



Clean Technologies for the Purification of Wastewaters: Adsorptive Parametric Pumping

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Abstract

The general objective of the thesis was to study the removal of phenolic species from effluents and from Kraft lignin oxidation process by adsorption, ion-exchange and membrane processes.

Adsorption of phenol, salicylic acid and p-nitrophenol from aqueous solutions onto polymeric resins (Sephabeads SP206 and SP207, Amberlite XAD16 and Duolite S861) and activated carbon (Filtrisorb F400) was studied. Batch equilibrium experiments were carried out at three different temperatures (293, 310 and 333 K) and equilibrium data fitted by the Langmuir isotherm. In order to ascertain the fixed bed implementation of the adsorbents, adsorption runs were carried out at laboratory scale and the effects of temperature and flow-rate were addressed. The linear driving force (LDF) approximation was used to predict the adsorption kinetics and simulate experimental breakthrough curves. Parametric pumping is an innovative technology that allows removing phenolic compounds from waste solutions to be recovered and recycled. Polymeric resin Sephabeads SP206 was the better adsorbent studied in this work for the recovery and/or purification of liquid streams containing phenol, salicylic acid and 4-nitrophenol by adsorptive parametric pumping. Different operating conditions were used in an automated pilot plant and experimental results compared to those simulated using home-made package.

Adsorption of synthetic vanillin onto non-ionic polymeric resins Sephabeads SP206 by using static and dynamic approach has been investigated. The impact of sodium hydroxide on the adsorption of vanillin was investigated and for this purpose, the modified Langmuir model of isotherm has been used. Increasing concentration of sodium hydroxide has significantly reduced the adsorbed amount of the vanillin onto polymeric adsorbent SP206. The mathematical model includes linear driving force for intraparticle mass transfer and reaction in liquid phase for the system vanillin/sodium hydroxide.

The membrane ultrafiltration process particularly focused to recovery of vanillin from Kraft lignin oxidation products. This process is considered as the first step of the vanillin recovery process. During the ultrafiltration process the vanillin as low molecular weight species is withdrawn in the permeate stream. For this purpose tubular ceramic membranes with different cut-offs: 1, 5, 15 and 50 kDa were selected and their performances compared. The influence of the lignin and vanillin concentration and pH of the feed mixture on the ultrafiltration process has been investigated as well. The mathematical model that considers concentration polarisation and gel layer formation phenomena has been developed to predict the flux decline during the ultrafiltration process.

The recovery of vanillin obtained in the oxidation of Kraft lignin process in alkali medium (pH 12-13) by using ion-exchange process with neutralization reaction in presence of a buffer solution (vanillate/vanillin) was studied. A set of batch equilibrium experiments (uptake curves) has been evaluated in order to obtain the concentration evolution of the vanillin, vanillate species and pH with time until equilibrium between liquid and resin phase is established. The fixed bed ion-exchange Na^+/H^+ has been analyzed at laboratory scale and the evolution of vanillin, vanillate and pH was studied. A mathematical model developed for both batch and fixed-bed systems consider intraparticle diffusion controlled neutralization of the cationic resin by the system vanillin/NaOH. The model predicts the curves evaluated by batch experiments and breakthrough and elution curves obtained from fixed bed experiments.

Resumo

O objectivo da tese é o estudo da remoção de compostos fenólicos de efluentes e do processo de oxidação de lenhina *Kraft* através de processos de adsorção, permuta iónica e membranas.

A adsorção de fenol, ácido salicílico e p-nitrofenol em soluções aquosas sobre resinas poliméricas (*Sephabeads SP206 and SP207, Amberlite XAD16 e Duolite S861*) e carvões activados (*Filtrisorb F400*) foi estudada em sistema descontínuo e de leito fixo a três temperaturas diferentes (293, 310 e 333 K) e ainda analisada a influência do caudal usando um modelo de força motriz linear.

A bombagem paramétrica é uma tecnologia avançada que permite a remoção de compostos fenólicos de efluentes que podem então ser recuperados e reciclados. A resina polimérica *Sephabeads SP206* mostrou o melhor desempenho na purificação de caudais líquidos contaminados com fenol, ácido salicílico e 4-nitrofenol. Experiências foram realizadas em uma unidade piloto automatizada usando diferentes condições operacionais. Os resultados experimentais foram comparados com os resultados obtidos através da simulação do processo.

A adsorção de vanilina sintética em resinas não poliméricas (*Sephabeads SP206*) foi estudada em condições estáticas e dinâmicas. O efeito da concentração de hidróxido de sódio sobre a adsorção da vanilina foi também investigado e, nesta análise, isotermas de *Langmuir* modificadas foram empregadas. O aumento da concentração de hidróxido de sódio acarretou uma redução substancial das quantidades de vanilina adsorvida sobre o adsorvente polimérico SP206. O modelo matemático usado inclui a aproximação de força motriz linear para a transferência de massa intraparticular para o sistema de vanilina/hidróxido de sódio.

Este trabalho também apresenta o estudo do processo de ultrafiltração voltado para a recuperação da vanilina da lenhina degradada proveniente do processo de oxidação da lenhina *Kraft*. Este processo com membranas é considerado o primeiro passo na recuperação da vanilina. Durante o processo da ultrafiltração, a vanilina bem como outras espécies de baixo peso molecular são retiradas na corrente de permeado. Neste estudo, membranas de cerâmica tubulares com diferentes *cut-offs* (1, 5, 15, e 50 kDa) foram empregadas e seus desempenhos comparados. A influência do pH e da concentração de lenhina e de vanilina no processo de ultrafiltração foi também analisada. Um modelo matemático que considera a polarização e a formação de uma camada de gel sobre a superfície da membrana foi desenvolvido para prever o declínio do fluxo do permeado durante o processo de ultrafiltração.

A obtenção da vanilina proveniente da oxidação da lenhina *Kraft* em meio alcalino (pH 12-13) usando processos de permuta iónica com reacções de neutralização na presença de uma solução vanilato/vanilina com pH controlado foi também objectivo deste trabalho. Experiências em sistema descontínuo e de leito fixo foram realizadas. O modelo matemático desenvolvido tanto para o sistema batelada como para o sistema de leito fixo considera a difusão intraparticular a etapa controladora da permuta iónica na resina catiônica para o sistema vanilina/hidróxido de sódio. O modelo permite prever a evolução das espécies vanilina, vanilato de sódio e pH em função do tempo.

Résumé

L'objectif général de cette thèse est d'étudier la soustraction des espèces phénoliques des effluents et des procédés d'oxydation de la lignine Kraft par adsorption, par des procédés d'échanges ioniques et membranaires

On a étudié l'adsorption du phénol, de l'acide salicylique et du p-nitrophénol issus de solutions ioniques sur des résines polymériques (Sephabeads SP206 and SP207, Amberlite XAD16 et Duolite S861) et sur des charbons actifs (Filtrisorb F400). Des expériences d'équilibre de type batch ont été réalisées à trois températures différentes (293, 310 and 333 K) et les données d'équilibre ont été ajustées par le modèle de Langmuir. Afin de s'assurer de l'application des adsorbants en lit fixe, les expériences d'adsorption ont été réalisées à l'échelle du laboratoire et les effets de la température et du débit ont été étudiés. L'approximation LDF (*Linear Driving Force*) a été utilisée pour prédire les cinétiques d'adsorption et simuler les courbes de perçage. Le pompage paramétrique est une technologie innovante qui nous a permis de retirer les composés phénoliques des solutions déchets afin de pouvoir les récupérer et les recycler. La résine polymère Sephabeads SP206 s'est révélée être le meilleur adsorbant dans ce travail de récupération et/ou de purification de courants liquides contenant du phénol, de l'acide salicylique et du 4-nitrophenol par pompage paramétrique. Différentes conditions opératoires ont été utilisées dans un pilote automatisé et les résultats expérimentaux ont été comparés à ceux de la simulation en utilisant un package fait maison.

Il a également été étudié l'adsorption de la vanilline synthétique sur des résines polymères non-ioniques Sephabeads SP206 en utilisant une approche statique et dynamique ; L'impact de l'hydroxyde de sodium sur l'adsorption de la vanilline a été analysé, et pour ce cas, le modèle de Langmuir modifié a été utilisé. L'augmentation de la concentration de l'hydroxyde de sodium a nettement réduit les quantités de vanilline adsorbées. Le modèle mathématique inclut un modèle LDF pour le transfert de matière intraparticulaire et pour la réaction dans la phase liquide pour le système vanilline/NaOH.

Le procédé d'ultrafiltration par membrane est centré particulièrement sur le recouvrement de la vanilline à partir de produits d'oxydation de la lignine Kraft. Ce procédé est considéré comme la première étape du procédé de recouvrement de la vanilline. Durant le procédé d'ultrafiltration la vanilline comme toutes espèces de faible masse moléculaire, est soutirée dans le courant du perméat. Dans ce cas, des membranes céramiques tubulaires avec différentes coupes : 1, 5, 15 and 50 kDa ont été sélectionnées et leurs performances comparées. L'influence de la concentration en lignine, en vanilline et le pH du mélange d'alimentation sur le procédé d'ultrafiltration ont également été étudiés. Le modèle mathématique considère une polarisation de la concentration et le phénomène de formation d'une couche de gel a été développé afin de prédire le déclin de flux durant le procédé d'ultrafiltration.

Nous avons également exploré le recouvrement de la vanilline obtenu dans le procédé d'oxydation de la lignine Kraft dans de l'alcali moyen (pH 12-13) en utilisant un procédé d'échange ionique avec une réaction de neutralisation en présence d'une solution tampon (vanilate / vanilline). Une série d'expériences d'équilibres de type batch ont été évaluées dans le but d'obtenir l'évolution des concentrations de la vanilline, de la vanilate et le pH jusqu'à ce que l'équilibre entre la phase liquide et la résine soit atteint. Le lit fixe à échange ionique Na^+ / H^+ a été analysé à l'échelle du laboratoire et les évolutions de la vanilline, de la vanilate et du pH ont été étudiées. Un modèle mathématique développé aussi bien pour les systèmes batch et lit fixe considère une diffusion intraparticulaire à neutralisation contrôlée de la résine cationique par le système vanilline/ NaOH. Le modèle est en accord raisonnable avec les courbes évaluées par les expériences batch et les courbes de perçage et d'élution obtenues par les expériences en lit fixe.

Resumé

Cieľom tejto práce bolo študovať odstránovanie fenolových zlúčenín z odpadových vôd a z Kraft lignín oxidačných procesov pomocou adsorpčných, ion výmenných a membranových metód.

Adsorpcia fenolu, kyseliny salicylovej a p-nitrofenolu z vodných roztokov sa študovala na polymerických adsorbentoch (Sephabeads SP206 a SP207, Amberlit XAD16 a Duolit S861) a aktivovanom uhlí (Filtrisorb F400). Experimentálne statické adsorpčné rovnováhy boli namerané pri troch rozličných teplotách (293, 310 a 333 K) a analyzované Langmuirovým modelom izotermy. Kolonové testy s adsorbentmi sa uskutočnili v laboratornej škále pričom sa študoval efekt teploty a prietoku na adsorpciu. Za účelom modelovania experimentálnych koncentračných profilov bola kinetika adsorpcie pre prenos hmoty do vnútra častice priblížená použitím priamej hnaciej sily (*linear driving force*, LDF). „*Parametric pumping*“ je inovačná technológia, ktorá umožňuje odstraňovanie fenolových zlúčenín z odpadových vôd za účelom izolácie a opätovného využitia. Polymerický adsorbent Sephabeads SP206 bol v tejto práci nájdený ako najvhodnejší zo študovaných adsorbentov na izoláciu a/alebo čistenie kvapalných zdrojov obsahujúcich fenol, kyselinu salicylovú a 4-nitrofenolu použitím adsorpčného „*parametric pumping*“. Na plno-automatizovanom skúšobnom zariadení boli testované rôzne operačné podmienky a experimentálne výsledky sa porovnali s teoretickými výsledkami z nášho modelovacieho programu. Adsorpcia syntetického vanilínu na neionický polymerický adsorbent Sephabeads SP206 bola študovaná použitím statických a dynamických metód. Zisťoval sa vplyv hydroxidu sodného na adsorpciu vanilínu a za týmto účelom bol použitý modifikovaný Langmuirov model izotermy. Zvyšujúca sa koncentrácia hydroxidu sodného významne znížila adsorbované množstvo vanilínu na polymerickom adsorbente SP206. Matematický model zahŕňal vnútročasticový prenos hmoty opísaný priamou hnaciou silou (*linear driving force*) a reakciu v kvapalnej fáze prebiehajúca v systéme vanilín/hydroxid sodný.

Membranová ultrafiltrácia bola špeciálne zameraná na získavanie vanilánu z Kraft lignín oxidačných produktov. Táto metóda je považovaná za prvý krok v procese získavania vanilínu. Počas ultrafiltrácie, vanilín ako látka s nízkou molekulovou hmotnosťou je odoberaná na strane permeátu. Za týmto účelom boli vybrané tubulárne keramické membrány s veľkosťami pórov: 1, 5, 15 a 50 kDa a efektívnosť separácie bola porovnaná. Vplyv koncentrácie lignínu a vanilínu v základnom roztoku a jeho pH na ultrafiltráciu bolo tiež predmetom štúdie. Matematický model zahŕňal jav koncentračnej polarizácie a formovania vrstvy gelu pre potreby modelovania poklesu fluxu počas ultrafiltrácie.

Získavanie vanilínu vyrobeného oxidáciou Kraft lignínu v alkalickom roztoku (pH 12 - 13) sa študoval na iónvýmennom materiáli. Proces bol spojený s neutralizačnou reakciou v prostredí tlmivého roztoku (vanilát/vanilín). Rad statických experimentov sa vykonával za účelom merania koncentračného profilu vanilínu a vanilátu a pH s časom až do dosiahnutia rovnovážneho stavu medzi kvapalnou a pevnou fázou. Vývoj koncentrácií vanilínu, vanilátu a zmena pH s časom boli taktiež zisťované v laboratornej škále použitím kolóny naplnenej iónvýmenným materiálom Na^+/H^+ . Navrhnutý matematický model pre statický a dynamický systém zahŕňal neutralizáciu v kyslom katexe kontrolovanú vnútročasticovou difúziou systémom vanilín/NaOH. Súlad bol nájdený medzi riešením matematického modelu a statickými i dynamickými experimentálnymi výsledkami.

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Chapter 3

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1. Introduction

1.1 Relevance and Motivation

The aim of this thesis is to apply clean technologies in the purification of wastewaters from different sources containing phenolic compounds and in the process of producing vanillin from Kraft lignin.

The present work “Clean Technologies for the Purification of Wastewaters: Adsorptive Parametric Pumping” is divided into two sections: The first section aims at the removal of phenolic species from effluents (phenol, salicylic acid, 4-nitrophenol) by using thermal parametric pumping. The second section deals with the recovery of vanillin from Kraft lignin oxidation, using membrane and ion-exchange process.

Widespread contamination of water by phenolic effluents has been recognized as an issue of growing importance in recent years. In fact, the main pollutants of aquatic ecosystems are considered to be phenols since they are harmful to plants, animals and human, even at low concentrations (Nigam *et al.*, 2000). By the extensive use of these compounds they readily enter ecosystems with industrial and municipal waste water, leachates emerging from waste deposits, by agricultural runoff of pesticides, by effluents from oil refineries, etc.(Li *et al.*, 2001; Li *et al.*, 2002).

Phenolic compounds are widely used in pharmaceutical, petrochemical and other chemical manufacturing processes. Most of them are toxic, potential or known human carcinogen and undesirable due to odours and unsightly colour (Martel and Morcellet, 1994) and cannot be discharged to the water recipient without treatment. The processes frequently involved are biological degradation, chemical oxidation of the waste organics and adsorption processes.

In the past, municipal treatment-systems were used for the purification of wastewater from industry. These systems depended on biological activity and were mostly found inefficient in the removal of the more resistant phenolic effluents. Nowadays, new treatment technologies are still constantly researched and developed. Current methods for removing phenolics from wastewater include microbial degradation, chemical oxidation (using ozone, hydrogen peroxide or chlorine dioxide), and adsorption on natural and synthesized adsorbent, incineration methods, solvent extraction and irradiation (Cooney, 1998).

It has been shown that biological degradation occurs too slowly (Kunin, 1976). Biological degradation and chemical oxidation are very sensitive to operation conditions and therefore can have unpredictable performance. Among the mentioned methods for removing pollutants adsorption still continues to be the most widely used process, especially in the cases with low pollutant concentrations. The adsorption processes have better performance and reproducibility and also they have advantage in economical point of view.

Major types of adsorbents in use are: activated alumina, activated carbon, silica gel, molecular sieve carbon, molecular sieve zeolites and polymeric adsorbents. Activated carbons are porous materials, with a large surface area containing predominantly micropores, which are used for purification and recovery in chemical and pharmaceutical processing as well as for environmental remediation. They are versatile adsorbents and are therefore used to remove a broad spectrum of dissolved organic and inorganic species from liquid and gaseous phases. Commercially available activated carbons are mainly derived from coal, wood or coconut shell, though there are an enormous range of potential source materials that could be used.

In view of the high cost and tedious procedure for the preparation and regeneration of activated carbon there is continuing search for alternative low cost potential adsorbents. This has encouraged research into speciality adsorbents using naturally occurring materials and synthetic resins that may lead to a cost-effective treatment process and energy efficient operation.

At present, polymeric adsorbents are widely employed for the isolation and purification of organic substances.

Due to their wide variations in functionality, surface area, and porosity, polymeric adsorbents have been increasingly viewed as an alternative to activated carbon for the selective removal of specific organic substances from contaminated water (Li *et al.*, 2001; Li *et al.*, 2002). Among the adsorbents used in adsorption technology, copolymers of polystyrene divinylbenzene are of great importance (Gusler *et al.*, 1993).

Parametric pumping is a cyclic process based upon the fact that the adsorption equilibrium isotherms of solutes onto some materials are strongly dependent on certain thermodynamic variables such as temperature, pressure, pH etc. There are two modes for operation: the direct mode when the temperature change is imposed through the column wall, and the recuperative mode, when the temperature change is carried by the liquid stream.

Parametric pumping was initially considered as a technology for the recovery of valuable products. Later it was used for wastewater purification purposes (Costa *et al.*, 1982) giving the starting point to other works carried out in our laboratory (Ferreira and Rodrigues, 1995b; Ferreira and Rodrigues, 1995a; Díez *et al.*, 1998; Davesac *et al.*, 2000).

Some potential advantages of parametric pumping are the possibility of continuous operation and the use of low potential thermal energy as a regenerant. A closed system parametric pumping has no feed or product streams and the system requires a feed reservoir and two reservoirs to collect the top and the bottom product. In an open system operating in recuperative mode the enrichment of the solute occurs in the top reservoir while an almost free-solute solution is obtained in the bottom reservoir.

The pulp and paper industry is a large water consumer and discharges effluents which produce high inorganic and organic pollution loadings. Pulp and paper industries are the main source of pure lignin. The Kraft process is at present dominating chemical pulping process of wood delignification and accounts for 2/3 of the lignin production. The black liquor is, after recovery of chemicals, burned in the boiler (Keyoumu *et al.*, 2004). The increase of capacity of pulp and paper plants is often limited by the boiler capacity which can justify the use of black liquor as lignin-source to produce vanillin. In the process of Kraft lignin oxidation to produce vanillin the reaction media at pH =12-13 contains degraded lignin and vanillin (most

in the vanillate form) (Fargues *et al.*, 1996). By using a membrane process the lignin can be extracted and the mixture vanillin/vanillate can be recovered in the permeate. The vanillin is then recovered from the mixture by using a column packed with strong acidic resin in H^+ form. The extracted lignin can be later converted into a useful biofuel, or used as dispersant or to produce biopolymers.

1.2 Objectives and Outline

There are two general objectives of this thesis. The first part is dedicated to purification of diluted wastewaters containing phenol, salicylic acid and 4-nitrophenol including the search for suitable adsorbents. For this purpose, the thermal parametric pumping has been considered as a clean technology which avoids the use of chemical regenerant and contributes to achieve the concept of zero-pollutant plant.

The objective of the second part of the thesis is to recover vanillin from the reaction media in the Kraft lignin oxidation process. The recovery includes ultrafiltration process using ceramic membranes to separate high molecular weight components (lignin) from vanillin. As following step nonionic polymeric adsorbent and strong cationic ion-exchanger has been tested in the process of recovery of vanillin.

Adsorption is one of the most common ways for wastewater treatment of phenolic compounds, which are undesirable pollutants in the environment, specifically in aquatic media. In the Chapter 2, the adsorption of phenol from aqueous solutions onto two polymeric resins (Sephabeads SP206, SP207) and onto activated carbon (Filtrisorb F400) was studied. Polymeric resins Amberlite XAD16 and Duolite S861 have been studied as well and are described in Appendix B. Batch equilibrium experiments were carried out at three different temperatures (293, 310 and 333 K) for each of the adsorbents and equilibrium data were fitted by the Langmuir isotherm. The breakthrough curves were predicted by using linear driving force (LDF) model. Polymeric resin Sephabeads SP206 was used to purify a phenolic solution by parametric pumping at pilot scale using hot and cold temperatures of 293 and 333 K.

Salicylic acid is a phenolic compound with a high production in a world scale, which is mainly linked to aspirin manufacture. Batch and fixed bed adsorption and desorption of salicylic acid onto activated charcoal (Filtrisorb F400) and onto polymeric adsorbents (Sephabeads SP207, Sephabeads SP206) was studied. Polymeric resins Amberlite XAD16

and Duolite S861 have been also studied and are described in Appendix B. The adsorptive behavior of these resins has been compared. The aim is to obtain a purified and a concentrated stream of salicylic acid, which allows recycling for the industrial process so contributing to achieve the concept of a zero-pollutant plant. For this purpose, the applicability of parametric pumping technology for the purification of salicylic acid in liquid phase has been evaluated in the Chapter 3.

The recovery and/or purification of liquid streams containing 4-nitrophenol by adsorptive parametric pumping were studied in the Chapter 4. An automated parametric pumping pilot unit was operated in semi-continuous recuperative mode. The heart of the system was a column packed with polymeric adsorbent Sephabeads SP206. Previously, the adsorption behaviour was obtained from batch equilibrium experiments and fixed bed adsorption. The Simplified *Equilibrium model* and a *linear driving force (LDF) model* were used to predict parametric pumping experimental results.

Chapter 5 considers the adsorption of synthetic vanillin at different pH onto non-ionic polymeric resins Sephabeads SP206. Batch experiments were carried out in order to obtain adsorption equilibrium isotherms at temperatures 293, 310, 333 K. The adsorption equilibrium isotherms have been described by the Langmuir model. The impact of sodium hydroxide on the adsorption of vanillin was investigated. The mathematical model used to predict fixed-bed adsorption results includes linear driving force for intraparticle mass transfer and reaction in liquid phase for the system vanillin/sodium hydroxide.

The membrane separation of the mixture lignin/vanillin using ceramic ultrafiltration tubular membranes is described in the Chapter 6. The influence of membrane pore size on the separation of vanillin from lignin/vanillin mixture was experimentally studied by testing ceramic membranes with different cut-offs (50 (described in appendix D), 15, 5 and 1 kD). The influence of concentration and pH of the mixture on the recovery of vanillin was evaluated as well.

The Chapter 7 deals with the recovery of vanillin from Kraft lignin oxidation using an ion exchange process accompanied by neutralization. In order to produce vanillin, oxidation of lignin takes place in the presence of alkaline medium (pH=12-13); under such condition almost all vanillin is present as vanillate. The vanillate solution is passed through the column packed with ion-exchange resin in H^+ form (Amberlite IR120H) and the vanillate is

converted to vanillin form. A set of batch equilibrium experiments (uptake curves) and fixed-bed experiments were evaluated in order to obtain the evolution of vanillin, vanillate species and pH with time until equilibrium between liquid and resin phase is established. The developed mathematical model predicts uptake curves and breakthrough curves and is based on intraparticle diffusion controlled neutralization of the cationic resin by the system vanillin/NaOH.

The conclusions of the thesis and suggestions for the future work are addressed in Chapter 8.

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2. Adsorptive purification of phenol wastewaters: parametric pumping operation¹

2.1 Introduction

Phenol-containing wastewater presents a serious environmental problem since biological degradation of phenol occurs too slowly or does not occur at all (Kunin, 1976). Adsorptive processes are widely used in the purification of such polluted streams and diluted wastewaters (Humphrey, 1995; Keller, 1995; Knaebel, 1995). For some target solutes, it is also interesting the fact that sorption operations are able to concentrate solutes, especially when these solutes are valuable compounds.

Phenols are the most extensively studied compounds in the field of wastewater treatment as they are persistent pollutants with high toxicity that are released in the wastewaters of a considerable number of industries (Morao *et al.*, 2004). Different techniques are used for the removal of phenolic compounds from wastewater (Lin *et al.*, 2002; Kujawski *et al.*, 2004).

¹ Based on the papers:

Adsorptive purification of phenol wastewaters: experimental basis and operation of a parametric pumping unit. by M. Otero, M. Zabkova, A.E. Rodrigues, Chemical Engineering Journal, 110, 101-111 (2005)

Phenolic wastewaters purification by thermal parametric pumping: modeling and pilot scale experiments. by M. Otero, M. Zabkova, A.E. Rodrigues, Water Research 39, 3467-3478 (2005)

Adsorption of phenolic compounds onto different polymeric adsorbents has been studied by various groups (Crook *et al.*, 1975; Costa, 1984; Ramalho, 1993; Deosarkar and Pangarkar, 2004).

The performance of any adsorption-based process greatly depends on the effectiveness of design and operating conditions. Therefore, rigorous approaches to the design and operation of the adsorption system must be used to ensure efficient applications. In order to get this, the mechanism and dynamics of adsorption must be understood, as well as the major variables that affect the adsorptive process.

Conventional fixed-bed processes involve a saturation, adsorption or loading step, followed by desorption, elution or regeneration steps. On the whole, wastewater purification by means of conventional fixed bed comprise two drawbacks: one is the low efficiency of the fixed bed operation, since only a fraction of the adsorbent is used and the other is the use of a chemical regenerant to get an operative bed, with the associated waste disposal and a new pollution problem.

Parametric pumping is a cyclic separation process in which a mobile phase percolates through a fixed bed upwards and downwards alternatively; a change in the temperature (or in another thermodynamic variable such as pressure, pH, etc) occurring simultaneously with the change in the flow direction (Simon *et al.*, 1998). In thermal parametric pumping, the temperature is the changing variable and the process is based upon the fact that the adsorption equilibrium isotherm of solutes onto some materials changes with temperature. The temperature change may be either carried out by the solution itself (in “recuperative mode”), which is heated or cooled by means of thermostatic baths, or imposed through the column wall (in “direct mode”). Also data on the combination of both modes have been published (Ghasem, 2003) but, no matter the mode in which thermal parametric pumping is operated, thermal energy is used as regenerant. Under appropriate conditions, wastewater to be purified passes through a bed of adsorbent in upward flow at a temperature T_h (hot half-cycle) followed by downward flow at a temperature T_c ($T_c < T_h$) (cold half-cycle) which will produce a concentrated solution at the top reservoir and a solute-free stream in the bottom one.

The basis of parametric pumping were established in the late sixties (Wilhelm *et al.*, 1966; Wilhelm *et al.*, 1968; Pigford *et al.*, 1969), when it was seen as a way to purify valuable compounds. It was not until the eighties that parametric pumping was considered for

wastewater purification purposes (Costa *et al.*, 1982) giving the starting point to other works carried out in our laboratory (Ferreira and Rodrigues, 1995b; Ferreira and Rodrigues, 1995a; Díez *et al.*, 1998; Davesac *et al.*, 2000).

Whether the problem is isolating or purifying a substance of commercial interest or cleaning wastewater, the technology to separate and purify molecules of choice is of critical importance.

The interest of parametric pumping for the wastewater treatment is that this technology would enable purification of industrial wastewaters avoiding the use of chemical regenerant and allowing the recycling of the concentrated stream for the industrial process so contributing to achieve the concept of zero-pollutant plant.

The aim of this chapter is to describe the adsorption of phenol onto different polymeric resins SP206, SP207 and activated charcoal (Filtrisorb F400). Thermal parametric pumping being based on the variation of temperature, both batch equilibrium and fixed bed tests were carried out at three different temperatures (293, 310 and 333 K) for each of the adsorbents in order to study the effect of temperature on the adsorption of phenol. Modeling of the fixed bed adsorption was made based on the results obtained for adsorption equilibrium isotherms. Also experiments at different flow rates of the feed solution were carried out. The final aim of the work is to use parametric pumping for the purification of phenolic wastewater and to compare experimental with simulated results obtained by a simulation package of parametric pumping cycles previously developed (Davesac *et al.*, 2000).

2.2 Experimental part

2.2.1 Chemicals and adsorbents

Phenol (C_6H_6O) was purchased from Sigma-Aldrich (Spain). The solutions of phenol were prepared with degassed and distilled water.

The activated carbon used was Filtrisorb F400, and was kindly provided by Chemviron Carbon (Belgium). The nonionic polymeric resins were Sephabeads SP206 and SP207 (Mitsubishi Chemical Corporation) purchased from Resindion (Italy). These resins have been previously used successfully for phenolic derivatives adsorption (Díez *et al.*, 1998).

In the *Table 2.1* are reported the physical characteristics provided by the producers for the adsorbents employed in this research work. As it may be seen, the polymeric adsorbents properties are very different from those of the activated charcoal.

2.2.2 Batch adsorption

Adsorption equilibrium experiments were carried out by contacting a given amount of adsorbent (0.05-6.0 g) with 100 mL of phenol solution in 250-mL Erlenmeyer flasks. Initial concentration of the solution was 500 mg L⁻¹ in most cases. Adsorption equilibrium isotherms were measured by batch equilibration placing the volumetric flasks in a shaking mixer at 150 rpm and using a thermostatic bath for temperature control.

Table 2.1 Physical properties of adsorbents used for phenol adsorption

Adsorbent	Filtrisorb F400	Sephabeads SP206	Sephabeads SP207
Matrix	Agglomerated coal based granular activated carbon	Aromatic porous resin with hydrophobic substituents-crosslinked copolymer of styrene	Aromatic porous resin with hydrophobic substituents-crosslinked copolymer of styrene
Physical form	Black granular carbon	Yellow opaque beads	Brown opaque beads
Humidity factor (f_h) (dry particle to wet particle mass ratio)	1	0.5	0.5
Specific surface area (m ² g ⁻¹)	1050	556	627
Density of wet adsorbent (g L ⁻¹)	700	1190	1180
Average Particle size (mm)	0.7	0.4	0.4

Equilibrium experiments were run at 293, 310 and 333 K for each adsorbent-phenol system. After shaking during 48 h, the solution was separated from the adsorbent and the final concentration of phenol in solution was determined by measuring the absorbance at a wavelength of 272 nm using UV-visible spectrophotometer Jasco (model 7800, Japan) and the amount of phenol adsorbed onto adsorbents, q^* (mg g⁻¹ dry resin), was calculated.

2.2.3 Fixed-bed adsorption

The adsorbents previously used in batch testes were also used in fixed bed operation. A peristaltic pump Watson-Marlow was used to pump the phenol solution through the beds of the adsorbents here considered. The temperature of the feeding solution was maintained by a thermostatic bath (Edmund Bühler). Phenol concentration at the column outlet was measured by an UV-visible spectrophotometer Jasco (model 7800, Japan) at a wavelength 272 nm.

Fixed bed adsorption of phenol onto different adsorbent was studied at temperatures 293, 310 and 333 K. Experiments at two different flow-rates were carried out as well. The flow-rates of the feed solution were 10 and 15 mL min⁻¹ for Filtrasorb F400, 10 and 5 mL min⁻¹ for SP 206 and 207. The feed concentration was always around 100 mg L⁻¹ of phenol. Dynamic column experiments were carried out by packing the adsorbents in lab-scale column (0.30 × 0.01 I.D m) and feeding with the phenol solution. A peristaltic pump (Watson-Marlow) was used to pump the phenol solution in downward flow. The temperature of the feed was maintained by a thermostatic bath (Edmund Bühler).

The height of the bed used in the experiments was 300 mm for the polymeric adsorbents and 100 mm for the activated carbon.

2.2.3.1 Parametric pumping operation

Figure 2.1 shows the pilot plant used to carry out the phenol purification by thermal parametric pumping. This is a completely automated system and it has been described with detail elsewhere (Ferreira and Rodrigues, 1995b). Basically, the core is a borosilicate column (90 I.D x 1000 mm) where the adsorbent is packed. Temperature waves in the cycles are measured by thermocouples installed at the inlet and outlet of the column. The solution is pumped through the column downward (cold half-cycle: 293K) and upward (hot half-cycle: 333K) alternatively by using the peristaltic pumps 15 or 16 respectively. The solenoid valves 11 and 12 are one open and the other closed while downward flow and on the contrary during the upward flow. Heating and cooling of the fluid phase is carried out by the hot 7 and the cold 6 heat exchangers. There are three reservoirs: top, bottom and feed reservoirs. The top and bottom reservoirs receive product when the solution is pumped through the column in upward or downward flow, respectively. From the feed reservoir, the feed solution is passed into the top reservoir, with the pump 18 on. Pressure transducers installed at the bottom of the

reservoirs allow detecting when all the solution contained in a reservoir was transferred, which means the end of one half cycle. Bottom and top products were collected at fixed time intervals by a fraction collector, with pumps 19 and 17 working. The solute concentration was determined by an UV-visible spectrophotometer Jasco (model 7800, Japan) at a wavelength 272 nm.

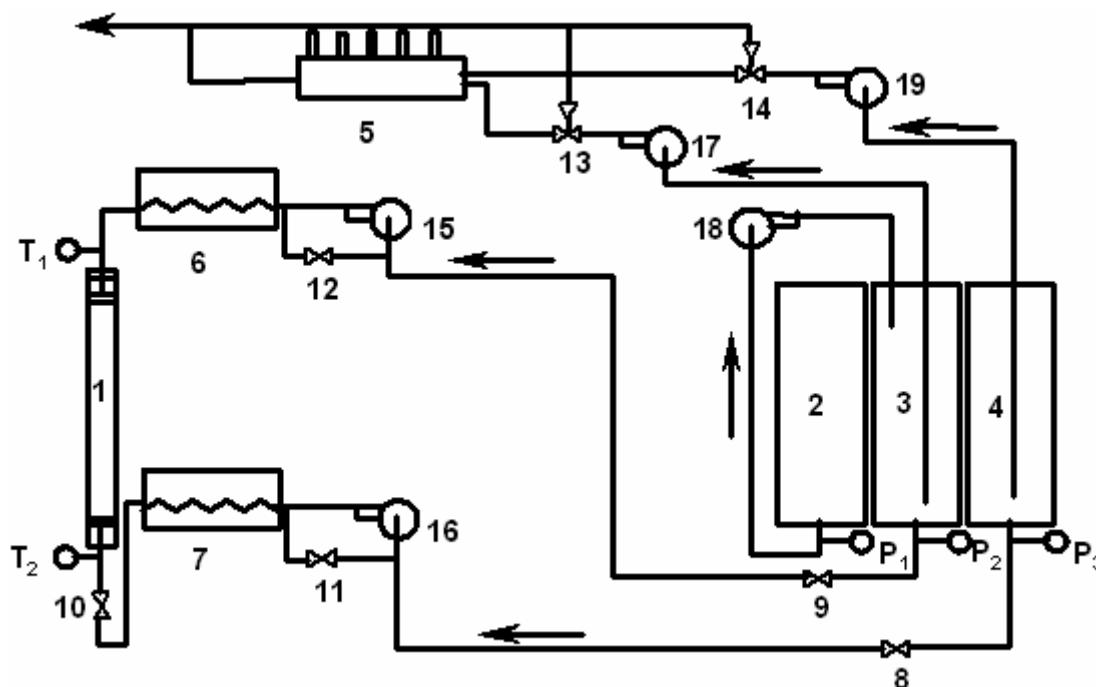


Figure 2.1 Experimental set-up of the parametric pumping pilot plant.

Legend:

- (1) Glass column G90-Amicon
- (2) Feed reservoir
- (3) Top reservoir
- (4) Bottom reservoir
- (5) Fraction collector Gilson
- (6)–(7) Heat exchangers
- (8)–(12) Two ways solenoid valves
- (13)–(14) Three ways solenoid valves
- (15)–(16) Peristaltic pumps Watson Marlow
- (17)–(19) Peristaltic pumps Gilson
- (T1)–(T2) Thermocouples (type K)
- (P1)–(P3) Pressure transducers Schwaevitz (type P510)

The experimental set-up described above was used for the system water-phenol-Sephabeads SP206. Also other systems have been previously studied (Ferreira and Rodrigues, 1995b; Ferreira and Rodrigues, 1995a; Díez *et al.*, 1998). Previously to the cyclic operation of the system, fixed bed adsorption runs were carried out in the pilot unit at both 293 and 333 K using Sephabeads SP206 as adsorbent. The feed concentration was around 500 mg L⁻¹ and the

flow-rate 600 mL min^{-1} , the height and the diameter of the SP206 bed being 800 and 90 mm respectively. Previously to each run, the temperature of the bed was stabilized by pumping deionised water at 600 mL min^{-1} and at 293 K or 333 K to later carry out the corresponding phenol isothermal fixed bed saturation.

The operation of the parametric pumping pilot plant was performed during 10 cycles in a recuperative mode. The regime of operation was semi-continuous, i.e., the sequence was: feed input and top product withdrawal during the upward hot half-cycle and bottom product withdrawal during the downward cold half-cycle. A simulation package (Davesac *et al.*, 2000) was used for the simulation of the cyclic operation. Experimental results were compared with the simulated ones obtained using a non-isothermal model which includes Linear Driving Force describing intraparticle mass transfer and axial dispersion.

2.3 Mathematical models

2.3.1 Adsorption isotherms

The amount of phenol adsorbed onto adsorbent q^* (mg g^{-1} dry resin), was calculated by a mass balance relationship (Eq. 2.1).

$$q^* = (C_0 - C^*) \frac{V}{W} \quad 2.1$$

where C_0 (mg L^{-1}) and C^* (mg L^{-1}) are the initial and equilibrium liquid-phase concentrations, respectively, V the volume of the solution (L) and W the dry weight (g) of the corresponding adsorbent. The volume of solution and mass of adsorbent used in experiment are described in Paragraph 2.2.2.

The adsorption equilibrium isotherms for phenol onto each adsorbent at various temperatures, q^* (mg g^{-1} dry resin) versus the adsorbate liquid concentration at equilibrium, C^* (mg L^{-1}) were fitted with the Langmuir model.

The Langmuir equation (Eq. 2.2) is based on a theoretical model, which assumes that adsorption occurs onto specific sites of a uniform energetic surface, without interactions between adsorbed molecules and adsorption is confined to monolayer coverage.

$$q^* = \frac{QK_L C}{1 + K_L C} \quad 2.2$$

where Q is the maximum adsorptive capacity and K_L a parameter which relates to the adsorption enthalpy (Guiochon *et al.*, 1994).

$$K_L = K_L^\infty \exp\left(-\frac{\Delta H_L}{RT}\right) \quad 2.3$$

The adsorption enthalpy in the Langmuir constant is generally a net value that includes the solvent desorption and the solute adsorption (Giles *et al.*, 1974). The empirical parameters were calculated by MATLAB 6.1 following the optimization routine and using the Simplex direct search method. The obtained parameters are given in *Table 2.2*.

Separation parameter:

From the equilibrium results, it may be found the separation to be expected as a function of temperature for each of the systems phenol-adsorbent. The separation parameter b , introduced by Pigford (1973), is indicative of the separation potential:

$$b = \frac{a}{1 + m} \quad 2.4$$

with the average slope $\bar{m} = \frac{m(T_1) + m(T_2)}{2}$ and the deviation $a = \frac{m(T_1) - m(T_2)}{2}$, considering

$T_1 < T_2$. The capacity parameter is defined as $m(T) = \frac{(1 - \varepsilon)\rho_p f_h K(T)}{\varepsilon}$, where $K(T) = QK_L$

is the slope of initial linear region of the isotherm corresponding to each temperature, ε is the bed porosity was assumed ($\varepsilon = 0.4$), ρ is the density and f_h the humidity factor of the corresponding adsorbent, which values appear in *Table 2.1*.

2.3.2 Fixed bed modeling

The model used to predict the fixed bed adsorption of the phenol comprises a mass balance, the adsorption equilibrium isotherm at the liquid/solid interface. The linear driving force (LDF) rate equation was used to describe the diffusional mass transfer inside adsorbent particles.

Species balance:

The mass balance in a bed volume element is:

$$D_{ax} \frac{\partial^2 C(z,t)}{\partial z^2} - u_i \frac{\partial C(z,t)}{\partial z} = \frac{\partial C(z,t)}{\partial t} + \frac{1-\varepsilon}{\varepsilon} \rho_p f_h \frac{\partial \langle q(z,t) \rangle}{\partial t} \quad 2.5$$

where D_{ax} is the axial dispersion coefficient, u_i is the interstitial velocity, ε is the bed porosity, z is the axial position, C is the concentration in the bulk fluid phase, $\langle q \rangle$ is the average adsorbed phase concentration in the adsorbent particles, ρ_p is the density of the adsorbent and f_h its humidity factor.

The boundary conditions for the mass balance equation are the Danckwerts boundary conditions:

$$z = 0 \quad D_{ax} \frac{\partial C(z,t)}{\partial z} \Big|_{z=0} = u_i (C(0,t) - C_0) \quad 2.6$$

$$z = L \quad \frac{\partial C(z,t)}{\partial z} \Big|_{z=L} = 0 \quad 2.7$$

The associated initial conditions for the adsorption are:

$$C(z,0) = 0 \quad 2.8$$

$$q(z,0) = 0 \quad 2.9$$

Intraparticle mass transfer:

The Linear Driving Force (LDF) approximation (Glueckauf, 1955) was used to describe intraparticle mass transfer:

$$\frac{\partial \langle q(z,t) \rangle}{\partial t} = k_{LDF} [q^*(z,t) - \langle q(z,t) \rangle] \quad 2.10$$

where k_{LDF} is the Linear Driving Force kinetic constant, $q^*(z,t)$ is the adsorbed phase concentration at particle surface in equilibrium with the bulk concentration.

In the previous equations, the axial dispersion was obtained from the following expression (Guiochon *et al.*, 1994):

$$\frac{u_0 d_p}{D_{ax}} = (0.2 + 0.011 \text{Re}^{0.48}) \quad 2.11$$

$$\text{where } \text{Re} = \frac{u_0 \rho_f d_p}{\eta}.$$

The k_{LDF} used in the model were estimated by the following expression (Azevedo, 2001):

$$k_{LDF} = \frac{\Omega D_{pe}}{r_p^2 \rho_f \frac{dq^*}{dC}} \quad 2.12$$

where D_{pe} ($\text{m}^2 \text{min}^{-1}$) is the effective pore diffusivity, r_p (m) is the radius of the particle of the adsorbent, Ω is the LDF factor, which is equal to 15 for spherical particles (Azevedo, 2001), and $(\frac{dq^*}{dC})$ is the slope of the adsorption equilibrium isotherm.

The D_{pe} was calculated from (Guiochon *et al.*, 1994):

$$D_{pe} = \frac{\varepsilon_p D_m}{\tau} \quad 2.13$$

where D_m is the molecular diffusivity of the solute in water, τ is the tortuosity of the adsorbent and ε_p its porosity.

The molecular diffusivity of phenol in water was calculated from the Wilke-Chang (Wilke and Chang, 1955) equation (Eq. 2.14), which estimates the D_m ($\text{cm}^2 \text{s}^{-1}$) as:

$$D_m = 7.4 \times 10^{-8} \frac{(\phi M_B)^{1/2} T}{\eta_B V_A^{0.6}} \quad 2.14$$

where V_A is the molar volume of the solute, the values of V_A were estimated by the Le Bas additive method (Reid *et al.*, 1987) giving $V_A = 108 \text{ cm}^3 \text{ mol}^{-1}$ for phenol. Wilke and Chang recommended that the dimensionless association factor of solvent, ϕ was chosen 2.6 if the solvent is water. The viscosity of water η_B (cp) at the corresponding temperature was used.

The partial differential equations of the model to describe the adsorption of phenol onto tested adsorbent were solved using the software package *gPROMS*[®] for general PROcess Modelling System. The orthogonal collocation method on finite elements (OCFE) was used with 50 finite elements and two interior collocation points in each element of the adsorption bed.

2.3.3 Parametric pumping simulation

From the batch and fixed bed tests results, the adsorbent Sephabeads SP206 is the one which adsorption performance is affected by temperature in a higher degree. Recuperative thermal parametric pumping being based in differences on adsorption capacity caused by changes in the temperature of the solution, this resin was selected for studying phenol purification by parametric pumping. The experimental results of the parametric pumping system Sephabeads SP206-Phenol were compared with the simulated ones using a Linear Driving Force model with axial dispersion. Equations corresponding to the model used include, apart of the mass balance (Eq. 2.5), the equilibrium isotherm (Eq. 2.2 and 2.3) and the mass transfer (Eq. 2.10), an energy balance and the balance equations of the reservoirs.

Energy balance

$$\begin{aligned} & \left[\rho_f C_{p_f} \varepsilon + \rho C_{p_s} (1 - \varepsilon) \right] \frac{\partial T(z, t)}{\partial t} = \\ & = K_{ae} \frac{\partial^2 T(z, t)}{\partial z^2} \pm \rho_f C_{p_f} u_0 \frac{\partial T(z, t)}{\partial z} - h_w A_w (T - T_{amb}) + (-\Delta H) \frac{\partial \langle q(z, t) \rangle}{\partial t} \end{aligned} \quad 2.15$$

where K_{ae} is the axial thermal conductivity, h_w is the heat transfer coefficient of the wall of the column and A_w is the wall specific area, ρ_f and ρ are the densities of the fluid and of the adsorbent, and C_{p_f} and C_{p_s} are the heat capacities of the fluid and of the adsorbent, respectively. Considering $z = 0$ at the bottom of the column and $z = L$ at the top, in the (Eq. 2.15), the term $\pm \rho_f C_{p_f} u_0 \frac{\partial T(z, t)}{\partial z}$ has the “+” sign for the cold half-cycle downwards, and the “-” sign for the hot half-cycle upwards.

Balance of the reservoirs

Hot half-cycle

$$\langle C_{BP} \rangle = \langle C_{BP} \rangle_{n-1} \quad 2.16$$

$$\langle C_{TP} \rangle = \frac{(1 - \phi_B) \langle C(L, t) \rangle_n}{(1 + \phi_T)} + C_F \frac{(\phi_B + \phi_T)}{(1 + \phi_T)} \quad 2.17$$

where $\langle C_{BP} \rangle$ and $\langle C_{TP} \rangle$ are the average concentration of phenol in the fluid which is in the bottom and in the top reservoirs, respectively, ϕ_B and ϕ_T are the fraction of the total reservoir displacement volume ($Q_{(\pi/\omega)}$) which are withdrawn as product from the bottom and the top reservoirs, respectively, and n refers to the number of cycles. Total reservoir displacement volume ($Q_{(\pi/\omega)}$) is the volume of solution percolated through the column during cold half-cycle.

Cold half-cycle

$$\langle C_{BP} \rangle = \langle C(0, t) \rangle_n \quad 2.18$$

The boundary conditions for the equations included in the parametric pumping model are:

Hot half-cycle

$$z = 0 \quad C(0, t) = \langle C_{BP} \rangle_n; \quad T = T_h \quad 2.19$$

$$z = L \quad \frac{\partial C(z, t)}{\partial z} = 0 \quad \frac{\partial T(z, t)}{\partial z} = 0 \quad 2.20$$

Cold half-cycle

$$z = 0 \quad \frac{\partial C(z, t)}{\partial z} = 0 \quad \frac{\partial T(z, t)}{\partial z} = 0 \quad 2.21$$

$$z = L \quad C(L, t) = \langle C_{TP} \rangle_n \quad T = T_c \quad 2.22$$

The initial conditions were:

$$t = 0 \quad C(z, 0) = C_F \quad T(z, 0) = T_c \quad 2.23$$

2.4 Results and discussion

2.4.1 Adsorption equilibrium isotherm

The adsorption equilibrium isotherms for phenol onto each adsorbent at various temperatures, q^* (mg g⁻¹ dry resin) versus the adsorbate liquid concentration at equilibrium, C^* (mg L⁻¹) were fitted with the Langmuir equation. Langmuir isotherm (Eq.2.2) is based on a theoretical model where the maximum adsorption capacity corresponds to a monolayer saturated with adsorbate molecules on the adsorbent surface, which is energetically homogeneous. The characteristic parameters corresponding to the fittings are shown in *Table 2.2*.

Table 2.2 Equilibrium parameters determined for the adsorption of phenol onto Filtrasorb F400, Sephabeads SP206 and Sephabeads SP207

Langmuir parameters	Filtrasorb F400	Sephabeads SP206	Sephabeads SP207
Q (mg g⁻¹)	169.1	85.0	88.8
K_L[∞] (L mg⁻¹)	1.32 x10 ⁻³	1.52 x10 ⁻⁸	2.99x10 ⁻⁷
ΔH_L (kJ mol⁻¹)	-12.12	-30.35	-23.22

The Q corresponding to the Filtrasorb is higher than those corresponding to the Sephabeads SP206 and SP207. On the contrary, the process is more exothermic in the case of phenol adsorption onto the polymeric resins than onto the activated charcoal as indicated by the value of ΔH_L .

The experimental adsorbed concentrations as a function of liquid phase concentration corresponding to the phenol adsorption onto Filtrasorb F400 at each of the temperatures considered are shown in *Figure 2.2*. The obtained fittings to the Langmuir model are shown together with the experimental points. The adsorption isotherms of phenol onto polymeric adsorbents SP206 and SP207 are shown on the *Figure 2.3* and *Figure 2.4*.

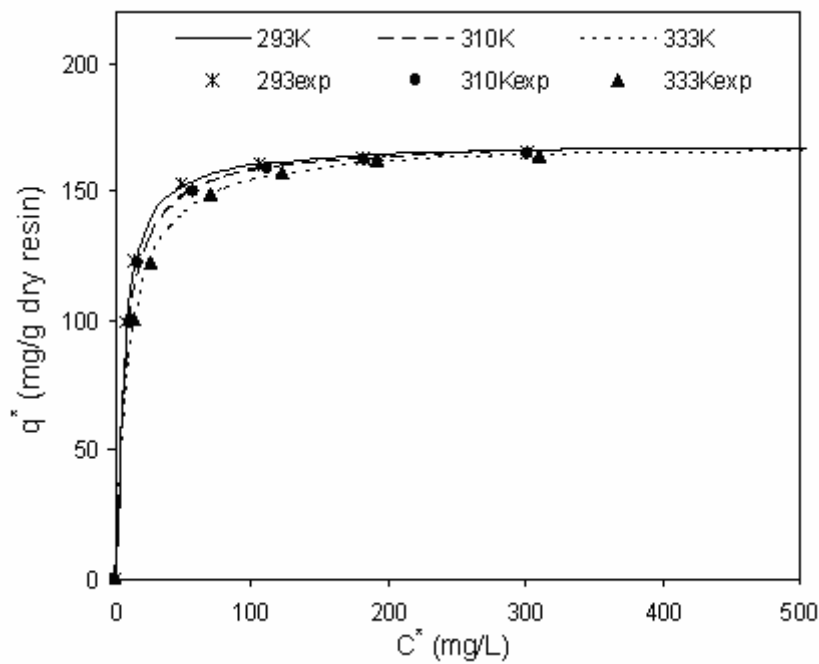


Figure 2.2 Experimental adsorption equilibrium (symbols), q^* versus C^* and fittings to Langmuir model (lines) at different temperatures (293, 310 and 333K) for the adsorption of phenol onto Filtrasorb F400

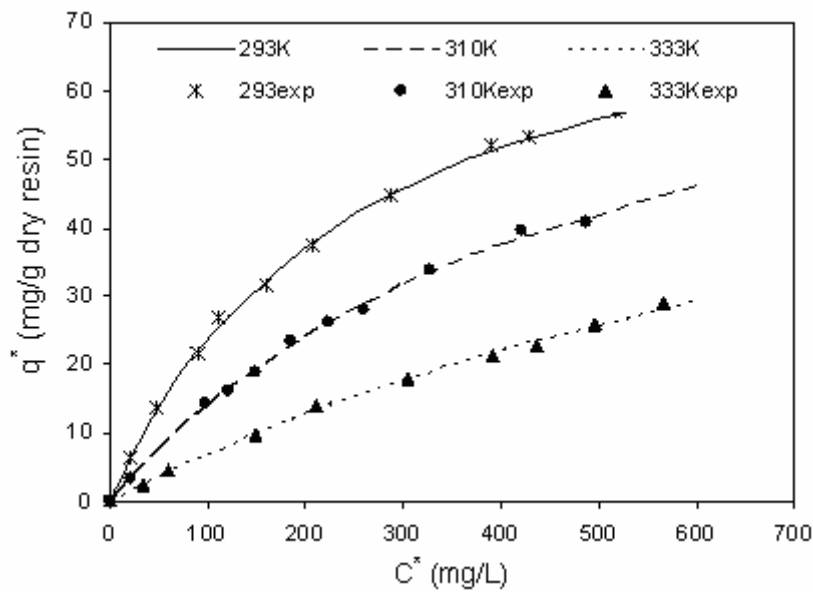


Figure 2.3 Experimental adsorption equilibrium (symbols), q^* versus C^* and fittings to Langmuir model (lines) at different temperatures (293, 310 and 333K) for the adsorption of phenol onto Sephabeads SP206

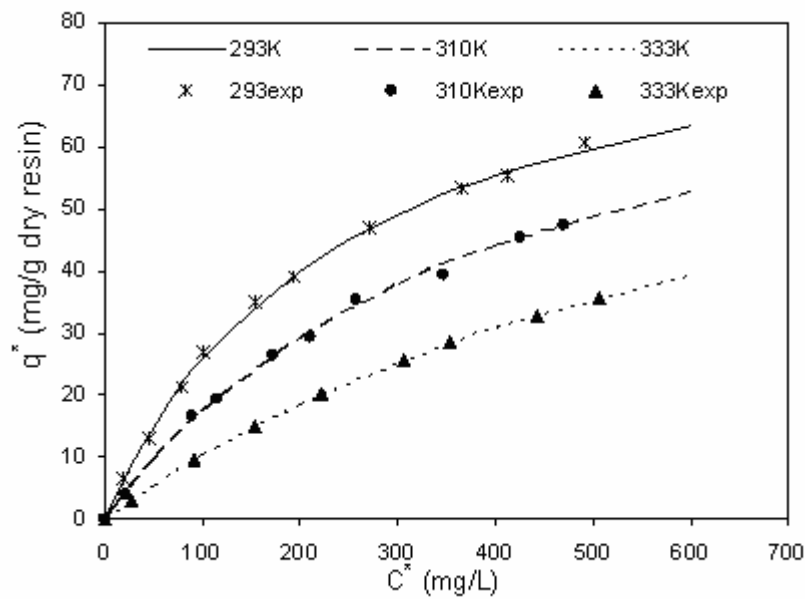


Figure 2.4 Experimental adsorption equilibrium (symbols), q^* versus C^* and fittings to Langmuir model (lines) at different temperatures (293, 310 and 333K) for the adsorption of phenol onto Sephabeads SP207

The adsorptive capacity of phenol is much higher for the activated carbon Filtrasorb F400 than for the polymeric resins. Nevertheless, the influence of temperature on equilibrium is much more noticeable in the case of the adsorption of phenol onto the resins, especially onto Sephabeads SP206. From the equilibrium results, it may be found the separation to be expected as a function of temperature for each of the systems phenol-adsorbent for different ranges of temperature. Table 2.3 shows for each of the adsorbents considered the corresponding separation parameter (b) regarding to the adsorption of phenol. The parameter b is indicative of the separation potential.

Table 2.3 Separation parameter, b , corresponding to the different systems adsorbent-phenol

Temperature range	293K-310K	310K-333K	293K-333K
Filtrasorb F400	0.14	0.16	0.29
Sephabeads SP206	0.33	0.39	0.63
Sephabeads SP207	0.26	0.30	0.52

As it may be observed in Table 2.3, in the temperature range studied, the largest b values correspond to the adsorption of phenol onto Sephabeads SP206. For this reason the system

phenol/SP206 was used in parametric pilot plant experiments at temperature range 293 K-333 K.

2.4.2 Fixed- bed adsorption

The breakthrough curves corresponding to the different adsorbents here considered confirm that the influence of temperature variable on the adsorption of phenol is much more noticeable for the polymeric resins Sephabeads SP 206 and SP 207 than for the activated carbon Filtrasorb F400. This can be seen by comparing runs at the same flow rate (10 mL min^{-1}) on the *Figure 2.5* (Filtrasorb 400) and *Figure 2.8* and *Figure 2.10* (SP206 and SP 207, respectively).

Experimental data are shown together with the predicted behaviors on *Figure 2.5 -2.10*. The *LDF* model seems to well describe the fixed bed adsorption of phenol onto the adsorbents here used at the conditions of temperature and flow-rate here studied.

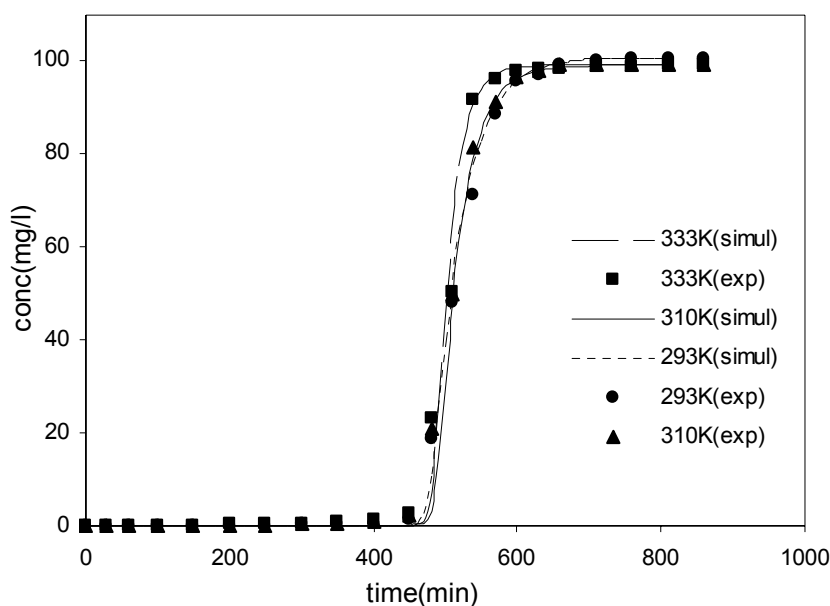


Figure 2.5 Fixed bed adsorption of phenol onto Filtrasorb F400. The bed length was 100 mm for Filtrasorb F400 and solution was fed at three temperatures (293K, 310K and 333K) at flow-rate 10 mL min^{-1} . Symbols correspond to the experimental results and full lines to the simulated ones.

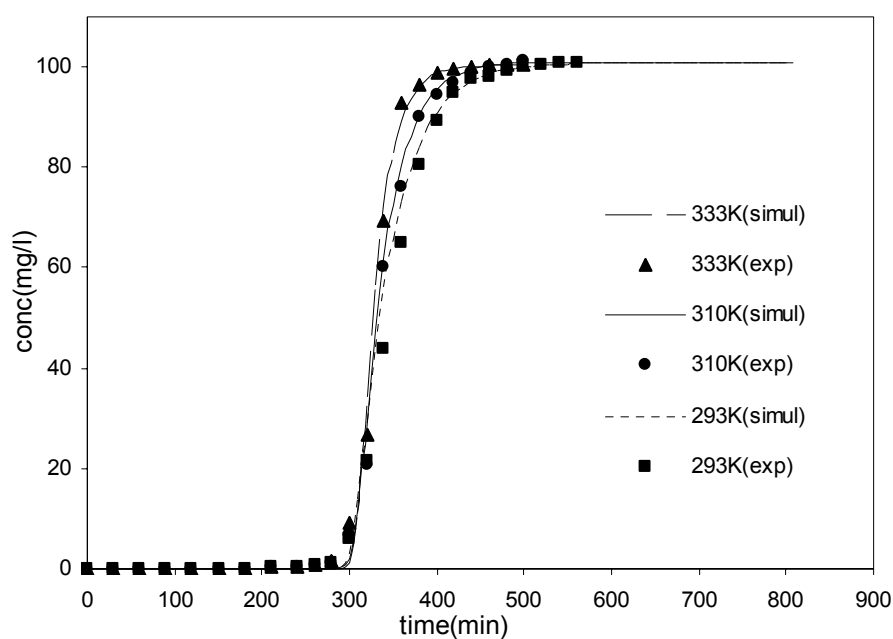


Figure 2.6 Fixed bed adsorption of phenol onto Filtrasorb F400. The bed length was 100 mm for Filtrasorb F400 and solution was fed at three temperatures (293K, 310K and 333K) at the flow-rate 15 mL min^{-1} . Symbols correspond to the experimental results and full lines to the simulated ones.

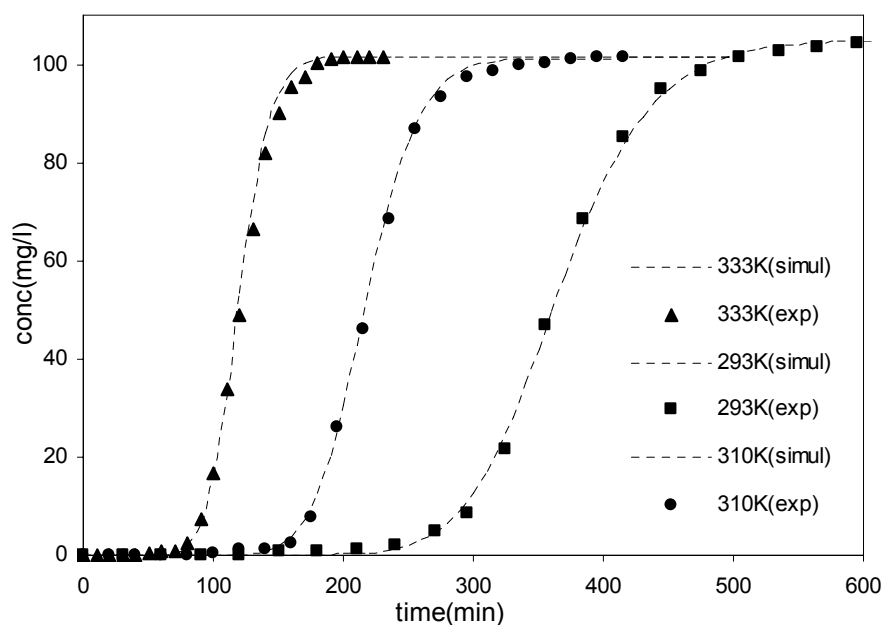


Figure 2.7 Fixed bed adsorption of phenol onto Sephabeads SP206. The bed length was 300 mm for Sephabeads SP206 and solution was fed at three temperatures (293K, 310K and 333K) at the flow-rate 5.5 mL min^{-1} . Symbols correspond to the experimental results and full lines to the simulated ones.

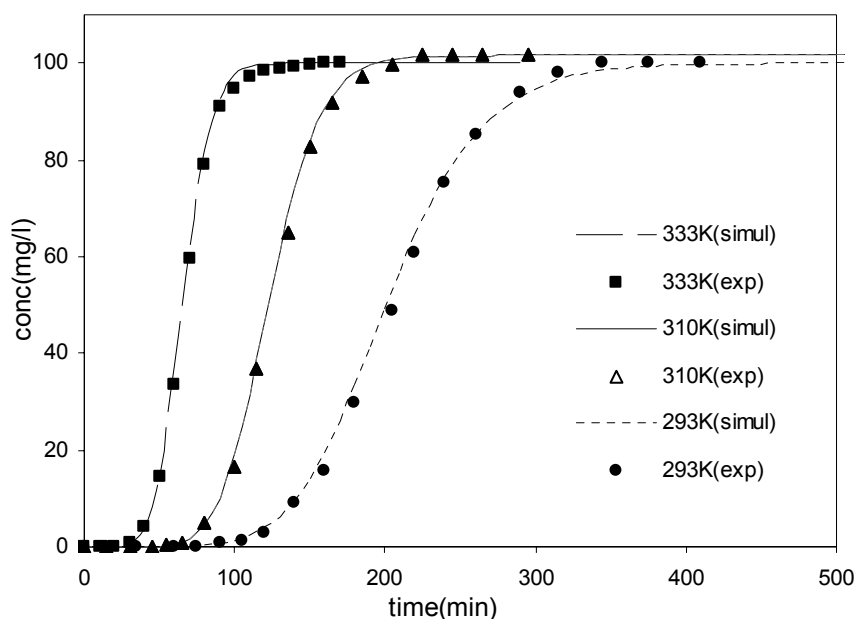


Figure 2.8 Fixed bed adsorption of phenol onto Sephabeads SP206. The bed length was 300 mm for Sephabeads SP206 and solution was fed at three temperatures (293K, 310K and 333K) at the flow-rate 10 mL min^{-1} . Symbols correspond to the experimental results and full lines to the simulated ones.

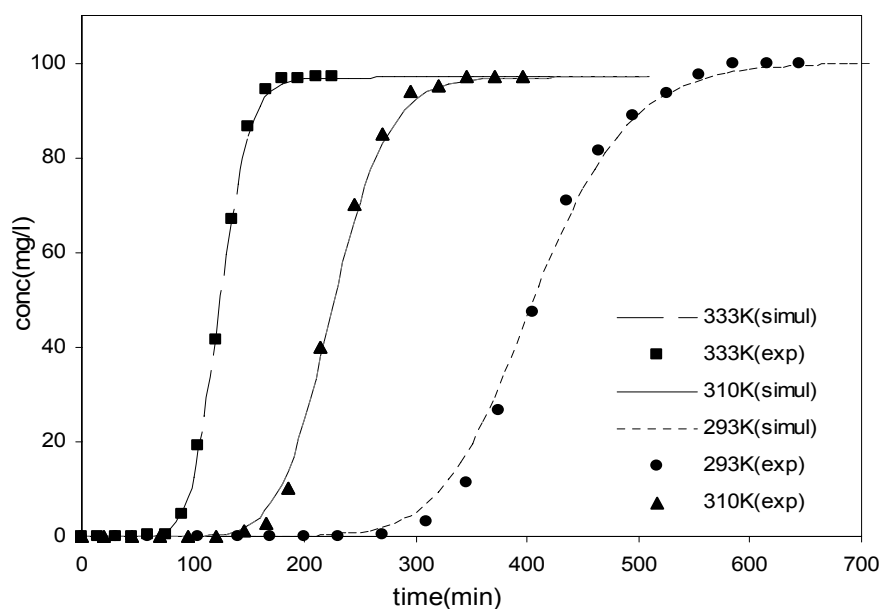


Figure 2.9 Fixed bed adsorption of phenol onto Sephabeads SP207. The bed length was 300 mm for Sephabeads SP207 and solution was fed at three temperatures (293K, 310K and 333K) at the flow-rate 5.5 mL min^{-1} . Symbols correspond to the experimental results and full lines to the simulated ones.

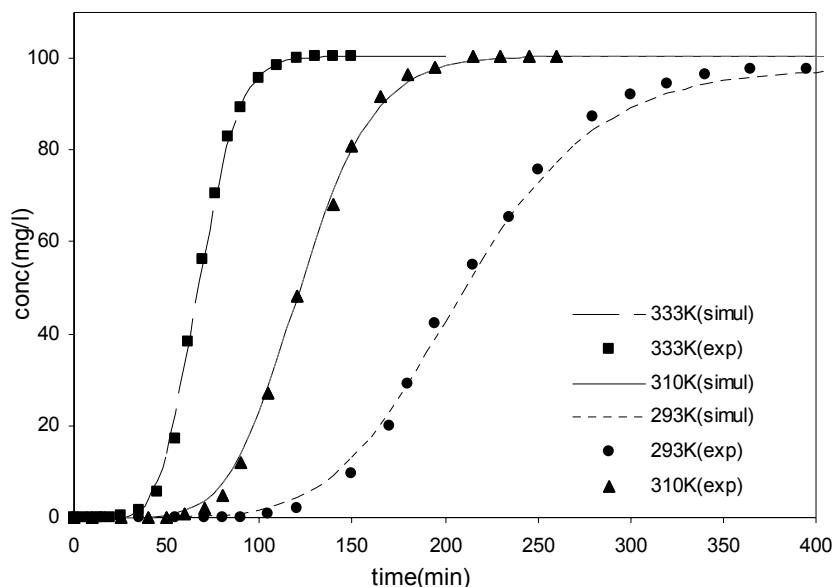


Figure 2.10 Fixed bed adsorption of phenol onto Sephabeads SP207. The bed length was 300 mm for Sephabeads SP206 and solution was fed at three temperatures (293K, 310K and 333K) at the flow-rate 10 mL min^{-1} . Symbols correspond to the experimental results and full lines to the simulated ones.

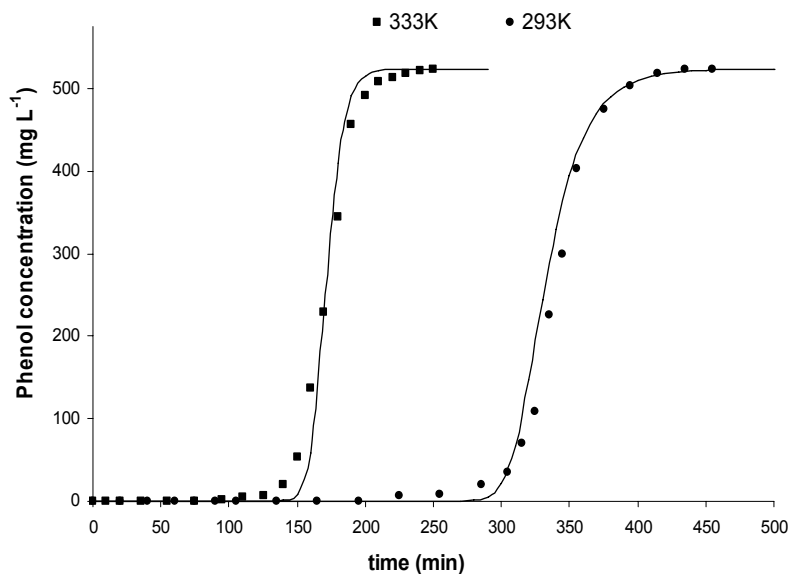


Figure 2.11 Fixed bed adsorption of phenol onto Sephabeads SP206 in pilot scale column (800x90 I.D. mm). The solution was fed at a flow rate of 600 mL min^{-1} and two runs, at 293K and 333K, respectively, were carried out.

The values of the Reynolds and the calculated axial dispersion D_{ax} used for the simulation of the breakthrough curves of phenol are shown in Table 2.4. The k_{LDF} rate constant used in the model is shown in the Table 2.5.

Table 2.4 Parameters used for estimating the D_{ax} corresponding to the different fixed bed systems considered at flow rate 10 mL min^{-1}

<i>adsorbent</i>	<i>T</i> (K)	<i>L</i> (mm)	Re	$D_{ax} (\text{cm}^2 \text{min}^{-1})$
Filtrisorb F400	293	100	1.45	4.18
	310		2.31	4.12
	333		3.13	4.07
Sephabeads SP206	293	300	0.46	1.35
	310		0.73	1.34
	333		0.98	1.33
Sephabeads SP207	293	300	0.46	1.35
	310		0.73	1.34
	333		0.98	1.33

Table 2.5 LDF kinetic rate constants estimated (k_{LDF}) for the adsorption of phenol onto each adsorbent.

Adsorbent	T (K)	D_m ($\text{m}^2 \text{min}^{-1}$)	ε_p	τ	D_{pe} ($\text{m}^2 \text{min}^{-1}$)	$k_{LDF} (\text{min}^{-1})$
Filtrisorb F400	293	5.34×10^{-8}	0.75	2	2.00×10^{-8}	0.027
	310	8.88×10^{-8}			3.33×10^{-8}	0.036
	333	1.32×10^{-7}			4.95×10^{-8}	0.054
Sephabeads SP206	293	5.34×10^{-8}	0.61	2	1.63×10^{-8}	0.074
	310	8.88×10^{-8}			2.71×10^{-8}	0.192
	333	1.32×10^{-7}			4.03×10^{-8}	0.409
Sephabeads SP207	293	5.34×10^{-8}	0.63	2	1.68×10^{-8}	0.053
	310	8.88×10^{-8}			2.80×10^{-8}	0.148
	333	1.32×10^{-7}			4.16×10^{-8}	0.330

2.4.3 Parametric pumping

From the batch and fixed bed tests results, the adsorbent Sephabeads SP206 is the one which adsorption performance is affected by temperature in a higher degree. Recuperative thermal parametric pumping being based in differences on adsorption capacity caused by changes in the temperature of the solution, this resin was selected for studying phenol purification by parametric pumping. Fixed bed adsorption of phenol at 293K and at 333K was carried out in the column of the parametric pumping set-up using a bed of Sephabeads SP206 (800 x 90 I.D mm). *Figure 2.11* shows the experimental results together with those simulated by the model previously used in lab-scale columns. This model well predicts the fixed bed adsorption of phenol onto Sephabeads SP206 also at a pilot scale. The characteristic parameters of the operated system and the conditions under which the parametric pumping runs were carried out are shown in *Table 2.6*. In the *Table 2.6* V_U represents volume which is percolated through the column during hot-half cycle, $Q_{(\pi/\omega)}$ is reservoir displacement volume, ϕ_B, ϕ_T are fraction of $Q_{(\pi/\omega)}$ withdrawn as a bottom and top product, respectively, Q_{TP}, Q_{BP} are flow-rates of removing the product from the top and bottom reservoir, respectively. Q_c, Q_h, t_c and t_h describes flow-rate of the fluid in the column during the cold and hot half-cycle and time of the cold and hot cycle.

Table 2.6 Experimental conditions used for the different parametric pumping runs in semi-continuous recuperative mode.

Operating variables	Run 1	Run 2	Run 3	Run 4
V_U (mL)	11616	29000	9500	17000
$Q_{(\pi/\omega)}$ (mL)	16940	31200	9600	20000
ϕ_B	0.31	0.068	0.068	0.15
ϕ_T	0.34	0.56	0.56	0.25
t_c (min)	55	120	60	100
t_h (min)	48	100	50	85
Q_c (mL.min ⁻¹)	308	260	160	200
Q_h (mL.min ⁻¹)	242	290	190	200
Q_{TP} (mL.min ⁻¹)	134	184	119.5	62.5
Q_{BP} (mL.min ⁻¹)	105	18	12	32

Figure 2.12 shows the simulated axial profiles of temperature and concentration corresponding to the operation of the parametric pumping unit under conditions for the run 4. The evolution of the temperature profile along the time of the 10th hot half-cycle and the 10th cold half-cycle may be seen in Figure 2.12 (A) and (B) respectively. The temperatures along the bed at the end of the hot and at the end of the cold half-cycles are in the Figure 2.12 (C). In Figure 2.12 (D) the simulated concentration profiles of phenol at the end of the hot and cold half-cycles are shown for cycles 1, 2, 5, 10 and 20. These historic profiles reflect the evolution of the concentration waves during the operation of the parametric pumping system.

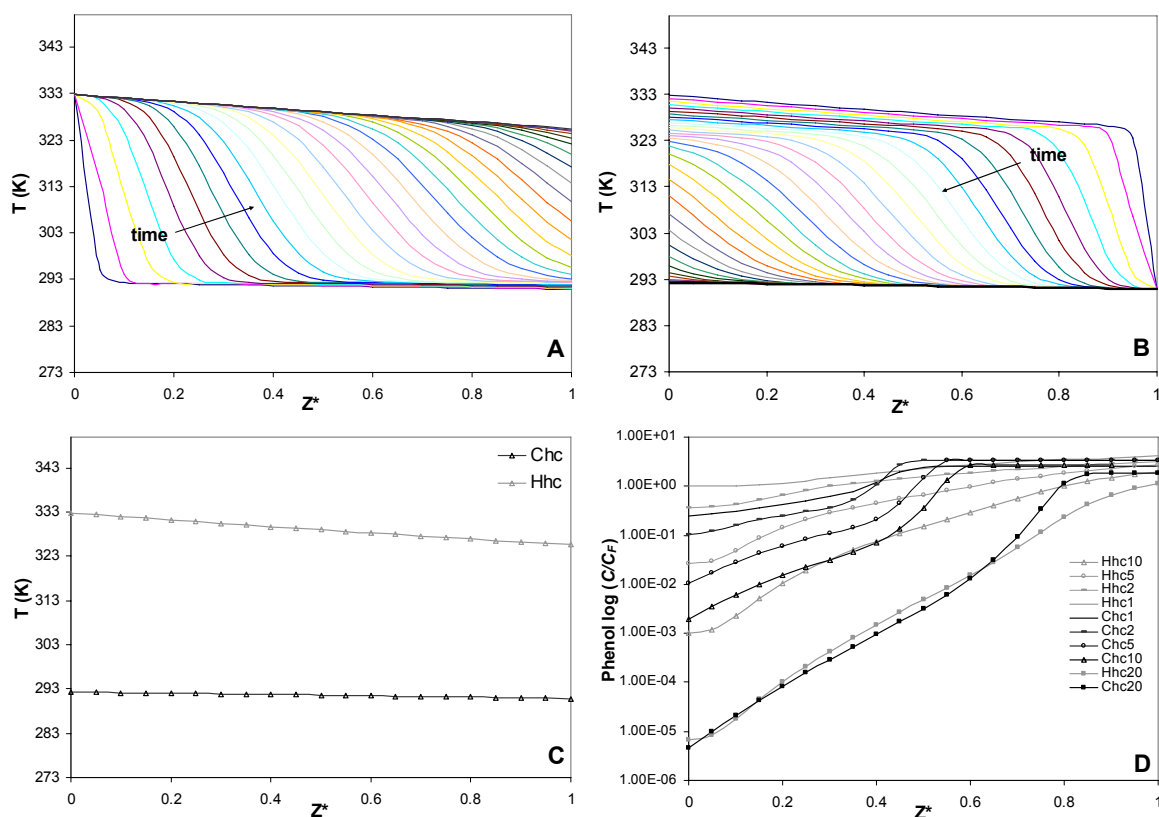


Figure 2.12 Simulated axial profiles of temperature and concentration during the operation of parametric pumping for phenol wastewater purification at the conditions corresponding to run 4. (A) Bed temperature profile evolution along the 10th hot half-cycle. (B) Bed temperature profile evolution along the 10th cold half-cycle. (C) Bed temperature profiles at the end of the hot half-cycle (Hhc) and at the end of the cold half-cycle (Chc). (D) Concentration profiles in the bed at the end of the hot half-cycle (Hhc) and cold half-cycle (Chc) for cycles 1, 2, 5, 10 and 20.

The experimental top and bottom temperatures in the bed at the conditions corresponding to run 4 are shown in Figure 2.13 along the 10 cycles of operation.

The parametric pumping unit was operated in a semi-continuous way, the aim being to obtain clean water as the bottom product and concentrated solution as the top product. Runs under different experimental conditions were carried out to ascertain the predictions of the models. The top and bottom concentrations of phenol are represented as a function of time in *Figure 2.14 – 2.17*. The experimental results were compared with the predicted by the *equilibrium* and by the *LDF* models. The characteristics of the adsorbent and the bed, the operating variables, the equilibrium isotherm and the thermal and mass transport parameters are introduced in the program to solve the previous equations.

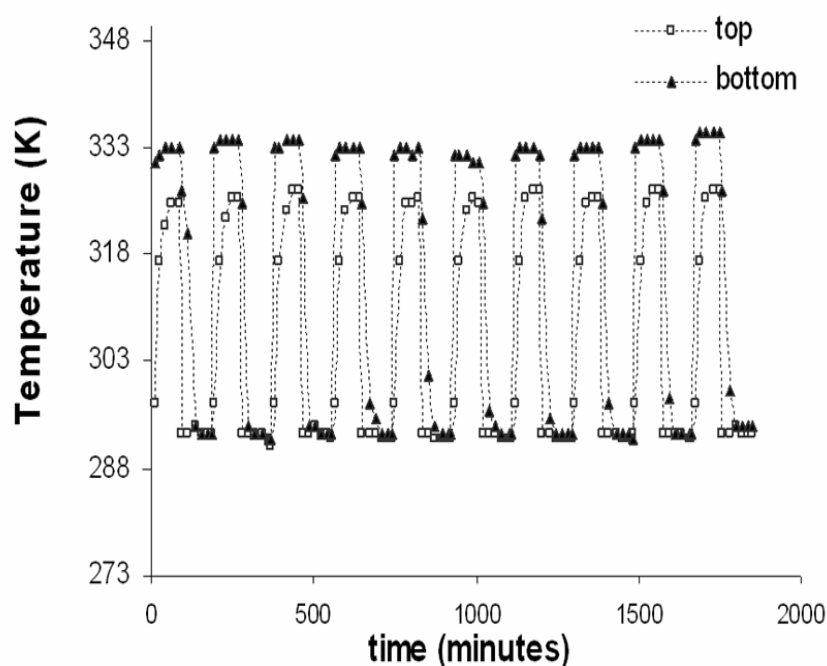


Figure 2.13 History of top and bottom temperatures measured during the recuperative parametric pumping

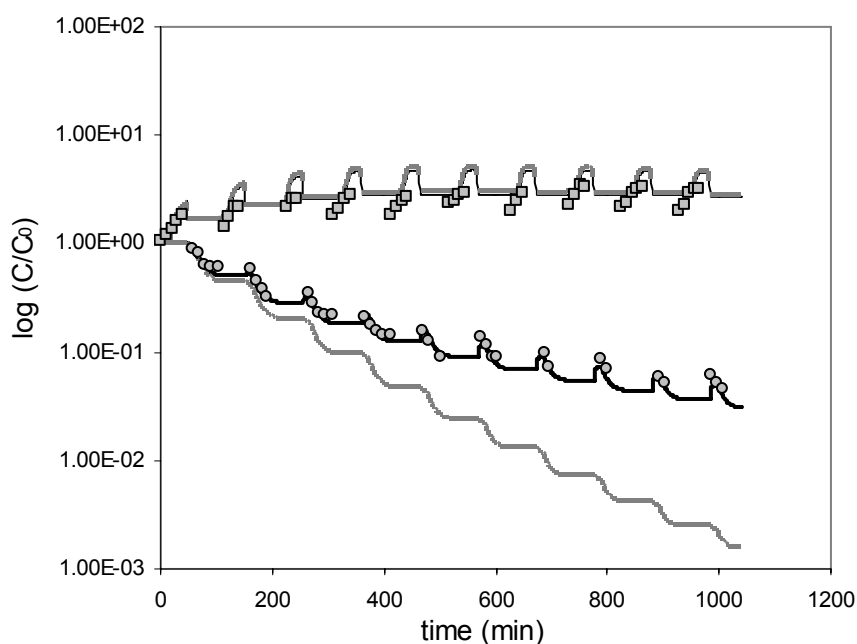


Figure 2.14 Experimental results (symbols) for the parametric pumping run 1 together with the equilibrium model (grey full lines) and the LDF model (black full lines) predictions. Top and bottom product concentrations of phenol are shown as a function of time in recuperative parametric pumping

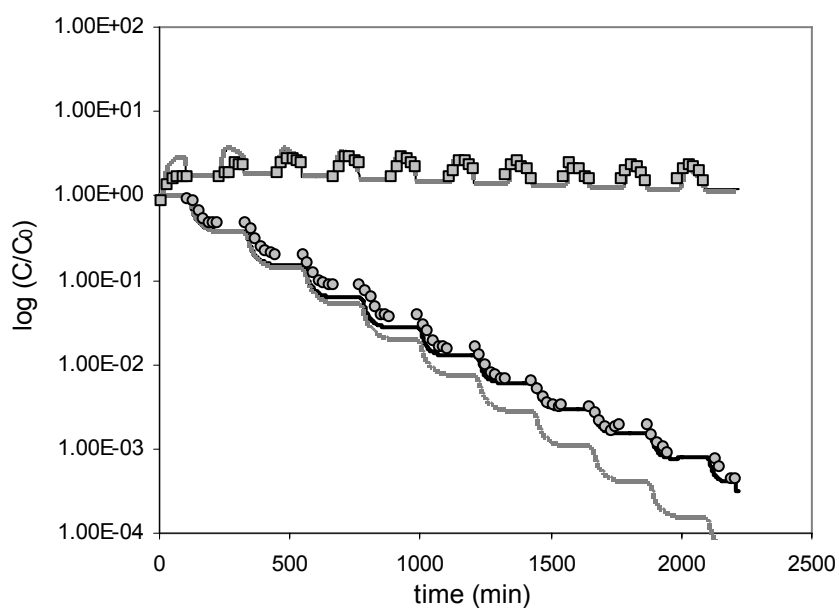


Figure 2.15 Experimental results (symbols) for the parametric pumping run 2 together with the equilibrium model (gray full lines) and the LDF model (black full lines) predictions. Top and bottom product concentrations of phenol are shown as a function of time in recuperative parametric pumping

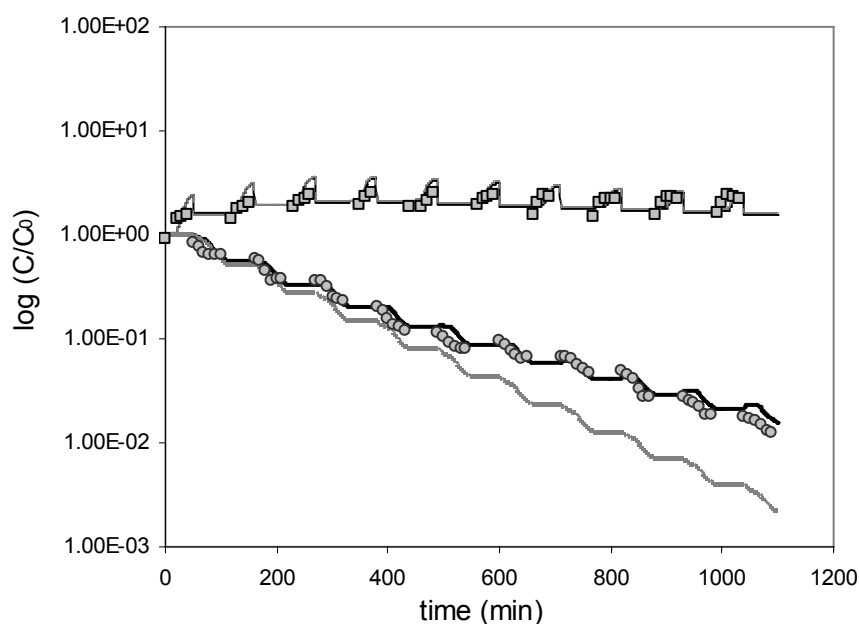


Figure 2.16 Experimental results (symbols) for the parametric pumping run 3 together with the equilibrium model (gray full lines) and the LDF model (black full lines) predictions. Top and bottom product concentrations of phenol is shown as a function of time in recuperative parametric pumping

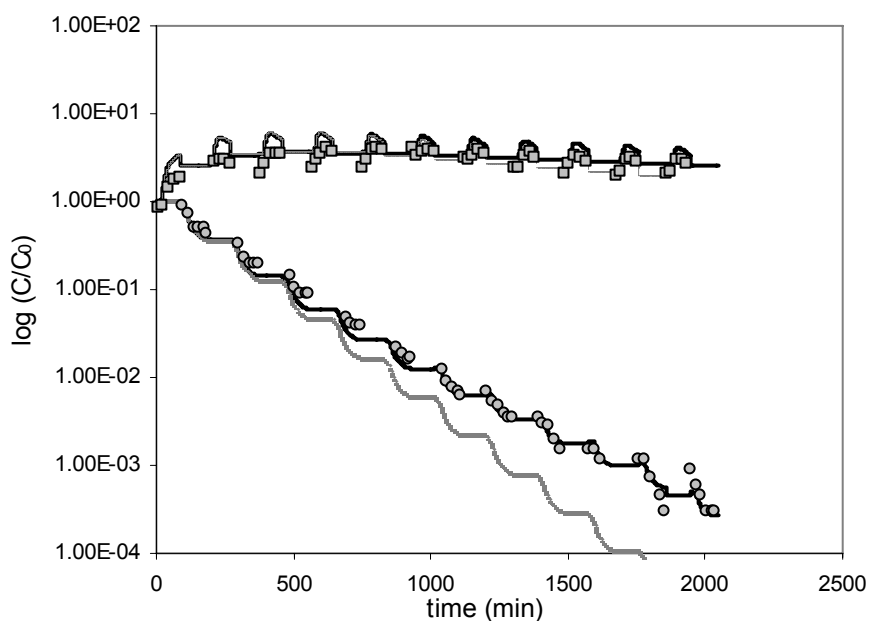


Figure 2.17 Experimental results (symbols) for the parametric pumping run 4 together with the equilibrium model (gray full lines) and the LDF model (black full lines) predictions. Top and bottom product concentrations of phenol are shown as a function of time in recuperative parametric pumping

The degree of purification of phenol varies depending on the operational conditions applied. The highest degree of purification was obtained under conditions applied in the run 4. It may be seen that the two models here used predict the first cycles of the operation for all runs.

Nevertheless, the equilibrium model with axial dispersion predicts unlimited separation so it is not appropriate for the simulation when the number of cycles increases. The Linear Driving Force model with axial dispersion, which considers also mass-transfer resistance inside the particle, is more accurate in its predictions. For the phenol, the *LDF* model seems to describe well the parametric pumping operation under the different conditions of the experimental runs. As it may be observed, the simulation predictions of the *LDF* model are in good agreement with experimental results, which indicates that the Linear Driving Force approximation is appropriate for describing mass transfer in this cyclic process.

A high level of purification was obtained after 10 cycles of the run 4 and the concentration of phenol in the bottom reservoir decreased to $C/C_F < 0.001$ and in the top reservoir triplicate that of the feeding.

2.5 Conclusions

Adsorption of phenol onto polymeric resins (Sephabeads SP206 and Sephabeads SP207) and activated carbon (Filtrisorb F400) was studied and focused on parametric pumping. Batch tests were carried out in order to make a screening of adsorbents related to the effect of temperature on the adsorptive behavior. On the basis of the separation parameter b , Sephabeads SP206 showed the higher separation potential in function of temperature for the adsorption of phenol. Dynamic studies were also done for the adsorption of phenol onto the polymeric resins and onto the activated carbon to ascertain the applicability of the LDF (Linear Driving Force) model in fixed bed. The effect of temperature on the fixed bed adsorption of phenol was also more noticeable for the polymeric resins, especially for Sephabeads SP206, rather than for the Filtrisorb F400.

Pilot scale fixed bed using Sephabeads SP206 as adsorbent was studied before operating the parametric pumping unit. Model equations including intraparticle mass transfer described by the LDF model satisfactorily predicted the breakthrough curves at pilot scale (in an 800x90 mm bed) carried out both at 293 and 333 K.

Thermal parametric pumping in recuperative mode was performed in a pilot plant using Sephabeads SP206 for phenol adsorption. By applying a $T_c = 293$ K and a $T_h = 333$ K a high level of purification was obtained; the concentration of phenol in the bottom reservoir was

going down and $C/C_F < 0.001$ from the 10th cycle, the $C_F = 544 \text{ mg L}^{-1}$. It was seen that the purification of liquid streams containing phenol might be achieved by thermal parametric pumping using Sephabeads SP206 as adsorbent. Runs under different conditions were carried out to confirm the quality of their predictions. Operational conditions define the degree of purification got by thermal parametric pumping. Two models, an *equilibrium model* with axial dispersion and a *Linear Driving Force model* with axial dispersion were used for simulating the operation of the parametric pumping unit.

In all cases, the LDF model, which has more restrictions, seems to predict better the performance of the system. Under appropriate conditions, at the 10th cycle it was possible to decrease C/C_F to 0.0003 (run 4) for phenol. A high degree of purification of phenolic wastewaters may then be achieved by thermal parametric pumping using Sephabeads SP206 as adsorbent and avoiding the use of any chemical regenerant.

2.6 Nomenclature

a	deviation in the separation parameter
A_w	wall specific area (4/D) (m^{-1})
ΔH_L	enthalpy of adsorption for the Langmuir isotherm (J mol^{-1})
b	separation parameter
C	concentration in the bulk fluid phase (g L^{-1})
C_0	initial liquid-phase concentration of phenol in the batch and in the fixed bed operation (mg L^{-1})
C^*	equilibrium liquid-phase concentration of phenol (mg L^{-1})
C_F	feed liquid-phase concentration of phenol in the operation of the parametric pumping unit (mg L^{-1})
C_{p_f}	heat capacity of the fluid $\text{kJ}/(\text{kg.K})$
C_{p_s}	heat capacity of the solid $\text{kJ}/(\text{kg.K})$
$\langle C_{BP} \rangle$	average concentration of the fluid in the bottom reservoir (mg L^{-1})

$\langle C_{TP} \rangle$	average concentration of the fluid in the top reservoir (mg L^{-1})
d_p	diameter of the particle of the adsorbent (cm)
D	bed diameter (mm)
D_{ax}	axial dispersion ($\text{m}^2\text{min}^{-1}$)
D_{pe}	the effective pore diffusivity ($\text{m}^2\text{min}^{-1}$)
D_m	molecular diffusivity ($\text{m}^2\text{min}^{-1}$)
f_h	humidity factor ($\text{g dry adsorbent/g adsorbent}$)
h_w	wall heat transfer coefficient $\text{kJ}/(\text{m}^2 \text{ s K})$
K_{ae}	axial thermal conductivity ($\text{kJ}/(\text{m.s.K})$)
K_L	parameter in the Langmuir isotherm model (L mg^{-1})
K_L^∞	equilibrium constant corresponding to the Langmuir model (L mg^{-1})
k_{LDF}	Linear Driving Force (LDF) kinetic rate constant (min^{-1})
L	bed length (m)
$\overline{m}(T)$	capacity parameter in the separation parameter b
m	average slope in the separation parameter b
M_B	molecular weight of solvent B (g mol^{-1})
n	number of cycles
Pe	Péclet number
Pe_h	thermal Péclet number
Q	constant in the Langmuir isotherm model (mg g^{-1}) related to the adsorptive capacity
$Q_{(\pi/\omega)}$	reservoir displacement volume (cm^3)
Q_c	flowrate of the fluid in the column during the cold half-cycle (mL min^{-1})
Q_h	flowrate of the fluid in the column during the cold half-cycle (mL min^{-1})

Q_{BP}	flowrate of removing the product from the bottom reservoir (mL min^{-1})
Q_{TP}	flowrate of removing the product from the top reservoir (mL min^{-1})
q	phenol adsorbed per dry mass of adsorbent at a certain time (mg g^{-1})
q^*	phenol adsorbed per dry mass of adsorbent in equilibrium with the phenol concentration in solution at a certain time (mg g^{-1})
Re	Reynolds number
r_p	radius of the particle of the adsorbent (m)
t	time (min)
t_c	cold half-cycle time (min)
t_h	hot half-time (min)
T	absolute temperature (K)
T_c	feeding temperature during the cold half-cycle (K)
T_h	feeding temperature during the hot half-cycle
T_{amb}	ambient temperature (K)
U	feed flow rate ($\text{cm}^3 \text{min}^{-1}$)
u_0	superficial velocity (m min^{-1})
u_i	interstitial velocity (m min^{-1})
V	volume of the solution (L)
V_U	volume percolated during hot-half cycle (L)
V_A	molar volume of solute a at its normal boiling temperature ($\text{cm}^3 \text{mol}^{-1}$)
W	dry weight (g) of the corresponding adsorbent
z	axial coordinate in the bed (cm)
Z^*	normalized axial coordinate in the bed

Greek Letters

ε	bed porosity
ε_p	porosity of the adsorbent
ϕ	dimensionless association factor of solvent B
ϕ_B	fraction of $Q_{(\pi/\omega)}$ that is withdrawn as bottom product
ϕ_T	fraction of $Q_{(\pi/\omega)}$ that is withdrawn as top product
η	viscosity of the solution (Pa.s)
η_B	viscosity of solvent B (cp)
Ω	LDF factor, which is equal to 3, 8 or 15 for slab, cylindrical or spherical geometry
ρ	density of the adsorbent (g L ⁻¹)
ρ_f	density of the fluid (g L ⁻¹)
τ	tortuosity of the adsorbent
ω	frequency of temperature change

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3. Removal of salicylic acid from effluents using natural and polymeric adsorbents¹

3.1 Introduction

Salicylic acid is a compound produced from phenol (Hanesian and Perna, 2000), which was once used as a painkiller being later replaced by aspirin since it causes severe stomach pain. Salicylic acid has many applications, but the most popular one is the manufacture of acetylsalicylic acid (aspirin), which is accompanied by the production of phenolic wastewaters. Aspirin (acetylsalicylic acid-ASA) is the salicylate ester of acetic acid and when ingested becomes in its active form, salicylic acid (Insel, 1990; Lutomski *et al.*, 1995). More than 10,000 tons of aspirin are consumed each year only in the United States.

Traditionally, drugs were rarely viewed as potential environmental pollutants and only recently started to capture the attention of the scientific or popular press (Velagaleti, 1997;

¹ Based on the papers:

Fixed bed adsorption of salicylic acid onto polymeric adsorbents and activated charcoal By M. Otero, M. Zabkova, C. A. Grande, A.E. Rodrigues, Industrial & Engineering Chemistry Research, 44, 927-936 (2005)

Salicylic acid adsorption onto Sephabeads SP206 in view of its purification by thermal parametric pumping. by M. Otero, M. Zabkova, A.E. Rodrigues, Adsorption 11, 887-892 (2005)

Halling-Sorenson *et al.*, 1998; Montague, 1998; Raloff, 1998; Daughton and Ternes, 1999); nevertheless, salicylic acid, which is a xenobiotic organic compound (Erikson *et al.*, 2003) may have several important metabolic effects that contribute to its toxicity (Kaplan *et al.*, 1954; Miyahara and Karlen, 1965; Schwart and Landry, 1965; Thurston *et al.*, 1970; Done and Temple, 1971; Hmicek *et al.*, 1974; Walters *et al.*, 1983; Bartels and Lund-Jacobsen, 1986). Also, if drugs are not captured from wastewaters during treatment they will remain in sewage sludge, which is actually a major pathway by which drugs enter the environment (Montague, 1998).

Adsorptive processes are an option for the purification of wastewaters containing pharmaceuticals. An additional interesting aspect of sorption operations, especially when dealing with valuable molecules, is their ability to concentrate solutes.

Traditional fixed bed adsorption systems suffer from two weaknesses: one is the need for a chemical regenerant, which implies an additional waste disposal problem and the other is the lack of efficiency, since only a fraction of the adsorbent is used in fixed bed operation.

As an alternative, thermal parametric pumping is a cyclic process based upon the fact that the adsorption equilibrium isotherm of solutes changes with temperature. A cyclic change of temperature in simultaneous with flow reversal will enable the separation process. In thermal parametric pumping, the temperature change can be imposed through the bed jacket in direct mode or through temperature change of the fluid stream in recuperative mode. If the feed stream (wastewater) passes through a bed of adsorbent in upward flow at a “hot” temperature and later in downward flow at a “cold” temperature, this cyclic process will produce a concentrated solution at a top reservoir and a solute-free solution in the bottom one. This will make possible the purification of salicylic acid industrial wastewaters without spending chemicals for regeneration and therefore avoiding a new pollution problem.

The aim of this chapter was to study the fixed bed adsorptive performance of polymeric adsorbents Sephabeads SP206 and Sephabeads SP207 and a well-known standard activated charcoal Filtrasorb F400 for the uptake of salicylic acid from aqueous solution. The influence of bed height and feed flow rate were considered. Special attention was given to the temperature effect on the adsorption of salicylic acid, purification technologies such as thermal parametric pumping being based on a marked differential adsorptive behavior in function of temperature. In this chapter, three adsorbents were also compared according to

their thermal separation potential. With the Sephabeads SP206 was subsequently used in the parametric pumping experiments to evaluate the feasibility of this technology for salicylic acid wastewater treatment.

3.2 Experimental section

3.2.1 Chemicals and adsorbents

Salicylic acid ($C_7H_6O_3$) was purchased from Sigma-Aldrich (Spain). Two different polymeric resins were used in this study: Sephabeads SP206 and SP207 (Mitsubishi Chemical Corporation), purchased from Resindion (Italy) and activated carbon Filtrasorb F400 was provided by Chemviron Carbon (Belgium). Physical characteristics data of all the adsorbents as supplied by the manufacturers are listed in *Table 2.1* (Chapter 2). The solutions of salicylic acid were prepared with degassed distilled water.

3.2.2 Batch adsorption studies

Adsorption equilibrium experiments were carried out by contacting the corresponding amount of adsorbent with 100 mL of salicylic acid solution in 250 mL Erlenmeyer flasks. Initial concentration on the solution was around 100 mg L^{-1} in all experiments. Adsorption equilibrium isotherms were measured by batch equilibration placing the volumetric flasks in a shaking mixer at 150 rpm and using a thermostatic bath for temperature control.

Equilibrium experiments were carried out at 293, 310 and 333 K for each adsorbent-salicylic acid system. After shaking for 48 h, the solution was separated from the adsorbent and the final concentration of salicylic acid in solution was determined by measuring the absorbance at 295 and 272 nm respectively by using the UV-visible spectrophotometer Jasco (model 7800, Japan).

3.2.3 Fixed bed adsorption and desorption of salicylic acid

Dynamic column experiments were carried out in a laboratory scale column with a peristaltic pump Watson-Marlow used to pump the salicylic acid solution into the column. The temperature of the feed solution was maintained by a thermostatic bath (Edmund Bühler). Salicylic acid concentration at the column outlet was determined by measuring the absorbance at a wavelength of 295 nm by using the UV-visible spectrophotometer Jasco (model 7800, Japan).

Runs at three different temperatures were carried out for each of the adsorbents by feeding the column with solutions at 293K, 310K and 333K. Different flow rates (10 and 15 mL min⁻¹) were also tested. With respect to the height of the bed, lengths of 15 and 30 cm were used for the polymeric adsorbents and beds of 10 and 5 cm for the activated carbon. Bed diameter was 1 cm for all runs. The feed concentration was around 100 mg L⁻¹ of salicylic acid in all cases.

The elution profiles of the salicylic acid saturated beds were also obtained. Distilled water was pumped through the columns at the same flow rate and temperature as those used for the saturation.

3.2.4 Operation of the pilot parametric pumping pilot plant

An automated pilot plant was used to carry out an experiment of water purification with a salicylic acid containing feed. *Figure 3.1* shows a schematic diagram of the unit used for parametric pumping experiment. Prior to the parametric pumping experiment, breakthrough curves of a solution with around 100 mg L⁻¹ of salicylic acid were performed at 293 and 333K to check effects of scale-up (axial dispersion, adsorbent packing and heat losses).

The parametric pumping experiment was performed with the following protocol: after saturation of the bed at 293K, the salicylic acid solution was pumped through the bed of Sephabeads SP206 in upward flow (hot half-cycle, at 333K) followed by downward flow pumping of the solution (cold half-cycle, at 293K). This was repeated for ten cycles, each cycle comprising one hot and one cold half-cycle. The top reservoir receives the concentrated salicylic acid product when the solution is pumped through the column in upward flow and the bottom reservoir receives the purified effluent when the solution is pumped in downward flow. The system was operated in a recuperative mode, i.e., the temperature change was carried out by the solution itself, which is heated or cooled by means of thermostatic baths). Direct mode implies that the temperature change is imposed through the column wall, but the recuperative mode is more appropriate for industrial purposes as this allows for larger diameter columns (Ramalho *et al.*, 1991). The combination of both modes has also been studied (Ghasem, 2003) but under appropriate conditions one can expect to get a concentrated solution at the top of the column and a free-solute effluent at the bottom, hence thermal energy is used as regenerant.

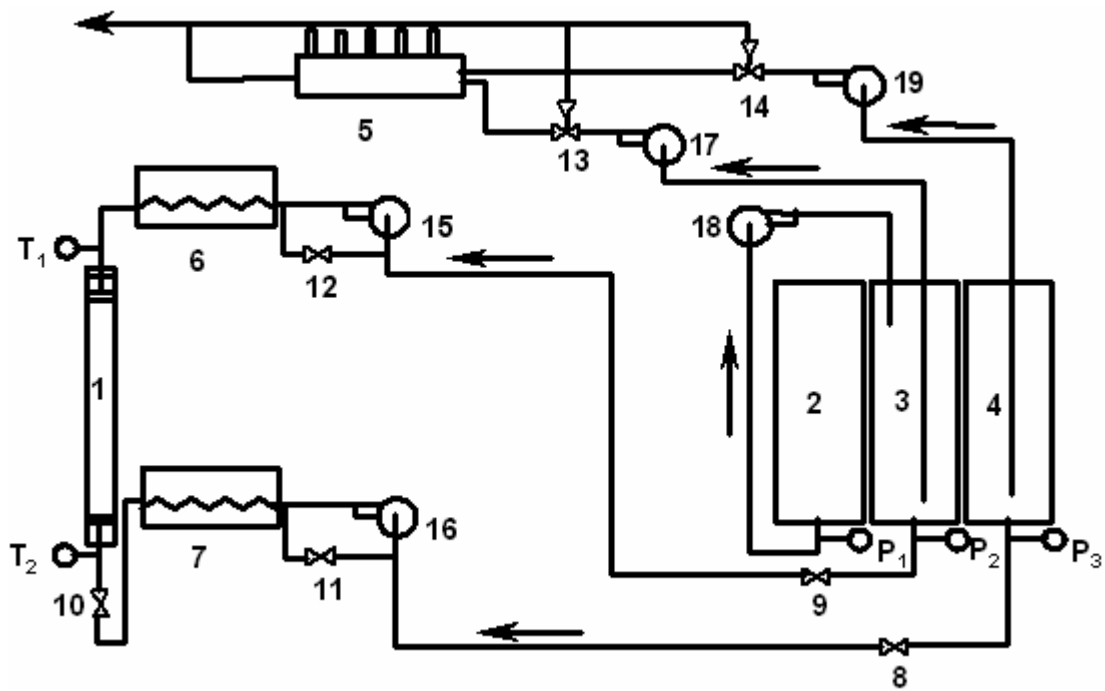


Figure 3.1 Experimental setup of the parametric pumping pilot plant.

Legend:

- (1) Glass column G90-Amicon
- (2) Feed reservoir
- (3) Top reservoir
- (4) Bottom reservoir
- (5) Fraction collector Gilson
- (6)–(7) Heat exchangers
- (8)–(12) Two ways solenoid valves
- (13)–(14) Three ways solenoid valves
- (15)–(16) Peristaltic pumps Watson Marlow
- (17)–(19) Peristaltic pumps Gilson
- (T1)–(T2) Thermocouples (type K)
- (P1)–(P3) Pressure transducers Schwaevitz (type P510)

3.3 Mathematical model

3.3.1 Thermal separation potential

The amount of salicylic acid adsorbed onto adsorbent q^* (mg g⁻¹ dry resin), was calculated by a mass balance relationship:

$$q^* = (C_0 - C^*) \frac{V}{W} \quad 3.1$$

where C_0 (mg L⁻¹) and C^* (mg L⁻¹) are the initial and equilibrium liquid-phase concentrations, respectively, V the volume of the solution (L) and W the dry weight (g) of the corresponding polymeric resin.

The equilibrium was described by the Langmuir and multisite Nitta model (Nitta *et al.*, 1984) for homogeneous adsorbents using statistical thermodynamic arguments.

Langmuir isotherm model:

$$q^*(z, t) = \frac{q_m K_L C^*}{1 + K_L C^*} \quad 3.2$$

Nitta isotherm model:

$$\theta = K_N C^* (1 - \theta)^n \quad 3.3$$

where $\theta = q^*/q_m$ is the fractional amount of the species in the adsorbed phase, q_m is the saturation capacity and n is the number of neighboring sites occupied by the adsorbate. The K_L , K_N are the constants corresponding to the Langmuir and to the Nitta model, respectively indicated by the subindexes L and N , which in a general form are given by:

$$K = K^\infty \exp\left(-\frac{\Delta H}{RT}\right) \quad 3.4$$

Taking into account the equilibrium results, the effect of temperature can be assessed for each of the systems salicylic acid - adsorbent considering the corresponding separation parameter. The separation parameter, b , introduced by Pigford (Pigford *et al.*, 1973) which indicatives of the separation potential.

$$b = \frac{a}{1 + m} \quad 3.5$$

where $\bar{m} = \frac{m(T_1) + m(T_2)}{2}$ is the average slope and $a = \frac{m(T_1) - m(T_2)}{2}$ is the deviation

considering $T_1 < T_2$. The capacity parameter is defined as: $m(T) = \frac{(1 - \varepsilon)\rho f_h K(T)}{\varepsilon}$, where

$K(T)$ is the slope of the initial linear region of the isotherm, which has been represented

either by $K(T) = QK_L$ or by $K(T) = q_m K_N$ corresponding to each temperature, ε is the bed porosity, ρ is the density of the adsorbent and f_h is the humidity factor.

3.3.2 Mathematical model

The mathematical model used comprises the mass balance in the liquid phase, the nonlinear adsorption equilibrium isotherm and a linear driving force (LDF) rate equation to describe the diffusional mass transfer inside adsorbent particles; moreover to simulate the operation of the parametric pumping unit a global energy balance was considered (Glueckauf and Coates, 1947; Shim *et al.*, 2004). The balance to the reservoirs containing the product from the hot and the cold cycles, top and bottom reservoirs are also considered. In the case of the adsorption and desorption runs in fixed bed, neither the balance in the reservoirs neither the energy balance were included.

Mass balance

The mass balance in a bed volume element is:

$$D_{ax} \frac{\partial^2 C(z,t)}{\partial z^2} - u_i \frac{\partial C(z,t)}{\partial z} = \frac{\partial C(z,t)}{\partial t} + \frac{1-\varepsilon}{\varepsilon} \rho f_h \frac{\partial \langle q(z,t) \rangle}{\partial t} \quad 3.6$$

where D_{ax} is the axial dispersion, u_i is the interstitial velocity, ε is the bed porosity, z is the axial position, t is the time variable, C is the concentration in the bulk fluid phase, $\langle q \rangle$ is the average adsorbed phase concentration in the particle, ρ is the density of the adsorbent and f_h its humidity factor. The axial dispersion, D_{ax} , was obtained from the following expression (Guiochon *et al.*, 1994a): $\frac{u_0 d_p}{D_{ax}} = (0.2 + 0.011 \text{Re}^{0.48})$ where $\text{Re} = \frac{u_i \rho_s \varepsilon d_p}{\eta}$.

Intraparticle mass transfer

The mass-transfer rate inside particles can be represented by the Linear Driving Force model:

$$\frac{\partial \langle q(z,t) \rangle}{\partial t} = k_s [q^*(z,t) - \langle q(z,t) \rangle] \quad 3.7$$

where k_s is the effective mass transfer coefficient, $q^*(C)$ is the adsorbed phase concentration in equilibrium with the bulk concentration.

The overall effective linear driving force rate constants for the experiments were estimated from the following correlation (Farooq and Ruthven, 1990; Silva and Rodrigues, 1997):

$$\frac{1}{k_s} = \frac{r_p}{3k_f} \rho f_h \frac{\partial q^*}{\partial C} + \frac{r_p^2}{15D_{pe}} \rho f_h \frac{\partial q^*}{\partial C} = \frac{r_p}{3k_f} \rho f_h \frac{\partial q^*}{\partial C} + \frac{1}{k_{LDF}} \quad 3.8$$

which considers macropore and film resistances to the mass transfer and where D_{pe} is the effective pore diffusivity, r_p is the radius of the particle of the adsorbent, 15 is the Ω factor that is equal to 15 for spherical particles (Azevedo, 2001), k_s is the global mass transfer coefficient, k_{LDF} is the linear driving force kinetic rate constant, k_f is the external film mass transfer coefficient, ρ and f_h are the density and the humidity factor of the adsorbent and the derivative $(\frac{dq^*}{dC})$ represents slope of the equilibrium data.

The external film mass transfer coefficient k_f was correlated by the Ranz-Marshall equation (Yang, 1987):

$$Sh = \frac{k_f d_p}{D_m} = 2.0 + 0.6 \left(\frac{\eta}{\rho_s D_m} \right)^{1/3} \left(\frac{u_0 \rho_s d_p}{\eta} \right)^{1/2} = 2.0 + 0.6 Sc^{1/3} Re^{1/2} \quad 3.9$$

where Sh , Sc and Re stand for the Sherwood, Schmidt and Reynolds numbers, respectively.

The values of the molecular diffusivity, D_m , of salicylic acid in water was approximated by

the Wilke – Chang equation (Wilke and Chang, 1955): $D_m = 7.4 \times 10^{-8} \frac{T \sqrt{\phi M}}{\eta V_m^{0.6}}$ where $T(K)$

is the absolute temperature, η its viscosity (cP). The molar volume of the adsorbate at its normal boiling temperature V_m ($\text{cm}^3 \text{mol}^{-1}$) was estimated by Le Bas method (Reid *et al.*, 1987).

Energy balance

A global energy balance for the column was used:

$$\begin{aligned} & \left[\rho_f C p_f \varepsilon + \rho C p_s (1 - \varepsilon) \right] \frac{\partial T(z, t)}{\partial t} = \\ & = K_{ae} \frac{\partial^2 T(z, t)}{\partial z^2} \pm \rho_f C p_f u_0 \frac{\partial T(z, t)}{\partial z} - h_w A_w (T - T_{amb}) + (-\Delta H) \frac{\partial \langle q(z, t) \rangle}{\partial t} \end{aligned} \quad 3.10$$

where K_{ae} is the axial thermal conductivity, h_w is the heat transfer coefficient of the wall of the column and A_w is the wall specific area, ρ_f and ρ are the densities of the fluid and adsorbent, and C_{pf} and C_{ps} are the heat capacities of the fluid and of the adsorbent, respectively. Considering $z = 0$ at the bottom of the column and $z = L$ at the top, in Eq.3.10 the term $\pm \rho_f C_{pf} u_0 \frac{\partial T(z, t)}{\partial z}$ has the “+” sign for the cold half-cycle downwards, and the “-” sign for the hot half-cycle upwards.

Balance of the reservoirs

Hot half-cycle

$$\langle C_{BP} \rangle = \langle C_{BP} \rangle_{n-1} \quad 3.11$$

$$\langle C_{TP} \rangle = \frac{(1 - \phi_B) \langle C(L, t) \rangle_n}{(1 + \phi_T)} + C_F \frac{(\phi_B + \phi_T)}{(1 + \phi_T)} \quad 3.12$$

Cold half-cycle

$$\langle C_{BP} \rangle = \langle C(0, t) \rangle_n \quad 3.13$$

where $\langle C_{BP} \rangle$ and $\langle C_{TP} \rangle$ are the average concentration of salicylic acid in the fluid in the bottom and in the top reservoirs, respectively, ϕ_B and ϕ_T are the fraction of the total reservoir displacement volume, $Q(\pi / \omega)$, that are withdrawn as product from the bottom and the top reservoirs, respectively, and n refers to the number of cycles.

Boundary and Initial conditions

In the case of the fixed bed adsorption and desorption, the boundary conditions for the mass balance (Eq 3.6) are the Danckwerts boundary conditions:

$$z = 0 \quad D_{ax} \frac{\partial C(z, t)}{\partial z} \Big|_{z=0} = u_i (C(0, t) - C_0) \quad 3.14$$

$$z = L \quad \frac{\partial C(z, t)}{\partial z} \Big|_{z=L} = 0 \quad 3.15$$

The initial conditions for the adsorption step are for a clean bed:

$$C(z, 0) = 0 \quad 3.16$$

$$q(z,0) = 0 \quad 3.17$$

For the simulation of the desorption step, initial conditions are:

$$C(z,0) = C_e \quad 3.18$$

$$q(z,0) = q^*(C_e) \quad 3.19$$

The boundary conditions for the equations included in the parametric pumping model are:

Hot half-cycle

$$z = 0 \quad C(0,t) = \langle C_{BP} \rangle_n; \quad T = T_h \quad 3.20$$

$$z = L \quad \frac{\partial C(z,t)}{\partial z} = 0; \quad \frac{\partial T(z,t)}{\partial z} = 0 \quad 3.21$$

Cold half-cycle

$$z = 0 \quad \frac{\partial C(z,t)}{\partial z} = 0; \quad \frac{\partial T(z,t)}{\partial z} = 0 \quad 3.22$$

$$z = L \quad C(L,t) = \langle C_{TP} \rangle_n; \quad T = T_c \quad 3.23$$

The initial conditions were:

$$C(z,0) = C_F; \quad T(z,0) = T_0 \quad 3.24$$

The partial differential equations corresponding to the fixed bed adsorption and desorption were solved using the software package *gPROMS*[®] for **g**eneral **PRO**cess **MO**delling **S**ystem. The orthogonal collocation method on finite elements (OCFE) was used with 50 finite elements and two interior collocation points in each element of the adsorption bed. The parametric pumping model was solved with a package (Davesac *et al.*, 2000) previously developed in Visual Basic.

3.4 Results and discussion

3.4.1 Thermal separation potential

Adsorption isotherms

The experimental adsorbed concentrations as a function of liquid phase concentration corresponding to the salicylic acid adsorption onto each of the adsorbents at each of the

temperatures considered are shown in *Figure 3.2*. The obtained fittings considering Langmuir and Nitta isotherm models are reported in *Table 3.1*. As it can be seen from *Figure 3.2*, the Nitta isotherm model describes better the equilibrium of salicylic acid onto the adsorbents than Langmuir isotherm model.

Table 3.1 Equilibrium determined for the adsorption of salicylic acid onto Filtrasorb F400 and Sephabeads SP206 and SP207

model	parameters	Filtrasorb F400	Sephabeads SP207	Sephabeads SP206
Langmuir	q_m (mg g ⁻¹)	351.0	81.6	45.2
	K_L^∞ (L mg ⁻¹)	1.85x10 ⁻⁵	2.03x10 ⁻⁷	1.27x10 ⁻⁸
	ΔH_L (kJ mol ⁻¹)	-19.69	-27.46	-37.19
Nitta	q_m (mg g ⁻¹)	432.8	91.5	66.2
	K_N^∞ (L mg ⁻¹)	1.51x10 ⁻⁵	8.48x10 ⁻⁸	1.41x10 ⁻⁸
	n	1.6	1.7	1.7
	ΔH_L (kJ mol ⁻¹)	-20.29	-30.58	-36.70

The values of the separation parameter (Eq. 3.5) allow easy comparison of the feasibility of thermal parametric pumping as purification process for different solute-adsorbent systems. As it may be observed in *Table 3.2* the largest b values are those corresponding to the system salicylic acid-Sephabeads SP206.

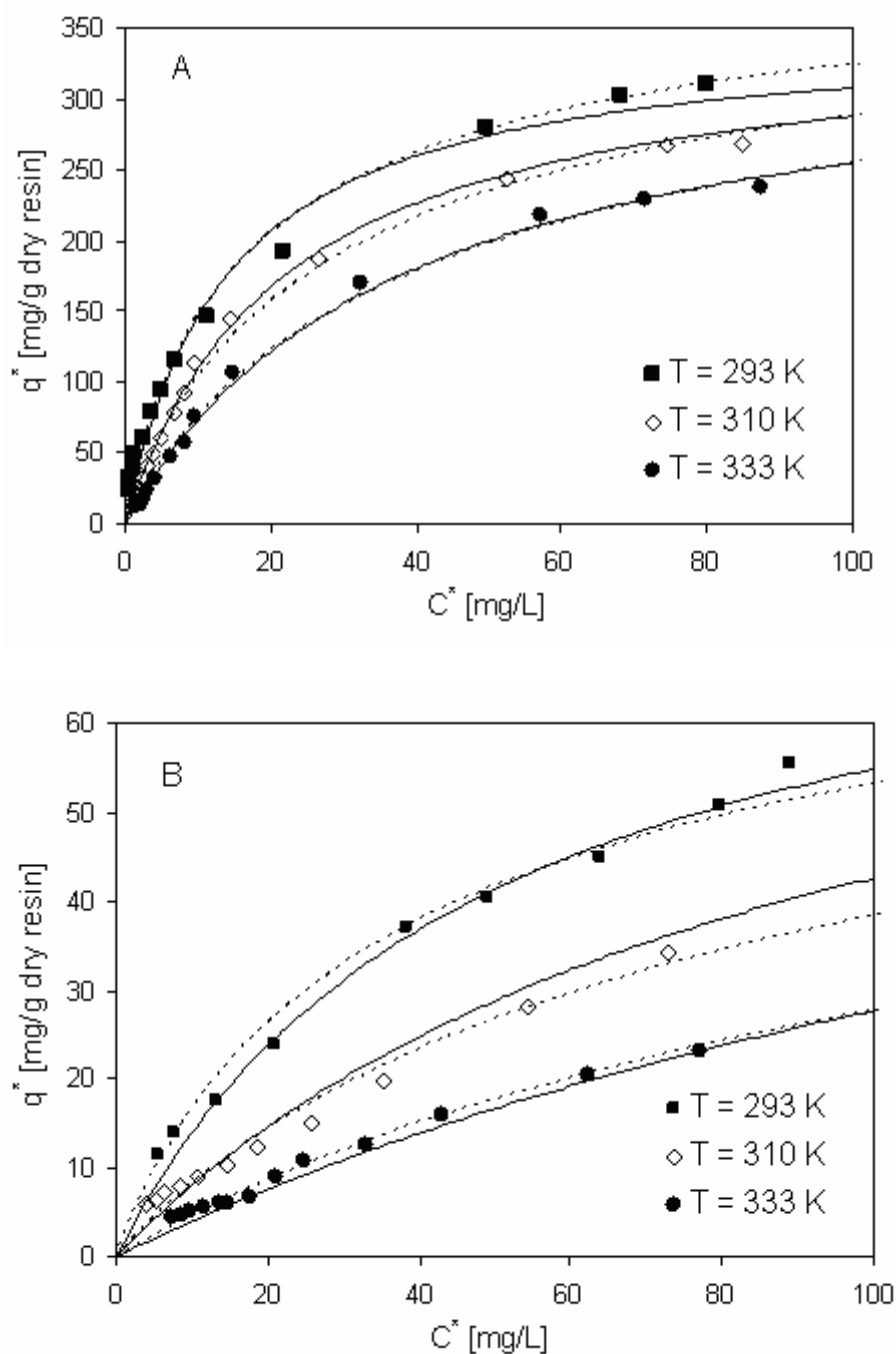


Figure 3.2 Experimental adsorption equilibrium, q^* versus C^* , for the adsorption of salicylic acid onto Filtrasorb F400 (A), Sephabeads SP207 (B) at different temperatures. Fittings to Langmuir (full lines) and Nitta (dotted lines) models are shown together with the experimental data points

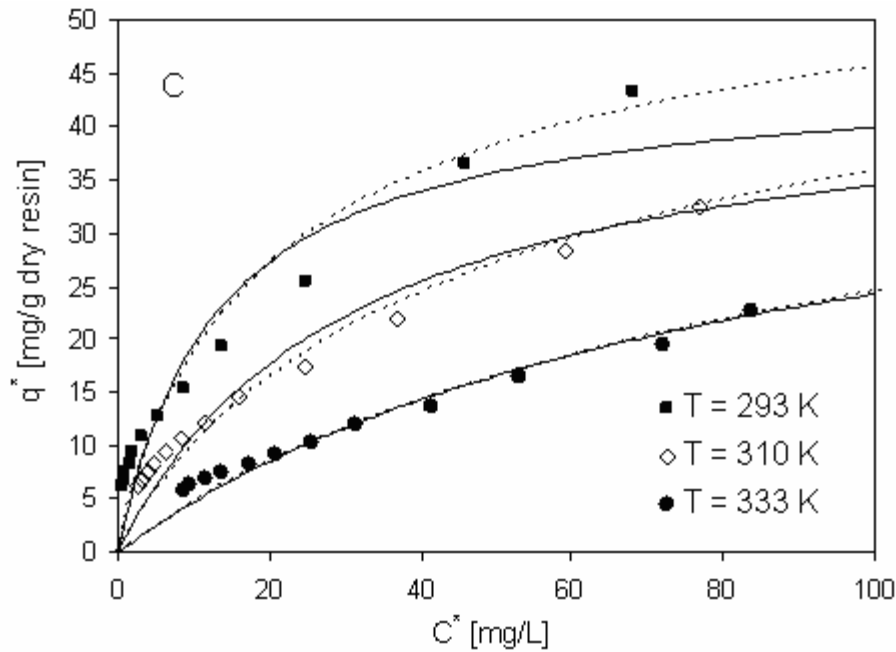


Figure 3.2 (continued) Experimental adsorption equilibrium, q^* versus C^* , for the adsorption of salicylic acid onto Sephabeads 206 (C) at different temperatures. Fittings to Langmuir (full lines) and Nitta (dotted lines) models are shown together with the experimental data points

Table 3.2 Separation parameter, b , corresponding to the different systems adsorbent-salicylic acid here considered

Temperature range	293K-310K		310K-333K		293K-333K	
model	Langmuir	Nitta	Langmuir	Nitta	Langmuir	Nitta
Filtrisorb F400	0.22	0.22	0.26	0.27	0.45	0.46
Sephabeads SP207	0.30	0.33	0.35	0.39	0.59	0.64
Sephabeads SP206	0.40	0.39	0.46	0.46	0.72	0.72

3.4.2 Laboratory scale fixed bed adsorption and desorption of salicylic acid

Experimental results corresponding to fixed bed adsorption of salicylic acid onto the adsorbents here considered are shown in Figure 3.3- Figure 3.5, desorption are shown in Figure 3.6. Full lines correspond to simulated results with the model including the mass balance equation, the Nitta equilibrium isotherm and the intraparticle mass transfer considering the global coefficient. No fitting parameters were applied for prediction of the

experimental data. The overall effective linear driving force rate constant was calculated by including the estimated external film mass transfer and pore diffusion resistance. Model parameters are reported in *Table 3.3* for all the systems considered together with the calculated k_f and the resulting values of k_s . Schmidt numbers, Sc at temperatures 293, 310, 333 K for salicylic acid were 1377, 817 and 561.

Effect of the temperature

The effect of temperature on the fixed bed performance of the adsorbents considered with respect of salicylic acid may be seen in *Figure 3.3*, which shows runs at 293, 310 and 333K. In all cases, the adsorption capacity of the bed decreases with increasing temperature, i.e., the adsorption is favored by lowering temperature. As it was for the batch tests, this is especially evident for the polymeric resins here used, which adsorption capacity of salicylic acid is strongly affected by temperature.

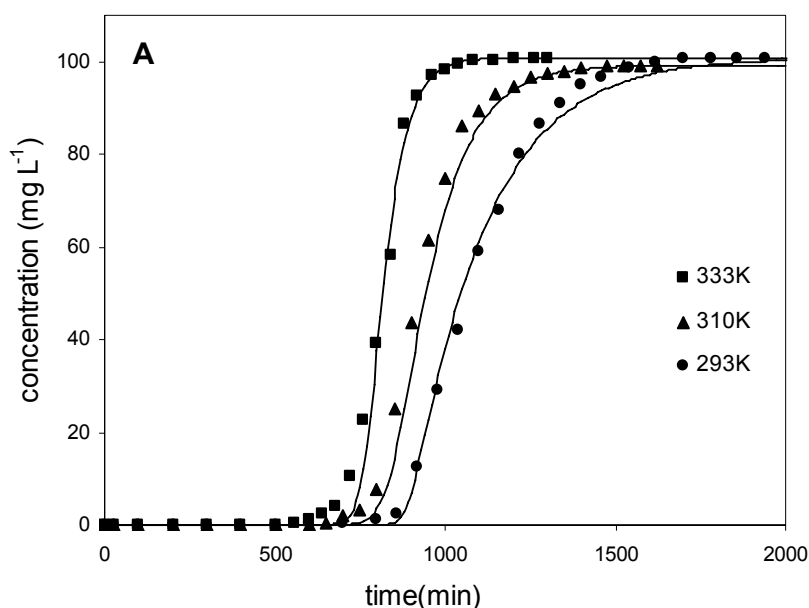


Figure 3.3 Effect of temperature on the fixed bed adsorption of salicylic acid onto Filtrasorb F400 (A). The bed length was 10 cm for (A) and solution was fed at three different temperatures (293K, 310K and 333K) at a flow-rate of 10 mL min⁻¹. Symbols are the experimental data and full lines are the simulated results obtained by the LDF model

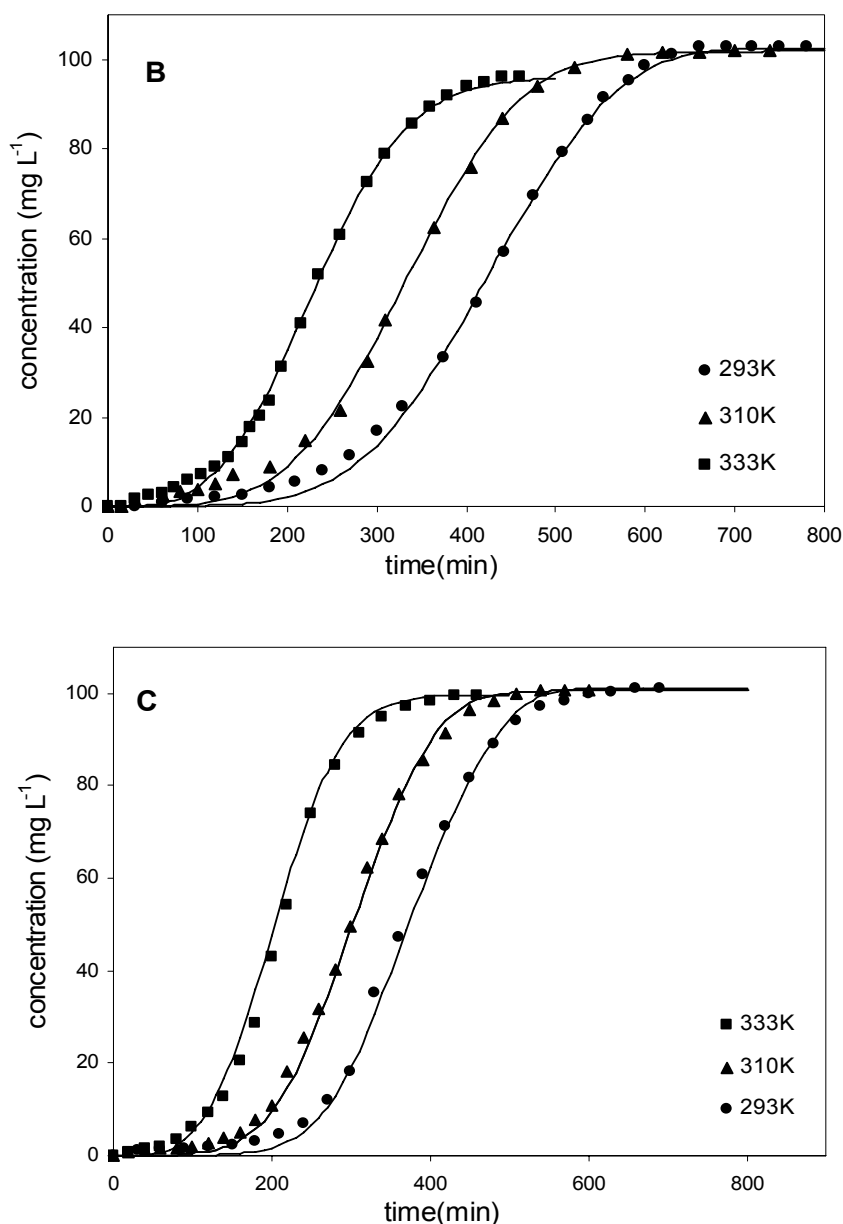


Figure 3.3 (continued) Effect of temperature on the fixed bed adsorption of salicylic acid onto Sephabeads SP207 (B) and Sephabeads SP206 (C). The bed length was 30 cm for (B) and (C) and solution was fed at three different temperatures (293K, 310K and 333K) at a flow-rate of 10 mL min^{-1} . Symbols are the experimental data and full lines are the simulated results obtained by the LDF model

In the case of the activated carbon, the effect of temperature on the adsorption of salicylic acid is not so marked, even though its adsorptive capacity is much higher than the ones of Sephabeads SP206 and SP207. From these results, the polymeric resins, especially Sephabeads SP206, would be more appropriate for carrying out a thermal parametric pumping process for the purification of salicylic acid, as it was also indicated by the separation parameter b .

Table 3.3 Parameters used for estimating D_{ax} and the intraparticle mass transfer coefficients k_f and k_s for the different fixed bed systems considered

adsorbent	T (K)	L (cm)	Flow-rate (mL min ⁻¹)	Re	D_{ax} (cm ² min ⁻¹)	Sh	D_m (cm ² min ⁻¹)	k_f (cm min ⁻¹)	k_s (min ⁻¹)
Filtrisorb F400	293	10	10	1.45	4.18	10.0	4.46x10 ⁻⁴	0.064	0.005
	310			2.31	4.12	10.5	4.72x10 ⁻⁴	0.071	0.013
	333			3.13	4.07	10.8	5.07x10 ⁻⁴	0.078	0.031
	293	10	15	2.18	6.19	11.9	4.46x10 ⁻⁴	0.075	0.005
	310			3.47	6.08	12.4	4.72x10 ⁻⁴	0.084	0.013
	333			4.70	5.99	12.7	5.07x10 ⁻⁴	0.092	0.032
	293	5	10	1.45	4.18	10.0	4.46x10 ⁻⁴	0.064	0.005
	310			2.31	4.12	10.5	4.72x10 ⁻⁴	0.071	0.013
	333			3.13	4.07	10.7	5.07x10 ⁻⁴	0.078	0.031
Sephabeads SP207	293	30	10	0.83	2.42	8.1	4.46x10 ⁻⁴	0.090	0.014
	310			1.32	2.40	8.4	4.72x10 ⁻⁴	0.100	0.043
	333			1.79	2.37	8.6	5.07x10 ⁻⁴	0.109	0.075
	293	30	15	1.24	3.60	9.4	4.46x10 ⁻⁴	0.105	0.015
	310			1.98	3.55	9.9	4.72x10 ⁻⁴	0.117	0.045
	333			2.68	3.51	10.1	5.07x10 ⁻⁴	0.128	0.078
	293	15	10	0.83	2.42	8.1	4.46x10 ⁻⁴	0.090	0.014
	310			1.32	2.40	8.4	4.72x10 ⁻⁴	0.100	0.043
	333			1.79	2.37	8.6	5.07x10 ⁻⁴	0.109	0.075
Sephabeads SP206	293	30	10	0.83	2.42	8.1	4.46x10 ⁻⁴	0.090	0.020
	310			1.32	2.40	8.4	4.72x10 ⁻⁴	0.100	0.035
	333			1.79	2.37	8.6	5.07x10 ⁻⁴	0.109	0.072
	293	30	15	1.24	3.60	9.4	4.46x10 ⁻⁴	0.105	0.021
	310			1.98	3.55	9.9	4.72x10 ⁻⁴	0.117	0.037
	333			2.68	3.51	10.1	5.07x10 ⁻⁴	0.128	0.075
	293	15	10	0.83	2.42	8.1	4.46x10 ⁻⁴	0.090	0.020
	310			1.32	2.40	8.4	4.72x10 ⁻⁴	0.100	0.035
	333			1.79	2.37	8.6	5.07x10 ⁻⁴	0.109	0.072

Effect of the flow-rate

The effect of flow-rate on the adsorption of salicylic acid may be seen in *Figure 3.4* for the Filtrasorb F400, Sephabeads SP207 and Sephabeads SP206, as A, B and C, respectively. The figures show the breakthrough curves corresponding to the pumping of solution at two

different flow-rates, 10 and 15 mL min⁻¹. Lowering the flow-rate leads to longer breakthrough times but, as it may be seen in *Figure 3.4*, for both the flow-rates tested a constant-pattern along the column has been reached.

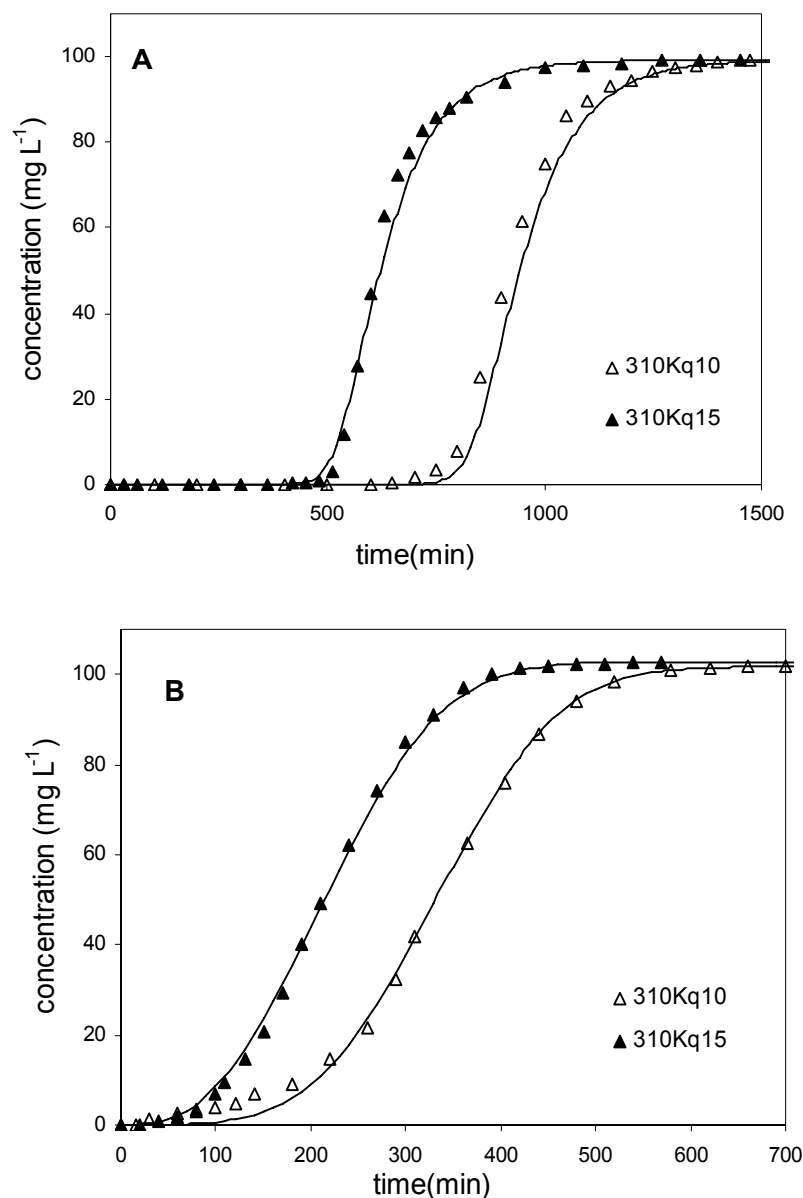


Figure 3.4 Effect of the flow-rate on the fixed bed adsorption of salicylic acid onto Filtrasorb F400 (A), Sephabeads SP207 (B). The bed length was 10 cm for (A) and 30 cm for (B) and solution was feed at 310 K and at two different flow-rates (q_{10} and q_{15} for 10 and 15 mL min⁻¹ respectively). Symbols are the experimental data and full lines are the simulated results obtained by the LDF model

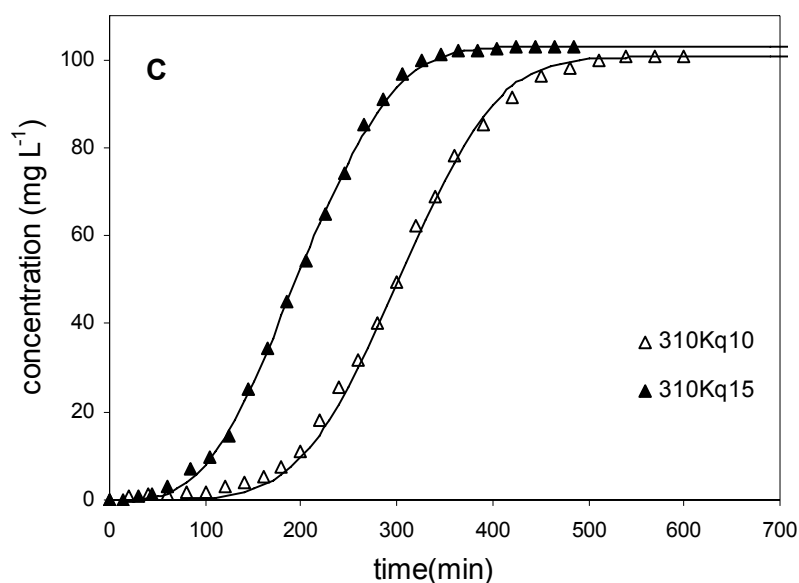


Figure 3.4 (continued) Effect of the flow-rate on the fixed bed adsorption of salicylic acid onto Sephabeads SP206 (C). The bed length was 30 cm for (C) and solution was feed at 310 K and at two different flow-rates (q_{10} and q_{15} for 10 and 15 mL min⁻¹ respectively). Symbols are the experimental data and full lines are the simulated results obtained by the LDF model

Effect of the bed length

Figure 3.5 A shows breakthrough curves corresponding to 10 cm and 5 cm beds (h10 and h5, respectively) of Filtrasorb F400. Figure 3.5 B and C shows the effect of the bed length for Sephabeads SP207 and Sephabeads SP206, respectively, for the runs carried out in beds of length 30 cm and 15 cm (h30 and h15, respectively).

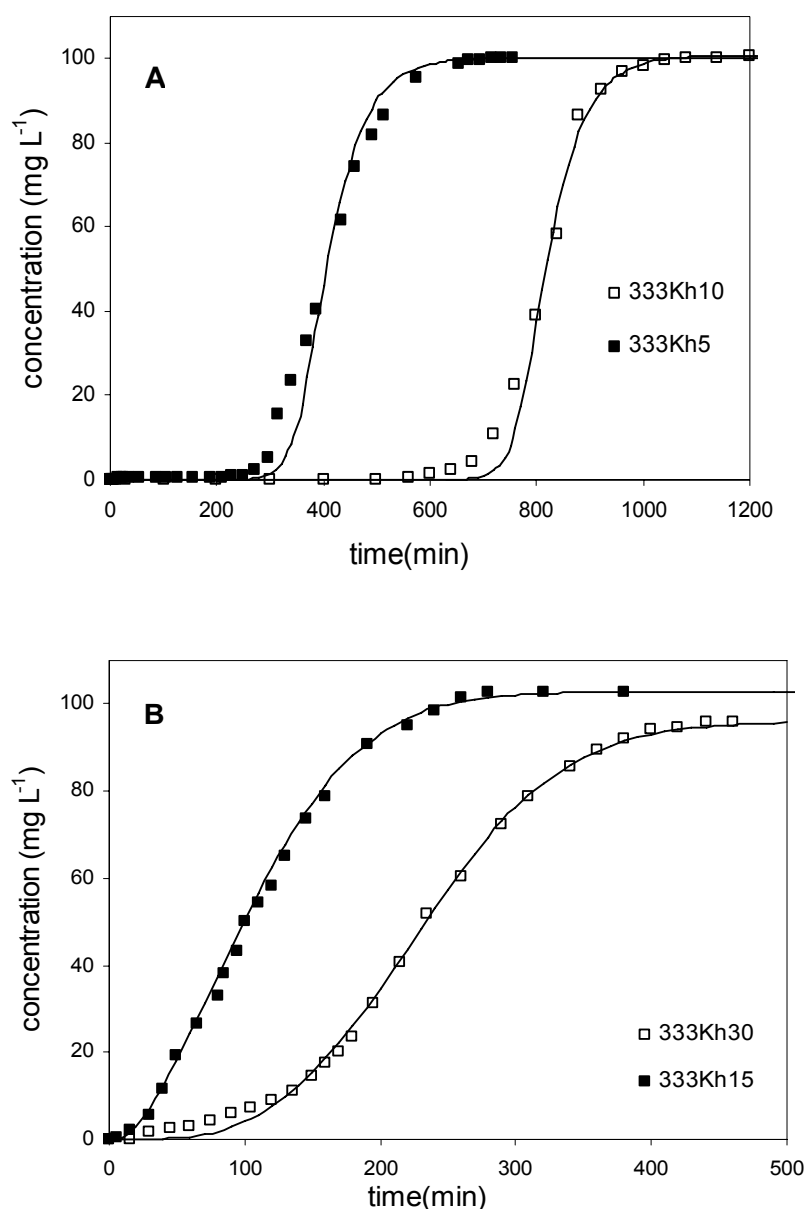


Figure 3.5 Effect of the height of the bed on the fixed bed adsorption of salicylic acid onto Filtrasorb F400 (A), Sephabeads SP207 (B). The bed length was 5 and 10 cm (h5 and h10 respectively) and 15cm and 30cm (h15 and h30 respectively) for Filtrasorb F400 and Sephabeads SP206. The solution was fed at 333K and at a flow-rate of 10 mLmin⁻¹. Symbols are the experimental data and full lines are the simulated results obtained by the LDF model

As it may be seen, having more adsorbent, the longer the bed, the longer the column takes to be saturated. Again, a constant pattern along the bed occurs for the different bed lengths here tested and no entrance effects (more dispersive fronts) have been observed because of using of a shorter bed.

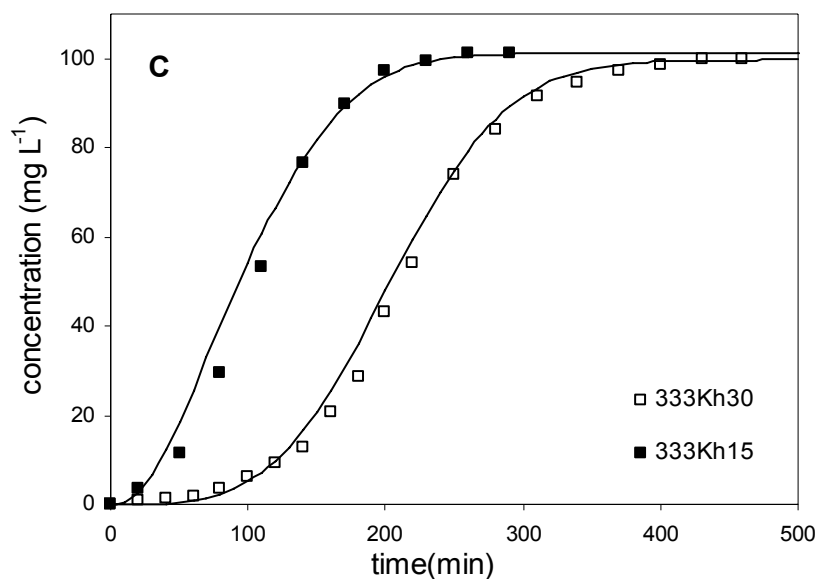


Figure 3.5 (continued) Effect of the height of the bed on the fixed bed adsorption of salicylic acid onto Sephabeads SP206 (C). The bed length was 15cm and 30cm (h_{15} and h_{30} respectively) for Sephabeads SP206 and SP207. The solution was fed at 333K and at a flow-rate of 10 mLmin^{-1} . Symbols are the experimental data and full lines are the simulated results obtained by the LDF model

Fixed bed desorption of salicylic acid

Desorption was carried out after complete saturation of the columns at the same temperature and flow-rate, except that water was pumped instead of salicylic acid solution. The Figure 3.6 A, B, C shows saturation-desorption cycles carried out in beds of Filtrasorb F400, Sephabeads SP207 and Sephabeads SP206, respectively. The comparison of the area corresponding to adsorption and desorption is within 5% difference, indicating that the operation is completely reversible. Because of the non-linearity of the adsorption equilibrium, the shape of the desorption curves is different from the adsorption ones (dispersive front). Note that kinetic effects are very noticeable in the case of desorption from the Filtrasorb F400 and the lower the temperature, the lower the mass transfer. The saturation-desorption cycles are much longer for the beds of Filtrasorb F400 than for Sephabeads SP207 and SP206.

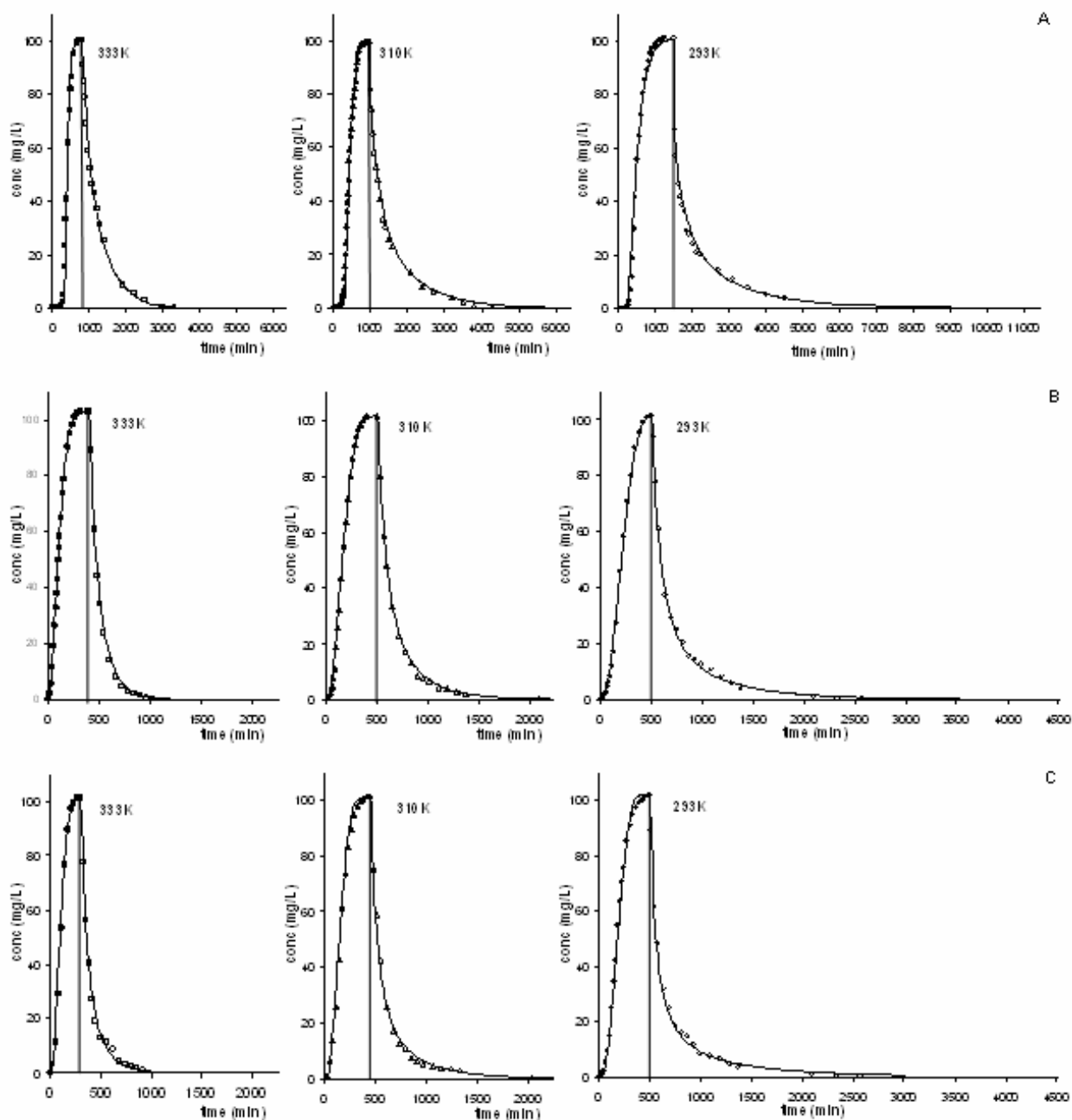


Figure 3.6 Salicylic acid saturation-desorption cycles in beds of Filtrasorb F400 (A), Sephadex SP207 (B) and Sephadex SP206 (C). The bed length was of 5 cm for Filtrasorb F400 and 15 cm for Sephadex SP207 and Sephadex SP206. Both solution (saturation step) and water (desorption step) were fed at a flow-rate of 10 mL min^{-1} and cycles at 293, 310 and 333K were carried out. Symbols are the experimental data and full lines are the simulated results obtained by the LDF model

Generally in all fixed bed experiments could be noticed slight differences between experimental and predicted capacities and are less than 6%. These differences could be due to experimental errors, either in adsorption equilibrium measurements or in flow rate measurements in the fixed-bed experiments. Some discrepancies were found between the predicted breakthrough and the experimental runs that may result from overestimation of the

external film mass transfer coefficient (Eq. 3.9). These differences are more pronounced for the polymeric resins than for the activated charcoal.

3.4.3 Parametric pumping operation

Pilot scale fixed bed adsorption of salicylic acid

With the aid of fixed bed experiments it was determined that the adsorbent with the higher separation parameter was the polymeric resin Sephabeads 206. For this reason, the pilot plant existing in our laboratory was loaded with it for parametric pumping experiments. Before the cyclic experiment it is desirable to carry out breakthrough experiments to check the fixed bed behavior in the real system to be used in parametric pumping runs. Fixed bed adsorption breakthrough curves of salicylic acid were carried out at 293K and at 333K, lower and upper temperatures where adsorption equilibrium data and kinetics are available. The corresponding experimental and simulated breakthrough curves are shown in *Figure 3.7*.

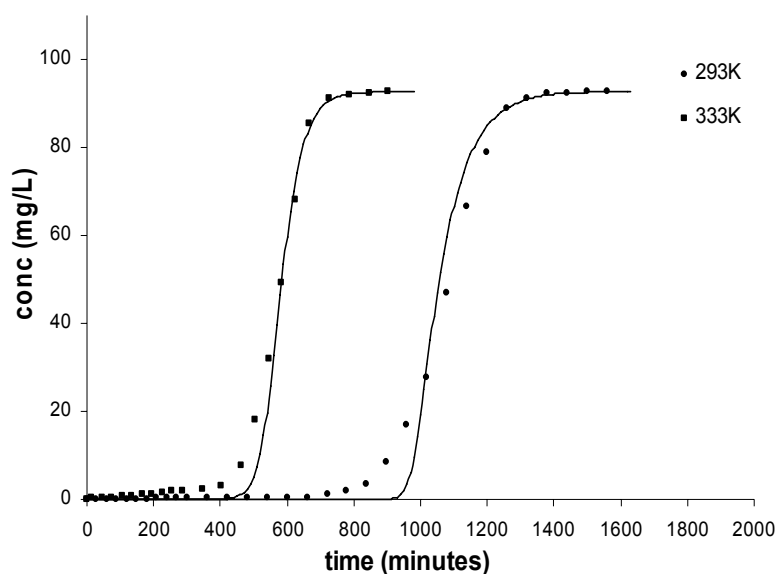


Figure 3.7 Breakthrough curves corresponding to the fixed bed adsorption of salicylic acid onto Sephabeads SP206 at pilot scale. Symbols are the experimental data and full lines are the simulated results obtained by the LDF model.

Full lines correspond to simulated results with the model including the mass balance equation, the Langmuir equilibrium isotherm and the intraparticle mass transfer equation considering the global coefficient. As for the laboratory scale fixed-bed experiments, some discrepancies between the model and the experimental data occur in the initial region of the pilot scale curves. As explained before, these discrepancies may result from overestimation of the external film mass transfer coefficient. Stoichiometric time at 293 K is nearly twice that at

333K, indicating the maximum amount of salicylic acid that can be desorbed in the hot half-cycle of the parametric pumping system.

Parametric pumping experiments

As mentioned before, the adsorbent Sephabeads SP206 was the one chosen for parametric pumping experiments due to the higher separation parameter b (Table 3.2). The characteristics of the resin, bed and the model parameters used for the simulations are reported in Table 3.4.

Table 3.4 Characteristics and parameters used for the simulations of the operated parametric pumping system

Resin properties	Bed characteristics	Thermal parameters	Transport parameters
$\rho = 1190 \text{ g L}^{-1}$	$L = 0.85 \text{ m}$	$Pe_h = 100$	$Pe = 120$
$f_h = 0.5$	$d = 0.09 \text{ m}$	$\xi_k = 1.205$	$D_m^{293} = 4.46 \times 10^{-8} \text{ m}^2 \text{ min}^{-1}$
$r_p = 2 \times 10^{-4} \text{ m}$	$\varepsilon = 0.4$	$h_w = 0.852 \text{ kJ}/(\text{m}^2 \text{ min K})$	$D_m^{333} = 5.07 \times 10^{-8} \text{ m}^2 \text{ min}^{-1}$
$\varepsilon_p = 0.607$			$D_{pe}^{293} = 1.36 \times 10^{-8} \text{ m}^2 \text{ min}^{-1}$
$\tau = 2$			$D_{pe}^{333} = 1.55 \times 10^{-8} \text{ m}^2 \text{ min}^{-1}$

The parametric pumping unit was operated in a semi-continuous way, the main aim was to obtain clean water as the bottom product, and salicylic acid concentrated solution as the top product. Runs under different experimental conditions were carried out to ascertain the effect of the cycle time, the flow rate and the ratio between bottom and top product volumes. The operating variables used in the parametric pumping experiments (temperatures, flow rates and step times) are listed in Table 3.5. The model used to predict the operation of the parametric pumping unit comprises the mass and energy balances, the Langmuir isotherm and the linear driving force (LDF) equations shown.

Effect of the cycle time

The effect of the cycle time on the system salicylic acid-Sephabeads SP206 has been studied by comparing runs 1, 2 and 3. The volume percolated in upward flow (hot half cycle) and downward flow was changed while the following conditions were set:

Production ($V_B + V_T$) = 8 L

Ratio (V_B / V_T) = 0.6

Flow-rate (Q_c and Q_h) = 200 mL min⁻¹

Table 3.5 Experimental conditions used for the different parametric pumping runs carried out in recuperative mode.

Run	C_F (mg L ⁻¹)	T_{amb} (K)	t_h (min)	t_c (min)	Q_h (mL min ⁻¹)	Q_c (mL min ⁻¹)	ϕ_T	ϕ_B	$Q_{(\pi/\omega)}$ (L)	Q_{TP} (mL min ⁻¹)	Q_{BP} (mL min ⁻¹)
1	101	298	85.0	100.0	200	200	0.25	0.15	20	62.50	31.58
2	108		35.0	50.0	200	200	0.50	0.30	10	166.67	66.67
3	106		110.0	125.0	200	200	0.2	0.12	25	47.62	25.00
4	109		56.6	66.6	300	300	0.25	0.15	20	96.77	48.65
5	114	300	106.25	125.0	160	160	0.25	0.15	20	49.38	25.00
6	109		75.0	100.0	200	200	0.15	0.25	20	42.86	52.63
7	104		95.0	100.0	200	200	0.35	0.05	20	77.78	10.53

The histories of top and bottom concentrations for the parametric pumping experiments show that during the hot half-cycle, the salicylic acid in the bed is desorbed and so the top concentration increases; then, during the cold-half cycle, it is possible to adsorb more salicylic acid so a less concentrated stream is collected as bottom product. Operating conditions were studied to ascertain the system response (*Table 3.5*). The effect of the cycle time is shown in *Figure 3.8*. A comparison between run 1, run 2 and run 3 shows that not only bottom purification but also top concentration are favored by longer cycle times. A long cycle time allows improving of interphase mass transfer and the operation to be closer to the equilibrium conditions so better results are attained.

Effect of the flow-rate

This effect was ascertained by comparing the runs 1, 4 and 5, which were carried out at different fluid flow-rates, both upward and downward the column. The following conditions were fixed: $\phi_B + \phi_T = 0.4$; $\phi_B / \phi_T = 0.6$.

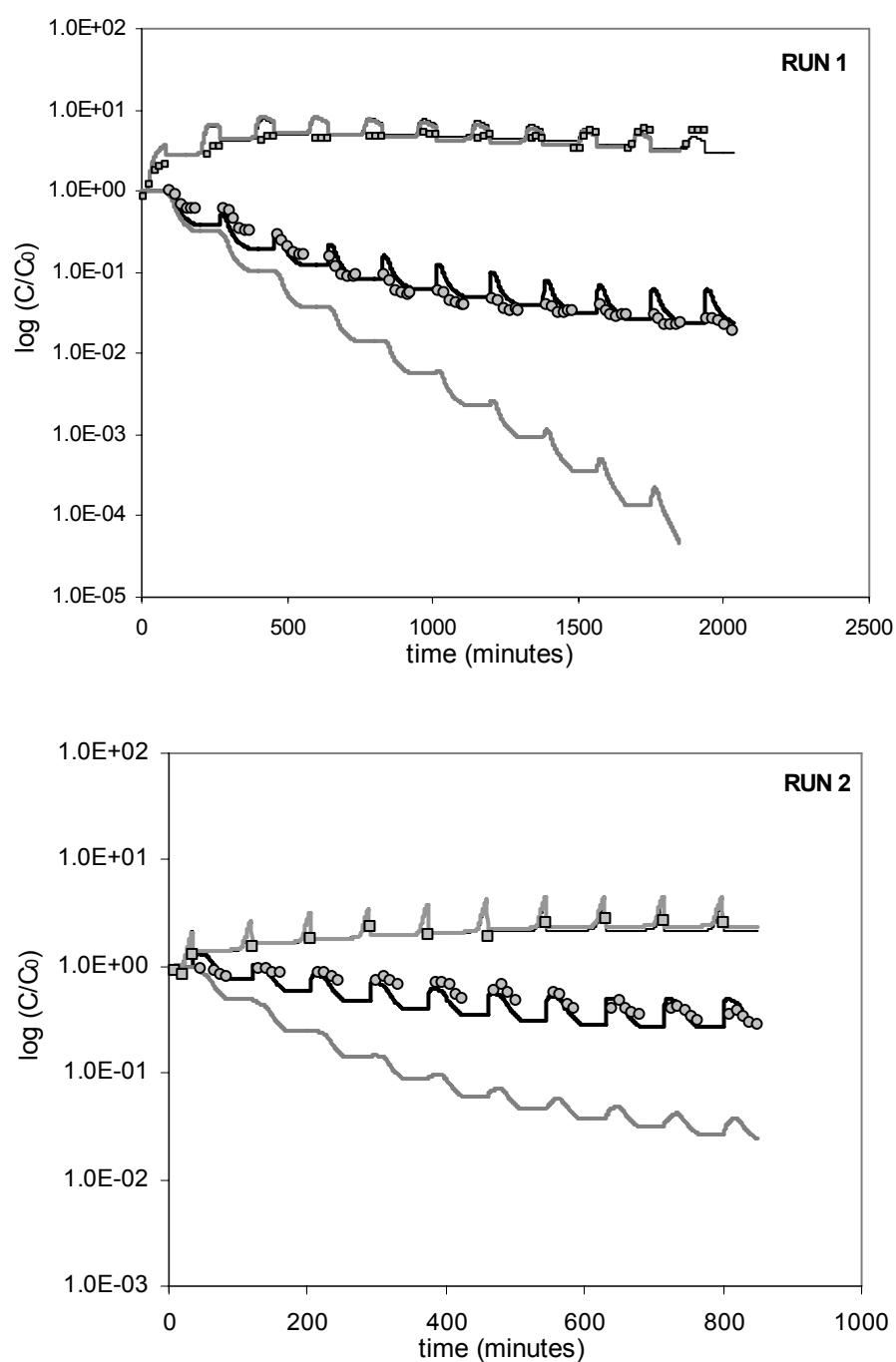


Figure 3.8 Experimental results and model predictions (grey line) Model I, (black line) Model II for the system salicylic acid/water/ SP206. Top and bottom product concentrations as a function of time in recuperative parametric pumping. Effect of the cycle time (RUN 2: 85 min; RUN 1: 185 min; RUN 3: 235 min)

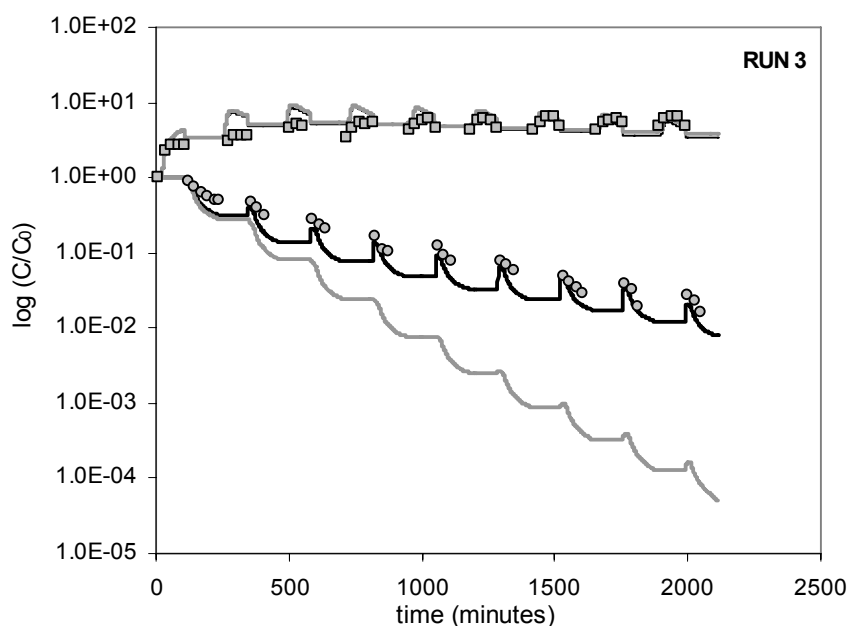


Figure 3.8 (continue) Experimental results and model predictions (grey line) Model I, (black line) Model II for the system salicylic acid/water/ SP206. Top and bottom product concentrations as a function of time in recuperative parametric pumping. Effect of the cycle time (RUN 2: 85 min; RUN 1: 185 min; RUN 3: 235 min)

The effect of the flow-rate and the ratio between bottom and top product volumes is shown in Figure 3.9.

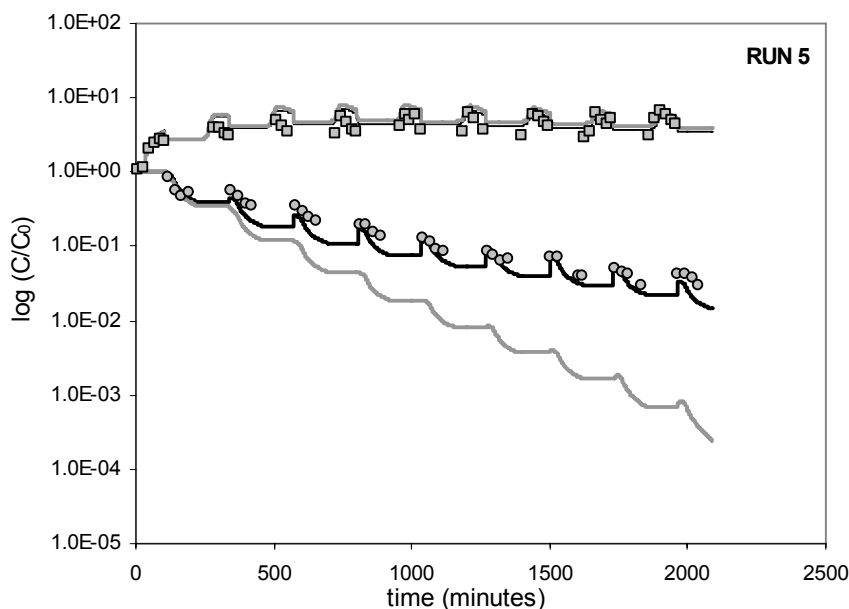


Figure 3.9 Experimental results and model predictions (grey line) Model I, (black line) Model II for the system salicylic acid/water/ SP206. Top and bottom product concentrations as a function of time in recuperative parametric pumping. Effect of the flow-rate (RUN 5: 160 mL min⁻¹; RUN 1: 200 mL min⁻¹; RUN 4: 300 mL min⁻¹)

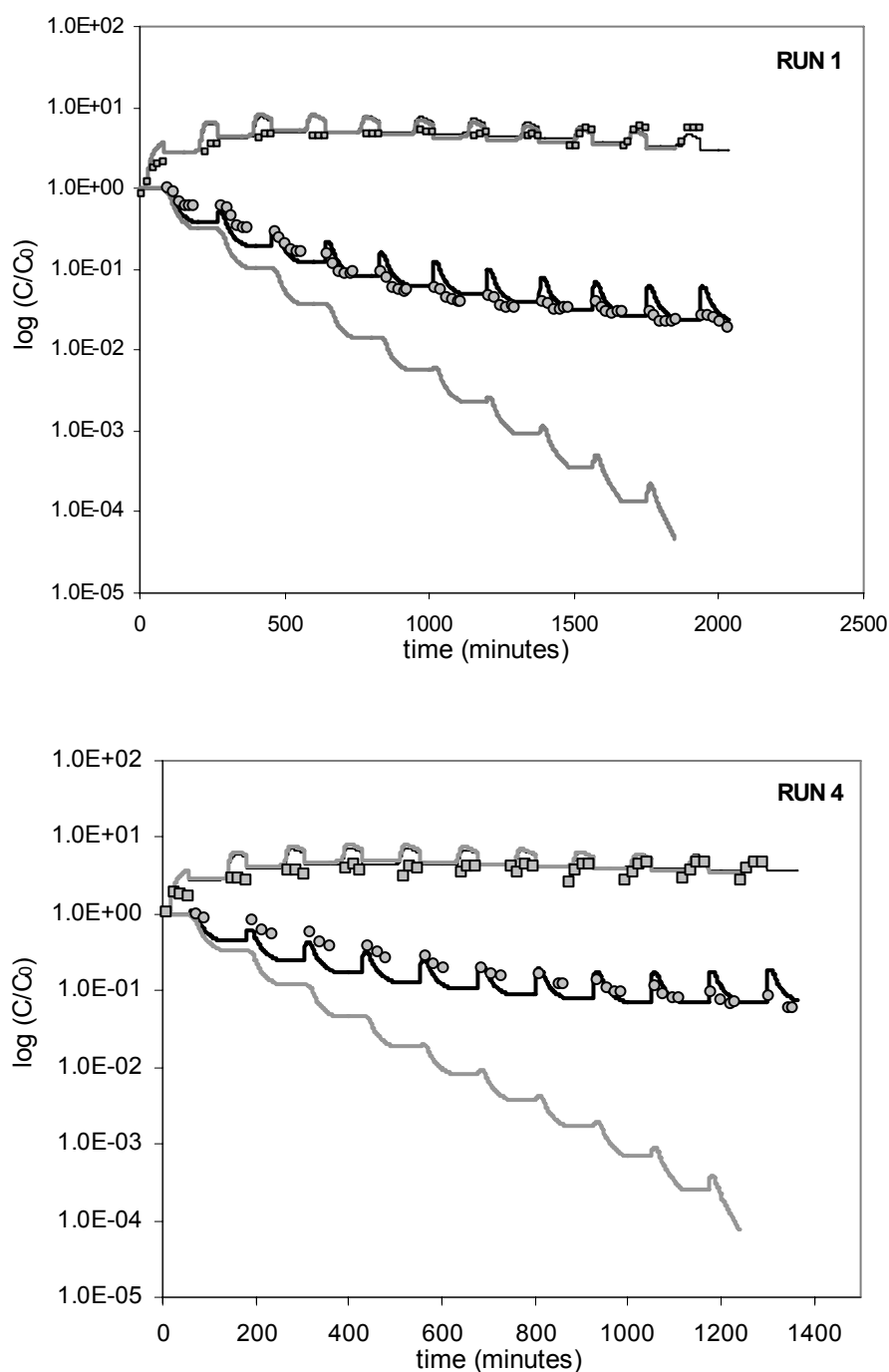


Figure 3.9 (continue) Experimental results and model predictions (grey line) Model I, (black line) Model II for the system salicylic acid/water/ SP206. Top and bottom product concentrations as a function of time in recuperative parametric pumping. Effect of the flow-rate (RUN 5: 160 mL min^{-1} ; RUN 1: 200 mL min^{-1} ; RUN 4: 300 mL min^{-1})

Lower flow-rates imply longer cycle times, which allow for better separation ratios and a higher purification level. The flow-rate does not influence the ratio of velocities of thermal and concentration waves. In this system, the thermal wave is much faster than the concentration wave. However, a minimum flow-rate is required to guarantee thermal

breakthrough up to the level of the feed temperature in each half-cycle. According to the results presented in *Figure 3.9*, operating conditions of run 5, for which the flow-rate is lower than for runs 4 and 1, give better separation results. The flow-rate (run 5) is able to maintain a difference of temperature enough to cause separation and the effect of longer contact between the phases is favorable.

Effect of the ratio between fractions of volume reservoir obtained as bottom and top product ϕ_B/ϕ_T

In order to find out the influence of the ϕ_B/ϕ_T , runs 1, 6 and 7 were compared. This ratio was changed for each of these three runs while setting the following: $\phi_B + \phi_T = 0.4$; average time of cycle = 185 min

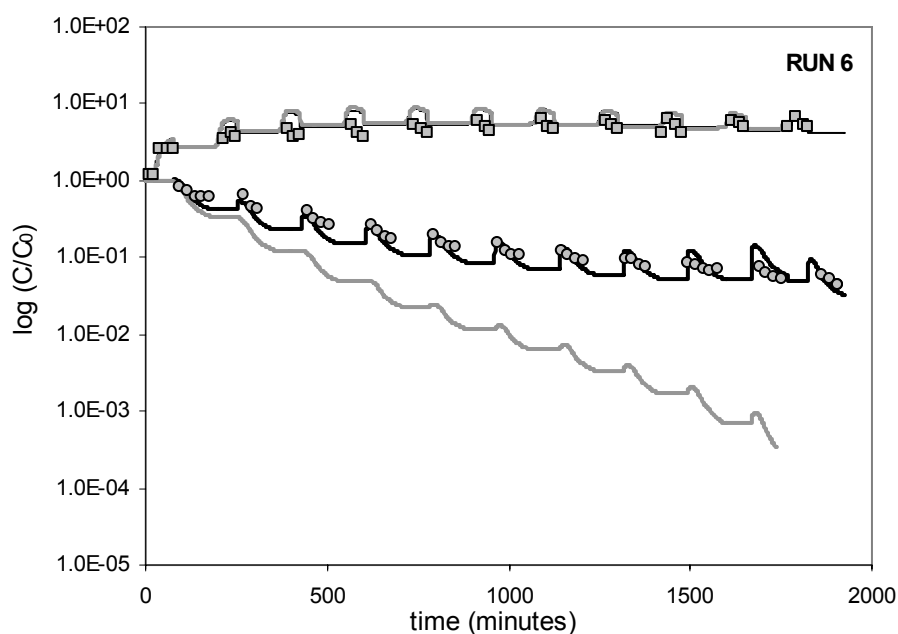


Figure 3.10 Experimental results and model predictions (grey line) Model I, (black line) Model II for the system salicylic acid/water/ SP206. Top and bottom product concentrations as a function of time in recuperative parametric pumping. Effect of the ratio ϕ_B/ϕ_T (RUN 6: 5/3; RUN 1: 3/5; RUN 7: 1/7)

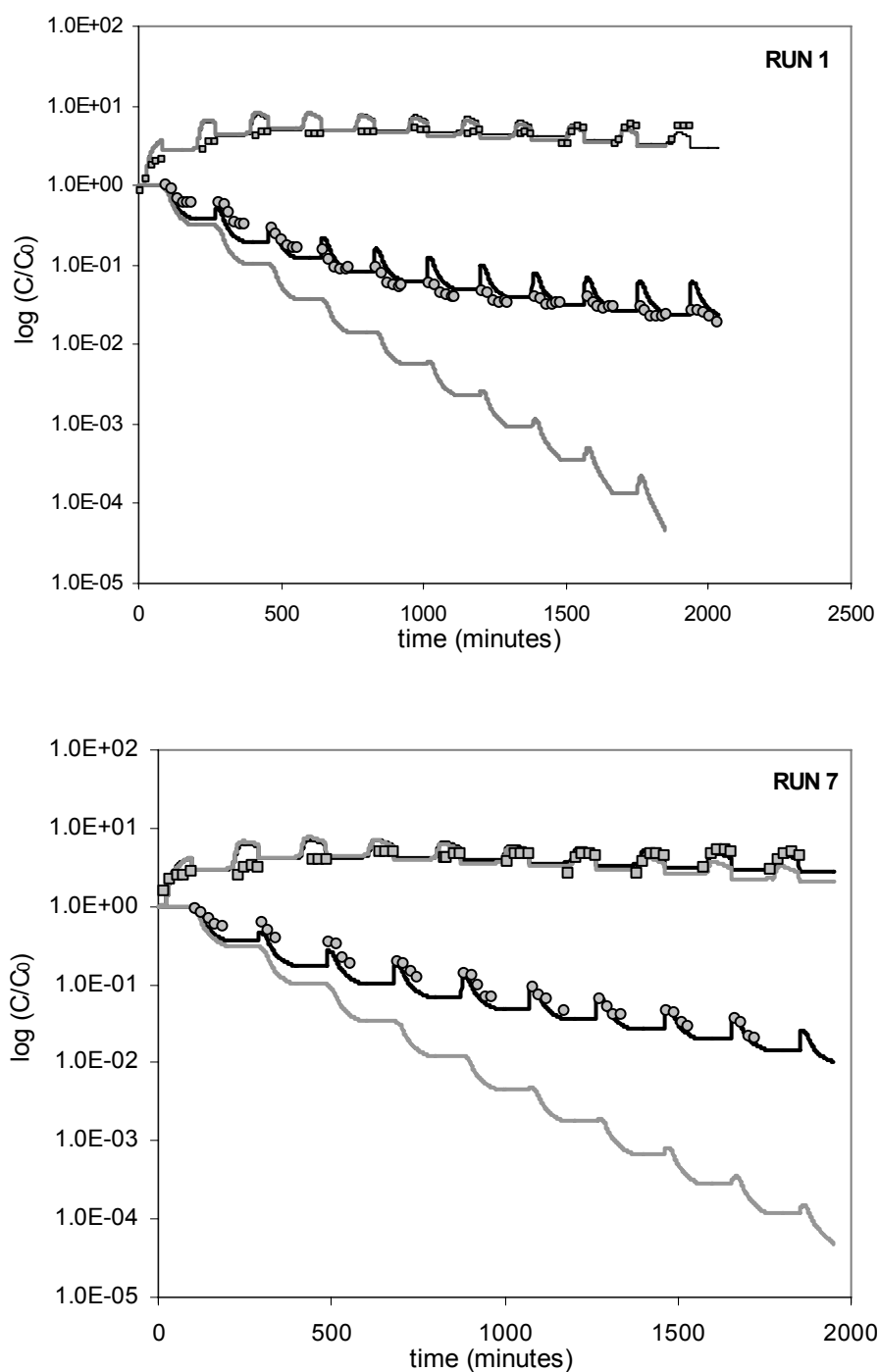


Figure 3.10 (continued) Experimental results and model predictions (grey line) Model I, (black line) Model II for the system salicylic acid/water/ SP206. Top and bottom product concentrations as a function of time in recuperative parametric pumping. Effect of the ratio ϕ_B / ϕ_T (RUN 6: 5/3; RUN 1: 3/5; RUN 7: 1/7)

The ratio ϕ_B / ϕ_T affects the volume of top and bottom reservoir which is percolated through the column, so, the larger this ratio is the larger is the top concentrated reservoir volume which is percolated downward flow and the smaller the purification with respect to the

starting concentration. Run 7 then results in a higher purification level than runs 6 and 1 although less bottom product is got.

The Model I and Model II predictions are very similar for the top concentrated product but not for the bottom purified one. On the whole, the LDF model (Model II) predictions are in better agreement with experimental results. The LDF approximation used in Model II seems to be adequate to describe intraparticle mass transfer for the cyclic process here considered. It may be seen in *Figure 3.8- Figure 3.10* that the LDF model explain the parametric pumping operation for the system salicylic acid/water/polymeric adsorbent SP206 to a great extent, except for small disparities related to deviation of the equilibrium results from the Langmuir model.

3.5 Conclusions

The effects of temperature, bed length and flow-rate were studied on fixed bed adsorption of salicylic acid using different polymeric adsorbents (Sephabeads SP207 and SP206) and activated carbon (Filtrisorb F400). The simulation of breakthrough curves based on a linear driving force (LDF) rate model to describe the diffusional mass transfer seems to fit well the experimental results. The polymeric adsorbents are much more sensitive to temperature when adsorbing salicylic acid than the Filtrisorb F400. This is especially true for the Sephabeads SP206, which shows the higher values of the separation parameter b based on the temperature. Thermal parametric pumping in recuperative mode was carried out in a pilot plant using Sephabeads SP206 for salicylic acid purification. A LDF model explained top and bottom concentrations of salicylic acid as a function of time. In terms of a purification of salicylic acid, thermal parametric pumping using Sephabeads SP206 as adsorbent may be an interesting option worth to be further studied.

3.6 Nomenclature

a	deviation in the separation parameter
A_w	wall specific area (4/D) (m^{-1})
ΔH	enthalpy of adsorption (J mol^{-1})
b	separation parameter
Bi	non-dimensional mass Biot number ($k_f r_p / D_{pe}$)

C	concentration in the bulk fluid phase (g L^{-1})
C_0	initial liquid-phase concentration of phenol (mg L^{-1})
C_e	equilibrium liquid-phase concentration of phenol (mg L^{-1})
C_F	feed phenol concentration in the liquid-phase (mg L^{-1})
Cp_f	heat capacity of the fluid $\text{kJ}/(\text{kg.K})$
Cp_s	heat capacity of the solid $\text{kJ}/(\text{kg.K})$
$\langle C_y \rangle$	average concentration of the fluid in a reservoir (mg L^{-1}), $y = BP$ or $y = TP$
d_p	diameter of the particle of the adsorbent (cm)
D	bed diameter (mm)
D_{ax}	axial dispersion ($\text{m}^2\text{min}^{-1}$)
D_{pe}	the effective pore diffusivity ($\text{m}^2\text{min}^{-1}$)
D_m	the molecular diffusivity ($\text{m}^2\text{min}^{-1}$)
f_h	humidity factor ($\text{g dry adsorbent}/\text{g adsorbent}$)
h_w	global wall heat transfer coefficient $\text{kJ}/(\text{m}^2 \text{ s K})$
K_{ae}	axial thermal conductivity ($\text{kJ}/(\text{m.s.K})$)
K	parameter in the isotherm model (L mg^{-1})
K^∞	infinite adsorption equilibrium constant for the equilibrium model (L mg^{-1})
k_{LDF}	Linear Driving Force (LDF) kinetic rate constant (min^{-1})
L	bed length (m)
$\bar{m}(T)$	capacity parameter in the separation parameter b
m	average slope in the separation parameter b
M_B	molecular weight of solvent B (g mol^{-1})
n	number of cycles

Pe	Péclet number
Pe_h	thermal Péclet number
Q	constant in the Langmuir isotherm model (mg g^{-1}) related to the adsorptive capacity
$Q(\pi / \omega)$	reservoir displacement volume (mL)
Q_x	flowrate of the fluid in the column during a half-cycle (mL min^{-1}), $x = c$ or $x = h$
Q_y	flowrate of removing the product from a reservoir (mL min^{-1}), $y = BP$ or $y = TP$
$\langle q \rangle$	average adsorbed phase concentration per dry mass of adsorbent (mg g^{-1})
q^*	solute adsorbed per dry mass of adsorbent in equilibrium with the solute concentration in solution at a certain time (mg g^{-1})
q_e	solute adsorbed per dry mass of adsorbent at equilibrium (mg g^{-1})
Re	Reynolds number
r_p	radius of the particle of the adsorbent (m)
t	time (min)
t_x	half-cycle time (min), $x = c$ or $x = h$.
T	absolute temperature (K)
T_x	feeding temperature during a half-cycle (K), $x = c$ or $x = h$.
T_{ab}	ambient temperature (K)
U	flow rate ($\text{cm}^3 \text{min}^{-1}$)
u_0	superficial velocity (m min^{-1})
u_j	interstitial velocity (m min^{-1})
V_U	volume percolated during hot-half cycle (mL)
V_A	molar volume of solute a at its normal boiling temperature ($\text{cm}^3 \text{mol}^{-1}$)
z	axial coordinate in the bed (cm)

Greek Letters

ε	bed porosity
ε_p	porosity of the adsorbent
ϕ	dimensionless association factor of solvent B
ϕ_B and ϕ_T	fractions of the $Q_{(\pi/\omega)}$ that are withdrawn as bottom and top products, respectively
θ	fractional coverage of solute on the adsorbed phase in the Nitta model
η	viscosity of the solution (Pa.s)
Ω	LDF factor, which is equal to 3, 8 or 15 for slab, cylindrical or spherical geometry
ρ	density of the adsorbent (g L^{-1})
ρ_f	density of the fluid (g L^{-1})
τ	tortuosity of the adsorbent
ξ_η	heat capacity parameter
ω	frequency of temperature change

Sub indexes

L	corresponding to the Langmuir equilibrium model
N	corresponding to the Nitta equilibrium model
c	relative to the cold half-cycle
h	relative to the hot half-cycle
BP	bottom product from cold half-cycle
TP	top product from hot half-cycle

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4. Purification of 4-nitrophenol wastewaters by thermal parametric pumping: modeling and pilot scale experiments¹

4.1 Introduction

Phenolic compounds are priority pollutants that enter water bodies through discharge from pharmaceutical, petrochemical and other chemical manufacturing processes. They are harmful to organisms at low concentrations and many of them have been classified as hazardous pollutants because of their potential to harm human health. Given their toxicity, phenols have been included in the US Environmental Protection Agency (USA EPA, 1987) list of priority pollutants.

Many methods including sorption (Mortland *et al.*, 1986; El-Geundi, 1997; Gao *et al.*, 2001), biological degradation (Gusler *et al.*, 1993; Haghighi-Podeh *et al.*, 1995; Gonzalez *et al.*, 2001), chemical oxidation (Pintar and Levec, 1992; Kiwi *et al.*, 1994; Alemzadeh *et al.*,

¹ Based on the paper: *Phenolic wastewaters purification by thermal parametric pumping: modeling and pilot scale experiments*. by M. Otero, M. Zabkova, A.E. Rodrigues, Water Research 39, 3467-3478 (2005)

2002), and solvent extraction (Dieckmann and Gray, 1996) have been used to separate these compounds from water. Among these, sorption is the most commonly applied and it is effective for low to medium levels of phenols. A large number of theoretical and experimental results have been published using different adsorbents such as activated carbons, polymeric resins and organoclays.

Sorption operations are able to concentrate solutes, especially in the case that these solutes are valuable and can be recycled. In conventional fixed-bed adsorption, there are two steps: the first one is saturation, adsorption or loading, which is followed by a second step of desorption, elution or regeneration. This operative scheme accounts for a low efficiency since only a fraction of the adsorbent capacity is used. Also, it is necessary to use a chemical regenerant to get an operative bed, so a new waste disposal problem comes out.

Parametric pumping enables purification of industrial wastewaters avoiding the use of chemical regenerant agents and allowing the recycling of the concentrated stream for the industrial process so contributing to achieve the concept of zero-pollutant plant. This is a cyclic separation process, which consists of a mobile phase that percolates through a fixed bed upwards and downwards cyclically, and, with the same periodicity, a cyclic change occurs in any thermodynamic variable, such as temperature, pressure, pH, etc (Simon *et al.*, 1998). In thermal parametric pumping the temperature is the changing variable and the process assumes that the adsorption equilibrium isotherm of the solute onto the adsorbent changes with temperature.

The fundamentals of parametric pumping were established in the late sixties (Wilhelm *et al.*, 1966; Wilhelm *et al.*, 1968; Pigford *et al.*, 1969). At the beginning it was seen as a way to purify valuable compounds but from the 1980's parametric pumping started to be considered for wastewater purification purposes (Costa *et al.*, 1982) what gave the starting point to previous works carried out in our laboratory (Ferreira and Rodrigues, 1995b; Ferreira and Rodrigues, 1995a; Díez *et al.*, 1998; Davesac *et al.*, 2000).

In this work, the purpose was to study the purification of 4-nitrophenol from water by thermal parametric pumping. The polymeric resin Sephabeads SP206 was chosen as adsorbent. Several runs under different conditions were carried out for each of the solutes. The aim of the work was to describe the adsorptive parametric pumping cyclic performance. Two different models: an equilibrium-dispersion model and a Linear Driving Force model with

axial dispersion were used. The Linear Driving Force Model with axial dispersion well predicts the pilot scale experimental results obtained both for phenol and 4-nitrophenol.

4.2 Experimental part

4.2.1 Chemicals and adsorbents

4-nitrophenol ($C_6H_5NO_3$) was purchased from Fluka (Spain). The solutions of 4-nitrophenol were prepared with degassed and distilled water.

The polymeric resin Sephabeads SP206 (Mitsubishi Chemical Corporation) was purchased from Resindion (Italy). This is a nonionic polymeric resin of polystyrene crosslinked with DVB and it has been previously used with success for other phenolic derivatives adsorption (Díez, et al., 1998; Davesac et al., 2000). According to the manufacturers, Sephabeads SP206 are yellow opaque beads with a radius (r_p) of 0.4 mm, the resin having a density (ρ_p) of 1190 g L⁻¹ and a moisture content of 50% ($f_h = 0.5$).

4.2.2 Batch adsorption

Adsorption equilibrium experiments were carried out by contacting the corresponding amount of adsorbent (0.1-3.0 g) with 100 mL of 4-nitrophenol solution in 250-mL Erlenmeyer flasks. Initial concentration of the solution was around 500 mg L⁻¹. Adsorption equilibrium isotherms were measured by batch equilibration placing the volumetric flasks in a shaking mixer at 150 rpm and using a thermostatic bath for temperature control.

Equilibrium experiments were run at 293, 310 and 333 K. After shaking during 48 h, the solution was separated from the adsorbent and the final concentration of solute in water was determined by measuring the absorbance by means of a UV-visible spectrophotometer Jasco (model 7800, Japan) and the wavelength was 372 nm. The amount of solute adsorbed onto the different adsorbents, q_e (mg g⁻¹ dry resin), was calculated by a mass balance relationship (Eq 4.1).

$$q_e = (C_0 - C_e) \frac{V}{W} \quad 4.1$$

where C_0 (mg L^{-1}) and C_e (mg L^{-1}) are the initial and equilibrium liquid-phase concentration of solute, V (L) the volume of the solution and W (g) the dry weight of the corresponding adsorbent.

The adsorption equilibrium isotherms for 4-nitrophenol onto Sephabeads SP206, which represent q_e (mg g^{-1} dry resin) versus the adsorbate liquid concentration at equilibrium, C_e (mg L^{-1}), were fitted with the Langmuir equation:

$$q_e(z, t) = \frac{QK_L C_e}{1 + K_L C_e} \quad 4.2$$

where Q is the maximum adsorptive capacity and K_L a parameter which relates to the adsorption enthalpy.

$$K_L = K_L^\infty \exp\left(\frac{(-\Delta H)}{RT}\right) \quad 4.3$$

Fittings of the equilibrium data to the Langmuir isotherm model were calculated by MATLAB 6.1 following the optimization routine and using the Simplex direct search method.

4.2.3 Fixed-bed adsorption

Dynamic column experiments were carried out in a laboratory scale jacketed column filled with Sephabeads SP206. The bed height and diameter were 15 and 2 cm, respectively. A peristaltic pump Watson-Marlow used to pump the solution into the column with a flowrate of 30 mL min^{-1} . The experiments at the temperatures 293 K, 310 K and 333 K were performed. The corresponding temperature was maintained by a thermostatic bath (Edmund Bühler). The solute concentration in the feed was around 100 mg L^{-1} in all cases. The concentrations of 4-nitrophenol at the column outlet were determined by measuring the absorbance at 372 nm, respectively, by means of a UV-visible spectrophotometer Jasco (model 7800, Japan).

The mathematical model used to predict breakthrough curves includes a mass balance, the adsorption equilibrium isotherm and the mass transfer governed by the Linear Driving Force (LDF) rate.

Species mass balance:

The mass balance in a bed volume element is:

$$D_{ax} \frac{\partial^2 C(z,t)}{\partial z^2} - u_i \frac{\partial C(z,t)}{\partial z} = \frac{\partial C(z,t)}{\partial t} + \frac{1-\varepsilon}{\varepsilon} \rho_p f_h \frac{\partial \langle q(z,t) \rangle}{\partial t} \quad 4.4$$

where D_{ax} is the axial dispersion, u_i is the interstitial velocity, ε is the bed porosity, z is the axial position, C is the concentration in the bulk fluid phase, $\langle q \rangle$ is the average adsorbed phase concentration in the adsorbent particles, ρ_p is the density of the adsorbent and f_h its humidity factor.

Adsorption equilibrium isotherm:

The equilibrium was described by the Langmuir isotherm, which was above specified by Eq 4.2 and Eq. 4.3.

Intraparticle mass transfer

The Linear Driving Force (LDF) approximation (Glueckauf, 1955) was used to describe intraparticle mass transfer:

$$\frac{\partial \langle q(z,t) \rangle}{\partial t} = k_{LDF} [q^*(z,t) - \langle q(z,t) \rangle] \quad 4.5$$

where k_{LDF} is the Linear Driving Force kinetic constant, $q^*(z, t)$ is the adsorbed phase concentration in equilibrium with the bulk concentration.

The boundary conditions for the mass balance equation are the Danckwerts boundary conditions:

$$z = 0 \quad D_{ax} \frac{\partial C(z,t)}{\partial z} \Big|_{z=0} = u_i (C(0,t) - C_0) \quad 4.6$$

$$z = L \quad \frac{\partial C(z,t)}{\partial z} \Big|_{z=L} = 0 \quad 4.7$$

The associated initial conditions for the adsorption are:

$$C(z,0) = 0 \quad 4.8$$

$$q(z,0) = 0 \quad 4.9$$

The axial dispersion was obtained from the following expression (Guiochon *et al.*, 1994):

$$\frac{u_0 d_p}{D_{ax}} = (0.2 + 0.011 \text{Re}^{0.48}) \quad 4.10$$

$$\text{where } \text{Re} = \frac{u_0 \rho_f d_p}{\eta}.$$

The k_{LDF} used in the model were estimated by the following expression (Azevedo, 2001):

$$k_{LDF} = \frac{\Omega D_{pe}}{r_p^2 \rho_f \frac{dq^*}{dC}} \quad 4.11$$

where D_{pe} ($\text{m}^2 \text{min}^{-1}$) is the effective pore diffusivity, r_p (m) is the radius of the particle of the adsorbent, Ω is the *LDF* factor, which is equal to 15 for spherical particles (Azevedo, 2001), and $(\frac{dq^*}{dC})$ is the slope of the equilibrium data.

The D_{pe} was calculated from (Guiochon *et al.*, 1994):

$$D_{pe} = \frac{\varepsilon_p D_m}{\tau} \quad 4.12$$

where D_m is the molecular diffusivity of the solute in water, τ is the tortuosity of the adsorbent and ε_p its porosity.

The molecular diffusivity of 4-nitrophenol in water was found from the Wilke-Chang (1955) method, which estimates the D_m ($\text{cm}^2 \text{s}^{-1}$) as:

$$D_m = 7.4 \times 10^{-8} \frac{(\phi M_B)^{1/2} T}{\eta_B V_A^{0.6}} \quad 4.13$$

where V_A is the molar volume of the solute, the values of V_A were estimated by the Le Bas additive method (Le Bas, 1915) giving $V_A = 127.9 \text{ cm}^3 \text{ mol}^{-1}$ for 4-nitrophenol. Wilke and Chang recommended that the dimensionless association factor of solvent, ϕ , was chosen 2.6 if

the solvent is water. The viscosity of water η_B (cp) at the corresponding temperature was used.

The partial differential equations of the model to describe the adsorption of 4-nitrophenol onto Sephabeads SP206 were solved using the software package *gPROMS*[®] for general **PRO**cess **MO**delling **S**ystem (gPROMS, 2003). The orthogonal collocation method on finite elements (OCFE) was used with 50 finite elements and two interior collocation points in each element of the adsorption bed.

4.2.4 Parametric pumping system

Figure 4.1 shows the automated parametric pumping pilot plant used for the purification of 4-nitrophenol from wastewater. The adsorbent, Sephabeads SP206, was placed in the borosilicate column of the plant. The adsorbent bed was 80 x 9 cm with a porosity $\varepsilon = 0.4$.

The operation of the plant was performed in a semi-continuous way, with feed to the top reservoir. The aim is to produce a concentrated solution at the top reservoir and a solute-free stream in the bottom one. After saturation of the bed at the cold temperature T_c , the solution was passed cyclically through the bed of adsorbent in upward flow at a temperature T_h (hot half-cycle) followed by downward flow at a temperature T_c ($T_c < T_h$) (cold half-cycle). The conditions (temperature range, flow-rates, products withdrawal) under which the operation is carried out determine the concentration and purification obtained.

The parametric pumping pilot plant was operated in a recuperative mode, i.e., temperature change is not imposed through the column wall (direct mode) but by the solution itself, which is heated or cooled by means of thermostatic baths. Recuperative mode was chosen as, compared to direct mode, it would be more appropriate for industrial purposes as this allows the use of larger diameter columns (Ramalho *et al.*, 1991).

The automated pilot plant used has three reservoirs: top, bottom and feed reservoirs. The top and bottom reservoirs receive product when the solution is pumped through the column in upward or downward flow, respectively. From the feed reservoir the feed solution, around 500 mgL^{-1} of 4-nitrophenol, is passed into the top reservoir. Pressure transducers installed at the bottom of the reservoirs to detect when all the solution contained in a reservoir was

transferred, which means one half-cycle ending. Bottom and top products were collected at fixed time intervals by a fraction collector and the solute concentration was later spectrophotometrically determined at the corresponding wavelength.

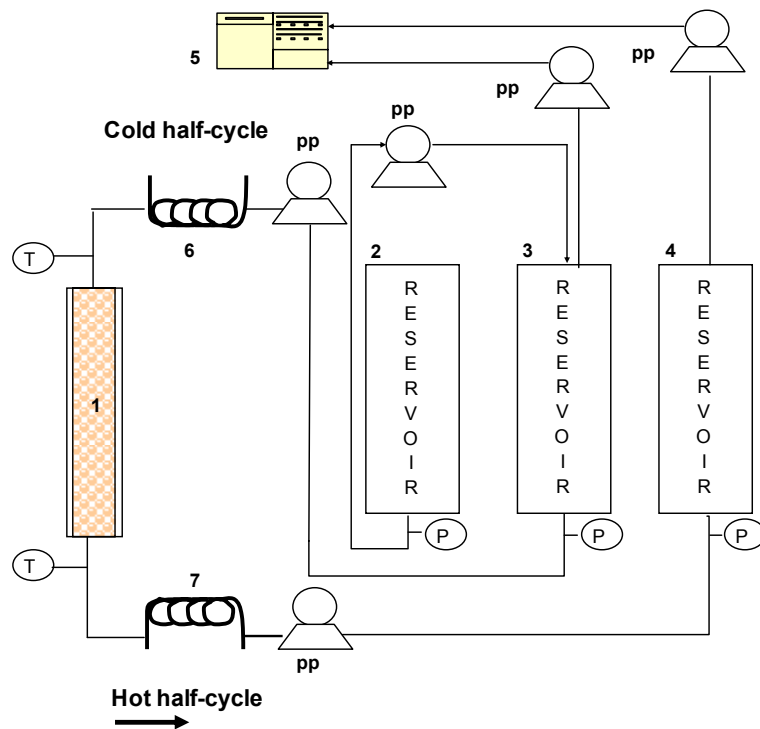


Figure 4.1 Experimental set-up of the parametric pumping pilot plant: 1.- Borosilicate column; 2.- Feed reservoir; 3.- Top reservoir; 4.- Bottom reservoir; 5.- Fraction collector; 6-7.- Heat exchangers; 8-12.- Two way solenoid valves; 13-14.- Three way solenoid valves; 15-19.- Peristaltic pumps; T_1 - T_2 - Thermocouples; P_1 - P_3 - Pressure transducers.

In this work, the experimental set-up above described was used for the systems water/4-nitrophenol/Sephabeads SP206. The ambient temperature (T_{amb}) was kept at around 295 K, the $T_h = 333$ K and the $T_c = 293$ K for all the experimental runs.

4.3 Mathematical model for parametric pumping

The predictive capability of two models was studied; first of all, a simple equilibrium model was used; later, the *LDF* model was used and results obtained by each of the models were compared.

4.3.1 Equilibrium model with axial dispersion

This model will be referred as the *equilibrium-dispersion model*, assuming that axial dispersion is also considered to simulate the operation of the parametric pumping unit. This mathematical model comprises a mass balance, a global energy balance and the adsorption equilibrium isotherm. The balances of the reservoirs containing the product from the hot and the cold cycles, top and bottom reservoirs are included as well.

The *equilibrium-dispersion model* assumes:

- a) mixing in the reservoirs is perfect
- b) radial temperature gradients in the bed are negligible
- c) one-dimensional pseudo-homogeneous model for the heat transfer
- d) constant physical properties of the fluid and the adsorbent
- e) the effect of the transient temperature regime on the heat and mass transfer parameters is negligible
- f) the film heat and mass transfer resistances are negligible
- g) the adsorption equilibrium is described by the Langmuir isotherm and the constant of equilibrium exponentially depends of temperature
- h) instantaneous equilibrium between the pore fluid concentration and the adsorbed concentration, i.e., mass transfer kinetics is infinitely fast

The model equations are the following:

Mass balance

The mass balance in a bed volume element is:

$$D_{ax} \frac{\partial^2 C(z,t)}{\partial z^2} \pm u_i \frac{\partial C(z,t)}{\partial z} = \frac{\partial C(z,t)}{\partial t} + \frac{1-\varepsilon}{\varepsilon} \rho_p f_h \frac{\partial \langle q(z,t) \rangle}{\partial t} \quad 4.14$$

where, in the *equilibrium model*, $\langle q(z,t) \rangle = q^*(z,t)$.

Considering $z=0$ at the bottom of the column and $z=L$ at the top, in the equation above, the term $\pm u_i \frac{\partial C(z,t)}{\partial z}$ has the “-” sign for the hot half-cycle upwards, and the “+” sign for the cold half-cycle downwards.

Energy balance

A global energy balance for the column was used:

$$\begin{aligned} & \left[\rho_f C_{p_f} \varepsilon + \rho_p C_{p_s} (1 - \varepsilon) \right] \frac{\partial T(z,t)}{\partial t} = \\ & = K_{ae} \frac{\partial^2 T(z,t)}{\partial z^2} \pm \rho_f C_{p_f} u_0 \frac{\partial T(z,t)}{\partial z} - h_w A_w (T - T_{amb}) + (-\Delta H) \frac{\partial \langle q(z,t) \rangle}{\partial t} \end{aligned} \quad 4.15$$

where K_{ae} is the axial thermal conductivity, h_w is the heat transfer coefficient of the wall of the column and A_w is the wall specific area, ρ_f and ρ_p are the densities of the fluid and of the adsorbent, and C_{p_f} and C_{p_s} are the heat capacities of the fluid and of the adsorbent, respectively. Again, in the *equilibrium-dispersion model*, $\langle q(z,t) \rangle = q^*(z,t)$.

Considering $z = 0$ at the bottom of the column and $z = L$ at the top, in the equation above, the term $\pm \rho_f C_{p_f} u_0 \frac{\partial T(z,t)}{\partial z}$ has the “+” sign for the cold half-cycle downwards, and the “-” sign for the hot half-cycle upwards.

Adsorption equilibrium isotherm

The adsorption equilibrium isotherms for 4-nitrophenol onto Sephabeads SP206 were described by Langmuir equations (Eq.4.2) and (Eq.4.3).

Balance of the reservoirs

- Hot half-cycle

$$\langle C_{BP} \rangle = \langle C_{BP} \rangle_{n-1} \quad 4.16$$

$$\langle C_{TP} \rangle = \frac{(1 - \phi_B) \langle C(L,t) \rangle_n}{(1 + \phi_T)} + C_F \frac{(\phi_B + \phi_T)}{(1 + \phi_T)} \quad 4.17$$

- Cold half-cycle

$$\langle C_{BP} \rangle = \langle C(0, t) \rangle_n \quad 4.18$$

where $\langle C_{BP} \rangle$ and $\langle C_{TP} \rangle$ are the average concentrations of solute in the fluid which is in the bottom and in the top reservoirs, respectively, ϕ_B and ϕ_T are the fraction of the total reservoir displacement volume ($Q(\pi/\omega)$) that are withdrawn as product from the bottom and the top reservoirs, respectively, and n refers to the number of cycles.

4.3.2 Model of Linear Driving Force (LDF) with axial dispersion

The *LDF model* was also used for the simulation of the operation of the parametric pumping unit. This model includes the equations above indicated for the *equilibrium-dispersion model* and, apart of the previous, one more equation corresponding to the *LDF* intraparticle rate, which was previously used for modeling the breakthrough curves (Eq. 4.5), to describe the diffusional mass transfer inside adsorbent particles.

The *LDF model* assumptions are the same as the equilibrium model except for:

- equilibrium between the bulk fluid concentration and the adsorbed concentration at the particle surface
- intraparticle mass transfer velocity described by the linear driving force (*LDF*) model

Intraparticle mass transfer

The Linear Driving Force (*LDF*) approximation, first introduced by Glueckauf (1955), imposes a restriction to the previous *equilibrium-dispersion model*. According to this model the average adsorbed phase concentration rate is proportional to the difference between the adsorbed phase concentration in equilibrium with the bulk fluid and the average adsorbed phase concentration, given by (Eq. 4.5).

Boundary and Initial conditions

For both models, the boundary conditions for the equations used to predict the parametric pumping operation, were the following:

- Hot half-cycle
- $z = 0 \quad C(0, t) = \langle C_{BP} \rangle_n \quad T = T_h \quad 4.19$

- $z = L \quad \frac{\partial C(z, t)}{\partial z} = 0 \quad \frac{\partial T(z, t)}{\partial z} = 0 \quad 4.20$

- Cold half-cycle

$$z = 0 \quad \frac{\partial C(z, t)}{\partial z} = 0 \quad \frac{\partial T(z, t)}{\partial z} = 0 \quad 4.21$$

$$z = L \quad C(L, t) = \langle C_{TP} \rangle_n \quad T = T_c \quad 4.22$$

The initial conditions were:

$$C(z, 0) = C_F \quad 4.23$$

$$T(z, 0) = T_0 \quad 4.24$$

The partial differential equations corresponding to both the *equilibrium* and the *LDF* parametric pumping models were solved with a package (Davesac et al., 2000) previously developed in our laboratory in Visual Basic.

4.4 Results and discussion

4.4.1 Adsorption isotherms

The characteristic parameters Q , K_L and ΔH corresponding to the fittings of the experimental data to the Langmuir isotherm model are shown in *Table 4.1*.

Table 4.1 Equilibrium parameters determined for the adsorption of phenol and 4-nitrophenol onto Sephabeads SP206 and the corresponding separation parameter b calculated for temperature range 293-310K, 310-333K and 293-333K .

Langmuir parametrs	4-Nitrophenol
Q (mg g ⁻¹)	101.1
K_L^∞ (L mg ⁻¹)	8.23×10^{-8}
ΔH_L (kJ mol ⁻¹)	-30.37
b (temperature range)	
b (293 K-310 K)	0.33
b (310 K-333 K)	0.39
b (293 K-333 K)	0.64

The experimental adsorbed concentrations as a function of liquid phase concentration corresponding to the 4-nitrophenol adsorption onto Sephabeads SP206 at each of the

temperatures considered are shown in *Figure 4.2*. The obtained fittings to the Langmuir model are shown together with the experimental points.

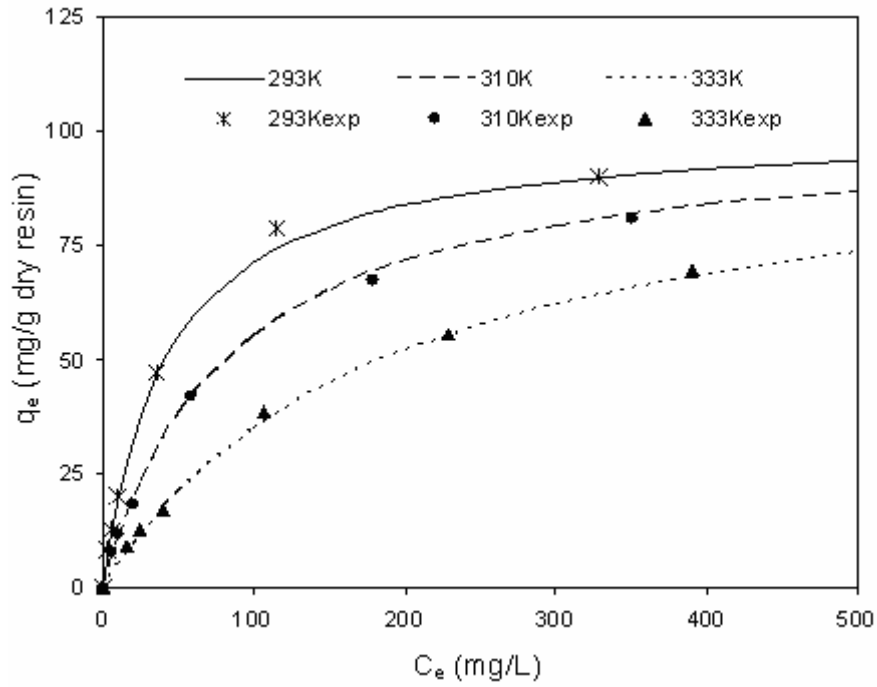


Figure 4.2 Experimental adsorption equilibrium (symbols), q_e versus C_e and fittings to Langmuir model (full lines) at three temperatures (293, 310 and 333 K) for the adsorption of 4-nitrophenol onto Sephabeads SP206.

Separation parameter:

From the equilibrium results, it may be found the separation to be expected as a function of temperature for the systems 4-nitrophenol-SP206. The separation parameter b , introduced by Pigford (Pigford *et al.*, 1973), is indicative of the separation potential:

$$b = \frac{a}{1 + m} \quad 4.25$$

with the average slope $\bar{m} = \frac{m(T_1) + m(T_2)}{2}$ and the deviation $a = \frac{m(T_1) - m(T_2)}{2}$, considering

$T_1 < T_2$. The capacity parameter is defined as $m(T) = \frac{(1 - \varepsilon)\rho_p f_h K(T)}{\varepsilon}$, where $K(T) = QK_L$

is the slope of initial linear region of the isotherm corresponding to each temperature, ε is the bed porosity ($\varepsilon = 0.4$), ρ is the density and f_h the humidity factor of the corresponding adsorbent, which values appear in *Table 2.1* (see Chapter 2). Together with the equilibrium

coefficients, the b parameters corresponding to the adsorption of 4-nitrophenol onto Sephabeads SP206 are shown in *Table 4.1*. In the range of temperature considered (293 K-333 K) the larger the temperature difference, the higher the separation parameter for 4-nitrophenol.

Fixed bed adsorption

The values of the Reynolds and the calculated axial dispersion D_{ax} used for the simulation of the breakthrough curves of 4-nitrophenol are shown in *Table 4.2*, which also shows the corresponding k_{LDF} rates included in the model here used.

Table 4.2 Estimated axial dispersions (D_{ax}) corresponding to the fixed bed systems considered and LDF kinetic rate constants estimated (k_{LDF}) for the adsorption of 4-nitrophenol onto Sephabeads SP206.

T (K)	Re	D_{ax} (cm ² min ⁻¹)	D_m (cm ² min ⁻¹)	ε_p	τ	D_{pe} (cm ² min ⁻¹)	k_{LDF} (min ⁻¹)
293	0.62	1.83	5.11x10 ⁻⁴	0.61	2	1.56x10 ⁻⁴	0.022
310	0.99	1.81	8.46x10 ⁻⁴			2.58x10 ⁻⁴	0.038
333	1.34	1.80	1.24x10 ⁻³			3.78x10 ⁻⁴	0.077
$L = 15$ cm							
$Flow\text{-}rate = 30$ mL min ⁻¹							

Fixed bed experimental results from the adsorption of 4-nitrophenol onto polymeric resin are shown together with the simulated ones in *Figure 4.3*. The *LDF model* seems to describe well the fixed bed adsorption of 4-nitrophenol onto Sephabeads SP206 at the temperatures considered.

4.4.2 Parametric pumping operation and simulation

The parametric pumping unit was operated in a semi-continuous way, the aim being to obtain clean water as the bottom product and concentrated solution as the top product. Experiments under different experimental conditions were carried out to ascertain the predictions of the models. Experimental conditions are shown in *Table 4.3*.

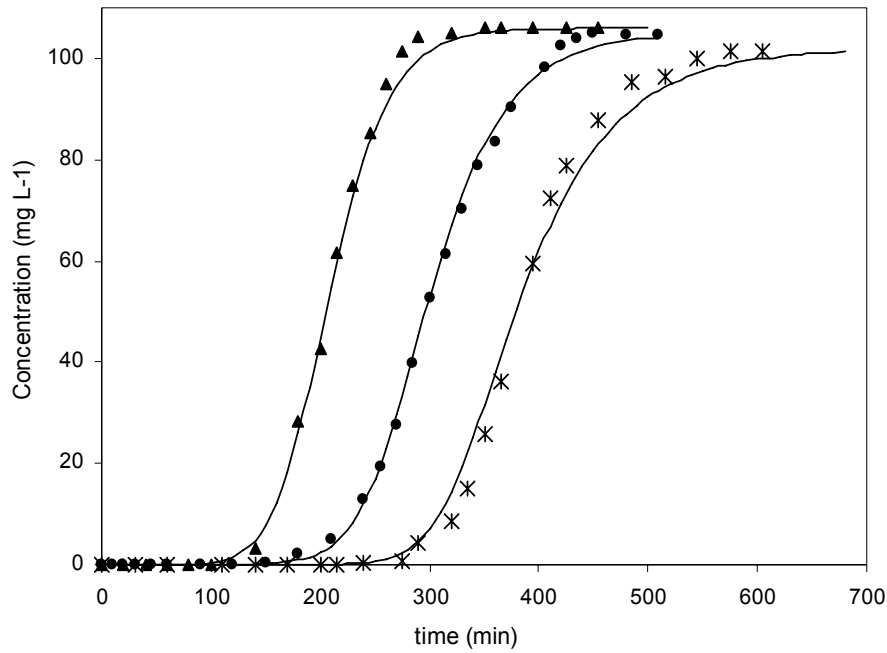


Figure 4.3 Fixed bed adsorption of 4-nitrophenol onto Sephabeads SP206. The bed length was 15 cm and solution was fed at three temperatures (293 K, 310 K and 333 K) at a flow-rate of 30 mL min⁻¹. Symbols correspond to the experimental results and full lines to the simulated ones.

The top and bottom concentrations of 4-nitrophenol are represented as a function of time in Figure 4.4-Figure 4.7. The experimental results were compared with the predicted by the *equilibrium* and by the *LDF* models. The characteristics of the adsorbent and the bed, the operating variables, the equilibrium isotherm and the thermal and mass transport parameters are introduced in the program to solve the previous equations.

In the Table 4.3 V_U represents volume which is percolated through the column during hot-half cycle, $Q_{(\pi/\omega)}$ is reservoir displacement volume, ϕ_B, ϕ_T are fraction of $Q_{(\pi/\omega)}$ withdrawn as a bottom and top product, respectively, Q_{TP}, Q_{BP} are flow-rates of removing the product from the top and bottom reservoir, respectively. Q_c, Q_h, t_c and t_h describes flow-rate of the fluid in the column during the cold and hot half-cycle and time of the cold and hot cycle.

Table 4.3 Experimental conditions used for the different parametric pumping runs in recuperative mode

Operating variables	Run 1	Run 2	Run 3	Run 4
V_U (mL)	11616	29000	9500	17000
$Q_{(\pi/\omega)}$ (mL)	16940	31200	9600	20000
ϕ_B	0.31	0.068	0.068	0.15
ϕ_T	0.34	0.56	0.56	0.25
t_c (min)	55	120	60	100
t_h (min)	48	100	50	85
Q_c (mLmin ⁻¹)	308	260	160	200
Q_h (mLmin ⁻¹)	242	290	190	200
Q_{TP} (mLmin ⁻¹)	134	184	119.5	62.5
Q_{BP} (mLmin ⁻¹)	105	18	12	32

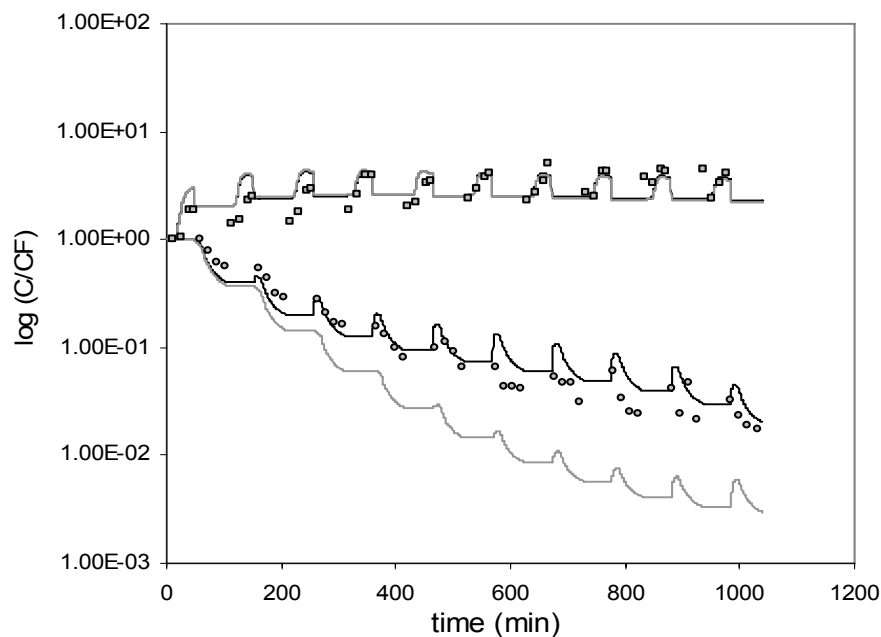


Figure 4.4 Experimental results (symbols) for the parametric pumping run 1 together with the equilibrium model (gray full lines) and the LDF model (black full lines) predictions. Top and bottom product concentrations 4-nitrophenol are shown as a function of time in recuperative parametric pumping.

The degree of purification of this pollutant varies depending on the operational conditions applied, and it is especially good for the run 4. It may be seen that the two models here used predict the first cycles of the operation at the same way. Nevertheless, the equilibrium model predicts unlimited separation so it is not appropriate for the simulation when the number of cycles increases. The Linear Driving Force model, which incorporates one more equation,

comprises more resistances than the equilibrium model and it is more accurate in its predictions.

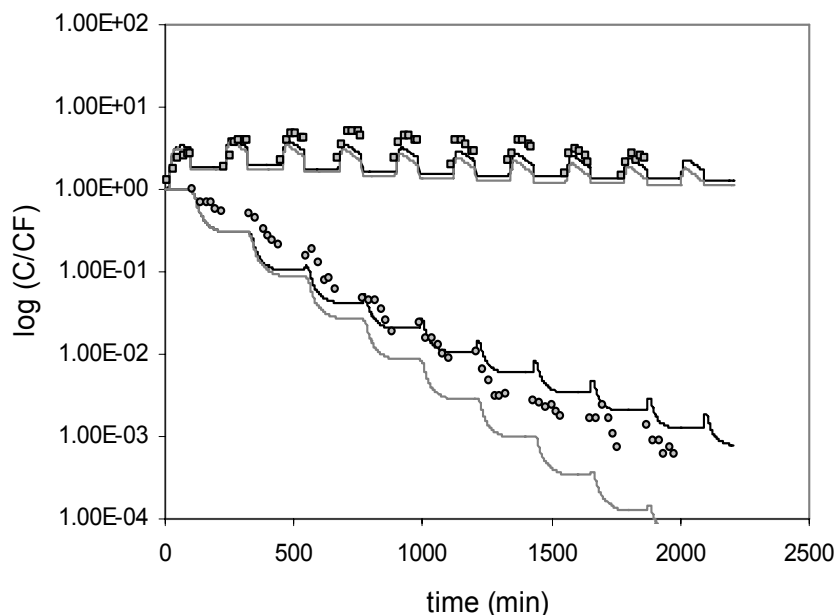


Figure 4.5 Experimental results (symbols) for the parametric pumping run 2 together with the equilibrium model (gray full lines) and the LDF model (black full lines) predictions. Top and bottom product concentrations of 4-nitrophenol are shown as a function of time in recuperative parametric pumping.

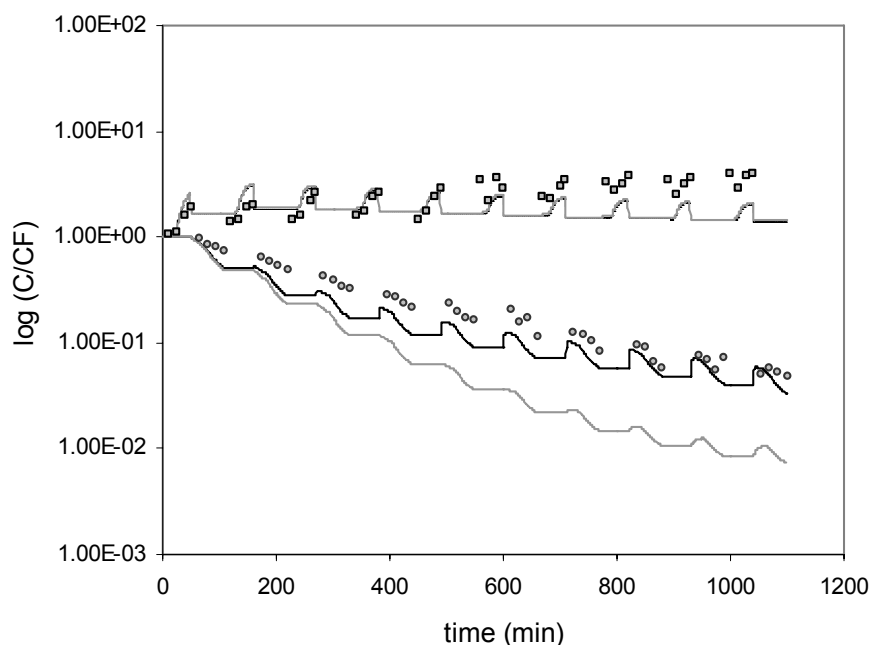


Figure 4.6 Experimental results (symbols) for the parametric pumping run 3 together with the equilibrium model (gray full lines) and the LDF model (black full lines) predictions. Top and bottom product concentrations of 4-nitrophenol are shown as a function of time in recuperative parametric pumping.

The *LDF* model seems to describe well the parametric pumping operation under the different conditions of the experimental runs. As it may be observed, the simulation predictions of the *LDF* model are in good agreement with experimental results, which indicates that the Linear Driving Force approximation is appropriate for describing mass transfer in this cyclic process.

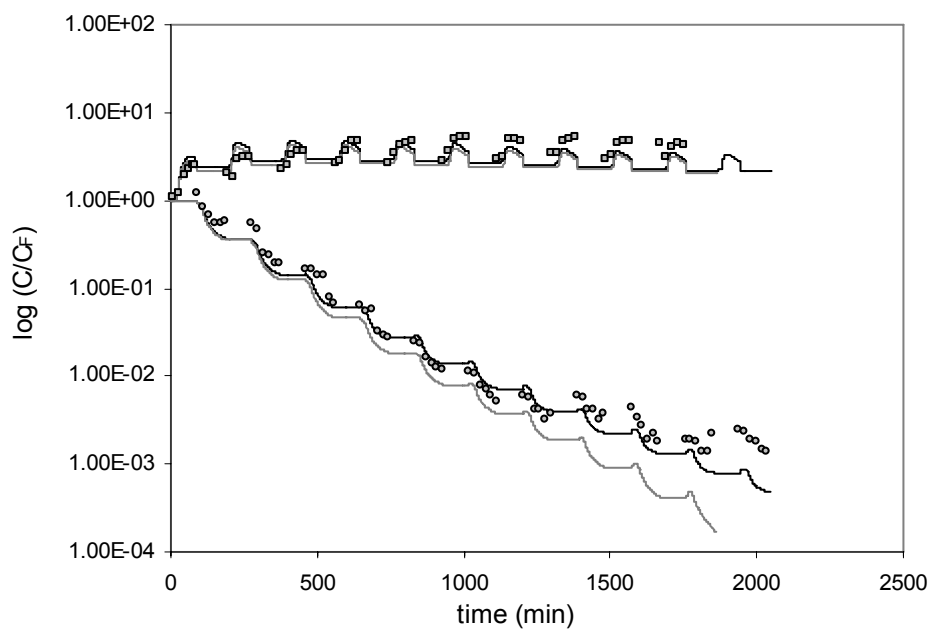


Figure 4.7 Experimental results (symbols) for the parametric pumping run 4 together with the equilibrium model (gray full lines) and the *LDF* model (black full lines) predictions. Top and bottom product concentrations of 4-nitrophenol is shown as a function of time in recuperative parametric pumping.

A high level of purification was obtained after 10 cycles and the concentration of 4-nitrophenol in the bottom reservoir decreased to $C/C_F < 0.0015$ and in the top reservoir the concentration was 3 times higher than the feed concentration.

4.5 Conclusions

Adsorption of 4-nitrophenol onto the polymeric resin Sephabeads SP206 was studied with a focus on parametric pumping.

Batch tests were carried out in order to determine the effect of temperature on the equilibrium. The Langmuir isotherm model well fitted the equilibrium of adsorption. The corresponding separation parameters b were evaluated for 4-nitrophenol in the 293–333 K range of temperature. Differences on adsorption capacity depending on temperature were confirmed by

dynamic experiments. The LDF model used well predicted the experimental results obtained for 4-nitrophenol.

Thermal parametric pumping in recuperative mode was carried out in a pilot plant using Sephabeads SP206 for 4-nitrophenol purification from water. Two models, an *equilibrium-dispersion model* with axial dispersion and a *Linear Driving Force model*, also with axial dispersion, were used for simulating the operation of the parametric pumping unit. Runs under different conditions were carried out to confirm the quality of their predictions. Operational conditions define the degree of purification obtained by thermal parametric pumping. In all cases, the LDF model, which has more restrictions, seems to better predict the performance of the system. Under appropriate conditions, at the 10th cycle it was possible to decrease to $C/C_F = 0.0013$ for 4-nitrophenol. A high degree of purification of phenolic wastewaters may then be achieved by thermal parametric pumping using Sephabeads SP206 as adsorbent and avoiding the use of any chemical regenerant.

4.6 Nomenclature

a - deviation in the separation parameter

A_w - wall specific area (4/D) (m^{-1})

ΔH_L - enthalpy of adsorption for the Langmuir isotherm (J mol^{-1})

b - separation parameter

C - concentration in the bulk fluid phase (kg m^{-3})

C_0 - initial liquid-phase concentration of 4-nitrophenol (kg m^{-3})

C_e - equilibrium liquid-phase concentration of 4-nitrophenol (kg m^{-3})

C_F - feed 4-nitrophenol concentration in the liquid-phase (kg m^{-3})

Cp_f - heat capacity of the fluid $\text{kJ}/(\text{kg.K})$

Cp_s - heat capacity of the solid $\text{kJ}/(\text{kg.K})$

$\langle C_{BP} \rangle$ - average concentration of the fluid in the bottom reservoir (kg m^{-3})

$\langle C_{TP} \rangle$ - average concentration of the fluid in the top reservoir (kg m^{-3})

- d_p - diameter of the particle of the adsorbent (m)
- D - bed diameter (m)
- D_{ax} - axial dispersion (m^2s^{-1})
- D_{pe} - effective pore diffusivity (m^2s^{-1})
- D_m - molecular diffusivity (m^2s^{-1})
- f_h - humidity factor ($\text{g dry adsorbent/g adsorbent}$)
- h_w - global wall heat transfer coefficient $\text{kJ}/(\text{m}^2 \text{ s K})$
- K_{ae} - axial thermal conductivity ($\text{kJ}/(\text{m.s.K})$)
- K_L - parameter in the Langmuir isotherm model ($\text{m}^3 \text{ Kg}^{-1}$)
- K_L^∞ - equilibrium constant corresponding to the Langmuir model ($\text{m}^3 \text{ Kg}^{-1}$)
- k_{LDF} - Linear Driving Force (LDF) kinetic rate constant (s^{-1})
- L - bed length (m)
- m - mass of adsorbent (kg)
- $\overline{m}(T)$ - capacity parameter in the separation parameter b
- m - average slope in the separation parameter b
- M_B - molecular weight of solvent B (g mol^{-1})
- n - number of cycles
- Pe - Péclet number = $u_i L / D_{ax}$ (-)
- Pe_h - thermal Péclet number = $\rho_f C_p L / K_{ae} / u_0$ (-)
- Q - constant in the Langmuir isotherm model related to the adsorption capacity (mg g^{-1})
- $Q_{(\pi/\omega)}$ - reservoir displacement volume (m^3)
- Q_c - flowrate of the fluid in the column during the cold half-cycle ($\text{m}^3 \text{ s}^{-1}$)
- Q_h - flowrate of the fluid in the column during the cold half-cycle ($\text{m}^3 \text{ s}^{-1}$)

- Q_{BP} - flowrate of removing the product from the bottom reservoir ($\text{m}^3 \text{s}^{-1}$)
- Q_{TP} - flowrate of removing the product from the top reservoir ($\text{m}^3 \text{s}^{-1}$)
- q - 4-nitrophenol adsorbed per dry mass of adsorbent at a certain time (mg g^{-1})
- q^* - 4-nitrophenol adsorbed per dry mass of adsorbent in equilibrium with the 4-nitrophenol concentration in solution at a certain time (mg g^{-1})
- q_e - 4-nitrophenol adsorbed per dry mass of adsorbent at equilibrium (mg g^{-1})
- Re - Reynolds number (-)
- r_p - radius of the particle of the adsorbent (m)
- t - time (s)
- t_c - cold half-cycle time (s)
- t_h - hot half-time (s)
- T - absolute temperature (K)
- T_c - feeding temperature during the cold half-cycle (K)
- T_h - feeding temperature during the hot half-cycle
- T_{amb} - ambient temperature (K)
- u_0 - superficial velocity (m s^{-1})
- u_i - interstitial velocity (m s^{-1})
- V - volume of the solution (m^3)
- V_U - volume percolated during hot-half cycle (m^3)
- V_A - molar volume of solute a at its normal boiling temperature ($\text{cm}^3 \text{mol}^{-1}$)
- W - dry weight of the corresponding adsorbent (kg)
- z - axial coordinate in the bed (m)

Greek Letters

- ε - bed porosity

ε_p - porosity of the adsorbent

ϕ - dimensionless association factor of solvent B

ϕ_B - fraction of the $Q_{(\pi/\omega)}$ that is withdrawn as bottom product

ϕ_T - fraction of the $Q_{(\pi/\omega)}$ that is withdrawn as top product

η - viscosity of the solution (Pa.s)

η_B - viscosity of solvent B (Pa.s)

Ω - LDF factor, which is equal to 3, 8 or 15 for slab, cylindrical or spherical geometry

ρ_p - density of the adsorbent (kg m^{-3})

ρ_f - density of the fluid (kg m^{-3})

τ - tortuosity of the adsorbent

4.7 References

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5. Separation of synthetic vanillin at different pH onto polymeric adsorbent Sephabeads SP 206¹

5.1 Introduction

Vanillin (4-hydroxy-3-methoxybenzaldehyde) is the major component of natural vanilla, which is one of the most used flavoring materials in the food industry, confectionery products and also as a fragrance (Walton *et al.*, 2003),(Walton *et al.*, 2000). Presently approximately 50% of the worldwide production of synthetic vanillin is used as an intermediate in the chemical and pharmaceutical industries for the production of herbicides, antifoaming agents or drugs (Walton *et al.*, 2003),(Hocking, 1997). Synthetic vanillin is also used in household product, such as air-fresheners and floor polishes. Vanillin displays antioxidant and antimicrobial properties and so has the potential for use as a food preservative (Krueger and Krueger, 1983; Burri *et al.*, 1989; Dausch and Pastore, 2005). It is active against both Gram-positive and Gram-negative food-spoilage bacteria but also shows antimutagenic effect (Cerrutti *et al.*, 1997; Keshava *et al.*, 1998; Fitzgerald *et al.*, 2004; Fitzgerald *et al.*, 2005). The source of vanilla is the bean, or pod of the tropical Vanilla orchid (principally Vanilla

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planifolia Andrews, syn. *V. fragrans* (Salisb. Ames) (Walton *et al.*, 2003; Dausch and Pastore, 2005). Vanillin occurs also in other plants, including commercial products such as tobacco (Makkar and Becker, 1994); however, the pods of the *Vanilla* orchid still remain the greatest commercial source of natural vanillin. In addition to vanillin, natural vanilla contains a large number of other organic compounds. About 200 of these constituents have so far been identified, of which only 26 occur in concentrations greater than 1 ppm (Anklam *et al.*, 1997). The five most important constituents are vanillin itself (2-2.8%), p-hydroxybenzaldehyde (about 0.2%), vanillic acid (about 0.2%), p-hydroxybenzylmethyl ether (about 0.02%) and acetic acid (about 0.02%) (Klimes and Lamparsky, 1977; Anklam and Muller, 1993).

Natural vanillin is mainly obtained after process of ageing by an alcoholic extraction of vanilla pods and industrial one is obtained by chemical synthesis from guaiacol or black liquors from the paper industry (Forss *et al.*, 1986). The world market consists of around 1800 tons of pods, industrial vanillin is around 12,000 tons and a market price is bellowing \$15 per kg, while the market price of natural vanillin is approximately \$1200-\$4000 per kg (Lomascolo *et al.*, 1999; Muheim and Lerch, 1999).

The main part of vanillin production is formed by oxidation of sulfite liquor, which is a side product of the wood pulping process. Vanillin is presented in oxidizing solution as a sodium salt of vanillin and its isolation can be provided by acidification of the liquor with subsequent extraction (Hibbert and Tomlinson, 1937). Disadvantage of this method is that a large amount of acidic solution is needed for neutralization and also the precipitation of the lignin makes this process more complicated. Another method used is extraction of sodium vanillate from the alkaline solution by alcohols (Sandborn *et al.*, 1936). The limited solubility of sodium vanillate in organic solvents is weak point in this case.

The goals of the chapter were to determine adsorption equilibrium isotherms of vanillin onto nonionic polymeric adsorbent Sephabeads SP206 at different temperatures (293 K, 310 K, and 333 K) and to evaluate adsorption kinetics in fixed-bed. The fixed-bed breakthrough curves of vanillin onto polymeric resin SP206 at different flow rates, feed concentrations, and at different temperatures have been studied. Influence of concentration of sodium hydroxide on adsorption of vanillin using static and dynamic approach has been investigated.

5.2 Experimental part

5.2.1 Chemicals and adsorbents

Vanillin ($\text{C}_8\text{H}_8\text{O}_3$) and sodium hydroxide (NaOH) were purchased from Sigma-Aldrich (Spain). The solutions of vanillin and sodium hydroxide were prepared with degassed and deionised water. The adsorption of vanillin from aqueous solutions by using non-ionic polymeric resin Sephabeads SP206 (Mitsubishi Chemical Corporation) was carried out purchased from Residion (Italy). The physical characteristics of polymeric resin SP206 provided by the manufacturer are summarized in *Table 5.1*.

Table 5.1 Physical and chemical properties of the polymeric adsorbent Sephabeads SP206

Color and physical form	Yellowish brown opaque spherical beads
Density of wet adsorbent (kg m^{-3})	1190
Moisture content at delivery (%)	50.0
Pore volume (mL g^{-1})	1.02
Surface area ($\text{m}^2 \text{g}^{-1}$)	556
Pore radius ($\text{\AA}$)	100-150
Particle size range (mm)	0.25-0.6
Particle size used in experiment (mm)	0.4
Porosity of the particle	0.61
Operating pH range	0-14

5.2.2 Equipment

The batch adsorption experiments by using Erlenmeyer flasks with the jacket were performed, which were placed in shaking mixer (GLF-3018, Germany). The temperature was controlled using thermostatic bath (Edmund Bühler, Germany). The solution was analyzed on UV-VIS spectrophotometer Jasco (model 7800, Japan) at the wavelength 254, 259 and 376 nm. The fixed bed adsorption studies were performed in glass column with the jacket (150×20 mm,

I.D.). The vanillin solution was pumped to the system by peristaltic pump Watson-Marlow (England).

5.2.3 Batch adsorption

Batch experiment has been carried out in two stages. The first stage of batch experiment without sodium hydroxide has been realized in order to obtain the adsorption equilibrium isotherm of vanillin onto adsorbent SP206. The adsorption equilibrium isotherm at three different temperatures has been studied. The second stage of batch experiment has been performed to study the influence of sodium hydroxide on adsorption of vanillin onto adsorbent SP206. The batch experiment has been performed in 250 mL Erlenmeyer flasks where 20 mL of vanillin solution with the same concentration and the different mass of the wet adsorbent have been added. The mass of wet adsorbent was in the range 0.05 g to 1.5 g. The humidity of the adsorbent SP206 was determined for each experiment as a difference between weight of wet adsorbent and after drying at 150 °C. The initial concentrations of the vanillin used in the first stage and in the second stage of batch experiment were $3.30 \times 10^{-3} \text{ mol L}^{-1}$ and $6.60 \times 10^{-3} \text{ mol L}^{-1}$, respectively. The concentrations of sodium hydroxide used were $1 \times 10^{-3} \text{ mol L}^{-1}$ and $5 \times 10^{-3} \text{ mol L}^{-1}$. Solutions were prepared in degassed and deionized water. Temperature was controlled by thermostatic bath. Equilibrium experiments at 293, 310 and 333 K for each adsorbent-vanillin and adsorbent/vanillin-sodium hydroxide system were performed. The volumetric flasks were placed in a shaking mixer at constant speed 150 rpm. The equilibrium in solid-liquid mixture has been reached approximately within 12 hours. The solution was separated from the adsorbent and the final concentration of vanillin was determined by measuring the absorbance using UV-VIS spectrophotometer. The absorbance of the vanillin solution without sodium hydroxide was measured at wavelength of 254 nm.

The total concentration of vanillin and vanillate species was determined by measuring the absorbance at the wavelength 259 nm, which is isobestic point. Additionally, the concentration of vanillate was determined at the wavelength of 376 nm.

5.2.4 Fixed-bed adsorption

The fixed bed adsorption studies on the polymeric adsorbent SP206 were performed by the same approach as was pointed out in previous section. The glass column with jacket (150 × 20 mm, I.D.) has been used in all fixed-bed experiment and solutions have been delivered by

peristaltic pump. Fixed bed adsorption experiments of vanillin without the presence of sodium hydroxide onto adsorbent SP206 were carried out at three different temperatures 293, 310 and 333 K. The temperature of the column was maintained by a thermostatic bath. Vanillin concentration at the column outlet was determined at wavelength of 254 nm by an UV-VIS spectrophotometer. Different runs by changing the flow rate (20, 30, 50 mL min⁻¹), concentration of vanillin in feed solution (3.30×10^{-3} mol L⁻¹ and 0.66×10^{-4} mol L⁻¹) and the temperature of the feed solution were carried out in the first stage.

In the second stage of experiment the influence of concentration of sodium hydroxide has been investigated. For this purpose 1×10^{-3} mol L⁻¹ and 5×10^{-3} mol L⁻¹ as initial concentrations of sodium hydroxide has been used. The concentration of vanillin and vanillate species in the same manner as was pointed out in the batch adsorption studies part has been determined. The total concentration of the feed solution was 8.25×10^{-3} mol L⁻¹ and 8.72×10^{-3} mol L⁻¹. The concentration of the vanillin species at the system adsorbent/vanillin-sodium hydroxide was set as difference of total concentration (sum of concentration of vanillin and vanillate species) and concentration of the sodium vanillate. Different runs by changing the flow rate (14 and 20 mL min⁻¹), pH and the temperature of the feed solution were carried out in the second stage.

5.3 Theoretical section

5.3.1 Adsorption equilibrium isotherms

The adsorption equilibrium isotherms from batch experiments of vanillin onto polymeric adsorbent SP206 at three temperatures (293, 310 and 333 K) were evaluated. The isotherms of vanillin were measured by static method batch equilibration of a known mass of adsorbent with a given volume of vanillin solution. After equilibrium in solution was reached the concentration of vanillin C^* was measured and the vanillin concentration adsorbed in the resin q^* was determined by mass balance. The amount of vanillin adsorbed onto adsorbent q^* (mol g⁻¹ of dry resin) was found from the initial and final concentration in the liquid phase. Mass balance in static system is given

$$q^* = \frac{V(C_0 - C^*)}{W} \quad 5.1$$

where C_0 and C^* (mol L^{-1}) are the initial and equilibrium concentrations of vanillin in liquid phase, respectively (Diez *et al.*, 1998), V the volume of the solution (L), and W the dry mass (g) of the adsorbent. The equilibrium adsorption isotherms for each temperature were measured in two parallel experiments to reduce experimental errors.

Adsorption equilibrium of vanillin onto polymeric resin SP206 without sodium hydroxide has been described by Langmuir isotherm model. The Langmuir model is based on assumption that adsorption occurs onto specific sites of a uniform energetic surface, without interactions between adsorbed molecules and adsorption is confined to monolayer coverage (Ruthven, 1984) and is given

$$q^* = q_s \frac{bC^*}{1 + bC^*} \quad 5.2$$

where q_s is the saturation capacity and b relates to the adsorption enthalpy given as

$$b = b_\infty \exp\left(-\frac{\Delta H}{RT}\right) \quad 5.3$$

where b_∞ is the pre-exponential factor of adsorption equilibrium constant, ΔH is heat of adsorption, R is the gas constant and T is the temperature.

The heat of adsorption can be determined at given loading by Claapeyron equation (Snyder, 1969)

$$\frac{\Delta H}{RT^2} = -\left(\frac{\partial \ln c}{\partial T}\right)_q \quad 5.4$$

The heat of adsorption at given loading was approximately calculated using integrated Claapeyron relationship (Snyder, 1969).

$$-\Delta H \approx \frac{\ln\left(\frac{c_2}{c_1}\right)}{\left(\frac{1}{T_1} - \frac{1}{T_2}\right)} R \quad 5.5$$

5.3.2 Adsorption equilibrium isotherm in the presence of sodium hydroxide

The effect of sodium hydroxide on the adsorption equilibrium of vanillin onto polymeric resin SP206 has been studied.

The reaction taking place in the liquid phase in static system between vanillin and sodium hydroxide is the following



The equilibrium constant of the reaction is given as

$$K_{eq} = \frac{[C_8H_7O_3^-]}{[C_8H_8O_3][OH^-]} \quad 5.7$$

It is well known that there is no adsorption of sodium salt of phenolic compounds onto nonionic polymeric resin (Garcia *et al.*, 2002). Therefore, vanillate as a sodium salt of vanillin was considered as non-adsorbed compounds, which allows studying the effect of pH on the adsorption equilibrium. Considering $C_T = C_V + C_{VN}$, where C_T is the total molar concentration, C_V is the concentration of vanillin and C_{VN} is the vanillate concentration and by combining equation (5.2) and (5.7) one can obtain the extended Langmuir equation (Garcia *et al.*, 2002), where the pH of solution is taken into account.

$$q_V = q_s \frac{bC_T}{1 + K_{eq} 10^{pH-14} + bC_T} \quad 5.8$$

where q_V is molar concentration of vanillin in the solid phase, q_s is the saturation capacity and b is the adsorption equilibrium constant, which was evaluated in previous experiment without the presence of sodium hydroxide in solution.

5.3.3 Fixed-bed modeling

In order to study the adsorption behavior of the vanillin, sodium hydroxide onto SP206 in a fixed-bed system, a dynamic model was used. This mathematical model comprises the mass balance in the liquid phase, a linear driving force (LDF) for homogeneous particle and the nonlinear adsorption isotherm. The model equations for an isothermal adsorption in a fixed bed are as follows:

Mass balance of species “ i ” in a bed volume element:

$$\frac{\partial C_i(z,t)}{\partial t} = D_{ax} \frac{\partial^2 C_i(z,t)}{\partial z^2} - u_i \frac{\partial C_i(z,t)}{\partial z} - \frac{1-\varepsilon}{\varepsilon} \rho_s f_h \frac{\partial q_i(z,t)}{\partial t} + \mathfrak{R}_i; \quad i = 1, 2, 3, \dots \quad 5.9$$

where D_{ax} is the axial dispersion coefficient, u_i is the interstitial velocity, ε is the bed porosity, z is the axial position, t is the time variable, C_i is the concentration in the bulk fluid phase for the species (vanillin, vanillate, sodium hydroxide), q_i is the average adsorbed phase concentration of species in the particle, ρ is the density of wet adsorbent and f_h is the dry particle to wet particle mass ratio. $\mathfrak{R}_i$ is the reaction term for homogenous reaction taking place in the liquid phase around the homogeneous particle. For the vanillate and sodium hydroxide species, the term $\frac{\partial q_i(z,t)}{\partial t} = 0$ since they are not adsorbed onto the polymeric resin.

5.3.4 Kinetics of reaction vanillin/sodium hydroxide

The kinetics of reaction taking place between vanillin and sodium hydroxide is described by a first order law on each species resulting in the overall rate law:

$$r_1 = k_1 C_V C_{OH} - k_2 C_{VN} \quad 5.10$$

where r_1 represents the velocity of vanillin disappearance, k_1 , k_2 reaction rate constants and C_V , C_{OH} , C_{VN} are the concentration of vanillin, sodium hydroxide and vanillate respectively. The chemical reaction between vanillin and sodium hydroxide is very fast and the equilibrium is established almost instantaneously. For the system under consideration, the equilibrium constant for the vanillin reaction is $K_{eq} = \frac{k_1}{k_2}$ and is shown in *Table 5.2*.

The intraparticle mass transfer has been approximated by linear driving force (LDF) as is given:

$$\frac{\partial q_i(z,t)}{\partial t} = k_{LDF} [q_i^*(z,t) - q_i(z,t)] \quad 5.11$$

where k_{LDF} is the linear driving force kinetic coefficient, q_i^* is the adsorbed phase concentration in equilibrium with the bulk concentration at the certain time and q_i is the average adsorbed phase concentration in the homogeneous adsorbent particle. Intraparticle

mass transfer has been described by a linear driving force model, indicating that the rate of adsorption into the particle is proportional to the driving force (difference between adsorbed phase concentration in equilibrium with the bulk fluid concentration and average adsorbed phase concentration in the particle) still required to reach equilibrium. The boundary conditions for the mass balance equation are the Danckwerts boundary conditions:

$$z = 0; \quad D_{ax} \frac{\partial C(z,t)}{\partial z} \Big|_{z=0} = u_i (C(0,t) - C_{feed}) \quad 5.12$$

$$z = L; \quad \frac{\partial C(z,t)}{\partial z} \Big|_{z=L} = 0 \quad 5.13$$

The associated initial conditions for the adsorption are:

$$C_i(z,0) = 0 \quad 5.14$$

$$q_i(z,0) = 0 \quad 5.15$$

The axial dispersion coefficient was obtained from the expression (Guiochon *et al.*, 1994b)

$$(0.2 + 0.011 \text{Re}^{0.48}) = \frac{u_0 d_p}{D_{ax}} \quad 5.16$$

$$\text{where } \text{Re} = \frac{u_i \rho \varepsilon d_p}{\eta}.$$

The values of the calculated axial dispersion coefficient D_{ax} are shown in *Table 5.4*.

The linear driving force coefficient, k_{LDF} for homogeneous particle, was estimated by (Eq. 5.17), (Glueckauf and Coates, 1947).

$$k_{LDF} = \frac{\Omega D_{pe}}{\rho_s f_h r_p^2 \frac{\Delta q}{\Delta C}} \quad 5.17$$

where D_{pe} is the effective pore diffusivity, r_p is the radius of the particle of the adsorbent, Ω is constant, which is equal to 15 for the spherical particles (Glueckauf and Coates, 1947) ρ_s is the density of adsorbent, f_h the dry particle to wet particle mass ratio and $\left(\frac{\Delta q}{\Delta C}\right)$ the slope of the equilibrium isotherm.

The effective pore diffusivity $D_{pe} = \frac{\varepsilon_p D_m}{\tau}$, where D_m is the molecular diffusivity of vanillin in water, $\tau=2$ is the tortuosity of the adsorbent and ε_p its porosity. Molecular diffusivities, D_m ($\text{cm}^2 \text{s}^{-1}$), of vanillin at different temperatures are estimated by the Wilke-Chang estimation method (Reid *et al.*, 1987).

$$D_m = 7.4 \times 10^{-8} \frac{T \sqrt{\phi M}}{\eta V_m^{0.6}} \quad 5.18$$

where M is molecular weight of solvent (g mol^{-1}), ϕ is association factor of solvent, which account for solute-solvent interactions and was set equal to 2.6 for water (Reid *et al.*, 1987), T is absolute temperature (K), η is viscosity of solvent (cP), V_m molar volume of solute at its normal boiling temperature is $142.64 \text{ (cm}^3 \text{mol}^{-1})$.

The model equations (Eqs.5.6-5.15) were solved with gPROMS (gPROMS, 2003). The mathematical model involves a system of partial differential equations and algebraic equations (PDAEs). The axial domain was discretized using orthogonal collocation method on finite elements (OCFEM) over 50 elements with third order polynomials in each element. The system of ordinary differential and algebraic equation (ODAEs) was integrated over time using the DASOLV integrator implemented in gPROMS. The model can predict breakthrough and desorption curves that can be compared with those obtained experimentally.

5.4 Results and discussion

5.4.1 Adsorption equilibrium isotherm

The equilibrium adsorption isotherms for vanillin onto nonionic polymeric resin SP206 have been measured. The equilibrium adsorption isotherms of vanillin onto nonionic polymeric resin SP206 have been measured and fitted with Langmuir isotherm equation. The heat of adsorption of vanillin was calculated from experimental adsorption equilibrium data using (Eq. 5.5) at constant loading. The average value is 29.2 kJ mol^{-1} . It was also calculated after fitting of equilibrium isotherm with Langmuir equation leading to a value of 28.5 kJ mol^{-1} which is independent of loading and is reported in Table 5.2.

The loading is defined as q^*/q_s . Based on this fact the saturation capacity of the resin has been considered independent of temperature and in the process of evaluation of the isotherm parameters it was set constant for all tested temperatures. Parameters of Langmuir model of isotherm were evaluated by nonlinear fitting. As a minimization algorithm to improve accuracy in the determination of the isotherm parameters Levenberg-Marquardt method was used, which is incorporated in Origin 6.0 (Microcal Software, USA). The obtained coefficients of Langmuir model of isotherm are reported in the Table 5.2.

Table 5.2 Langmuir isotherms parameters and equilibrium constant at the temperature 293, 310 and 333 K

T (K)	q_s (mol g ⁻¹)	b_∞ (L mol ⁻¹)	$(-\Delta H)$ (kJ mol ⁻¹)	b (L mol ⁻¹)	K_{eq} (L mol ⁻¹)
293	7.534×10^{-4}	3.58×10^{-2}	28.5	4599.3	0.39×10^7
310				1912.5	0.44×10^7
333				1116.5	0.49×10^7

The experimental adsorbed concentrations as a function of liquid-phase concentration corresponding to the vanillin adsorption onto SP206 at each of the temperatures involved are shown in Figure 5.1. The obtained fittings using Langmuir model are shown in Figure 5.1 as well.

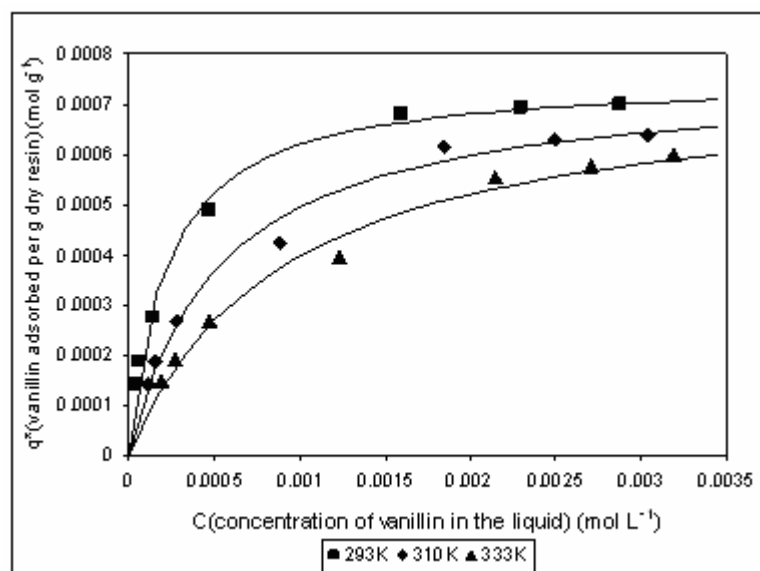


Figure 5.1 Adsorption equilibrium isotherms fitted by the Langmuir equation for the vanillin solution without sodium hydroxide onto polymeric resin SP206. Initial concentration of vanillin was 3.30×10^{-3} mol L⁻¹ with the corresponding pH = 5.3

The adsorption equilibrium constants decrease when increasing temperature. Although, vanillin shows the highest saturation capacity among phenolic compounds family reported in literature onto non-ionic polymeric resin SP206, the influence of temperature is not as strong as in other systems (Otero *et al.*, 2004; Otero *et al.*, 2005a; Otero *et al.*, 2005b).

The set of the experiments with the presence of sodium hydroxide were performed in order to study an effect on the adsorption equilibrium of vanillin. The comparison between calculated and experimental adsorption isotherms of vanillin at different pH of solution adjusted by 1 mM and 5 mM concentration of sodium hydroxide are given in the *Figure 5.2 - Figure 5.4* at temperatures of 293 K, 310 K and 333 K, respectively. The x- axis indicates according modified Langmuir (see Eq. 5.8) total concentration (sum of concentration of vanillin and vanillate) after reaching equilibrium and y-axis indicates amount of adsorbed vanillin per gram of dry resin. The full line represents extended Langmuir model at various pH values and points are experimental results. The numbers at each point indicate the final equilibrium pH for each experiment. As it has been pointed out above sodium hydroxide and vanillate are not adsorbed onto resin SP206. It can be seen that the amount of vanillin adsorbed is decreasing with the increasing pH of the solution or amount of sodium hydroxide added to solution of vanillin.

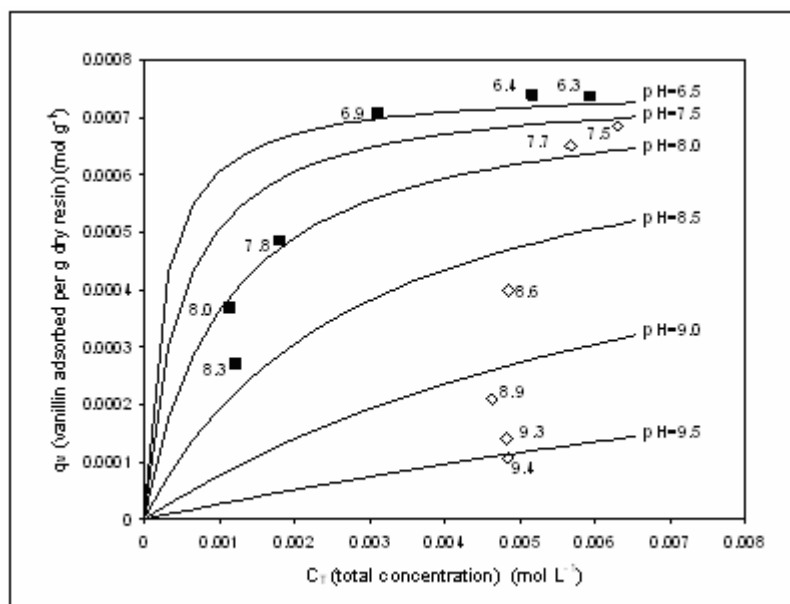


Figure 5.2 Adsorption isotherms of the vanillin adsorbed per gram of dry resin as a function of the total concentration (vanillin + vanillate). The initial solution was prepared by mixing 1×10^{-3} M NaOH, 5×10^{-3} M respectively and 6.60×10^{-3} mol L⁻¹ of vanillin. Initial pH of the solution was 6.5, 7.6 respectively. $K_{eq} = 0.39 \times 10^7$ L mol⁻¹. The temperature is 293 K.

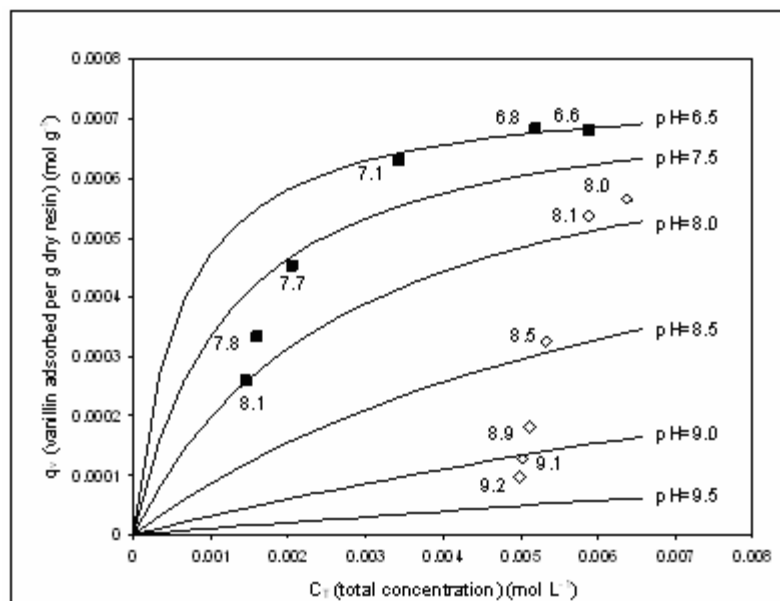


Figure 5.3 Adsorption isotherms of the vanillin adsorbed per gram of dry resin as a function of the total concentration (vanillin + vanillate). The initial solution was prepared by mixing 1×10^{-3} M NaOH, 5×10^{-3} M respectively and 6.60×10^{-3} mol L⁻¹ vanillin. Initial pH of the solution was 6.5, 7.6 respectively. $K_{eq} = 0.44 \times 10^7$ L mol⁻¹. The temperature is 310 K

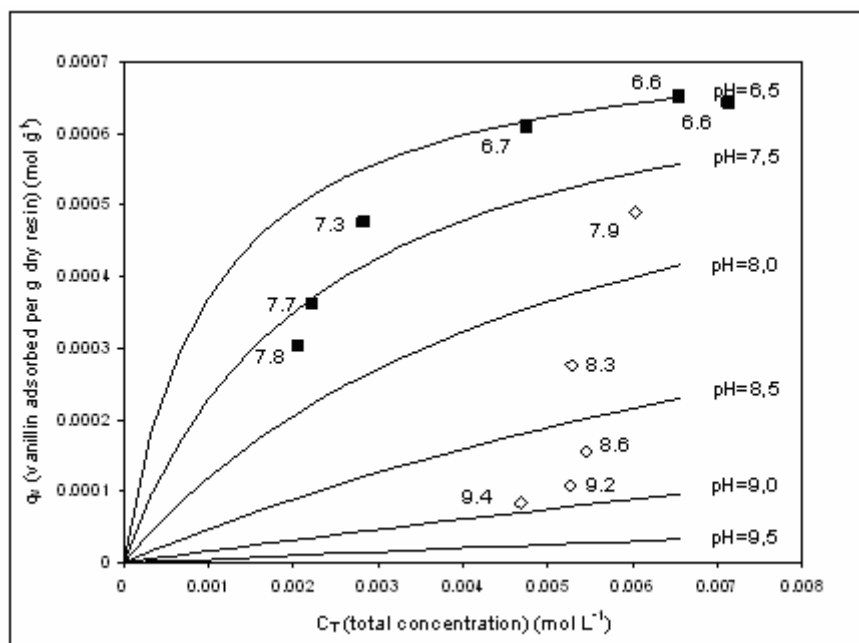


Figure 5.4 Adsorption isotherms of the vanillin adsorbed per gram of dry resin as a function of the total concentration (vanillin + vanillate). The initial solution was prepared by mixing 1×10^{-3} M NaOH, 5×10^{-3} M respectively and 6.60×10^{-3} mol L⁻¹ vanillin. Initial pH of the solution was 6.5, 7.6 respectively. $K_{eq} = 0.49 \times 10^7$ L mol⁻¹. The temperature is 333 K

5.4.2 Fixed- bed adsorption

The fixed bed adsorption of vanillin was studied onto the polymeric resin SP206 on a laboratory scale to investigate the influence of feed concentration of vanillin, temperature, flow rate and pH on the process performance. The breakthrough curve experiments without sodium hydroxide were performed under conditions reported in *Table 5.3*. The parameters of mathematical model used to predict breakthrough curves are summarized in *Table 5.3*. The calculated values of molecular diffusivity and kinetic coefficient k_{LDF} are summarized in *Table 5.4*.

Table 5.3 Experimental conditions for the fixed-bed adsorption of vanillin onto polymeric adsorbent Sephabeads SP 206.

Q (mL min ⁻¹)	T (K)	$C_{V,feed}$ (mmol L ⁻¹)	pH	Re	D_{ax} (cm ² min ⁻¹)
30	293	0.66	5.8	0.622	1.830
	310			0.893	1.815
	333			1.311	1.797
50	293	0.66		1.037	3.015
	310			1.489	2.984
	333			2.185	2.947
20	293	3.30	5.3	0.415	1.229
	310			0.596	1.221
	333			0.874	1.211
30	293	3.30		0.622	1.830
	310			0.893	1.815
	333			1.311	1.797

Table 5.4 Calculated values of molecular diffusivity and k_{LDF} for vanillin in absence of sodium hydroxide.

$C_{V,feed}$ (mmol L ⁻¹)	T (K)	D_m (cm ² min ⁻¹)	k_{LDF} (min ⁻¹)
0.66	293	4.44×10^{-4}	0.015
	310	6.76×10^{-4}	0.027
	333	10.80×10^{-4}	0.047
3.30	293	4.44×10^{-4}	0.034
	310	6.76×10^{-4}	0.055
	333	10.80×10^{-4}	0.085

The experimental and theoretical transient concentration profiles for vanillin at the feed concentration $6.60 \times 10^{-4} \text{ mol L}^{-1}$, and at the flow rate 30 mL min^{-1} and 50 mL min^{-1} are presented in *Figure 5.5* and *Figure 5.6*, respectively. The mathematical model used, which involved linear driving force for the intraparticle mass transfer describes satisfactorily the fixed-bed adsorption of vanillin onto Sephabeads SP206 at the temperatures considered. It can be observed that lowering the flow-rate of the feeding leads to later breakthrough times.

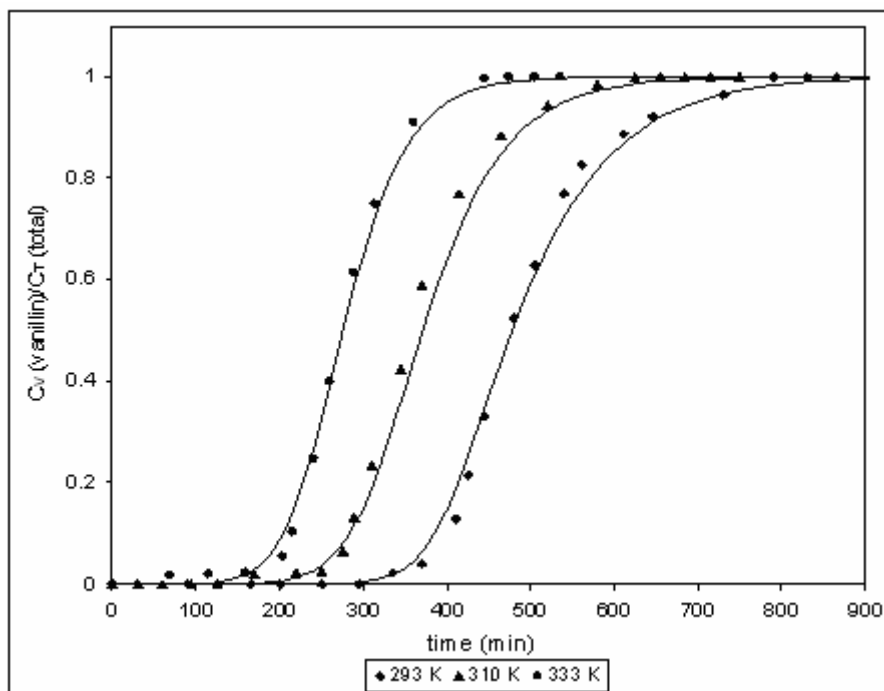


Figure 5.5 Experimental and simulated adsorption curves of vanillin onto polymeric resin SP206 at the temperature 293 K, 310 K and 333 K using column ($150 \times 20 \text{ mm}$, I.D.). (flow rate: 30 mL min^{-1} , feed concentration $6.60 \times 10^{-4} \text{ mol L}^{-1}$).

The predicted and experimental breakthrough curves for vanillin at the feed concentration $3.30 \times 10^{-3} \text{ mol L}^{-1}$ and at the flow rate 20 mL min^{-1} and 30 mL min^{-1} are shown in *Figure 5.7* and *Figure 5.8*, respectively. In the calculation of the mass transfer coefficient k_{LDF} , the slope of the chord ($\frac{\Delta q}{\Delta C}$) was used instead of the local slope of the adsorption isotherm. It can be observed that increasing the concentration, the derivative decreases and as a result the mass transfer coefficient is higher. The external mass transfer resistance was neglected since Biot number $Bi = k_f d_p / D_{pe}$ is always higher than 100.

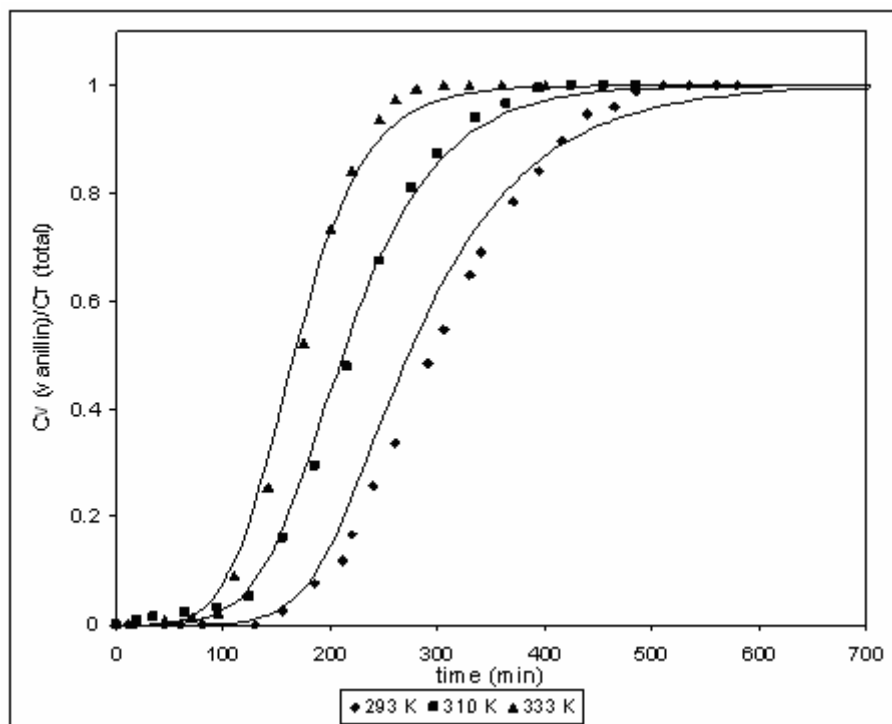


Figure 5.6 Experimental and simulated adsorption curves of vanillin onto polymeric resin SP206 by the temperature 293 K, 310 K and 333 K using column (150 x 20 mm, I.D.). (flow rate 50 mL min^{-1} , feed concentration $6.60 \times 10^{-4} \text{ mol L}^{-1}$)

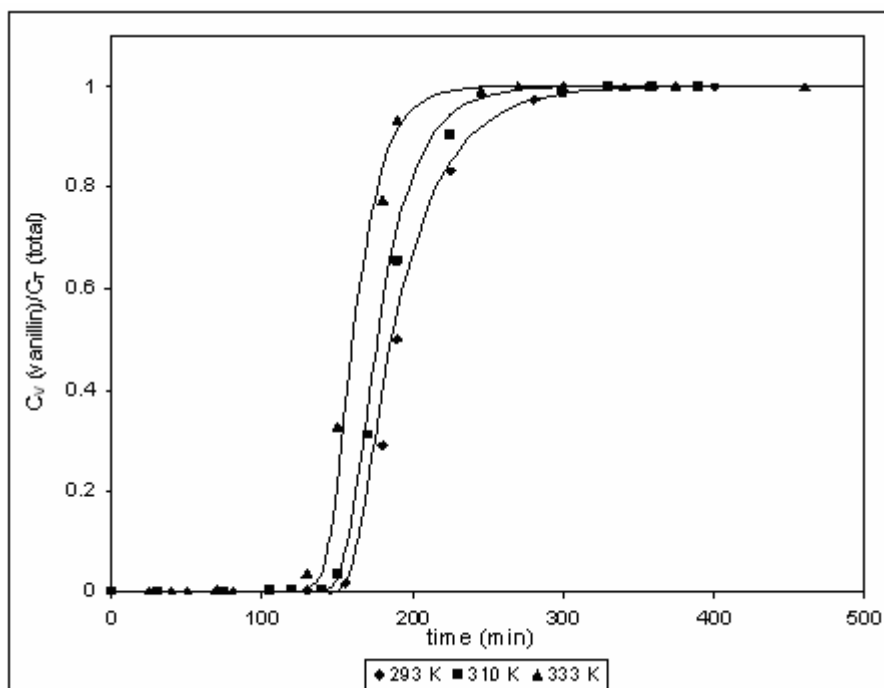


Figure 5.7 Experimental and simulated adsorption curves of vanillin onto polymeric resin SP206 by the temperature 293 K, 310 K and 333 K using column (150 x 20 mm, I.D.). (flow rate 20 mL min^{-1} , feed concentration $3.30 \times 10^{-3} \text{ mol L}^{-1}$)

It should be pointed out that with increasing temperature of the system the saturation of the bed occurs earlier at both tested concentrations of feed solution of vanillin (see *Figure 5.5 - Figure 5.8*). Furthermore, the influence of temperature with increasing feed concentration is decreasing and therefore the separation of vanillin is decreasing by the temperature of the system.

The breakthrough curve experiments in the presence of sodium hydroxide were performed under experimental conditions reported in *Table 5.5*. The parameters of mathematical model used to predict concentration profiles of vanillin, vanillate and sodium hydroxide are summarized in *Table 5.5*. The calculated values of molecular diffusivity and kinetic coefficient k_{LDF} are summarized in

Table 5.6.

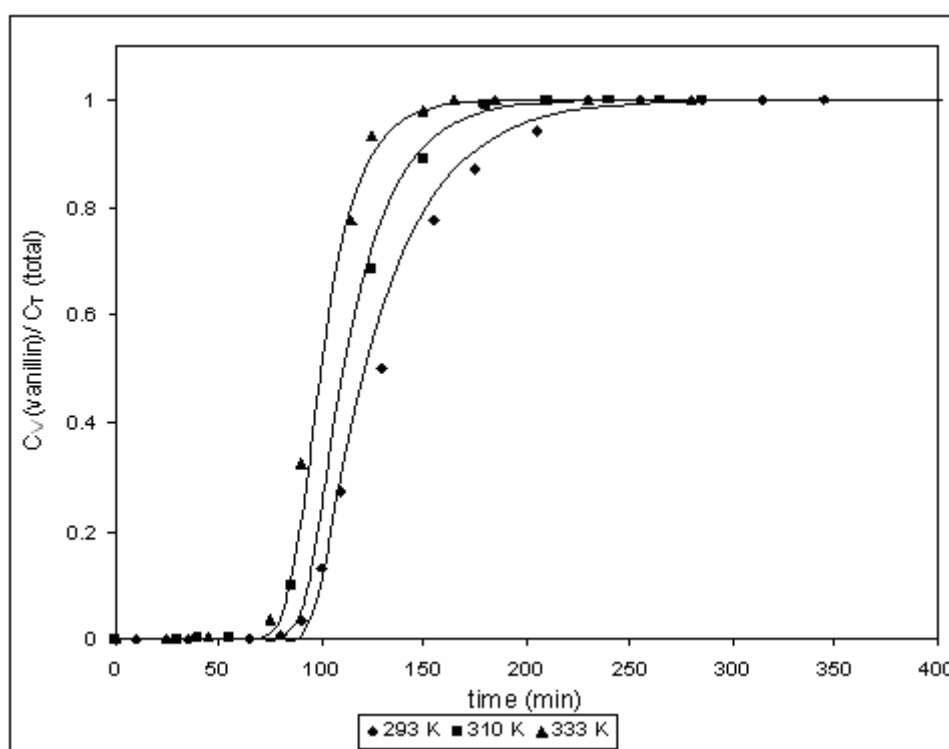


Figure 5.8 Experimental and simulated adsorption curves of vanillin onto polymeric resin SP206 by the temperature 293 K, 310 K and 333 K using column (150 x 20 mm, I.D.). (flowrate 30 mL min⁻¹, feed concentration 3.30×10^{-3} mol L⁻¹)

Table 5.5 Experimental conditions for the fixed-bed adsorption of vanillin in presence of sodium hydroxide in feed solution

Q (mLmin ⁻¹)	T (K)	Re	D_{ax} (cm ² min ⁻¹)	pH	$C_{V,feed}$ (mmol L ⁻¹)	$C_{T,feed}$ (mmol L ⁻¹)	$C_{VN,feed}$ (mmol L ⁻¹)
14	293	0.290	0.865	6.7	6.72	8.25	1.53
	310	0.417	0.860	6.6	6.74	8.25	1.51
20	293	0.415	1.229	7.4	3.54	8.72	5.18
	310	0.596	1.221	7.5	3.57	8.72	5.15

Table 5.6 Calculated values of molecular diffusivity and k_{LDF} for vanillin in presence of sodium hydroxide.

$C_{VN,feed}$ (mmol L ⁻¹)	T (K)	$C_{V,feed}$ (mmol L ⁻¹)	$C_{T,feed}$ (mmol L ⁻¹)	pH	D_m (cm ² min ⁻¹)	k_{LDF} (min ⁻¹)
1.53	293	6.72	8.25	6.7	4.44×10^{-4}	0.050
1.51	310	6.74	8.25	6.6	6.76×10^{-4}	0.080
5.18	293	3.54	8.72	7.4	4.44×10^{-4}	0.055
5.15	310	3.57	8.72	7.5	6.76×10^{-4}	0.092

Figure 5.9 and Figure 5.10 show experimental and theoretical transient concentration profiles for vanillin, vanillate and sodium hydroxide on the column (150 x 20 mm, I.D.) packed with resin SP 206 at the total feed concentration 8.25×10^{-3} mol L⁻¹ and at temperatures 293 K and 310 K, respectively.

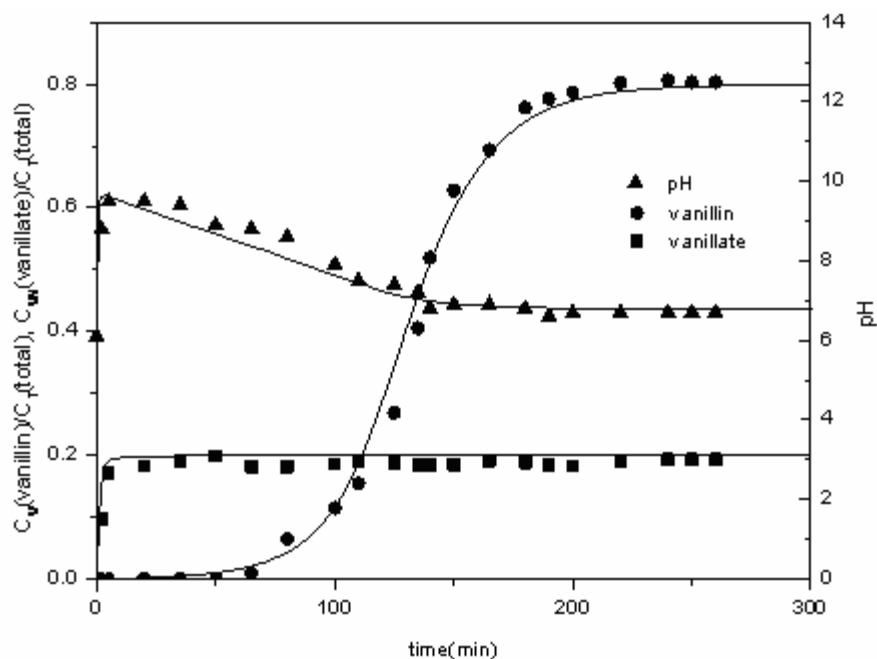


Figure 5.9 Breakthrough curve of the vanillin. The y-axis is shown as a concentration of vanillin, vanillate / total concentration. The feeding solution was prepared by mixing 1×10^{-3} M NaOH and 8.25×10^{-3} mol L⁻¹ vanillin and pH was 6.7. The initial pH in the zero time was 6.1. The flow rate is 14 mL min⁻¹, the temperature was 293 K. The points are showing experimental points full line demonstrates simulated curves

The predicted and experimental breakthrough curves for vanillin, vanillate and sodium hydroxide at the total molar concentration 8.72×10^{-3} mol L⁻¹ are shown in Figure 5.11 and Figure 5.12 at temperatures 293 K and 310 K, respectively. By adding the sodium hydroxide to the vanillin solution the sodium vanillate is formed according to the chemical reaction (see Eq. 5.6).

The equilibrium constant of the reaction $K_{eq} = k_1/k_2$ was evaluated from a series of experiments. The reaction is very fast and equilibrium is established instantaneously. The kinetic constant k_1 was set as an adjustable parameter with the value 1×10^6 L mol⁻¹ min⁻¹. This value was kept constant in all simulations performed in the work.

Sodium hydroxide and sodium vanillate are not adsorbed onto non-ionic resin SP206 and they are leaving at the time equal to the space time of the column. As soon as vanillin is removed from the solution by the adsorbent the equilibrium described by (Eq. 5.6) is displaced to the left side which leads to an increase of pH values. At a point the bed after saturation with vanillin the pH must decrease again to the value of feed solution.

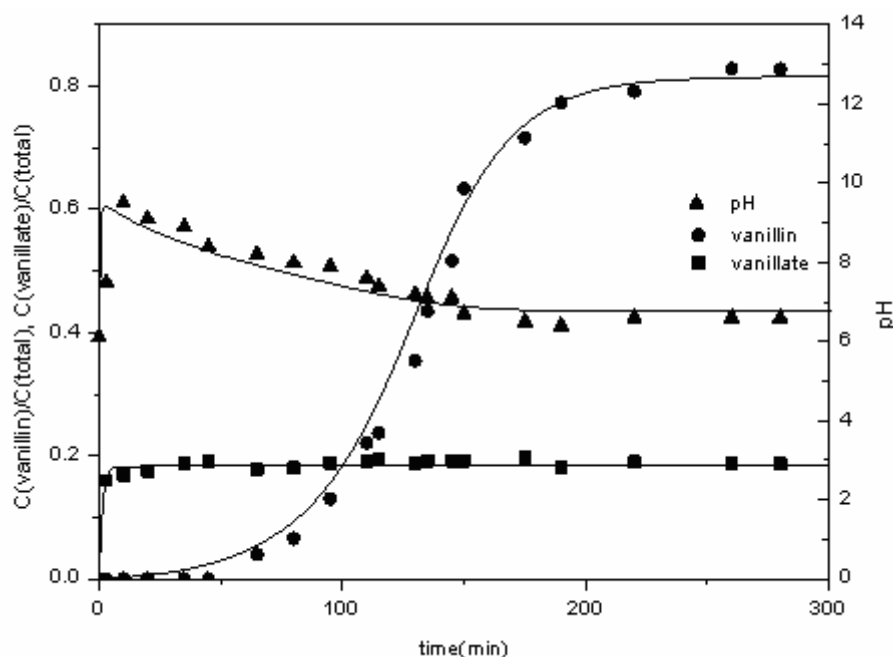


Figure 5.10 Breakthrough curve of the vanillin. The y-axis is shown as a concentration of vanillin, vanillate / total concentration. The feeding solution was prepared by mixing 1×10^{-3} M NaOH and 8.25×10^{-3} mol L^{-1} vanillin and pH was 6.6. The initial pH at time zero was 6.1. The flow rate is 14 mL min^{-1} , the temperature was 310 K. The points are showing experimental points, full line demonstrate simulated curves

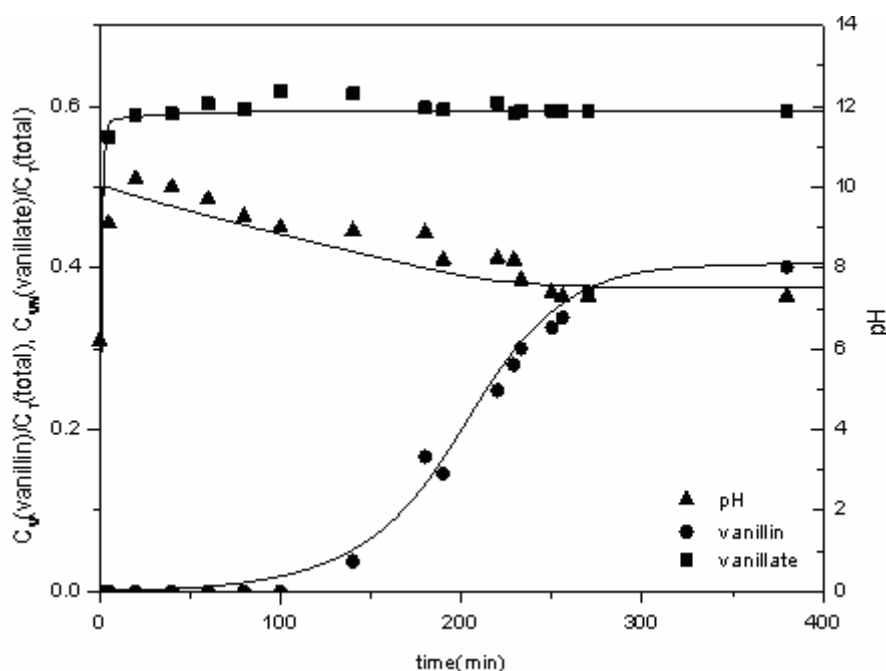


Figure 5.11 Breakthrough curve of the vanillin. The y-axis is shown as a concentration of vanillin, vanillate / total concentration. The feeding solution was prepared by mixing 5×10^{-3} M NaOH and 8.72×10^{-3} mol L^{-1} vanillin and pH was 7.4. The initial pH at the zero time was 6.1. The flow rate is 20 mL min^{-1} , the temperature was 293 K. The points are showing experimental points, full line demonstrate simulated curves

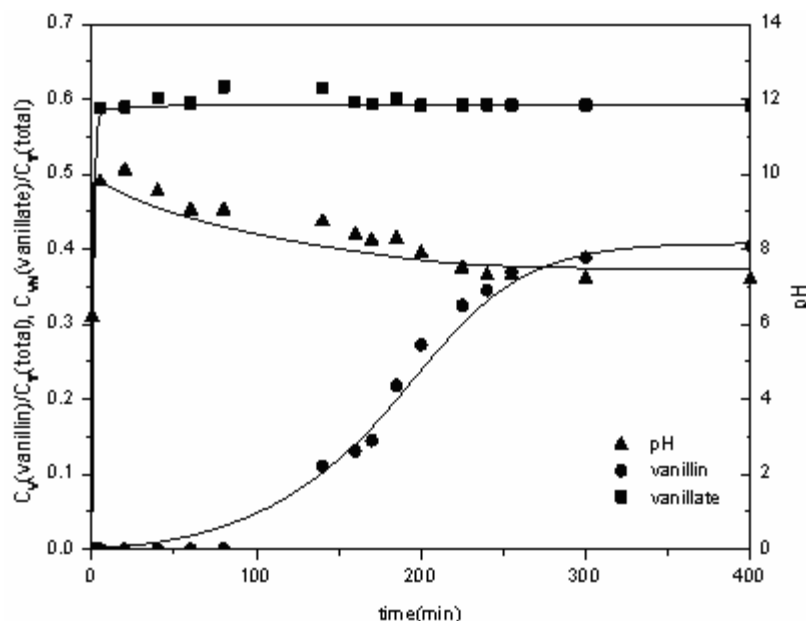


Figure 5.12 Breakthrough curve of the vanillin. The y-axis is shown as a concentration of vanillin, vanillate / total concentration. The feeding mixture of 5×10^{-3} M NaOH and 8.72×10^{-3} mol L^{-1} vanillin and pH was 7.5. The initial pH was 6.1. The flow rate is 20 mL min^{-1} , the temperature was 310 K

It can be seen that increasing the concentration of sodium hydroxide in the feed solution leads to later breakthrough times of vanillin. The explanation is because of the coupling of nonlinear adsorption of vanillin and reaction of vanillin with sodium hydroxide (Rodrigues, 1982).

The regeneration of the bed has been performed as well. For this purpose high concentration of sodium hydroxide (0.1 M) has been used. The initial conditions of the bed before regeneration is summarized in Table 5.5 (see condition for flow rate 14 mL min^{-1} , 293 K). Regeneration of the bed is presented in Figure 5.13. Reaction of vanillin and sodium hydroxide is very fast and once sodium hydroxide breaks the bed of adsorbent vanillate as a product of reaction is formed and vanillin is vanished from the outlet of the bed. After this short time period the diffusion of vanillate in the pores of adsorbent and diffusive and convective effect in the fixed-bed will carry on the process of regeneration.

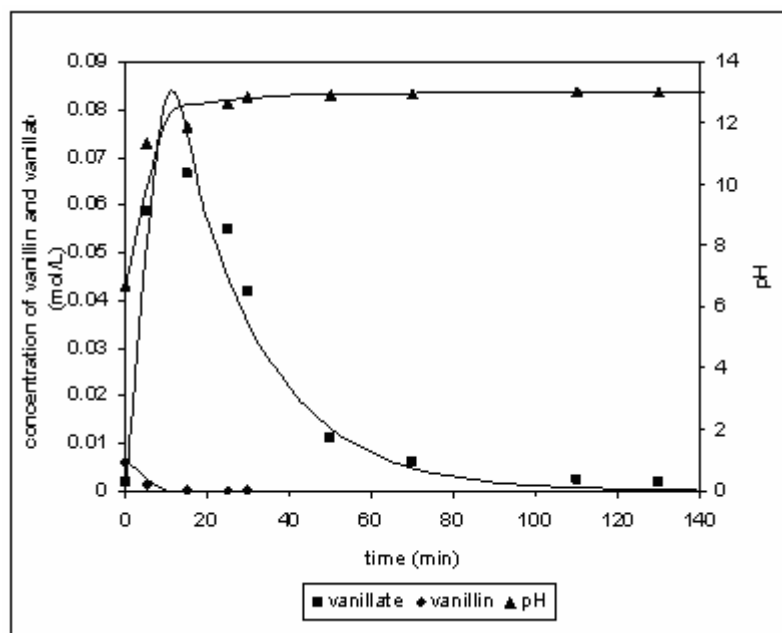


Figure 5.13 The regeneration of polymeric adsorbent SP 206 saturated with the solution of vanillin and sodium hydroxide at the experimental conditions reported in the Table 5.5 (see condition for flow rate 14 mL min^{-1} , 293 K) was achieved by using 0.1 M sodium hydroxide. The used flowrate of regeneration was 5 mL min^{-1}

5.5 Conclusions

Adsorption of vanillin onto non-ionic polymeric resins Sephabeads SP206 at different temperatures and concentration of sodium hydroxide were studied. Batch experiments were carried out in order to obtain adsorption equilibrium isotherms at temperatures 293 , 310 , 333 K . The adsorption equilibrium isotherms are nonlinear in the investigated concentration range and described by Langmuir model. Saturation capacity of Sephabeads SP206 was found to be independent of the temperature. Furthermore, the impact of sodium hydroxide on the adsorption of vanillin was investigated. For this purpose the modified Langmuir model of isotherm has been applied. Increasing concentration of sodium hydroxide higher than 1 M has significantly reduced the adsorbed amount of the vanillin onto polymeric adsorbent SP206.

The fixed-bed adsorption of vanillin onto polymeric resin SP206 at different flow rates, feed concentrations, and at different temperatures has been studied. The influence of concentration of sodium hydroxide on adsorption of vanillin in fixed-bed operation has been investigated. The mathematical model including linear driving force for intraparticle mass transfer and reaction in liquid phase for system vanillin/sodium hydroxide satisfactorily predicts all dynamic adsorption experiments in column.

5.6 Nomenclature

b	adsorption equilibrium constants (L mol^{-1})
b_{∞}	pré-exponential factor (L mol^{-1})
Bi	Biot number (-)
C^*	bulk liquid phase concentration (mol L^{-1})
C_0	initial concentration in batch system (mol L^{-1})
C_{feed}	feed concentration (mol L^{-1})
C_i	concentration in the bulk fluid phase (mol L^{-1})
C_{OH}	molar concentration of sodium hydroxide (mol L^{-1})
C_T	total molar concentration as a sum of concentration of vanillin (C_V) and vanillate (C_{VN}) (mol L^{-1})
C_V	molar concentration of vanillin (mol L^{-1})
C_{VN}	molar concentration of vanillate (mol L^{-1})
D	diameter of the column (m)
D_{ax}	axial dispersion coefficient ($\text{m}^2 \text{s}^{-1}$)
D_m	molecular diffusivity ($\text{m}^2 \text{s}^{-1}$)
d_p	diameter of the particle of the adsorbent (m)
D_{pe}	effective pore diffusivity ($\text{m}^2 \text{min}^{-1}$)
f_h	dry particle to wet particle mass ratio (g dry adsorbent / g adsorbent)
$-\Delta H$	heat of adsorption (J mol^{-1})
k_1	reaction rate constant ($\text{L mol}^{-1} \text{s}^{-1}$)
k_2	reaction rate constant (s^{-1})
K_{eq}	equilibrium constant of the reaction (L mol^{-1})

k_f	external mass transfer coefficient (m s^{-1})
k_{LDF}	linear driving force kinetic coefficient (min^{-1})
L	length of the bed (m)
M	molecular weight of the solute (g mol^{-1})
Q	flow rate ($\text{m}^3 \text{s}^{-1}$)
q	average adsorbed phase concentration in the homogeneous particle (mol g^{-1})
q^*	equilibrium adsorbed concentration (mol g^{-1} of dry resin)
q_i	average adsorbed phase concentration in the particle (mol g^{-1} of dry resin)
q_s	saturation capacity of the adsorbent (mol g^{-1})
q_v	molar concentration of vanillin in the solid phase (mol g^{-1} of dry resin)
$\Delta q/\Delta C$	slope of the equilibrium isotherm
R	gas constant ($\text{J mol}^{-1} \text{K}^{-1}$)
Re	Reynolds number (-)
r_1	velocity of vanillin disappearance (s)
r_p	radius of the particle of the adsorbent (m)
T	temperature (K)
t	time variable (s)
u_i	interstitial velocity (m s^{-1})
V	volume of solution (L)
V_m	molar volume of solute a at its normal boiling temperature ($\text{m}^3 \text{mol}^{-1}$)
W	dry weight of adsorbent (g)
z	axial variable (m)
<i>Greek letters</i>	
ε	bed porosity (-)

ε_p	porosity of the adsorbent (-)
ϕ	dimensionless association factor of solvent B
η	viscosity of the solvent (cP)
ρ	fluid density (kg m ⁻³)
ρ_s	density of the solid (kg m ⁻³)
Ω	LDF factor, which is equal to 3, 8 or 15 for slab, cylindrical or spherical geometry
Θ	loading defined as q^*/q_s (-)
τ	bed tortuosity (-)
$\mathfrak{R}_i$	reaction law for species “i”

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6. Recovery of vanillin from lignin/vanillin mixture by using tubular ceramic ultrafiltration membranes

6.1 Introduction

Since the late sixties membrane filtration processes have found industrial applications and started to compete with processes like distillation, evaporation or extraction. Membranes take advantage of their physical and chemical stability, reproducible performance, selectivity and high surface area per unit volume (Charcosset, 2006). They have broad applications in the wastewater treatment, food processing, biotechnology and pharmaceutical industry for the concentration of solutions and size-selective separation of large molecules from low molecular weight species. (Sondhi *et al.*, 2003).

Membrane filtration processes are pressure-driven separation techniques generally classified according to the size of particles retained by the membrane. The main categories of membranes cover microfiltration, ultrafiltration, nanofiltration and RO with the range of pore size from 2 μm to 0.5 nm. Microfiltration membranes have pores with size in the range from 50 nm to 2 μm and operating pressures below 2 bars and are mostly used to separate particles and bacteria from the solution. Ultrafiltration membranes have pore size between 50 nm to 2 nm and operating pressure difference between 1 and 10 bar. Ultrafiltration membranes retain highmolecular-mass solutes (polymers, proteins, colloids) and small molecules like water,

salts can pass through. Ultrafiltration is utilized for the concentration of macromolecular species such as proteins, polysaccharides, various polymers and the elimination of macrosolutes from effluents or in water for industrial or medical applications.

Nanofiltration membranes have pore size between 0.5 nm and 2 nm and operating pressures (transmembrane pressure) between 5 and 40 bars. The main utilization of these membranes is in sugar separation, separation of multivalent from monovalent salts for selective demineralization and concentration of organic compounds with low molecular weight.

There are already several papers about the treatability of Kraft pulp liquors using ultrafiltration process (Nuortila-Jokinen and Nystrom, 1996; Keyoumu *et al.*, 2004; Dafinov *et al.*, 2005; Wallberg *et al.*, 2005; Wallberg and Jonsson, 2006). The Kraft pulp liquor coming from paper industry is a waste which must be treated before disposal. On the other hand, organic compounds present in liquors, especially lignin, is a very useful raw material from which many valuable substances or materials can be produced, such as: vanillin, vanillic acid, dispersing agents, synthetic tannins, polymer filter sand binding agents, active carbon, ion-exchanger, etc. The main purpose of lignin removal from the liquor is to separate the cooking chemicals, NaOH and Na₂S to avoid losses of these chemicals from the mill (Wallberg *et al.*, 2005). The processes used for lignin removal are precipitation and ultrafiltration. Fractionation of the cooking liquor from Kraft and sulphite pulps by ultrafiltration has been studied for thirty years (Jokela and Salkinojasalonen, 1992; Carlsson *et al.*, 1998; Gilarranz *et al.*, 1998). In most of the applications the objective of ultrafiltration process was to purify the lignin fraction in order to use it as a fuel or valuable product.

In the process of Kraft lignin oxidation to produce vanillin the reaction media contains degraded molecules of lignin and sodium salt of vanillin (vanillate) and other species. The isolation of vanillate from the oxidized solution is an important stage in the vanillin production. During the ultrafiltration process vanillin goes to the permeate stream because of its low molecular weight. The lignin as a macromolecule stays in the retentate and its concentration significantly increased during the batch ultrafiltration process. Therefore, the ultrafiltration technique can be used as a first step in the process of recovery of vanillin from Kraft lignin oxidation.

The main goal of the work presented in this chapter was to study the membrane ultrafiltration process particularly focused on the recovery of vanillin from Kraft lignin oxidation media.

For this purpose tubular ceramic membranes Kerasep supplied by Orelis, France with molecular weight cut-off of 15 kDa, 50 kDa and Filtanium membranes with molecular weight cut-off of 1 kDa, 5 kDa supplied by Tami Industries, France were used. The influence of the lignin and vanillin concentration and pH of the mixture on the ultrafiltration process has been studied as well.

6.2 Experimental part

6.2.1 Chemicals and methods

Vanillin ($C_8H_8O_3$, purity $\geq 98\%$), pellets of sodium hydroxide (NaOH, purity $\geq 98\%$), and lignin alkali were used in experimental work. Lignin alkali used has an average molecular weight $M_w = 60000$ g/mol and the amount of sulfur total impurities was 9 wt % according to the supplier Sigma-Aldrich. Hydrochloric acid at concentration 1 M was used for acidification of the samples. All chemicals were supplied by Sigma Aldrich.

The mixtures of vanillin and lignin and sodium hydroxide were prepared with degassed and deionised water with conductivity value lower than 1 $\mu S/cm$. The pH of the mixture was adjusted by adding NaOH solution.

The vanillin and lignin concentration was measured by UV-VIS spectrophotometer Jasco (model 7800, Japan) after pretreatment of the samples.

The samples were acidified by concentrated hydrochloric acid to precipitate high molecular weight components (lignin). The precipitated solid was separated by centrifugation during 15 minutes at 5000 rpm. The supernatant was separated from the precipitated solid, diluted in deionised water and analyzed by UV spectrophotometer for vanillin content at the wavelength of 259 nm (Fargues *et al.*, 1996).

The precipitated solid was diluted in 2 N solution of sodium hydroxide in order to dissolve the lignin content. The amount of lignin was measured by UV spectrophotometer at the wavelength of 280 nm (Rojas *et al.*, 2006). Due to inclusion of vanillin inside the lignin precipitate (Fargues *et al.*, 1996), the calibration samples were treated by the same technique as above.

6.2.2 Equipment and experimental set-up

All experiments have been performed by using the experimental set-up shown in *Figure 6.1*. It consists of a feed tank, peristaltic pump (Watson-Marlow, England), damper, and ultrafiltration unit (Orelis, France). The membranes used in experiments were Kerasep membranes with molecular weight cut-off (molecular weight at which the membrane rejects 90 % of solute molecules) of 15 kDa, and 50 kDa supplied by Orelis, France and Filtanium membranes with molecular weight cut-off of 1 kDa, 5 kDa supplied by Tami Industries, France. Kerasep membranes were made of $\text{Al}_2\text{O}_3\text{-TiO}_2$ active layer on the ceramic support, with the service differential pressure of 0-4 bars and resistant to pH 0-14. The total membrane area was 0.008m^2 ; length was 400mm, inside diameter 6 mm and outside diameter 10 mm. Filtanium membranes for fine ultrafiltration were made of TiO_2 active layer on the ceramic support, with the operating differential pressure of 0-10 bars and resistant to pH 2-14. The membranes with cut-off below 15 KDa are usually called fine ultrafiltration membranes. In another literature sources are defined as nanofiltration membranes. The supplier's used term is "fine" ultrafiltration membranes.

The complete ultrafiltration experimental set-up is shown in *Figure 6.1 a* and ceramic membranes are shown in *Figure 6.1 b*.

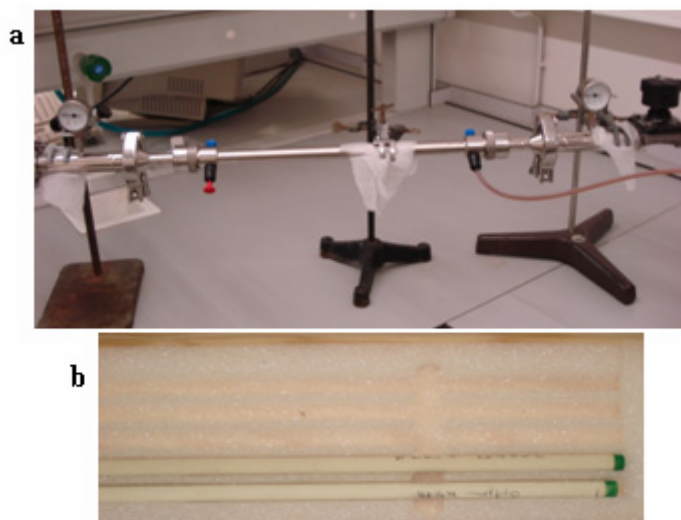


Figure 6.1 Ultrafiltration setup installed in the laboratory (a) and ceramic membranes (b) used in experiments

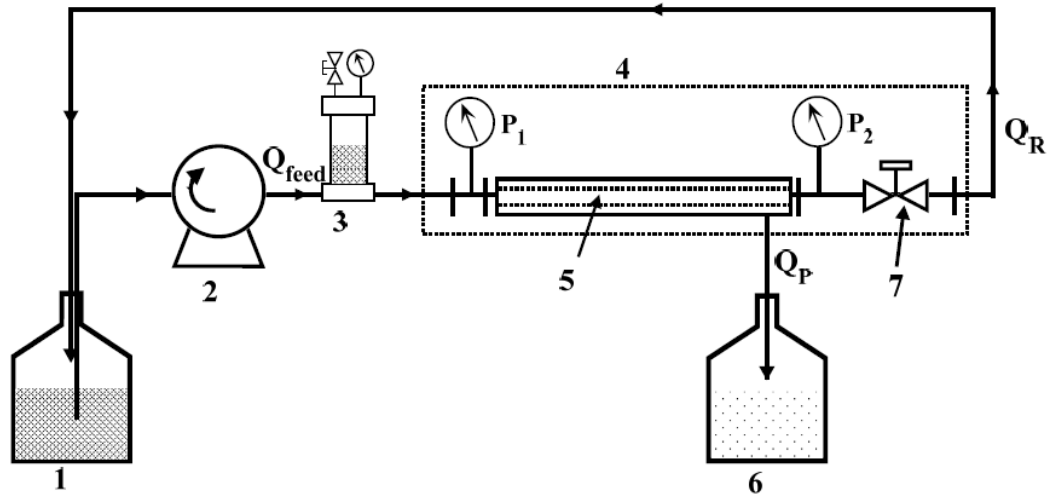


Figure 6.2 Scheme of the experimental set-up for batch ultrafiltration

1-tank with feed mixture; 2-peristaltic pump; 3-damper; 4-membrane module; 5-membrane
6-tank with permeate solution; 7-circulating valve: P_1 -pressure gauge inlet, P_2 -pressure
gauge outlet, Q_{feed} - feed flowrate, Q_p - permeate flowrate, Q_r - retentate flowrate

6.2.3 Measurement of water flux through membrane

The pure water permeate flowrate was measured for each membrane prior to starting experiments in order to obtain the water flux at different transmembrane pressure and to determine the membrane resistance (R_m). Water flowrate in the permeate side was measured at different pressures which were adjusted by a recirculation valve on the system starting from the lowest to the highest pressure and vice versa. The value of the membrane resistance was also used as an indicator of the membrane cleaning effectiveness.

The values measured during the experiment were: Q_r -Retentate flow rate ($L h^{-1}$) Q_p - Permeate flow rate ($L h^{-1}$), ΔP_1 - Relative inlet pressure on the feed side (bar) ΔP_2 -Relative outlet pressure on the retentate side (bar) T -Temperature ($^{\circ}C$).

The average water permeate flux is the flow of water divided by the surface area of the membrane and calculated as:

$$J = \frac{Q_p}{A_m} \quad 6.1$$

where J is permeate flux at time t ($L h^{-1} m^{-2}$) and A_m is membrane surface area (m^2). The water permeate flux was measured at different average transmembrane pressures at $25^{\circ}C$.

The average transmembrane pressure ΔP (bar) was calculated by

$$\Delta P = \frac{\Delta P_1 + \Delta P_2}{2} \quad 6.2$$

where ΔP_1 is the relative pressure at the inlet of the membrane module (bar), ΔP_2 is the relative pressure at the outlet of the membrane module (retentante side) (bar). Pure water permeate flux data are used to evaluate the membrane hydraulic resistance (R_m) according to Darcy's law:

$$J = \frac{\Delta P}{\eta_0 R_m} \quad 6.3$$

where η_0 is the solvent viscosity (Pa.s).

6.2.4 Membrane cleaning after experiments

The retained molecules accumulate on the membrane surface leading to the decrease of the membrane performance and periodically cleaning of the membrane must be carried out after each run.

The lignin solubility increases with increasing pH. If deionised water is used (pH = 6.1), some lignin can precipitate with lowering the pH and thus block the membrane. Therefore, 0.1-0.2M NaOH solution was used to clean the membrane after each experiment. In the first step of the cleaning procedure the membrane and feeding tubes were rinsed with solution of NaOH without opening the circulation valve to remove residues inside the system; later on the circulation valve was opened and the transmembrane pressure $\Delta P = 2.0$ bar adjusted. By “open the valve” was meant that there is permeate flow out of the membrane. This is the expression used in literature but in fact to have permeate flow the valve must be closed.

The time of cleaning procedure was 5-6 hours. In the next step, the system was rinsed with deionised water, to obtain neutral pH which was measured in the permeate and retentante side. After each cleaning procedure the permeate flux of water was measured and compared with the reference value.

6.2.5 Ultrafiltration of vanillin/lignin mixture

The experiments were performed by using the lab-scale experimental set-up shown in *Figure 6.2*. All experiments were carried out in the batch concentration mode. It is a commonly used method where retentate is recirculated back to the feed tank and the permeate is withdrawn to a separated reservoir. The lignin/ vanillin mixture was prepared in the feed tank with an initial feed volume depending on the experiment (7 L, 5 L or 4 L). The studied composition of the feed mixture were approximately 60 g/L lignin - 6 g/L of vanillin, 20 g/L of lignin - 2 g/L of vanillin, 5 g /L of lignin -0.5 g/L of vanillin, and the pH tested was in the range 8.5 and 12.5.

Prior to starting the experiment, the feed tank was filled with 0.1 M solution of sodium hydroxide and the whole system including the tubes was properly washed in order to remove foreign bodies that membrane can contain. Subsequently, deionised water was passed through the system and the experimental rig was ready for use. The pH of the mixture was adjusted with 0.1 M NaOH. Then the system was filled with the feed solution and the feed flowrate adjusted, which was kept constant during all the experiment duration. The experiment started when the circulation valve was open and the average transmembrane pressure (ΔP) adjusted to the value of 1.3 or 1.55 bars.

During the experiment the samples of permeate and retentate were collected and retentate flowrate, permeate flowrate, ΔP_1 and ΔP_2 were measured. After each experiment the final volume of permeate withdrawn and the volume of concentrated solution in the feed tank was measured and the volume reduction calculated:

$$VR = \frac{V_p}{V_0} \quad 6.4$$

where V_p is the permeate withdrawn volume and V_0 is the initial volume of the feed tank.

6.2.6 Measurement of viscosity

Viscosity measurements were made with routine capillary viscosimeter Jenna-Glass Schott Mainz (Germany). The viscosimeter has been designed in such a way that correction of kinetic energy may be ignored when flow time exceeds 200 second. The solution at the

concentration 5, 20, 40, 60 and 80 g L⁻¹ of lignin at pH=8.5 and 12.5 was prepared. The viscosimeter was filled with the sample of lignin and the flow time between two marks written on the viscosimeter was measured. The measurement was repeated three times for each sample at the temperature 26 °C. To evaluate the viscosity (Pa. s), the equation $\eta = K \times t$ was used where the constant $K = 0.002865$. The viscosity determined for each concentration of lignin was used to calculate the intrinsic viscosity $[\eta]$ (L g⁻¹).

6.3 Mathematical model

The membrane ultrafiltration is a size-exclusion based on pressure-driven process. The important characteristics of ultrafiltration process are the volumetric flux (permeate flux) and the rejection of the solutes by the membrane. The basic flux equation in a tubular membrane may be expressed as:

$$J = \frac{\Delta P}{\eta R_m} \quad 6.5$$

where J is the volumetric flux, ΔP is the transmembrane pressure ($= P(z) - P_p$); where $P(z)$ is the pressure distribution along the flow channel and P_p is the permeate pressure of the shell side. For the case of a perfectly mixed system, both pressures are assumed to be constant and R_m is the membrane hydraulic resistance. The term ηR_m can be found as the thickness of membrane to the permeability ratio and, then, the volumetric flux depends inversely upon the thickness of the membrane. One of the major challenges with the modelling of ultrafiltration process is the estimation of the decline of the flux with time.

Konieczny and Rafa (Konieczny and Rafa, 2000) have reported that the basic problems involving the ultrafiltration of pressure membrane process are:

- flux decline driving the operation of system;
- efficiency of the process is becoming independent of transmembrane pressure (limiting flux);
- fouling and concentration polarization leading to the reduction of efficiency of membrane;

As it is, Eq.(6.5) does not include any phenomena accounting the lost of efficiency in the filtration. These phenomena are the gel formation, the membrane polarization, the fouling of the membrane, resulting from reversible or irreversible pore plugging, which are very important in UF and need to be included in any detailed analysis.

Fouling is the accumulation of material on the surface or in the pores of the membrane. The permeate flux decline caused by reversible fouling can be recovered by cleaning the membrane with de-ionized water, whereas the flow decline caused by irreversible fouling can be only recovered by replacing the membrane or cleaning it using chemical reagents (Van der Bruggen *et al.*, 2002). The irreversible case is more critical membrane pores are blocked by the foulants or the foulants are adsorbed on the membrane surface (Speth *et al.*, 1998).

As mentioned before, the rejection coefficient is also an important parameter to characterize an UF membrane. The rejection represents a measure of the amount of solute retained by the membrane. The most common definition of rejection is the observed rejection (R_{obs}^i) because both permeate and concentrate solute concentration can be measured:

$$R_{obs}^i = 1 - \frac{C_{pi}}{C_{bi}} \quad 6.6$$

where C_{pi} and C_{bi} are the permeate and the bulk concentration of the species “i”, in the feed side of the membrane, respectively (Kovasin and Nordén, 1984). However, the observed rejection can be taken as an approximation of the separation properties of the membrane. For impermeable membrane, the rejection will be equal to 1.

There are other definitions of rejection, named intrinsic rejection (R_O), when phenomena leading to decline flux are taking place in UF processes, such as:

- with concentration polarization

$$R_O = 1 - \frac{C_p}{C_w} \quad 6.7$$

where C_w is the concentration of the rejected solute at the membrane surface.

- with gel formation,

$$R_o = 1 - \frac{C_p}{C_g} \quad 6.8$$

where C_g is the gel concentration of the rejected solute.

Combining (Eq. 6.6) and (Eq. 6.7) or (Eq. 6.6) and (Eq. 6.8), one can obtain the relation between the observed and intrinsic rejection coefficients.

A variety of models for volumetric flux calculation have been reported in literature. Cheng and Wu (Cheng and Wu, 2001) mentioned some used models for analysing the mean volumetric flux of ultrafiltration: the gel-polarization model (Porter, 1972), the resistance-in-series model (Yeh and Cheng, 1993), the osmotic pressure model (Nabetani *et al.*, 1990), the boundary layer model (Wijmans *et al.*, 1985). In this work, the unsteady-state model of the current ultrafiltration system is addressed using the osmotic pressure with polarization concentration and gel layer controlled flux decline. Both models are explained below. The osmotic pressure model is used only for one case when initial mixture of lignin and vanillin in UF process is diluted in the feed tank.

6.3.1 Osmotic pressure and polarization layer controlled flux decline

The concentration polarization is a phenomenon in which the solute that is rejected by the membrane accumulates on the membrane surface and then its concentration at surface is higher than that in the bulk. *Figure 6.3* shows a scheme of the polarization on membrane surface. Since the flux of the species through the membrane is low, its concentration will build up at the membrane wall and such build up will result in back diffusion of the solute into the bulk fluid.

From *Figure 6.3*, the steady state mass balance for the membrane with polarization in the case when rejection is not equal to 1 is:

$$J C_i + D \frac{dC_i}{dz} = J C_{p,i} \quad 6.9$$

Using the boundary conditions $C_i = C_{wi}$ at $z = 0$ and $C_i = C_{bi}$ at $z = \delta_{pol}$, the concentration of the rejected species “*i*” at the membrane wall (C_{wi}) can be calculated from the equation:

$$\frac{C_{wi}}{C_{bi}} = \frac{\exp(J/k)}{R_o + (1 - R_o)\exp(J/k)} \quad 6.10$$

where k is the mass transfer coefficient ($= \frac{D}{\delta_{pol}}$); δ_{pol} is thickness of polarization layer and D is diffusivity of species within polarization layer.

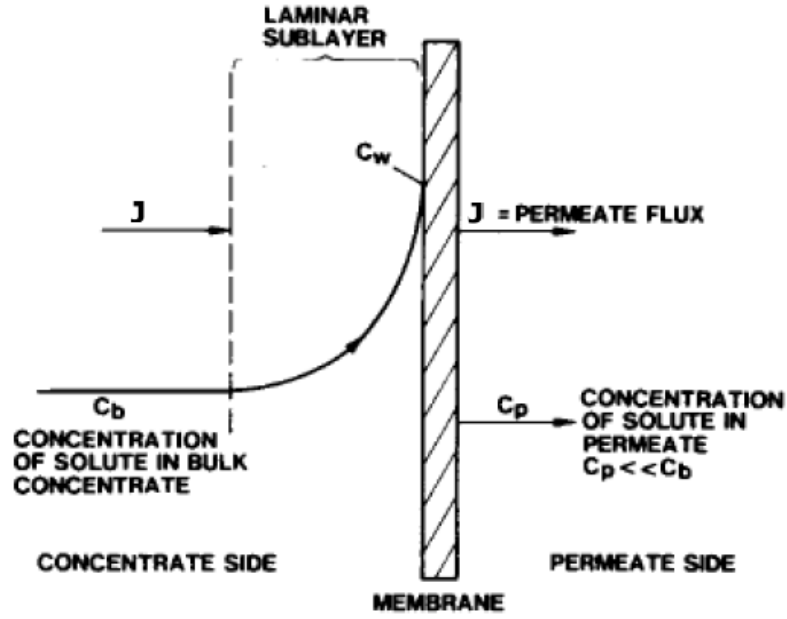


Figure 6.3 Concentration polarisations in ultrafiltration (Kovasin and Nordén, 1984)

Concentration polarization may cause a lowering in flux due to an increase in osmotic pressure difference across the membrane (Kozinski and Lightfoot, 1972). Therefore, the equation for the volumetric flux considering concentration polarization and osmotic pressure can be written as (Goldsmith, 1971):

$$J = \frac{\Delta P - \Delta \pi}{\eta R_m} \quad 6.11$$

where $\Delta \pi = \pi(C_{wi}) - \pi(C_{pi})$, η is the viscosity of the solution, R_m is the hydraulic membrane resistance and $\Delta \pi$ is the osmotic pressure.

The osmotic pressure can be measured directly or estimated from other thermodynamic quantities. For the case of very diluted (and ideal) solutions, the van't Hoff equation can be useful to assume a linear dependence on concentration, as shown in Eq. 6.12.

$$\pi(C) = a' C \quad 6.12$$

where a' is an empirically determined constant. The osmotic pressure for macromolecular solution increases much faster than linearly and Eq.6.12 usually becomes a polynomial function of the concentration.

6.3.2 Gel layer controlled flux decline

In ultrafiltration, some rejected solutes can form gels, cakes or slimes at the membrane wall. The gel layer model is based on the assumption that the concentration of the rejected solute on the membrane cannot exceed a certain value, named gel concentration (C_g). At the beginning of ultra-filtration only a polarization layer is taking place. After some time, gel concentration can be reached and then the net solute flux does not lead to a further increase of the concentration at the membrane surface; however, the thickness of the gel layer can change (Zaidi and Kumar, 2005). Since the gel layer works as a porous solid which causes an additional resistance to flow, the volumetric flux can be given by,

$$J_v = \frac{\Delta P}{\eta R_m + \eta R_g} \quad 6.13$$

where η is the viscosity of the solution, R_m is the membrane resistance and R_g is the resistance due to the gel layer. The term ηR_g can be expressed as δ_g / K_g where δ_g represents the thickness of gel layer that can vary with time and K_g is the permeability of the gel layer.

The value of K_g can be obtained from the Kozeny-Carman equation (Wankat, 1991):

$$K_g = \frac{d_p^2 \varepsilon_g^3}{150 \eta (1 - \varepsilon_g)^2} \quad 6.14$$

where d_p is particle diameter and ε_g is the porosity of gel layer. The gel permeability is very sensitive to the particle diameter in the gel layer, as discussed in (Wankat, 1991). The lignin is a very complex molecule and forms molecule associations which can affect the value of the diameter of the particle to be considered in the estimation of K_g and, consequently, the hydraulic resistance of gel.

The use of a gel layer model with variable diameter of the particle in bulk and a growing gel layer includes a time-dependent hydrodynamic resistance to the flow ($R_g(t)$). Therefore, the fitting parameter of this model is the gel resistance which is affected by operation conditions (feed flow rate and concentration, pH), as seen later.

Governing Mass Balances Equations

Considering the system shown in *Figure 6.3*, the overall mass balance is

$$-\frac{d(V)}{dt} = A_m J = Q_p \quad 6.15$$

where $V(t)$ is the volume of the solution in the entire system (feed tank, pipes and UF module) and A_m is membrane area.

The mass balance of the species (i = lignin, vanillin) over the system can be written as,

$$\frac{d(VC_{fi})}{dt} = Q_r C_{ri} - Q_f C_{fi} = -Q_p C_{pi} \quad 6.16$$

where Q_n is flow rate in stream n of the membrane module and C_{ni} is concentration of the species “i” in the “n” stream. The subscripts f , r and p mean feed, retentate and permeate stream, respectively, in the module of membrane. Eq.6.16 can be rewritten as:

$$\frac{d(C_{fi})}{dt} = \frac{Q_p}{V} (C_{fi} - C_{pi}) \quad 6.17$$

The global and solute mass balances for the membrane module are,

$$Q_f = Q_r + Q_p \quad 6.18$$

$$C_{fi} Q_f = C_{ri} Q_r + C_{pi} Q_p \quad 6.19$$

The system is assumed as perfectly mixed, the concentration of the species in retentate is the same as the bulk concentration (C_{bi}). The concentration of species i in the retentate or bulk is:

$$C_{ri} = C_{bi} = \frac{C_{fi}}{(1 - \theta R_{obs}^i)} \quad 6.20$$

where θ is permeate to feed flowrate ratio ($= \frac{Q_p}{Q_f}$). It is worth noting that for batch operation, the parameter θ is not constant during the UF process because the permeate flow rate is decreasing.

Concentration polarization can cause an increase in solute concentration as shown in *Figure 6.3* or it can cause a gel or cake layer to form. Under high-pressure operation, the concentration at the membrane can increase to the point of incipient gel precipitation, and a dynamic secondary membrane is formed on the top of the primary structure. In a batch operation, because of the increased concentration of lignin in the feed tank, the lignin solute may form a gel layer on the feed surface of the membrane

Table 6.1 Model describing concentration polarisation in the case of diluted solution 2/6 g/L lignin vanillin.

Concentration polarisation model	Gel layer model
$\frac{d(V)}{dt} = -A_m J$	$\frac{d(V)}{dt} = -A_m J$
$\frac{d(C_{fi})}{dt} = \frac{A_m J}{V} (C_{fi} - C_{pi})$ $i = \text{lignin, vanillin}$	$\frac{d(C_{fi})}{dt} = \frac{A_m J}{V} (C_{fi} - C_{pi})$ $i = \text{lignin, vanillin}$
$C_{ri} = C_{bi} = \frac{Q_f C_{fi}}{(Q_f - A_m J R_{obs}^i)}$ $i = \text{lignin, vanillin}$	$C_{ri} = C_{bi} = \frac{Q_f C_{fi}}{(Q_f - A_m J R_{obs}^i)}$ $i = \text{lignin, vanillin}$
$C_{wL} = C_{bL} \frac{\exp(J/k)}{R_o + (1 - R_o) \exp(J/k)}$ ⁽¹⁾ , $L = \text{lignin}$	$J = \frac{\Delta P}{\eta R_m + \eta R_g(t)}$ ⁽²⁾
$J = \frac{\Delta P - a' R_o C_{wL}}{\eta R_m}$, $L = \text{lignin}$	$C_{pi} = C_{bi} (1 - R_{obs}^i)$, $i = \text{lignin, vanillin}$
$R_o = (1 - R_{obs}^L) \frac{C_{bL}}{C_{wL}} + 1$, $L = \text{lignin}$	
$C_{pi} = C_{bi} (1 - R_{obs}^i)$, $i = \text{lignin, vanillin}$	

⁽¹⁾ $\Delta\pi = \pi(C_{wL}) - \pi(C_{pL}) = a' R_o C_{wL}$ with $\pi(C) = a' C$. An estimative from van't Hoff equation is made for the value of the “a” parameter. The used value is $42.1 \text{ Pa m}^3 \text{ kg}^{-1}$.

⁽²⁾ The time-dependent equation for the hydrodynamic resistance of the gel in different operational conditions (cut-off, feed flowrates, concentration, pH,...) is obtained from experimental results.

6.4 Results and discussion

6.4.1 Measurement of the water flux through the membrane

The viscosity of water at 25 °C is $0.891 \times 10^{-3} \text{ kg m}^{-1} \text{ s}^{-1}$ and the value of the membrane resistance (R_m) obtained from experimental results was $2.806 \times 10^{13} \text{ m}^{-1}$ for 1 kDa membrane, $1.222 \times 10^{13} \text{ m}^{-1}$ for 5 kDa and $2.806 \times 10^{12} \text{ m}^{-1}$ for 15 kDa membrane. The permeate fluxes of water as a function of transmembrane pressure (ΔP) for membranes of 1, 5 and 15 kDa are shown in Figure 6.4.

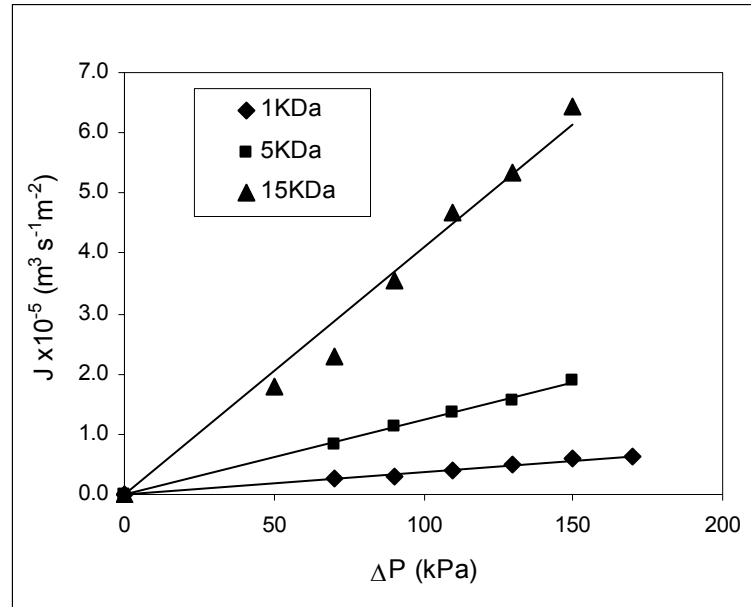


Figure 6.4 Water permeate flux ($\text{m}^3 \text{ s}^{-1} \text{ m}^{-2}$) through the membrane as a function of the transmembrane pressure (ΔP) (kPa). The membranes tested were 1, 5 and 15 kDa cut-offs. The surface area of each membrane is $S = 0.008 \text{ m}^2$. Open system.

As it is obvious from Figure 6.4, with increasing the cut-off of the membrane the water flux is higher. The cleaning efficiency is shown in Figure 6.5 where the water flux in the new membranes and after each experiment/cleaning is reported.

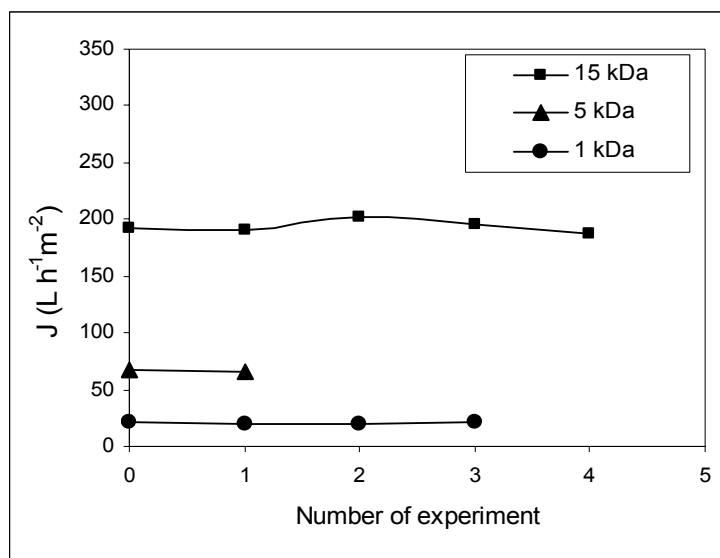


Figure 6.5 Flux of water with the new membrane and after each experiment and subsequent cleaning. The membrane used was 15, 5 and 1 kDa. The cleaning was done by using 0.1M solution NaOH. The transmembrane pressure ΔP at which the flux was measured is 1.3 bar for membrane 15 kDa and 1.5 bar for membrane 1 and 5 kDa.

The use of 0.1 - 0.2 M NaOH as a cleaning agent seems to be acceptable. In the case of membrane 1, 5 and 15 kDa after each experiment and subsequent cleaning the water flux obtained was almost the same as with the “new” membranes.

6.4.2 Ultrafiltration of vanillin/lignin mixture

The intrinsic viscosity $[\eta]$ characterizes the capacity of the solute to increase the viscosity of the solution and is defined as the limiting value of the specific viscosity/concentration ratio at zero concentration and given by: $[\eta] = \lim_{c \rightarrow 0} \frac{\eta_{sp}}{c}$. The intrinsic viscosity is expressed in unit of reciprocal concentration (L g^{-1}). The specific viscosity is defined as: $\eta_{sp} = (\eta - \eta_0)/\eta_0$, where η_0 is the viscosity of the pure solvent and η is the viscosity of the solution. The variation of the viscosity number $\frac{\eta_{sp}}{c}$ with concentration depends on the type of molecule as well as the solvent. To obtain the intrinsic viscosity it is necessary to find the viscosity at different concentrations and then extrapolate to zero concentration (infinite dilution). The intrinsic viscosity $[\eta]$ expressed in L g^{-1} was obtained from extrapolation of experimental data. The data were extrapolated in two ways to yield the intrinsic viscosity:

- 1) From viscosity number $((\eta - \eta_0)/\eta_0 c)$ versus concentration plot;

2) From a plot of $([\ln(\eta/\eta_0)]/c)$ versus concentration

The equations which are extrapolated to zero concentration are:

$$(\eta - \eta_0)/\eta_0 c = [\eta] + K_1 [\eta]^2 c \quad 6.21 a$$

$$[\ln(\eta/\eta_0)]/c = [\eta] + K_2 [\eta]^2 c \quad 6.21 b$$

where K_1 and K_2 are the constants (Albrecht, 1971).

The values of intrinsic viscosities obtained by extrapolation are slightly different. The value of the intrinsic viscosity obtained from the extrapolation of data plotted as viscosity number versus concentration was 0.00386 L g^{-1} and from data logarithmic viscosity number versus concentration 0.00395 L g^{-1} . The constants K_1 and K_2 are dimensionless with values of 2.345 and 1.167 for pH=8.5, respectively. The values of intrinsic viscosity determined from the viscosity number plot were employed in future calculations of hydrodynamic radius of molecule.

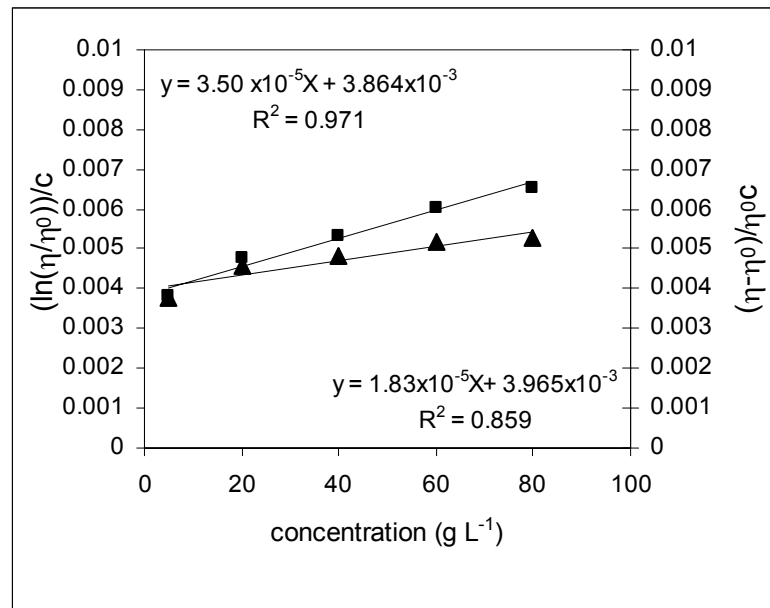


Figure 6.6 Viscosity number η_{sp}/c (■) and $[\ln(\eta/\eta_0)]/c$ (▲) versus concentration of lignin solution (g L^{-1})

The hydrodynamic radius of the molecule of solubilised lignin was calculated according to the Einstein viscosity relation (Bird *et al.*, 1994) if the porous sphere particle model is used.

$$[\eta] = 0.025 \frac{N_A}{M} \left(\frac{4}{3} \pi R_e^3 \right) \quad 6.22$$

which leads to:

$$R_e = \left(\frac{30[\eta]M}{\pi N_A} \right)^{1/3} \quad 6.23$$

where N_A is Avogadro's number, $[\eta]$ is the intrinsic viscosity (L g^{-1}), M is molecular weight. The value of molecular weight used in the calculation was the average molecular weight of lignin $M_w = 60000 \text{ g mol}^{-1}$ which is given by the supplier Sigma Aldrich. The hydrodynamic radius obtained for lignin molecule in water solution at pH=8.5 was 155 Å.

The diffusion coefficient is given by the Stokes-Einstein equation (Kovasin and Nordén, 1984):

$$D = \frac{kT}{6\pi\eta_0 R_e} \quad 6.24$$

where k is the Boltzmann constant, T is the temperature, η_0 is the solvent viscosity. The calculated value of the diffusion coefficient for pH=8.5 was $D = 1.623 \times 10^{-11} \text{ m}^2 \text{ s}^{-1}$.

Numerous correlations have been presented for the calculation of the mass transfer coefficient. In the turbulent regime, the most widely used equation is the Deissler correlation (Gross *et al.*, 1958; Brown, 1967) given by:

$$Sh = 0.023 \text{Re}^{0.875} Sc^{0.25} \quad 6.25$$

where $\text{Re} = \frac{d_h v \rho}{\eta_0}$ is the Reynolds number, ρ is the density (kg m^{-3}), d_h is hydraulic diameter of the flow channel (m), η_0 is viscosity of solvent ($\text{kg m}^{-1} \text{ s}^{-1}$) and v is the velocity in the flow channel (m s^{-1}), Schmidt number: $Sc = \eta / \rho D$, Sherwood number $Sh = k d_h / D$, where k is the mass transfer coefficient (m s^{-1}).

6.4.2.1 Experimental results with membrane of 1 kDa cut-off

The optimal membrane cut-off used to recover vanillin from lignin vanillin mixture is not so obvious as one could expect, indeed, there are two important parameters involved that should be considered. These parameters are purity of the vanillin and optimal permeate flux. Therefore when membrane with a low cut-off is used the vanillin in the permeate is obtained with high purity. In contrast, the permeate flux on such membrane is very low and that implies the use of high membrane area.

The permeate flux is the permeate flow per unit area of the membrane ($\text{L h}^{-1} \text{m}^{-2}$). It is an important parameter because it influences the full scale operation cost. The factors affecting the permeate flux are the feed composition, cut-off of the membrane and temperature. The variation of the permeate fluxes with time for the mixture of lignin and vanillin at concentrations 60 g L^{-1} and of 6 g L^{-1} on the ceramic membrane of 1 kDa cut-off at different pH are shown in *Figure 6.7*. It can be noticed that through the ultrafiltration of lignin/vanillin mixture at the same composition but different pH the flux differs slightly. This fact can be caused by changing the properties of lignin as well as the solubility in aqueous solvent with increasing pH.

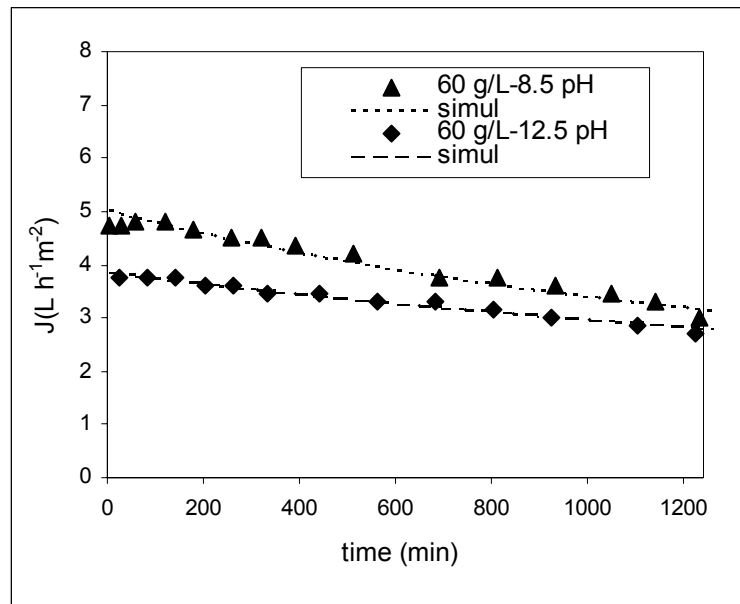


Figure 6.7 Permeate flux in membrane of 1 kDa cut-off at $\text{pH}=8.5$ and 12.5 . Concentration of lignin was 60 g L^{-1} and vanillin 6 g L^{-1} . Transmembrane pressure was constant during all experiment $\Delta P = 1.55 \text{ bar}$. Feed flow-rate: $Q_{\text{feed}} \approx 130$ and 120 L h^{-1} , respectively

It is clear from *Figure 6.7* that the flux decreases slightly from the beginning of experiment and no steady state was reached. We have noticed that the permeate flux was very low immediately after permeate started to be collected. The flux of pure water at the transmembrane pressure of 1.55 bar was $21 \text{ L h}^{-1} \text{m}^2$ while the flux of lignin/vanillin mixture was only $4\text{--}5 \text{ L h}^{-1} \text{m}^2$. In general, during the ultrafiltration process the gel layer is not formed in the beginning of the process and the main of resistance is caused by the resistance of membrane ($R_g \langle R_m$). From our experimental data, we can notice that gel resistance is always higher than membrane resistance from the beginning of experiments. This suggests that even at the beginning of experiments when the solution circulates through the system without opening the permeate valve, the gel layer formed at the membrane surface.

The mathematical model used to describe experimental permeate fluxes for lignin concentration of 60 g L⁻¹ pH=8.5 and pH = 12.5 assumes that increasing gel layer thickness leads to the increase of gel resistance (R_g). The model parameters applied in the simulations are shown in the *Table 6.2*.

Table 6.2 The model parameters used in the simulation for membrane 1 kDa cut-off.

Run	C_{feed}^0 (g L ⁻¹)		pH	R_{obs} (Lignin)	R_{obs} (Vanillin)	η (kg m ⁻¹ s ⁻¹)	Q_{feed} (L h ⁻¹)	V_0 (L)
	Lignin	Vanillin						
1	60	6	8.5	0.951	≈ 0	1.19×10^{-3}	130	5
2	60	6	12.5	0.972	≈ 0	1.19×10^{-3}	120	4
* the value of R_m is 2.806×10^{13} m ⁻¹ , transmembrane pressure $\Delta P = 1.55$ bar The membrane area $A_m = 0.008$ m ²								

The gel resistance as a function of time obtained from experimental data using Eq. 6.13 is shown in *Figure 6.8* for the studied pH range. The resistance of gel layer (R_g) is always higher than the membrane resistance ($R_m = 2.806 \times 10^{13}$ m⁻¹) measured using pure water and is increasing with time. As it was mentioned before, the gel layer resistance depends mostly on gel layer thickness but it is also influenced by the change of solution properties with time since the batch method is applied. The solution is becoming more concentrated, more viscous and the molecular weight distribution changes since certain molecular weight fraction is withdrawn in the permeate.

To include all factors which influence the permeate flux during the filtration, the gel resistance (R_g) increasing with the time was used as a fitting parameter. The predicted permeate flux obtained during the filtration of 60-6 g L⁻¹ at the pH=12.5 and 8.5 is shown along with the experimental data in *Figure 6.7*.

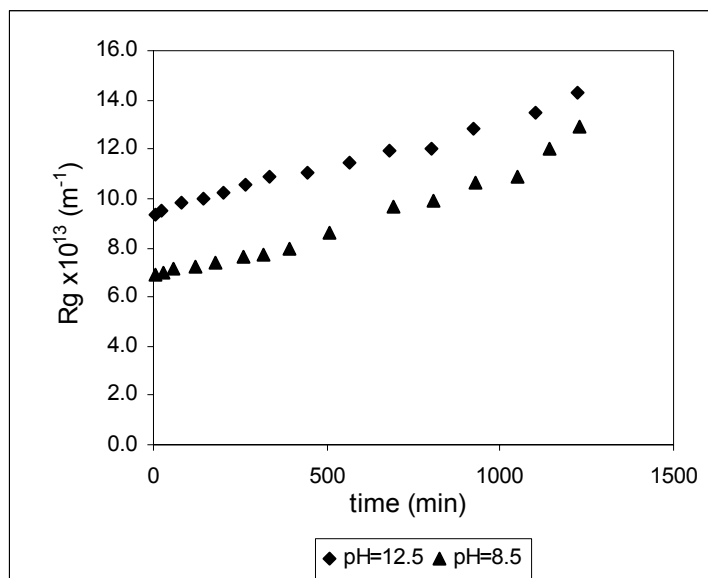


Figure 6.8 The values of gel resistance with the time obtained from experimental permeate flux results. The lignin and vanillin concentration was 60 g L^{-1} - 6 g L^{-1} , the $\text{pH}=8.5$ and 12.5

Experimental values of volume reduction, retention of lignin and vanillin measured at the end of experiment performed on the membrane with cut-off 1 kDa are summarized in Table 6.3. The final volume of permeate collected at the end of the experiment (≈ 21 hours) due to very low permeate flux was approximately 10 % of initial volume in the tank.

Although the permeate flux was very low comparing to higher cut-off membranes (see sections below) the highest observed rejection of lignin was obtained ($R_{obs} = 0.972$). It can be noticed that the observed rejection coefficient of lignin increases at higher pH. A possible explanation could be in the higher degree of association of lignin molecules due to a decrease of number of lignin molecules available to penetrate the membrane (Rudatin *et al.*, 1989). In addition, the observed rejection of vanillin as low molecular weight compound is zero at both tested pH of solution. Based on these facts a large quantity of pure vanillin can be recovered. On the other hand, the effectiveness of the ultrafiltration process is low mainly due to low permeate flux from the beginning of the experiment (see Figure 6.7) and with a tendency to decrease more with volume reduction.

Table 6.3 Volume reduction and retention for vanillin (VH) and lignin(L) obtained from experiments onto 1 kDa membrane

pH	$C(L) [\text{g L}^{-1}]$	$C(VH) [\text{g L}^{-1}]$	VR	R_{obs} lignin	R_{obs} vanillin
8.5	60	6	0.102	0.951	≈ 0
12.5	60	6	0.103	0.972	≈ 0

Each stream (retentate and permeate) was analyzed for lignin and vanillin content. The concentration histories of vanillin and lignin in retentate and permeate at concentration of lignin 60 g L^{-1} and vanillin 6 g L^{-1} and at pH of solution 8.5 and 12.5 using membrane of 1 kDa cut-off are presented in *Figure 6.9* and *Figure 6.10*, respectively. The experiments were performed at constant transmembrane pressure $\Delta P = 1.55 \text{ bar}$ and feed flow rate 130 L h^{-1} .

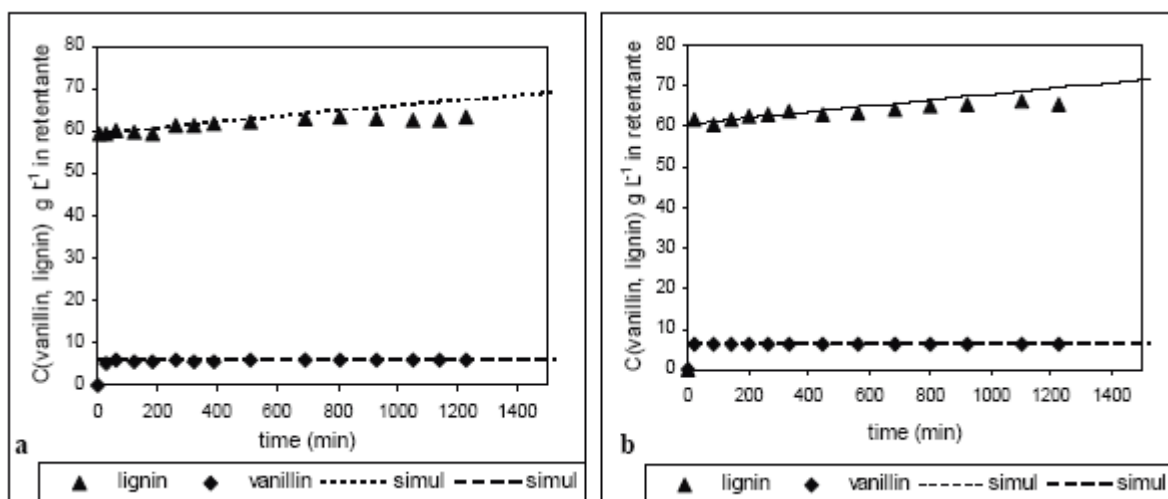


Figure 6.9 Vanillin and lignin concentration in retentate versus time using membrane of cut-off 1 kDa. The initial concentration of lignin was 60 g L^{-1} and vanillin 6 g L^{-1} , pH=8.5 (a) and pH=12.5 (b). Transmembrane pressure was constant during all experiment $\Delta P = 1.55 \text{ bar}$. Feed flow-rate: $Q_{\text{feed}} \approx 130 \text{ L h}^{-1}$ (a); $Q_{\text{feed}} \approx 120 \text{ L h}^{-1}$ (b)

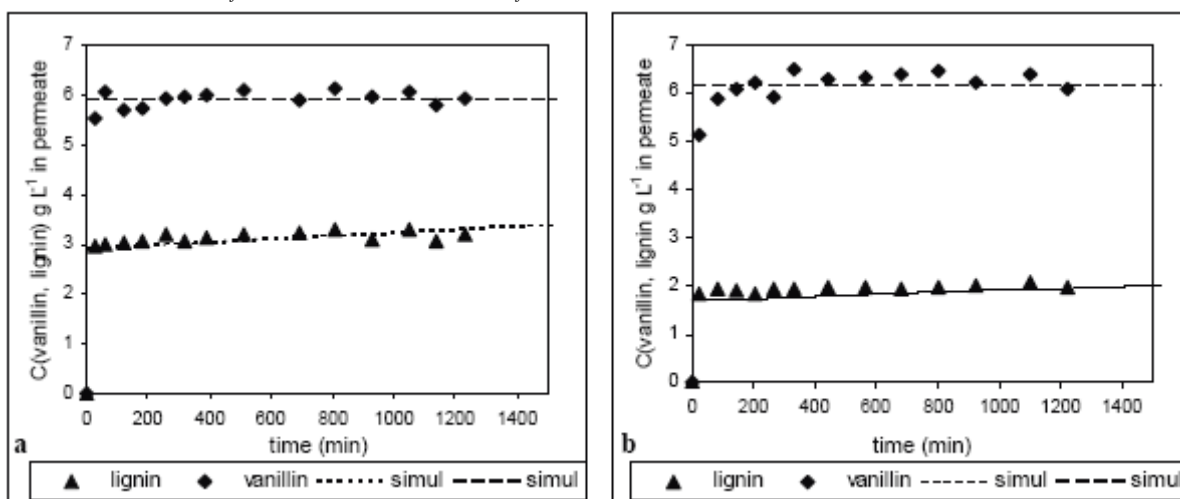


Figure 6.10 Vanillin and lignin concentration in permeate versus time using membrane of 1 kDa cut-off. The initial concentration of lignin was 60 g L^{-1} and vanillin 6 g L^{-1} , pH=8.5 (a); pH=12.5 (b). Transmembrane pressure was constant during all experiment $\Delta P = 1.55 \text{ bar}$. Feed flow-rate: $Q_{\text{feed}} \approx 130 \text{ L h}^{-1}$ (a). $Q_{\text{feed}} \approx 120 \text{ L h}^{-1}$ (b)

The variation of lignin and vanillin concentration in the retentate and the permeate with time was predicted using model equations shown in the *Table 6.1*.

The predicted curves for both species vanillin and lignin in the retentate and permeate are shown in *Figure 6.9* and *Figure 6.10*, respectively. The concentration of lignin and vanillin in the permeate or the retentate stream depends on the observed rejection. Since the batch method was applied, the feed concentration increases with the time as the retentate is recycled to the tank. Thus the concentration of lignin in the tank increased from 60 g L^{-1} to 63 g L^{-1} in the feed solution with $\text{pH}=8.5$ and from 60 g L^{-1} to 67 g L^{-1} for the feed solution with $\text{pH}=12.5$. If the observed lignin rejection is constant, the concentration of lignin in each stream must increase with increasing concentration in the feed. Because the permeate flux using membrane of 1 kDa cut-off is very low and only 10% volume reduction was reached, the concentration of lignin in the feed did not increase significantly as well as the lignin concentration in the retentate and permeate (*Figure 6.9, Figure 6.10*). Similarly, vanillin concentration (see *Figure 6.9, Figure 6.10*) measured in the samples of retentate and permeate remained constant during the experiments.

6.4.2.2 Experimental results with membrane of 5 kDa cut-off

Experimental values of volume reduction, retention of lignin and vanillin measured at the end of experiment performed on the membrane with cut-off 5 kDa are summarized in *Table 6.4*. The permeate flux at concentrations of lignin 60 g L^{-1} and vanillin 5 g L^{-1} and at $\text{pH}=12.5$ is shown in *Figure 6.11*.

Table 6.4 The values of volume reduction and retention for vanillin and lignin obtained from experiments onto 5 kD membrane.

$C(L)$ [g L ⁻¹]	$C(VH)$ [g L ⁻¹]	VR	R_{obs} lignin	R_{obs} vanillin
60*	5	0.275	0.968	≈ 0

The observed rejection of lignin ($R_{obs} = 0.968$) is slightly lower than for the membrane 1 kDa cut-off ($R_{obs} = 0.972$) but the permeate flux was practically ten times bigger. The collected volume of permeate was 27% from initial solution volume in the tank. The concentration of lignin measured in the tank at the end of experiment increased from 60 g L^{-1} to 90 g L^{-1} .

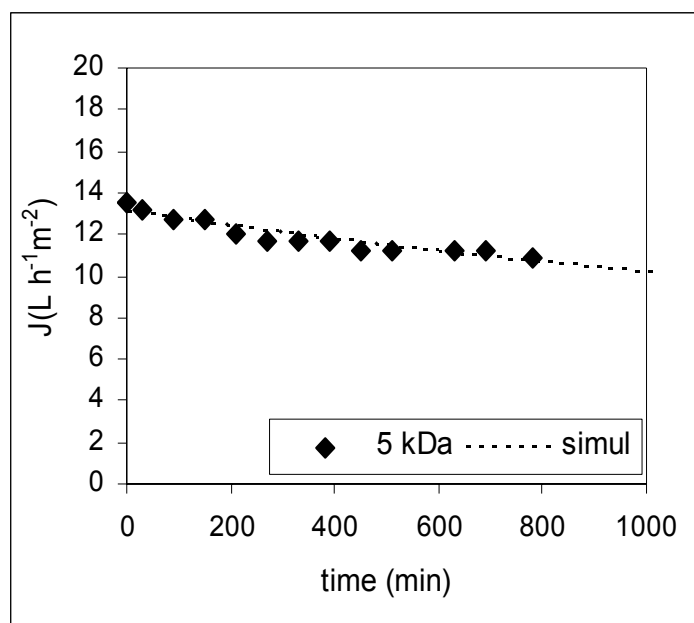


Figure 6.11 Permeate flux in membrane of 5 kDa cut-off at pH= 12.5. The concentration of lignin was 60 g L^{-1} and vanillin 5 g L^{-1} . Transmembrane pressure was constant during all experiment $\Delta P = 1.55 \text{ bar}$. Feed flow-ratet: $Q_{\text{feed}} \approx 120 \text{ L h}^{-1}$.

The permeate flux has very similar behavior compared to that observed on the membrane with cut-off 1 kDa (see Figure 6.7) under the same condition and it decreases slowly with time. The concentrations of vanillin in each stream of permeate and retentante were similar and the rejection was found to be close to zero. The permeate flux was predicted by using the gel layer model where the gel resistance was the fitting parameter. The model parameters used to predict data are listed in the Table 6.5. The change of gel resistance (R_g) with time is shown in Figure 6.12.

Table 6.5 The model parameters used in simulation for the membrane of 5 kDa cut-off

Run	$C_{\text{feed}}^0 \text{ (g L}^{-1}\text{)}$		pH	R_m (m^{-1})	η ($\text{kg m}^{-1} \text{ s}^{-1}$)	Q_{feed} (L h^{-1})	ΔP (bar)	V_0 (L)
	Lignin	Vanillin						
1	60	5	12.5	1.222×10^{13}	1.190×10^{-3}	120	1.55	4
* $R_{\text{obs}} = 0.968$ for lignin and $R_{\text{obs}} = 0$ for vanillin								

The concentration histories of vanillin and lignin in retentante and permeate using membrane of 5 kDa cut-off are presented in Figure 6.13 and Figure 6.14. The concentration of lignin and vanillin in feed was 60 g L^{-1} , 5 g L^{-1} , respectively, and pH of mixture was 12.5.

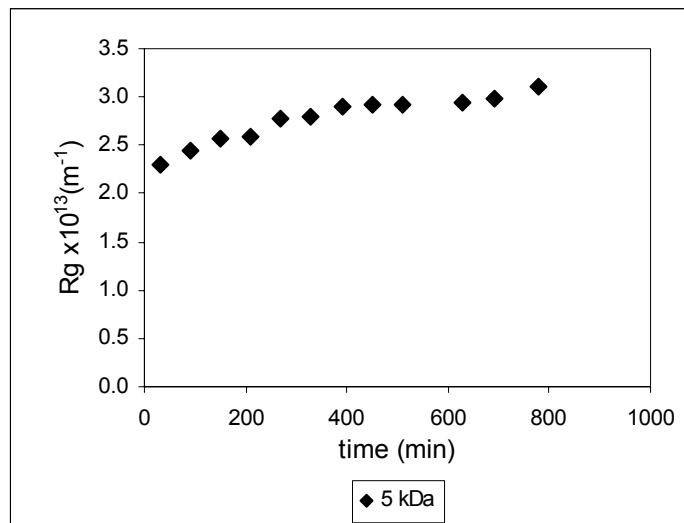


Figure 6.12 Gel resistance versus time obtained from experimental permeate flux results. Lignin and vanillin concentration were 60 g L^{-1} and 6 g L^{-1} , $\text{pH}=12.5$

The experiment was performed at constant transmembrane pressure $\Delta P = 1.55 \text{ bar}$ and feed flow rate was adjusted to 120 L h^{-1} . The concentration histories of lignin in the permeate and retentate were calculated by model equations reported in the Table 6.1. The predicted concentration histories of lignin and vanillin in each stream together with the experimental points are shown in Figure 6.13-Figure 6.14.

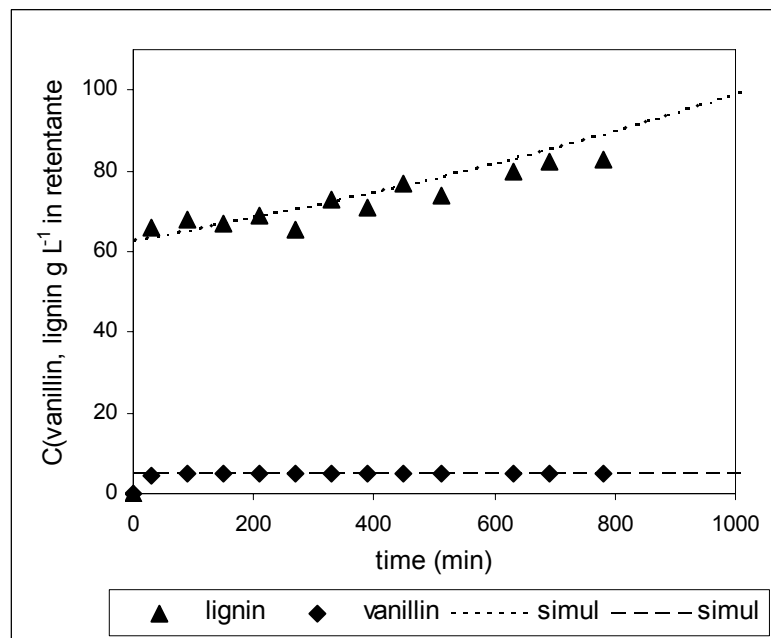


Figure 6.13 Vanillin and lignin concentration in retentate versus time using membrane of 5 kDa cut-off. The initial concentration of lignin was 60 g L^{-1} and vanillin 5 g L^{-1} , $\text{pH}=12.5$. Transmembrane pressure was constant during all experiment $\Delta P=1.55 \text{ bar}$. Feed flowrate t : $Q_{\text{feed}} \approx 120 \text{ L h}^{-1}$

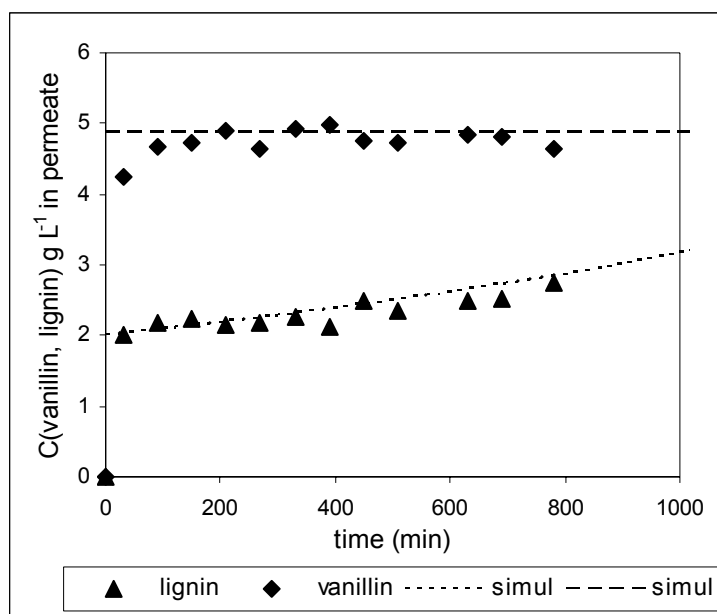


Figure 6.14 Vanillin and lignin concentration in permeate versus time using membrane of 5 kDa cut-off. The initial concentration of lignin was 60 g L^{-1} and vanillin 5 g L^{-1} , $\text{pH}=12.5$. Transmembrane pressure: $\Delta P = 1.55 \text{ bar}$. Feed flowrate: $Q_{\text{feed}} \approx 120 \text{ L h}^{-1}$

The predicted concentration profiles using the gel layer model are in good agreement with experimental data. It is shown that the lignin concentration in the permeate and retentante are slightly increasing while the vanillin concentration remains constant. The increase of the lignin concentration in both streams is due to application of batch filtration method. Similarly as in the case of membrane of 1 kDa cut-off the concentration of vanillin in the permeate was constant and no obstruction for the penetration of vanillin molecule was found.

6.4.2.3 Experimental results with membrane of 15 kDa cut-off

The experimental results performed with membrane of 15 kDa cut-off are summarized in Table 6.6 and the variation of permeate fluxes with time at different concentrations and pH of solution are shown in Figure 6.15-6.18.

Table 6.6 The values of volume reduction and retention for vanillin and lignin obtained from experiments onto 15 kD membrane.

pH	$C(L)$ [g L ⁻¹]	$C(VH)$ [g L ⁻¹]	VR	R_{obs} lignin	R_{obs} vanillin
8.5	5	0.5	0.500	0.916	≈ 0
	20	2.0	0.440	0.958	≈ 0
	60	6	0.313	0.943	≈ 0
12.5	20	2.0	0.440	0.873	≈ 0
	60	6	0.340	0.865	≈ 0

Figure 6.15 shows the permeate flux as a function of time for concentrations 60/6 g/L of lignin/vanillin solution at pH=8.5 and 12.5.

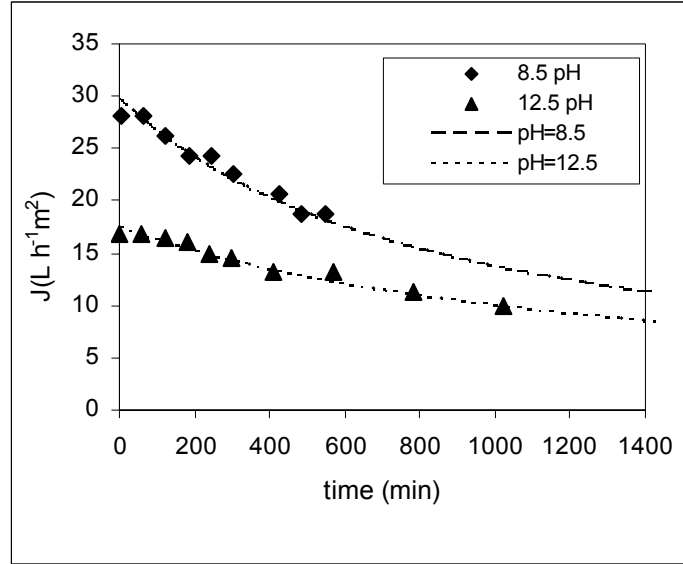


Figure 6.15 Permeate flux in membrane of 15 kDa cut-off at pH=8.5 and 12.5. The concentration of lignin was 60 g L⁻¹ and vanillin 6 g L⁻¹. Transmembrane pressure: $\Delta P = 1.3$ bar. Feed flowrate: $Q_{feed} \approx 101$ L h⁻¹.

The difference between the permeate fluxes of the lignin/vanillin solution at same concentration but at different pH was noticed also when using membrane of 1 kDa. In the case of membrane with 15 kDa cut-off the permeate flux for the solution of lignin/vanillin at concentration of 60/6 g L⁻¹ was almost two times higher for lower pH. As it was pointed out above the difference could be due to the change of the properties of lignin in an alkali media such as higher solubility and association of macromolecules and became more significant with increasing the lignin concentration (Rudatin *et al.*, 1989). The difference between permeate fluxes at the concentration 20 g L⁻¹ at different pH was also present but not so noticeable as at the higher concentration. The permeate fluxes at different concentration but the same pH were also compared. The initial permeate flux always decreases as the concentration of lignin in the initial feed solution increases.

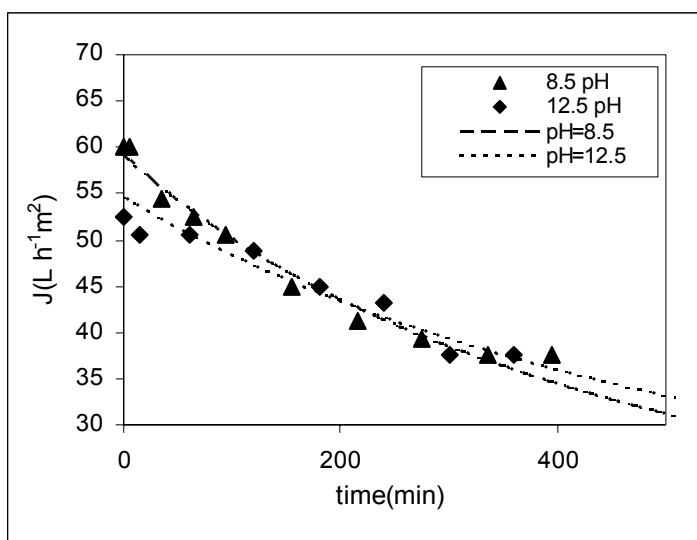


Figure 6.16 Permeate flux in membrane of 15 kDa cut-off at pH=8.5 and 12.5. The concentration of lignin was 20 g L^{-1} and vanillin 2 g L^{-1} . Transmembrane pressure: $\Delta P = 1.3 \text{ bar}$. Feed flow-rate: $Q_{\text{feed}} \approx 102 \text{ L h}^{-1}$

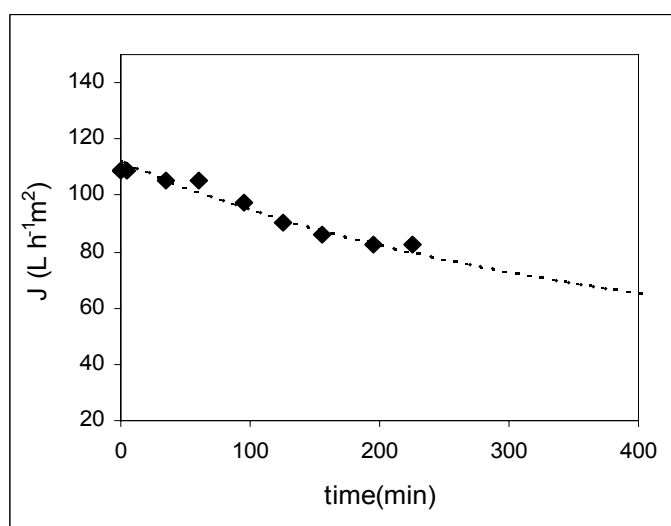


Figure 6.17 Permeate flux in membrane of 15 kDa cut-off at pH=8.5. The concentration of lignin was 5 g L^{-1} and vanillin 0.5 g L^{-1} . Transmembrane pressure $\Delta P = 1.3 \text{ bar}$. Feed flow-rate: $Q_{\text{feed}} \approx 109 \text{ L h}^{-1}$

The permeate fluxes were predicted using the gel resistance obtained from experimental data. The change of gel resistance with the time is shown in Figure 6.18 for all concentration range and the model parameters are in Table 6.7

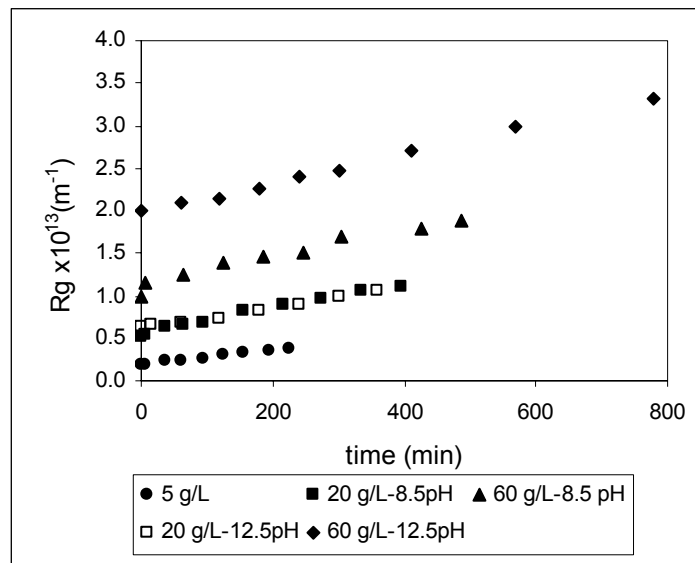


Figure 6.18 The change of gel resistance (R_g) with time when filtrating lignin/vanillin solution at the concentrations 5-0.5, 20-2, 60-6 g L^{-1} , $\text{pH}=8.5$ and 12.5

Table 6.7 Model parameters used in simulations for membrane of 15 kDa cut-off

Run	C_{feed}^0 (g L^{-1})		pH	R_{obs} Lignin	R_{obs} Vanillin	η ($\text{kg m}^{-1} \text{s}^{-1}$)	Q_{feed} (L h^{-1})	V_0 (L)
	Lignin	Vanillin						
1	5	0.5	8.5	0.916	≈ 0	0.887×10^{-3}	109	5
2	20	2	8.5	0.958	≈ 0	0.954×10^{-3}	102	5
3	20	2	12.5	0.873	≈ 0	0.954×10^{-3}	102	5
4	60	6	8.5	0.943	≈ 0	1.190×10^{-3}	101	5
5	60	6	12.5	0.865	≈ 0	1.190×10^{-3}	101	5
* the value of R_m is $2.806 \times 10^{12} \text{ m}^{-1}$, ΔP for all runs is 1.3 bar								

The observed rejection of lignin, R_{obs} , was 0.958 for the solution of lignin/vanillin at concentration of 20/2 g L^{-1} at $\text{pH}=8.5$ and $R_{obs}=0.873$ for $\text{pH}=12.5$. The rejection of lignin significantly decreased also at concentration of lignin/vanillin 60/6 g L^{-1} at $\text{pH}=12.5$ and it was 0.865. It could be noticed that the rejection of lignin at each tested concentrations 20 and 60 g L^{-1} decreases with increasing pH of the mixture. This is contrary to the results observed on the membrane of 1 kDa cut-off where at pH 12.5 the rejection was higher than at $\text{pH}=8.5$.

For the case of feed concentration 60 g L^{-1} of lignin, 6 g L^{-1} of vanillin and pH of mixture equal to 8.5 and 12.5 the histories of vanillin and lignin concentration in retentate and permeate for the membrane of cut-off 15 kDa are presented in Figure 6.19, Figure 6.20. The experiment was performed at constant transmembrane pressure $\Delta P=1.3$ bar. Feed flow-rate was adjusted to 102 L h^{-1} .

The predicted concentration curves for lignin in the retentante and permeate using equations reported in Table 6.1 are showed in Figure 6.19, Figure 6.20.

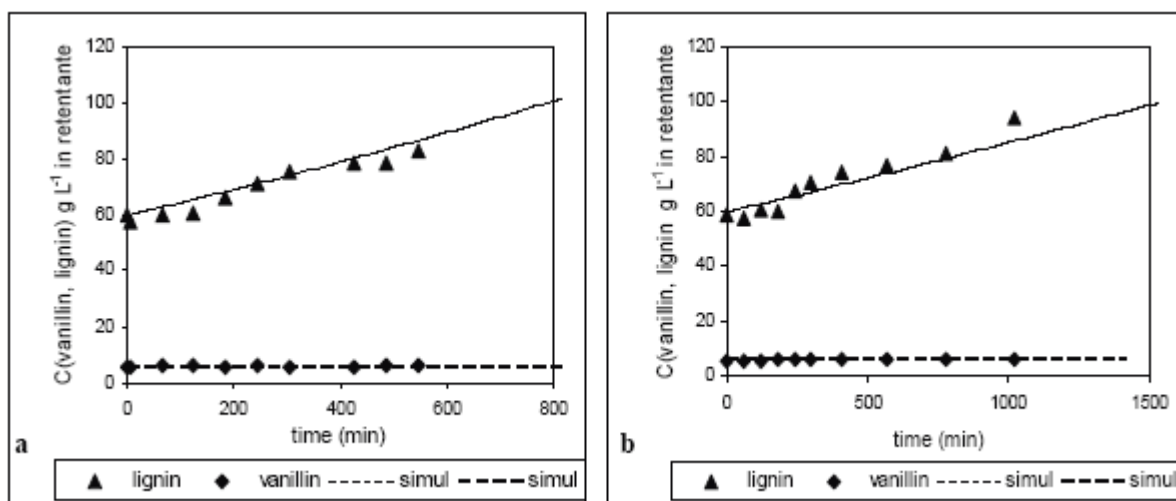


Figure 6.19 Vanillin and lignin concentration in retentante versus time using membrane of 15 kDa cut-off and at pH=8.5(a); pH=12.5(b). The initial concentration of lignin was 60 g L⁻¹ and vanillin 6 g L⁻¹. Transmembrane pressure: $\Delta P = 1.3$ bar. Feed flowrate: $Q_{feed} \approx 102$ L h⁻¹

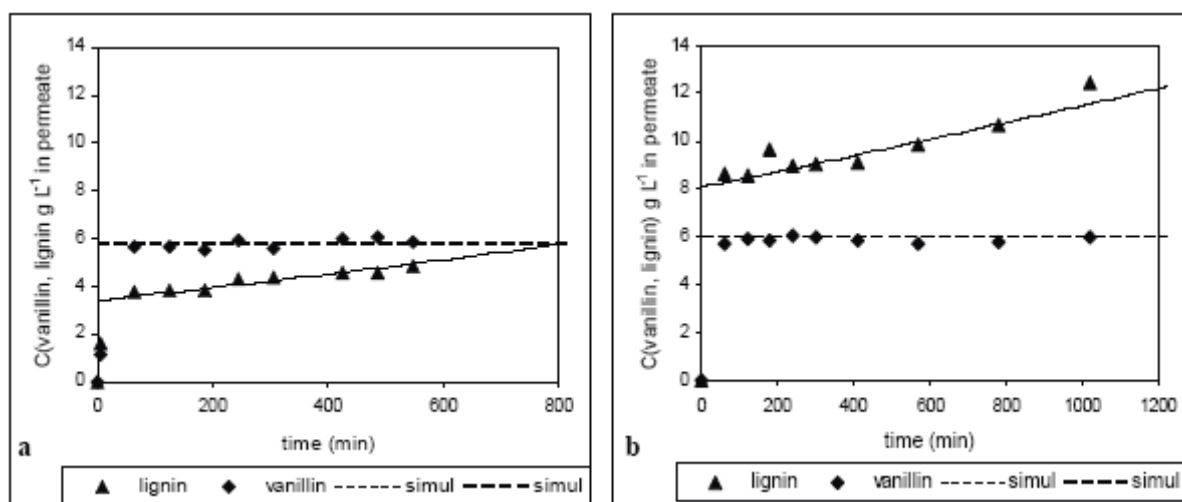


Figure 6.20 Vanillin and lignin concentration in permeate versus time using membrane of 15 kDa cut-off and at pH=8.5(a); pH=12.5(b). The initial concentration of lignin was 60 g L⁻¹ and vanillin 6 g L⁻¹. Transmembrane pressure: $\Delta P = 1.3$ bar. Feed flowrate: $Q_{feed} \approx 101$ L h⁻¹

For feed concentration of lignin 20 g L⁻¹ and vanillin 2 g L⁻¹ and pH of mixture equal to 8.5 and 12.5 the behavior of vanillin and lignin concentration in retentante and permeate for the membrane of cut-off 15 kDa are presented in Figure 6.21 and Figure 6.22, respectively. The experiment was performed at constant transmembrane pressure $\Delta P = 1.3$ bar. Feed flow-rate was adjusted to 102 L h⁻¹.

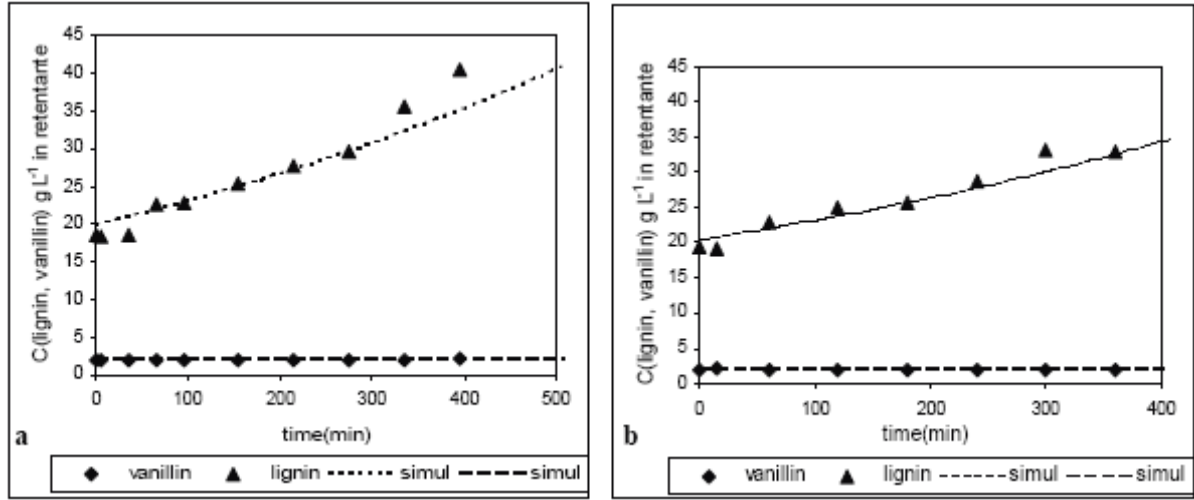


Figure 6.21 Vanillin and lignin concentration in retentate versus time using membrane of 15 kDa cut-off at pH=8.5(a), pH=12.5(b). The initial concentration of lignin was 20 g L⁻¹ and vanillin 2 g L⁻¹. Transmembrane pressure $\Delta P = 1.3$ bar. Feed flowrate: $Q_{feed} \approx 102$ L h⁻¹.

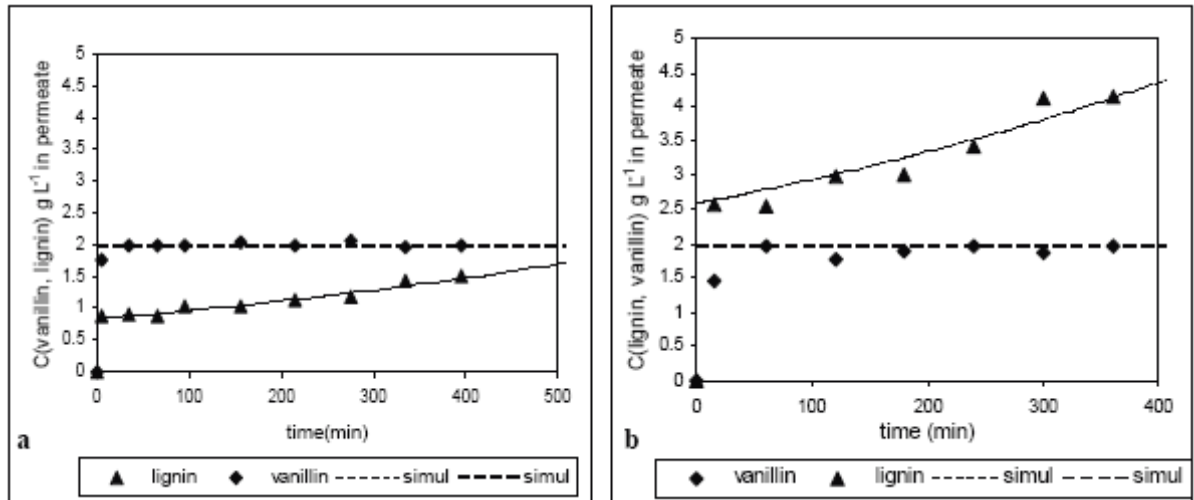


Figure 6.22 Vanillin and lignin concentration in permeate versus time using membrane of 15 kDa cut-off and at pH=8.5(a), pH=12.5(b). The initial concentration of lignin was 20 g L⁻¹ and vanillin 2 g L⁻¹. Transmembrane pressure $\Delta P = 1.3$ bar. Feed flow-rate: $Q_{feed} \approx 102$ L h⁻¹.

Depending on the permeate flux and the rejection of the lignin the concentration of lignin increases during the experiment in the retentate (see Figure 6.21). It is also evident as the feed concentration is increasing with time, lignin concentration increases in the permeate as well but the observed rejection of lignin remains constant. The observed rejection of vanillin calculated from experimental results was close to zero and the same concentration of vanillin was observed in the permeate and in the retentate during the experiments.

For feed concentration of lignin 5 g L⁻¹ and vanillin 0.5 g L⁻¹ and pH of mixture equal to 8.5 the concentration histories of vanillin and lignin in retentate and permeate using membrane

of 15 kDa cut-off are presented in *Figure 6.23* and *Figure 6.24*, respectively. The experiment was performed at constant transmembrane pressure $\Delta P = 1.3$ bar. Feed flow-rate was adjusted to 109 L h^{-1} .

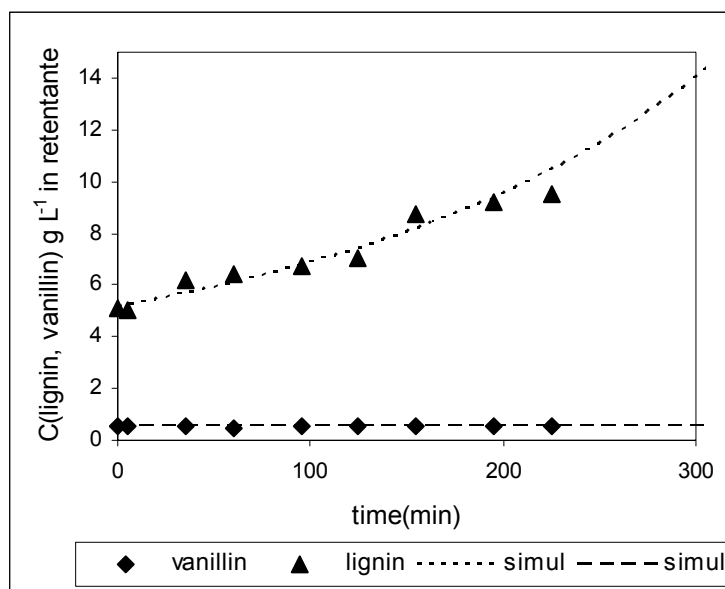


Figure 6.23 Vanillin and lignin concentration in retentate versus time using membrane of 15 kDa cut-off and at $\text{pH} = 8.5$. The initial concentration of lignin was 5 g L^{-1} and vanillin 0.5 g L^{-1} . Transmembrane pressure $\Delta P = 1.3$ bar. Feed flow-rate: $Q_{\text{feed}} \approx 109 \text{ L h}^{-1}$

The phenomena of lignin molecule association and aggregation to different degrees in various solvents lead to different molecular weight distributions. This fact has been already investigated in the literature (Lindström, 1979; Sarkanen *et al.*, 1984; Woerner and McCarthy, 1988; Gilardi and Cass, 1993) and the main mechanism of molecular association: are hydrogen bonding, stereoregular bonding, lyophobic bonding and charge transfer bonding (Rudatin *et al.*, 1989). Generally, it can be stated that association of molecules is strongly dependent on the molecular weight and pH of filtrated macromolecular solution (Sarkanen *et al.*, 1984).

It was found that for small molecular weight compounds the major association is in pH between 10-13; in contrast for high molecular weight compounds the considerable association occur at pH between 12 - 13.5 (Garver and Callaghan, 1991).

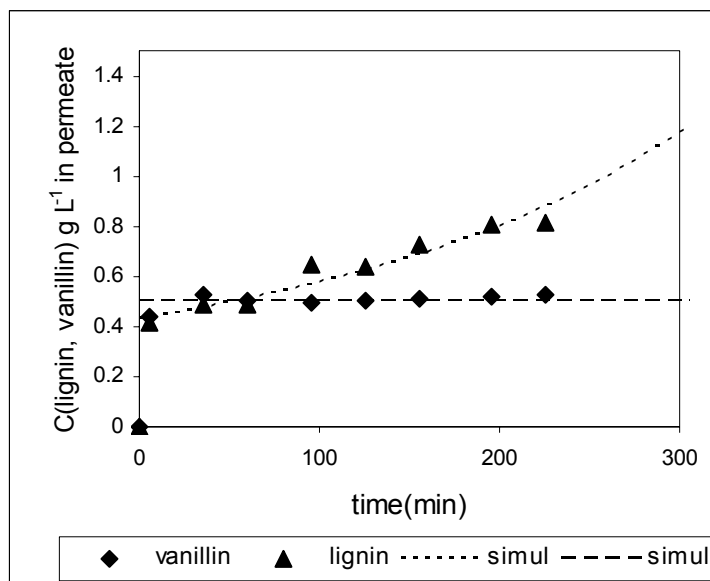


Figure 6.24 Vanillin and lignin concentration in permeate versus time using membrane of 15 kDa cut-off. The initial concentration of lignin was 5 g L^{-1} and vanillin 0.5 g L^{-1} , $\text{pH}=8.5$. Transmembrane pressure $\Delta P = 1.3 \text{ bar}$. Feed flow-rate: $Q_{\text{feed}} \approx 109 \text{ L h}^{-1}$

The association of the molecules at high pH lead to particle size increase mostly due to polyelectrolyte swelling and dissociation of ionisable functional groups (Lindström, 1979) while when pH decreases the association is due to the formation of hydrogen bonds. Glasser and Ross (Ross *et al.*, 1986) noticed from the experiments using membrane of 10 kDa and 20 kDa cut-off, respectively that the rejection of the Kraft lignin decreased with increasing pH of the solution. The same results were found in our experiments using membrane of 15 kDa cut-off but they are in contradiction with those observed on the membrane of 1 kDa cut-off. Unfortunately, there are no references in the literature presenting the influence of pH on the rejection using the membrane with lower cut-off. This disagreement between the rejection of lignin at two different pH of solution and using different membrane cut-off (1 kDa and 15 kDa) could be related to a change of governing mechanism.

One can speculate that at $\text{pH}=12.5$, the bigger molecules provide more sites for association compared with small molecules and therefore can be more effectively rejected by 1 kDa membrane while using 15 kDa membrane even associated molecules can pass through the membrane to the permeate. On other hand, the association of molecules with lowering the pH can be predominant leading to the formation of bigger aggregates which are not allowed to pass through the membrane of 15 kDa cut-off.

6.4.3 Experimental results of ultrafiltration of permeate obtained using membrane of 1 kDa cut-off

It was observed that with the membrane of lower cut-off, higher rejection could be obtained (see section 6.4.2.1). On the other hand, ultrafiltration of solution at high concentration of lignin using low cut-off membrane leads to significant decline of the permeate flux. One approach to solve the difficulty is to introduce more ultrafiltration stages. For this purpose, one experiment was carried out with lignin and vanillin solution at the similar concentration of both components as obtained by ultrafiltration of lignin/vanillin solution at a concentration 60/6 g L⁻¹ using membrane of 1kDa cut-off (see section 6.4.2.1). The permeate flux during ultrafiltration of lignin/vanillin mixture at the concentration 2 g L⁻¹ of lignin and 6 g L⁻¹ of vanillin is shown in *Figure 6.25*. It is very important to point out that the solution was prepared from fresh lignin and this model solution did not reflect the real permeate composition of the mentioned experiment essentially due to the content of high molecular weight fraction.

The permeate flux through the membrane was predicted by using the mathematical model which includes osmotic pressure and concentration polarisation and by the gel layer model and both mathematical models are compared with experimental permeate flux in *Figure 6.25*. *Table 6.8* reports the model parameters used in simulations. The series of mathematical equations involved in the simulations are listed in *Table 6.1*. The membrane area was $A_m = 0.008 \text{ m}^2$ and a' empirically determined constant from van't Hoff equation was 42.9 Pa m³ kg⁻¹. The gel layer resistance (R_g) as a function of time obtained by linear regression is:

$$R_g = 5.19 \times 10^7 t + 6.81 \times 10^{12}, R^2 = 0.982.$$

Table 6.8 Model parameters used in simulations considering osmotic pressure and concentration polarisation.

Run	C_{feed}^0 (g L ⁻¹)		pH	R_m (m ⁻¹)	η (kg m ⁻¹ s ⁻¹)	Q_{feed} (L h ⁻¹)	ΔP (bar)	V_0 (L)	k (m s ⁻¹)
	Lignin	Vanillin							
1	2	6	12.5	2.806×10^{13}	1.190×10^{-3}	120	1.55	4	2.49×10^{-6}
* the value of R_{obs} is 0.986 for lignin and zero for vanillin									

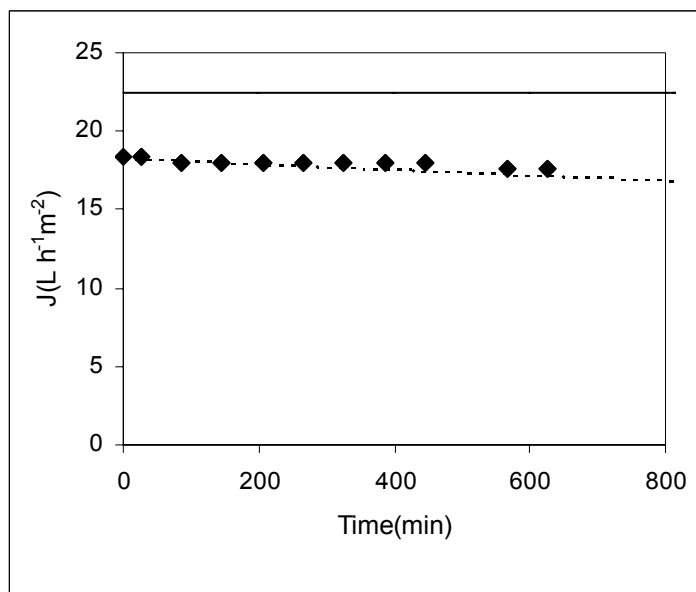


Figure 6.25 Permeate flux in membrane of 1 kDa cut-off at pH = 12.5. The concentration of lignin was 2 g L^{-1} and vanillin 6 g L^{-1} . Transmembrane pressure $\Delta P = 1.55 \text{ bar}$. Feed flowrate: $Q_{\text{feed}} \approx 120 \text{ L h}^{-1}$. The full line represents concentration polarisation model and the dotted line gel layer model.

The predicted permeate flux using concentration polarisation model is higher than the flux experimentally obtained. The reason of disagreement between the predicted and experimental permeate flux can be in mass transfer coefficient calculated according to Deissler correlation (Eq. 6.25). Mass transfer coefficient was calculated using diffusion coefficient D (Eq. 6.24) which includes hydrodynamic radius of the lignin molecule (R_e) estimated only for the average molecular weight ($M_w = 60000 \text{ g mol}^{-1}$). It is evident that mass transfer coefficient is not constant but is varying with the time due to change of lignin molecular weight during the process. Table 6.9 reports the values of volume reduction and retention of lignin and vanillin on ceramic membrane with cut-off 1 kDa measured at the end of the experiment. The volume of permeate and feed in the tank was measured and each stream was analyzed for lignin and vanillin content. The permeate flux was significantly higher in comparison to that when high concentration was filtrated. During the time of experiment the volume in the tank was reduced to almost 41% from the initial volume.

Table 6.9 The values of volume reduction and retention for vanillin and lignin obtained from experiments onto 1 kDa membrane

C(L) [g L ⁻¹]	C(VH) [g L ⁻¹]	VR	R_{obs} lignin	R_{obs} vanillin
2	6	0.405	0.986	≈ 0

The concentration histories of vanillin and lignin in retentate and permeate at concentration of lignin 2 g L^{-1} and vanillin 6 g L^{-1} and at pH of solution 8.5 and 12.5 using membrane of 1 kDa cut-off are presented in *Figure 6.26 a, b* and *Figure 6.27 a, b* respectively. The simulated concentration profiles for both species in the permeate and in the retentate were obtained using series of equations reported in the *Table 6.1* and are shown along with experimental data.

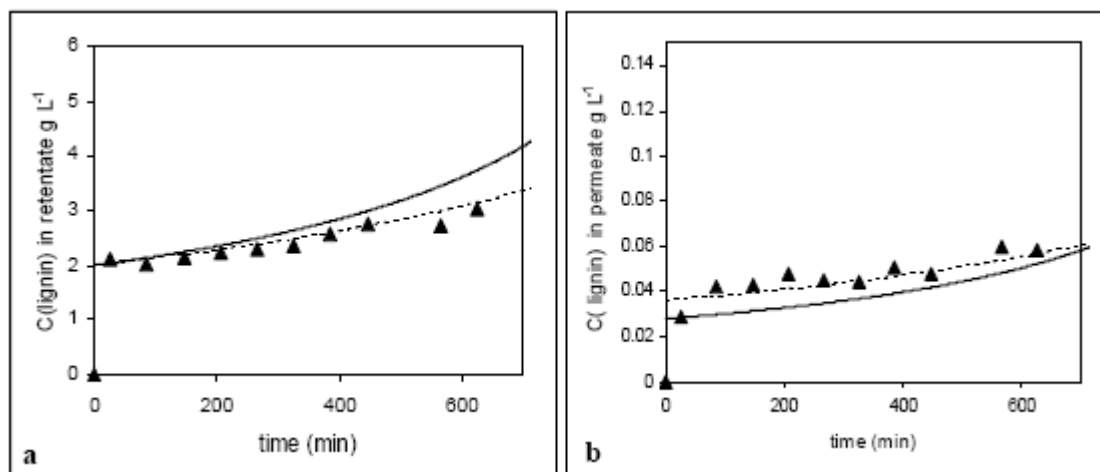


Figure 6.26 Lignin concentration in retentate (a) and permeate (b) as a function of time using membrane of 1 kDa cut-off. The initial concentration of lignin was 2 g L^{-1} and vanillin 6 g L^{-1} , pH=12.5. Transmembrane pressure $\Delta P = 1.55 \text{ bar}$. Feed flow-rate: $Q_{\text{feed}} \approx 120 \text{ L h}^{-1}$. The full line represents concentration polarisation model and the dotted line gel layer model.

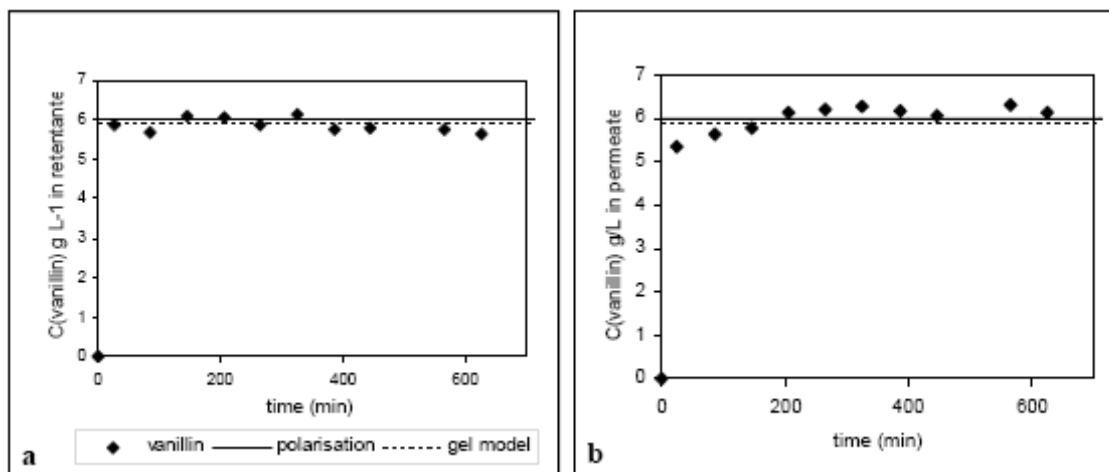


Figure 6.27 Vanillin concentration in retentate (a) and permeate (b) as a function of time using membrane of 1 kDa cut-off. The initial concentration of lignin was 2 g L^{-1} and vanillin 6 g L^{-1} , pH=12.5. Transmembrane pressure $\Delta P = 1.55 \text{ bar}$. Feed flow-rate: $Q_{\text{feed}} \approx 120 \text{ L h}^{-1}$. The full line represents concentration polarisation model and the dotted line gel layer model.

The concentration of lignin in the tank analysed at the end of experiment increased from 2 g L⁻¹ to 3.2 g L⁻¹. The observed rejection of vanillin was zero and the concentration in the permeate and retentate was constant. The process was carried out up to 41% volume reduction and 9.7 g of vanillin was recovered in the permeate. Since the low concentration of lignin in the solution, the flux decline does not represent significant limitation in the process as it is at high concentrations (see section 6.4.2.1). This could be a way to optimize the recovery of vanillin from Kraft lignin oxidation media using ultrafiltration

6.5 Conclusion

The recovery of vanillin from Kraft lignin oxidation product by the ultrafiltration techniques was investigated and it was shown that it can be employed as an efficient way for such purpose. The appropriate size of membrane cut-off can significantly reduce the high molecular components from the lignin/vanillin mixture. Due to high physical and chemical resistance the ceramic membranes can be applied under strong pH conditions and high temperature.

The tubular ceramic membranes with different molecular weight cut-offs: 1, 5 and 15 kDa were used in the experiments to compare their performance. The influence of the lignin and vanillin concentration and pH of the mixture on the ultrafiltration process has been studied as well.

The highest value of lignin rejection was obtained with the membrane 1 kDa cut-off. By filtrating the lignin/vanillin mixture at the concentration 60/6 g L⁻¹ and pH=12.5 the lignin observed rejection was 0.972. On the other hand, using the membranes with small cut-off leads to significant decline of permeate flux comparing with the membranes with bigger cut-off. For example the permeate flux using 1 kDa membrane was only 4 L h⁻¹m², while for membrane 5 kDa was 14 L h⁻¹m². One possibility to solve this problem can be to introduce more ultrafiltration stages starting from bigger cut-off membrane.

The influence of pH of the lignin/vanillin mixture on observed rejection was observed as well. It was found that increasing pH of the solution leads to decrease of lignin rejection using membranes with 15 kDa cut-off while the opposite was found using membrane 1 kDa. These phenomena can be explained by different mechanism of macromolecules association depending on molecular weight, pH and cut-off of the membrane.

We assume that the formation of a gel layer takes place on the membrane surface and thus has influence on the separation process because it is responsible for significant flux decline. On the other hand it was observed that very high cleaning efficiency can be obtained using alkali cleaning (NaOH). There was no evidence of irreversible fouling or plugging the membrane pores. All tested cut-off membranes recovered after experiments and subsequent cleaning procedure the same permeability as was found with “new” membranes.

6.6 Nomenclature

a'	coefficient in van't Hoff equation ($\text{Pa m}^3\text{kg}^{-1}$)
A_m	membrane surface, (m^2)
C_b	solute concentration in the bulk, (g L^{-1})
C_g	gel concentration of the rejected solute, (g L^{-1})
C_p	solute concentration in the permeate, (g L^{-1})
C_w	concentration of the rejected solute at the membrane surface, (g L^{-1})
d_h	Hydraulic diameter of the flow channel (m)
d_p	Particle diameter, (m)
D	Diffusion coefficient ($\text{m}^2 \text{s}^{-1}$)
J	Permeate flux, ($\text{L h}^{-1} \text{m}^{-2}$)
k	Mass transfer coefficient, (m s^{-1})
k	Boltzmann constant, ($1.3806503 \times 10^{-23} \text{ m}^2 \text{kg s}^{-2} \text{K}^{-1}$)
K_1, K_2	Constant in Eqs.6.19 a,b, (-)
K_g	Permeability of the gel layer ($\text{m}^2 \text{Pa}^{-1} \text{s}^{-1}$)
L	Length of the membrane, (m)
M_w	average molecular weight of the solute, (g mol^{-1})
N_A	Avogadro's number, ($6.0221415 \times 10^{23} \text{ mol}^{-1}$)

ΔP_1	Relative inlet pressure on the feed side, (bar)
ΔP_2	Relative outlet pressure, (bar)
P_p	Permeate pressure of the shell side (bar)
Q_{feed}	Feed flow-rate, (L h ⁻¹)
Q_p	Permeate flow rate, (L h ⁻¹)
Q_r	Retentante flow rate, (L h ⁻¹)
R^0	Intrinsic rejection, (-)
R_e	Hydrodynamic radius, (m)
Re	Reynolds number, $Re = d_h v \rho / \eta_0$ (-)
R_g	Resistance of the gel layer, (m ⁻¹)
R_m	Membrane hydraulic resistance, (m ⁻¹)
R_{obs}	Observed rejection, (-)
Sc	Schmidt number, $Sc = \eta / \rho D_{AB}$, (-)
Sh	Sherwood number (-)
t	Time, (s)
T	Temperature, (K)
ΔP	Average transmembrane pressure, , (bar)
VR	Volume reduction (-)
V_0	Initial volume of the feed tank, (m ³)
V_p	Permeate withdrawn volume, (m ³)
z	Axial variable, (m)

Greek symbols

ε_g	Porosity of gel layer, (-)

θ Flow rate ratio of permeate and feed, (-)

$\Delta\pi$ Osmotic pressure, (Pa)

ρ Density of the solute, (kg m^{-3})

η_0 Solvent viscosity, (Pa.s)

η Viscosity of the solution, (Pa.s)

$[\eta]$ Intrinsic viscosity (L g^{-1})

δ_{pol} Thickness of the polarization layer, (m)

δ_g Thickness of the gel layer, (m)

v Velocity in the flow channel, (m s^{-1})

Indexes

“ i ” specie vanillin or lignin

6.7 Reference

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7. Recovery of vanillin from Kraft lignin oxidation by ion-exchange with neutralization¹

7.1 Introduction

Vanillin (4-hydroxy-3-methoxybenzaldehyde) is one of the most common aromatic molecules used in the food, pharmaceutical and cosmetic industries. There are two commercial types of vanillin, pure vanillin obtained by chemical synthesis from guaiacol or black liquors from paper industry and a vanilla extract obtained by the ageing and alcoholic extraction of the pod of tropical *Vanilla orchid* (principally *Vanilla planifolia* Andrews, syn. *V. fragrans* (Salisb. Ames)) (Thibault *et al.*, 1998; Walton *et al.*, 2003; Dausch and Pastore, 2005). The natural vanillin is very expensive compared to synthetic vanillin produced by oxidation of spent sulfite liquor. Therefore, synthetic vanillin as the alkaline oxidation product of sulfite waste liquor is an interesting product to be studied.

The world market consists of around 1800 tons of pods, with the market price approximately \$1200-\$4000 per kilo, while industrial vanillin is around 12,000 tons and a market price is bellowing \$15 per kilo (Lomascolo *et al.*, 1999; Muheim and Lerch, 1999). That means

¹ Based on the paper “*Recovery of vanillin from Kraft lignin oxidation by ion-exchange with neutralization* by M. Zabkova, E.A. Borges da Silva and A.E. Rodrigues, Separation and Purification Technology (2006).

vanilla extract is 250 times more expensive than synthetic vanillin, because of the complexity of the culture and tedious ageing process (Thibault *et al.*, 1998). Nowadays, approximately 50% of the worldwide production of synthetic vanillin is used by the chemical and pharmaceutical industries for the production of herbicides, antifoaming agents, household products or drugs (Hocking, 1997; Walton *et al.*, 2000; Walton *et al.*, 2003). The antioxidant and antimicrobial properties are applied in use of vanillin as a food preservative (Krueger and Krueger, 1983; Burri *et al.*, 1989; Dausch and Pastore, 2005). It exhibits the activity against both Gram-positive and Gram-negative food-spoilage bacteria and also shows antimutagenic effect, for instance, as a suppressor of chromosomal damages (Cerrutti *et al.*, 1997; Keshava *et al.*, 1998; Fitzgerald *et al.*, 2004; Fitzgerald *et al.*, 2005).

Industrial vanillin is produced apart from guaiacol and glyoxylic acid route by oxidation of spent sulfite liquor, which is a byproduct of the sulfite wood pulping process (Bjorsvik, 1999; Bjorsvik *et al.*, 2000). The spent sulfite liquor usually consists of dry solids content (12-15%), of lignosulfonates (55-60%), monosacharides (20-30%) and salts of organic and inorganic acids (Forss *et al.*, 1986). Borregaard is one of the world's largest producers of vanillin, supplying vanillin from two different processes: one based on guaiacol route and another is based on oxidation of lignosulfonates (sulfite spent liquor) (Bjorsvik *et al.*, 2000).

The presence of vanillin in the alkaline oxidation products of sulfite waste liquor is of theoretical interest from the point of view of lignin chemistry (Pearl, 1942). It has been well known since 1920s that lignin heated under reflux conditions for long times in the presence of active alkali produces a maximum yield of vanillin (Van Ness, 1983). Pressure, temperature and reaction time influence the yield and nature of phenolic compounds obtained.

During the oxidation process, in addition of vanillin other reaction products can be formed such as oxidized lignin, acetovanillone, dehydrodivanillin, guaiacol, p-hydroxibenzaldehyde, and aromatic acids (Pearl, 1942). In the process of Kraft lignin oxidation to produce vanillin the reaction media at pH =12-13 contains degraded lignin and vanillin (most in the vanillate form) (Fargues *et al.*, 1996). After a membrane separation step the permeate will contain sodium vanillate and excess *NaOH* and the objective is to recover vanillin from this mixture by flowing it through a packed bed of acid resin in H^+ form. *Figure 7.1* shows a simplified flow sheet of the lignin oxidation for recovery of the synthetic vanillin.

Generally, the isolation of vanillin from the oxidized solution is an important stage in vanillin production. The concentration of vanillin in solution cannot be significantly increased by evaporation because of the high solids content and the vanillin present as sodium vanillate is difficult to extract.

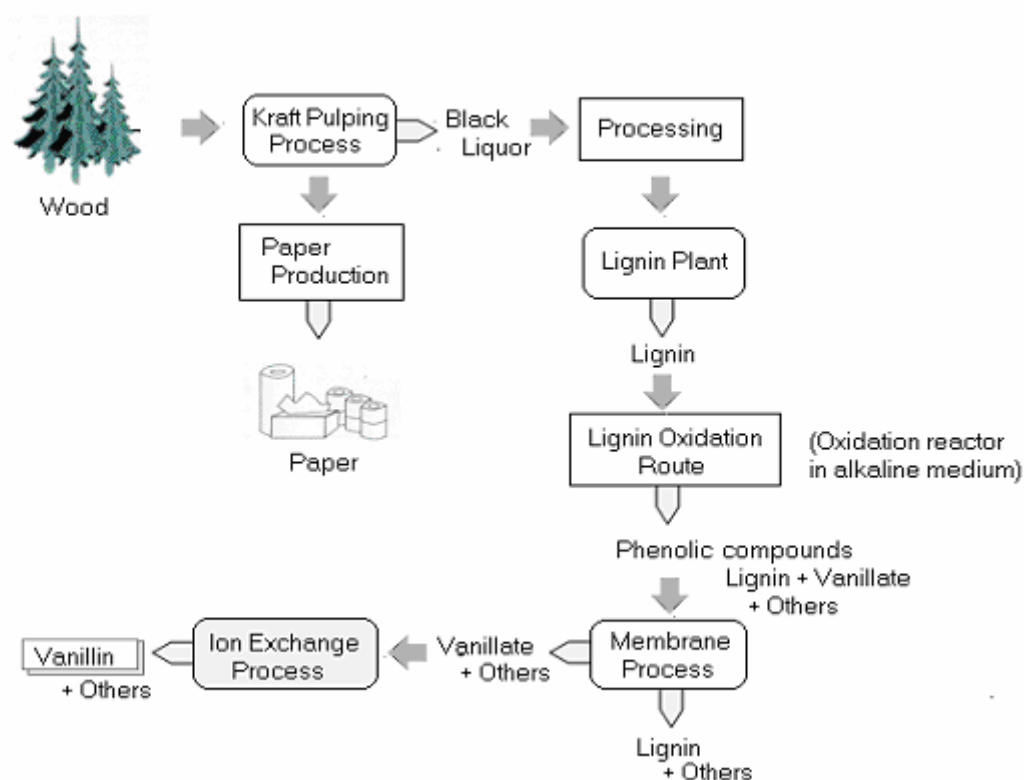


Figure 7.1 Simplified flow sheet of the lignin oxidation for recovery of the synthetic vanillin

Vanillin can be extracted from the solution with suitable solvents such as benzene or toluene after acidification of the liquor. Disadvantage of this method is that a large amount of acidic solution is required for neutralization and also the precipitation of the lignin complicates the extraction and causes loss of vanillin (Hibbert and Tomlinson, 1937).

The Lignin precipitation can be avoided by extraction of sodium vanillate from the alkaline solution, for instance with n-butyl alcohol or isopropyl alcohol (Sandborn and Salvesen, 1936; Bryan, 1955). However, the limited solubility of sodium vanillate in organic solvents is a disadvantage of this process.

In 1971, Craig and Logan provided an experiment using weak cation-exchange resins in acid form for vanillin isolation. The alkaline solution is eluted through the column filled with such

a resin, sodium vanillate and other phenolates are converted into a phenolic form (Craig and Logan, 1971). This presented process seems interesting and it became the main goal of the work presented here.

The target of the work is to study ion-exchange equilibrium between Na^+ from vanillin/ $NaOH$ solution and H^+ from the strong cationic resin Amberlite IR120H at the temperature 293 K and to evaluate ion exchange kinetics in fixed-bed. The breakthrough curves of directly measured vanillate, vanillin and calculated Na^+ of a fixed bed packed with cationic resin Amberlite IR120H in H^+ form, at different feed concentrations, have been studied. The influence of alkalinity of the vanillin solution on ion-exchange process using static and dynamic approach has been investigated.

7.2 Experimental Methods

7.2.1 Chemicals and ion-exchanger

Vanillin ($C_8H_8O_3$) and sodium hydroxide ($NaOH$) were purchased from Sigma-Aldrich (Spain). The solutions of vanillin and sodium hydroxide were prepared with degassed and deionised water. Demineralized water was used with conductivity value lower than $1\mu S/cm$. The strong cationic resin Amberlite IR120H supplied from Rohm & Haas (France) was used as an ion exchanger. The physical characteristics of polymeric ion-exchange resin Amberlite IR 120 H are summarized in *Table 7.1*. The resin was pretreated with the chlorohydric acid (HCl) and demineralized water before use.

Table 7.1 Properties of the ion exchanger Amberlite IR120H

Matrix	Styrene divinylbenzene copolymer (8% DVB; gel type)
Functional groups	Sulphonic
Total exchange capacity (equiv/g dry resin)*	0.0050 a; 0.0055 b
Density of the resin (kg dry resin/m ³)	560
Average particle diameter (m)	$5.50 \cdot 10^{-4}$ a; $7.04 \cdot 10^{-4}$ c
Moisture content (%)	47 to 62
^a Rodriguez et al. (Rodriguez et al., 1998) ^b Melis et al. (Melis et al., 1996) ^c Valverde et al. (Valverde et al., 2004) *From manufacturer (Rohm&Haas) ≥ 1.8 equiv/L wet resin	

7.2.2 Equipment

The batch adsorption experiments by using Erlenmeyer flasks with the jacket were performed, which were placed in shaking mixer (GLF-3018, Germany). The temperature was controlled using thermostatic bath (Edmund Bühler, Germany). The solution was analyzed on UV-VIS spectrophotometer Jasco (model 7800, Japan). The fixed bed ion-exchange experiments were performed in glass column with the jacket (150 × 20 mm, I.D.). The vanillin solution was pumped to the system by peristaltic pump Watson-Marlow (England). The pH of the solution was measured by pH meter Crison microPH 2002.

7.2.3 Ion-exchange equilibrium experiments

Contacting a different weight of strong cationic resin Amberlite IR120H and the same volume of the solution at the same initial concentration the batch ion exchange experiments were carried out. The moisture content of the resin Amberlite IR120 in H^+ form was determined for each experiment as a difference between weight of wet resin and after drying at 423 K. The solution was prepared by dissolving 0.033 equiv (≈ 5 g) of vanillin in 1L of sodium hydroxide solution with the concentration 0.03 equiv L^{-1} . Immediately after dissolution, according the chemical reaction between sodium hydroxide and vanillin, the vanillate is formed and equilibrium is characterized by the equilibrium constant of the reaction. The batch experiment has been performed in 250 mL Erlenmeyer flasks where 70 mL of prepared solution with the same concentration and an amount of the wet resin have been added. The weight of wet resin was in the range 0.005 g to 1.6 g. The temperature (293 K) was controlled by thermostatic bath. The volumetric flasks were placed in a shaking mixer at constant speed 150 rpm. The equilibrium in resin-liquid mixture has been reached approximately within 24 hours. The solution was separated from the ion-exchanger and the final concentration of vanillin was determined by measuring the absorbance using UV-VIS spectrophotometer. The total concentration of vanillin and vanillate species was determined by measuring the absorbance at the wavelength 259 nm, which is isobestic point. Additionally, the concentration of vanillate was determined at the wavelength of 376 nm.

In the case of ordinary binary Na^+ / H^+ ion-exchange isotherm the solution was prepared as a mixture of 0.1 equiv/L sodium chloride ($NaCl$) and pH was 5.34. The excess of H^+ ion was determined by measuring the pH after equilibrium was established.

In order to obtain the data and parameters of ion-exchange equilibrium isotherm, the following mass balance is used

$$q_i^* = \frac{V}{W f_H} (C_{0i} - C_i^*) \quad 7.1$$

where q_i^* represents the resin-phase equilibrium concentration, C_{0i} and C_i^* are initial and equilibrium concentrations in the bulk fluid phase, V is the volume of bulk solution, W is the wet mass of resin and f_H is dry particle to wet particle mass ratio.

7.2.4 Uptake ion-exchange experiments

The batch uptake experiment has been performed in 250 mL Erlenmeyer flasks where 50 mL of vanillin solution with the same concentration and the different mass of the wet resin have been added. The mass of wet resin was 0.3 g, 0.8 g, 1.0 g, 1.5 g and 2.0 g. The moisture content of the resin was determined for each experiment as a difference between weight of wet resin and after drying at 423 K. Temperature (293 K) was controlled by thermostatic bath. The volumetric flasks were placed in a shaking mixer at constant speed 150 rpm. The liquid samples (0.1 mL) were taken and analyzed during the time till the system reaches the equilibrium. The equilibrium in resin-liquid mixture has been reached after time which depends on the mass of the resin. The concentration of vanillin and vanillate in each sample was determined by measuring the absorbance using UV-VIS spectrophotometer in the same way as is described above.

7.2.5 Fixed-bed performance

The fixed bed ion-exchange experiments on the polymeric ion exchange resin Amberlite IR120H were performed. The glass column with jacket (150 × 20 mm, I.D.) has been used in all fixed-bed experiments and solutions have been delivered by peristaltic pump. Fixed bed ion-exchange experiments onto ion-exchanger Amberlite IR120H were provided at the temperature 293 K. The temperature of the column was maintained by a thermostatic bath. Vanillin concentration at the column outlet was determined at wavelength of 254 nm by an UV-VIS spectrophotometer. Different runs by changing the pH of the feed solution, which leads to different ratio vanillin and vanillate in the feed were carried out. Four different initial

pH of the vanillin solution 8.2, 11.4, 11.9 and 12.1 and the flow rate 19 mL min^{-1} have been used.

7.3 Theory and Modelling

7.3.1 Equilibrium for the ordinary binary ion-exchange

Ion exchange equilibrium is attained when an ion exchanger is placed in contact with an electrolyte solution containing a counterion which is different from that in the ion-exchanger. The ion-exchanger is initially in the $\overline{H}^+$ form, and the counterion in the solution is Na^+ . Counterion exchange occurs, and the ion $\overline{H}^+$ in the ion exchanger is partially replaced by Na^+ :



where the barred quantities represent species in the resin phase. In this reversible equilibrium, both the ion exchanger and the solution contain both competing counterion species, Na^+ and H^+ . The reversible ion exchange reaction between the liquid and resin phases resulting in an equilibrium constant K_{Na-H} for the binary system (Pieroni and Dranoff, 1963):

$$K_{Na-H} = \frac{y_{Na^+} x_{H^+}}{y_{H^+} x_{Na^+}} \quad 7.3$$

The ionic fraction is introduced as follows: $x_{Na^+} = \frac{C_{Na^+}}{C_T}$, $x_{H^+} = \frac{C_{H^+}}{C_T}$, in the liquid-phase;

$y_{Na^+} = \frac{q_{Na^+}}{q_T}$, $y_{H^+} = \frac{q_{H^+}}{q_T}$, in the resin-phase. The variable C_i is the concentration of ionic

species in solution, C_T is the total ionic concentration in the solution phase or the solution normality, q_i is the ion concentration in the resin phase, and q_T is the total exchange capacity of the resin. *Figure 7.2* illustrates two cases of ion-exchange equilibria: an ion-exchange isotherm for an ordinary binary system and an isotherm when the process of ion-exchange is accompanied by irreversible reaction. Generally, the former takes place when the solution contains only a neutral salt; the equilibrium shows the usual pattern for the ordinary ion-exchange process without reaction. This system was broadly revised by many researchers and

equilibrium data of the conventional equilibrium of a salt of strong acid or base on several ion-exchangers have already been reported. (Delucas *et al.*, 1992).

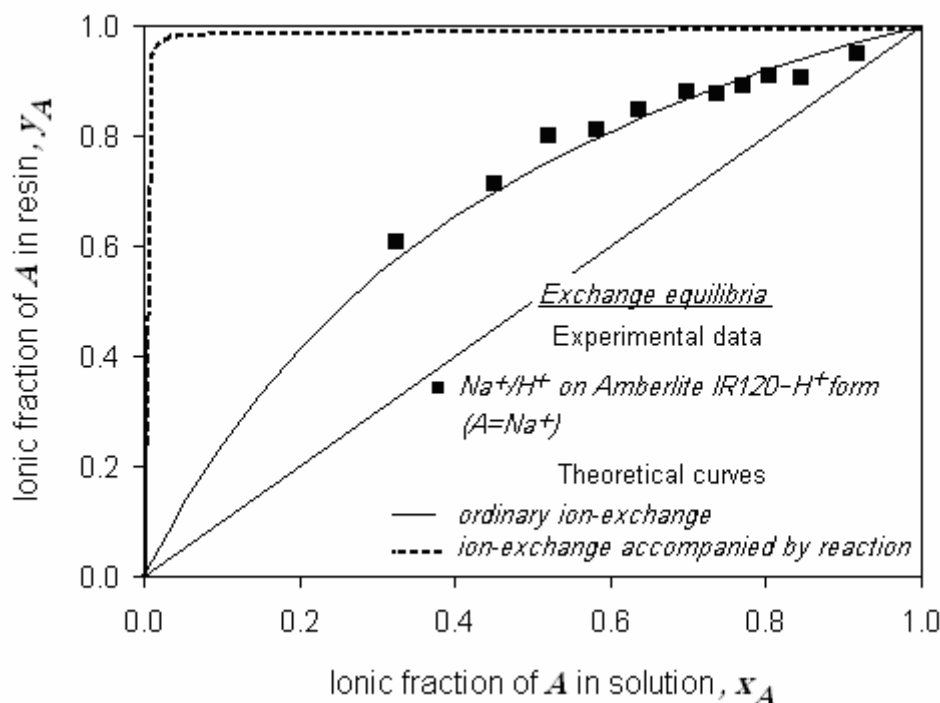


Figure 7.2 Theoretical ion-exchange equilibrium isotherms: ordinary and accompanied by chemical reaction. (dots) – experimental points for ordinary ion-exchange equilibrium of the Na^+/H^+ ions onto Amberlite IR120H. Initial solution: mixture of 0.1 equiv L^{-1} sodium chloride (NaCl) and $\text{pH} = 5.3$ (at 293 K)

The case of ion-exchange in presence of reaction has been introduced by Helfferich (1965), who derived rate laws for some typical ion-exchange processes involving neutralizations, association and complex formation. The bulk solution containing a base in contact with a H-form resin, such as $\bar{\text{H}}^+ + \text{Na}^+\text{OH}^- \rightarrow \bar{\text{Na}}^+ + \text{H}_2\text{O}$, is an example of ion-exchange accompanied by neutralization. For this situation, the ion-exchange becomes irreversible and the equilibrium isotherm rectangular – as seen in Figure 7.2. Some experimental points of the conventional ion-exchange equilibrium of the Na^+/H^+ ions onto Amberlite IR120H are also shown in Figure 7.2 and discussed later.

7.3.2 Ion-exchange equilibrium of the system vanillin/ NaOH -Amberlite IR120H

The ion-exchange process under consideration includes the consumption of the counter-ion released by the ion exchange (i.e. H^+) and therefore is accompanied by reaction (neutralization). Theoretical analysis of typical ion exchange processes involving reactions

has been introduced by Helfferich (Helfferich, 1965). Reactions such as neutralizations, association or complex-formation reactions have been already described (Helfferich, 1965). The equations of fractional approach for equilibrium taking into account diffusion controlling mechanisms— film and intraparticle based on Nernst-Planck equations, have already been developed (Helfferich, 1965; Haub and Foutch, 1986a). The experimental studies of the rate of neutralization of a strong acid ion exchanger by strong bases (Blickenstaff *et al.*, 1967a) and weak base (Blickenstaff *et al.*, 1967b) have supported the theory developed by Helfferich (Helfferich, 1965).

Here the studied system includes a bulk liquid phase and a resin phase. The bulk phase is an aqueous liquid where the slight dissociation of vanillin and water dissociation occur. The dissociation degree is characterized by dissociation constants K_d and K_w :

$$VH \leftrightarrow V^- + H^+; \quad K_d = \frac{C_{V^-} C_{H^+}}{C_{VH}} \quad 7.4$$

$$H_2O \leftrightarrow OH^- + H^+; \quad K_w = C_{H^+} C_{OH^-} \quad 7.5$$

where VH and V^- correspond to undissociated and dissociated vanillin form, respectively.

The liquid phase has been prepared as a mixture of vanillin and sodium hydroxide, which is a strong base and dissociate completely. The stoichiometric amount of OH^- anions reacts entirely with an equivalent amount of H^+ ions released by the weak acid (vanillin). The stoichiometric amount of weak acid is ionized and neutralized as well as the sodium salt of vanillin (VNa) is formed (Eq.7.6). The sodium vanillate, the salt of strong base and weak acid in the presence of water breaks completely into its ions.



The resin-phase added to the system provides sites with fixed charges for ion exchange process. The resin-phase is ion-exchange resin Amberlite IR120H, in which the exchangeable ion is H^+ . There are non-exchangeable co-ions V^- , OH^- and the counter ions Na^+ , H^+ in the studied system.

There are two situations that can occur during the preparation of the solutions to be processed by ion-exchange: (i) the solution contains the mixture of vanillin and its salt, i.e., a buffer solution; or (ii) the solution contains an amount of sodium hydroxide higher than the amount

of vanillin (above the equivalent point), all acid is converted to its salt and hydroxide is in excess in the initial solution. The equivalence point corresponds the situation when vanillin has been titrated and essentially none vanillin (VH) as well none ability to neutralize base remains in the system.

7.3.3 Batch ion-exchange modelling

The volume V_r of strong acid resin is introduced into contact with a volume V_s of diluted aqueous solution of vanillin/ $NaOH$ in the batch process. The rates of ion-exchange occur under condition of intraparticle and external film diffusion rate control as it is already reported (Helfferich, 1965). In the studied system, the ion-exchange operation and additional reactions take place in a well-stirred batch reactor and the process is assumed to be controlled by intraparticle diffusion. Thus, the concentration gradients in the bulk liquid phase are neglected.

The ion-exchange reactions can be written as follow:



Equation 7.7a shows the case where the solution contains a base: the H^+ ion from resin is exchanged with Na^+ ion from solution and it is converted in water by an irreversible reaction with OH^- co-ion in solution. As a result, the equilibrium isotherm would show a rectangular shape (Kataoka and Yoshida, 1988). Once the studied system contains vanillate and vanillin in solution (or only vanillate if the pH value is high enough), the reaction shown by Eq.7.7b is taking place and after the H^+ ion exchanges for Na^+ ion, vanillin is produced. As can be seen later, this system leads to a reversible condition since the isotherm obtained for exchange Na^+/H^+ is very favourable but not irreversible.

In the resin phase, the interdiffusion of counterions in the ion exchanger is not affected by the co-ions. The co-ions V^- and OH^- are assumed to be excluded from the interior of the resin particle (*Donnan* effect). Therefore, in modelling equations describing the ion-exchange in the resin phase, the reaction consuming H^+ ion interferes only with the boundary condition at the resin particle surface (Helfferich, 1965).

Ion flux equations are based on the Nernst-Plank theory and can be written:

$$\bar{N}_i = -D_i^{ef} \left(\nabla q_i + z_i q_i \frac{F}{RT} \nabla \phi \right) \quad 7.8$$

where $\bar{N}_i$ is the flux of the i -th ion in resin phase, z_i is valence, ϕ is electric potential, T is temperature, F and R are the *Faraday* and the ideal gas constants, respectively. The coefficient D_i^{ef} represents an effective diffusivity of the ion in the resin-phase considered as homogeneous structure.

The assumptions include the following: individual diffusion coefficients remain constant in process; activity coefficients are unity; the system is isothermal; reactions of the Eqs.7.4 -7.6 are instantaneous in comparison to the rate of exchange. Moreover, ion exchanger particle is considered spherical and uniform; the swelling changes are neglected in the model. The mobile co-ions are confined to liquid phase, since there is no interaction between them and resin phase. However, a few of them can diffuse into the resin accompanied by neutralising counter-ions. This action can increase the number of ions in the resin, causing its swelling and subsequently increase resin exchange capacity slightly above the capacity connected to the fixed ionic groups alone. The process of swelling is a result of hydrophobic and hydrophilic interactions between the solvent and the resin matrix (de Lucas *et al.*, 2002) and can be dependent on cross-linking and exchange capacity of the resin, as well as temperature and solution composition (Rodrigues, 1986). In the studied system the swelling phenomena was neglected. It is already reported that H^+ ion is more mobile than Na^+ (Rodriguez *et al.*, 1998). The resin matrix has negative charge and the co-ion moves away from it. Consequences of using these assumptions in some related models have been discussed elsewhere (Haub and Foutch, 1986a; Haub and Foutch, 1986b).

The ion-exchange kinetics has been evaluated by measuring the amount of exchange ions between resin and bulk phase. The electro-neutrality and zero current constraints for the resin phase requires that

$$q_{H^+} + q_{Na^+} = q_T \quad 7.9$$

$$\bar{N}_{H^+} + \bar{N}_{Na^+} = 0 \quad 7.10$$

By combination of Eq.7.8 and Eq.7.10 to substitute q_{H^+} and electrical potential term, we can obtain:

$$\bar{N}_{Na+} = -D^{ef} \nabla q_{Na+} \quad 7.11$$

where total resin-phase effective diffusivity D^{ef} is expressed by

$$D^{ef} = \frac{D_{Na+}^{ef} q_T}{q_T + q_{Na+}(\alpha - 1)} \quad 7.12$$

with $\alpha = D_{Na+}^{ef} / D_{H+}^{ef}$.

The transport equation of counter-ions through the resin with spherical shape can be written by using Eq. 7.11 leading to,

$$\frac{\partial q_{Na+}}{\partial t} = \frac{D_{Na+}^{ef} q_T}{q_T + q_{Na+}(\alpha - 1)} \left(\frac{\partial^2 q_{Na+}}{\partial r^2} + \frac{2}{r} \frac{\partial q_{Na+}}{\partial r} \right) - \frac{D_{Na+}^{ef} q_T (\alpha - 1)}{(q_T + q_{Na+}(\alpha - 1))^2} \left(\frac{\partial q_{Na+}}{\partial r} \right)^2 \quad 7.13$$

The situation appearing in the derivation of Eq.7.13 is analogous to coupled *Fickian* interdiffusion with non-constant effective interdiffusion coefficient.

Initial and boundary conditions are

$$t = 0 \quad (0 < r < R_p) \quad q_{Na+} = 0 \quad 7.14$$

$$r = 0 \quad (t > 0) \quad \frac{\partial q_{Na+}}{\partial r} = 0 \quad 7.15$$

$$r = R_p \quad (t > 0) \quad q_{Na+} = \frac{q_T K_L c_{Na+}}{1 + K_L c_{Na+}} \quad 7.16$$

where q_T is the total capacity of the ion exchanger and K_L is a Langmuir model parameter for the ion-exchange equilibrium. Since the model considers resin-phase as a homogeneous particle, the parameter D_{Na+}^{ef} represents an homogeneous effective diffusivity of ion sodium.

The H^+ ion from the resin exchanged for Na^+ ion diffuses to the particle surface in the radial direction and is consumed by instantaneous irreversible reaction with OH^- anion to form water at the resin/liquid interface. Additionally, it is assumed that the concentration of the Na^+ ion at the resin surface is at equilibrium with the bulk liquid. Therefore, an equilibrium relation (as shown in Eq.7.16) must be taken into account. As an example, ion-exchange process between resin in H^+ form and $NaOH$ solution accompanied by neutralization reaction the equilibrium is characterized by a rectangular isotherm.

The differential mass balance for the liquid phase in batch system can be written as:

$$\frac{\partial c_{Na+}}{\partial t} = -\frac{W}{V} f_H \frac{\partial \langle q_{Na+} \rangle}{\partial t} \quad 7.17$$

$$\text{with } \langle q_{Na+} \rangle = \frac{3}{R_p^3} \int_0^{R_p} r^2 q_{Na+} dr \quad 7.18$$

where $\langle q \rangle$ represents the average resin-phase concentration over the pellet, V is liquid phase volume, W is the wet mass of the resin and f_H is dry particle to wet particle mass ratio. The initial conditions are: $c_{Na+} = c_{oNa+}$ and $\langle q_{Na+} \rangle = 0$. The H^+ ion from resin is consumed at the particle surface and its variation in bulk phase depend on the reactions described by Eqs.7.4 - 7.7. The prediction of H^+ concentration in the liquid phase is provided by calculating pH of the solution. The pH value can be evaluated according to the proportion of vanillate sodium salt and vanillin in the solution and above equivalent point from the concentration of OH^- anions.

Using the electroneutrality principle in the bulk liquid phase, we have:

$$c_{Na+} + c_{H+} = c_{V-} + c_{OH-} \quad 7.19$$

Following Eq.7.4 and Eq.7.5 the amount of H^+ ion in bulk phase comes from dissociation of vanillin and water in the solution. When the dissociation constant of the weak acid is low, the amount of H^+ ions in solution can be neglected as well as OH^- anions below the equivalent point and then the concentration of sodium ions is equal to concentration of vanillate.

Keeping the above mentioned assumptions, the dissociation of vanillin is very fast and the equilibrium of dissociation reaction can be considered. During the ion-exchange process before the equivalent point is reached some vanillin has been neutralized with strong base ($NaOH$) and the solution contains a weak acid and its salt. The buffering power of vanillin is determined by $pKa = 7.4$. Both vanillin and vanillate molecules contain benzyl ring which can be determined by UV spectrophotometer at the wavelength of 259 nm. As a result, the total amount of these species in the solution can be measured and the following equation can be written:

$$C_V^T = C_{VH} + C_{VNa} \quad 7.20$$

where C_V^T is a total amount of vanillin and vanillate experimentally determined. Since we assume the co-ion species are not interacting with the resin the value of C_V^T should be always constant.

When pH is higher than that in the equivalent point, the solution contains vanillate but also sodium hydroxide. As a consequence, the pH value is controlled only by the amount of hydroxyls anions (OH^-) in the solution.

Since pH value influences the composition of the vanillin/vanilate in liquid phase we can state: (i) if reaction described by Eq.7.7b occurs the vanillin is produced and as a result pH of the solution decreases; (ii) if reaction described by Eq.7.7a occurs the pH of the solution decreases and consequently vanillin is formed by Eq. 7.4. The set of six variables (q_{Na^+} , q_{H^+} , C_{Na^+} , C_{H^+} , C_{V^-} and C_{VH}) can be obtained by solving Eq.7.4, Eq. 7.9, Eq.7.13), Eq.7.17, Eq.7.19 and Eq.7.20.

7.3.4 The fixed-bed operation

In order to study the fixed bed ion exchange behaviour, a differential mass balance in a bed volume element for the liquid phase can be written:

$$\frac{\partial c_{Na^+}}{\partial t} = D_{ax} \frac{\partial^2 c_{Na^+}}{\partial z^2} - u \frac{\partial c_{Na^+}}{\partial z} - \frac{1-\varepsilon}{\varepsilon} \rho_s f_h \frac{\partial \langle q_{Na^+} \rangle}{\partial t} \quad 7.21$$

where D_{ax} is the axial dispersion, u is the interstitial velocity, ε is the bed porosity, ρ_s is the wet resin density and f_H is dry particle to wet particle mass ratio. At the initial time,

$$C_{Na^+} = 0 \text{ and } \langle q_{Na^+} \rangle = 0 \quad 7.22$$

The boundary conditions for the mass balance equation are the *Danckwerts* boundary conditions:

$$z = 0 ; D_{ax} \left. \frac{\partial c_{Na^+}(z, t)}{\partial z} \right|_{z=0} = u(c_{Na^+}(0, t) - c_{oNa^+}) \quad 7.23$$

$$z = L ; \left. \frac{\partial c_{Na^+}(z, t)}{\partial z} \right|_{z=L} = 0 \quad 7.24$$

The intraparticle mass transfer term is modelled as discussed in batch model.

The set of algebraic and partial differential equations derived above has been solved using the software package *gPROMS*[®] (*general PROcess Modelling System*) (gPROMS, 2003). The orthogonal collocation method on finite elements (OCFEM) was used with minimum 40 finite elements and two interior collocation points in each element of the fixed bed. The model predicts breakthrough and desorption curves that are compared with those obtained experimentally.

7.4 Results and Discussion

7.4.1 Ion-exchange equilibrium isotherm and uptake profiles

The binary ion-exchange equilibrium isotherm Na^+ / H^+ has been evaluated by using sodium chloride solution as a source of counterion Na^+ . The experimental equilibrium points along with the fitted curve are shown on the *Figure 7.2*. The experimental points represent the relation between Na^+ ion fraction (x_{Na^+}) in the liquid phase and ion fraction (y_{Na^+}) in the resin-phase (in this case, A ion refers to the Na^+ ion in *Figure 7.2*). The equilibrium constant is obtained from fitting of the experimental points and its value is $K_{Na-H} = 2.82$. For the calculation of the resin-phase equilibrium concentration, the dry particle to wet particle mass ratio equal to 0.4 (g dry resin /g wet resin) which is an average value found in resin samples was used.

The ion-exchange equilibrium of the studied system vanillin- $NaOH$ /Amberlite IR120H is shown on the *Figure 7.3*. The x -axis shows concentration of Na^+ ions remaining in the liquid phase and y -axes concentration of Na^+ ions in the resin phase.

A Langmuir model is used to describe the experimental equilibrium data, $q_{Na+}^* = \frac{q_T K_L c_{Na+}}{1 + K_L c_{Na+}}$,

where q_T is the total capacity of the ion exchanger and K_L is a Langmuir model parameter for the ion-exchange equilibrium. The values of q_T and K_L are 0.0053 equiv g⁻¹ dry resin and 3 422.0 L equiv⁻¹, respectively. As a minimization algorithm to improve accuracy in the determination of the isotherm parameters Levenberg-Marquardt method was used, which is incorporated in Origin 6.0 (Microcal Software, USA).

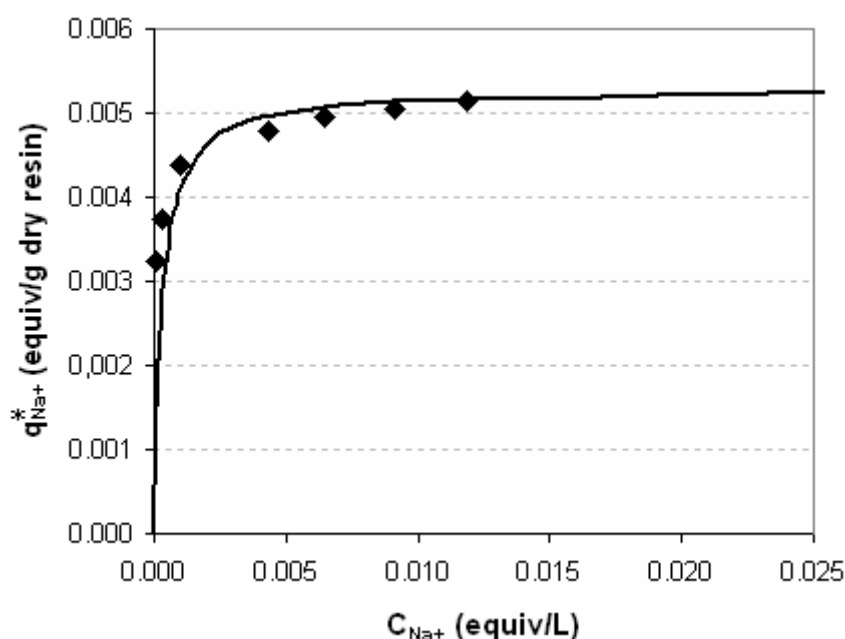


Figure 7.3 Ion-exchange equilibrium of the Na^+/H^+ ions onto Amberlite IR120H (in presence of vanillin – weak acid – in solution). Initial solution: mixture of 0.03 equiv L⁻¹ sodium hydroxide and 0.033 equiv L⁻¹ (≈ 5 g L⁻¹) of vanillin, pH = 8.3 (at 293 K); (dots) – experimental points, (lines) – predicted curves by simulation

Simultaneously, the set of batch experiments were performed in order to obtain the concentration behaviour of the vanillate, vanillin and pH according the time till equilibrium between liquid and resin phase is established. The experimental points along with the simulated behaviours are shown on the Figure 7.4, where amounts of resin phase added were 0.3g, 0.8g, 1.0g, 1.5g and 2.0g, respectively. In Table 7.2, the amount of wet resin, experimental initial and equilibrium concentrations of vanillin and vanillate, measured pH and calculated pH according the (Eq. 7.4) are shown.

Table 7.2 Initial and equilibrium experimental concentrations of vanillin (C_{VH}), vanillate (C_{VNa}), total (C_V^T) and measured pH and calculated pH^T (according to the Eq.7.4 – Batch system)

W (g wet resin)	C_{0i} (equiv L ⁻¹)					C_i^* (equiv L ⁻¹)				
	C_{VNa}	C_{VH}	C_V^T	pH ^T	pH	C_{VNa}	C_{VH}	C_V^T	pH ^T	pH
0.3	0.035	0.003	0.038	8.5	8.4	0.025	0.013	0.038	7.7	7.7
0.8	0.036	0.0024	0.038	8.5	8.3	0.003	0.035	0.038	6.3	6.3
1.0	0.036	0.0023	0.038	8.5	8.3	0.001	0.037	0.038	5.8	5.8
1.5	0.036	0.0014	0.037	8.7	8.3	0.0006	0.036	0.037	5.6	5.5
2.0	0.036	0.0014	0.037	8.7	8.3	0.0006	0.036	0.037	5.6	5.3

With the increasing mass of adsorbent added to the vanillate/vanillin solution, the equilibrium concentration of vanillate decreases and as a consequence, the concentration of vanillin increases. The agreement between calculated and measured pH values is good; although for cases of 1.5g and 2.0g of wet resin in solution, one can notice small differences between these values of pH. The discrepancy is more noticeable when very low concentration of vanillate is in the solution and can not be measured with high accuracy.

It is worth noting that the model considers the particle resin as a homogeneous solid. The diffusional resistance in such model is taken into account by a homogeneous effective diffusivity (D_i^{ef}) related with the effective diffusivity in a porous particle (D_{pi}) by $D_i^{ef} = D_{pi} [\Delta q_i^* / \Delta c_i]^{-1}$ where $\Delta q_i^* / \Delta c_i$ is the slope of the chord of the equilibrium isotherm. Correlations to evaluate diffusivity of ions in resin-phase are very limited and some values proposed in the literature are somewhat differing. The pore diffusivity D_{pi} is $[\varepsilon_p D_i^o / \tau]$, with D_i^o the diffusivity for the counter-ions in water, τ and ε_p is the tortuosity and porosity of the resin particle, respectively. As Amberlite IR120H resin is a gel type resin its particle porosity can be assumed lower than 0.1. The self diffusivity coefficient for the counterions in the liquid-phase were calculated according the *Nernst-Einstein* equation given as (Anderko and Lencka, 1998),

$$D^o = \frac{RT}{|z|F} \lambda^0 \quad 7.25$$

where λ^0 is limiting diffusivity. The temperature dependence of λ^0 can be reproduced for the range up to 550 K using Smolyakov's (1969) (Smolyakov, 1969) equation.

$$\ln \lambda^0(T) \eta(T) = A + B/T \quad 7.26$$

where η is the viscosity of pure water and A, B are adjustable constants for ions tabulated by Anderko and Lencka (Anderko and Lencka, 1997). The calculated values for

$$D_{H^+}^o = 8.380 \cdot 10^{-9} \text{ m}^2 \text{ s}^{-1} \text{ and } D_{Na^+}^o = 1.147 \cdot 10^{-9} \text{ m}^2 \text{ s}^{-1}.$$

For all cases, we assume the values of $D_{Na^+}^{ef} = 2.436 \cdot 10^{-12} \text{ m}^2/\text{s}$ and $\alpha^{-1} = 7.3$ (this last assumed as the hydrogen and sodium diffusivity ratio in free solution). The sodium homogeneous effective diffusivity was determined from a fit of the experimental data. For the cases studied, the slope of the chord of equilibrium isotherm has an order of magnitude between $O[10^2]$ and $O[10^3]$ which gives acceptable values of diffusivity for the purpose of this work. For simplicity, we assume only an average from homogeneous effective diffusivities obtained by fitting procedure. However, as expected, one can verify from *Figure 7.4* that when there is a lower equilibrium concentration of sodium in solution, the chord of equilibrium isotherm increases and a lower value of homogenous effective diffusivity must be expected.

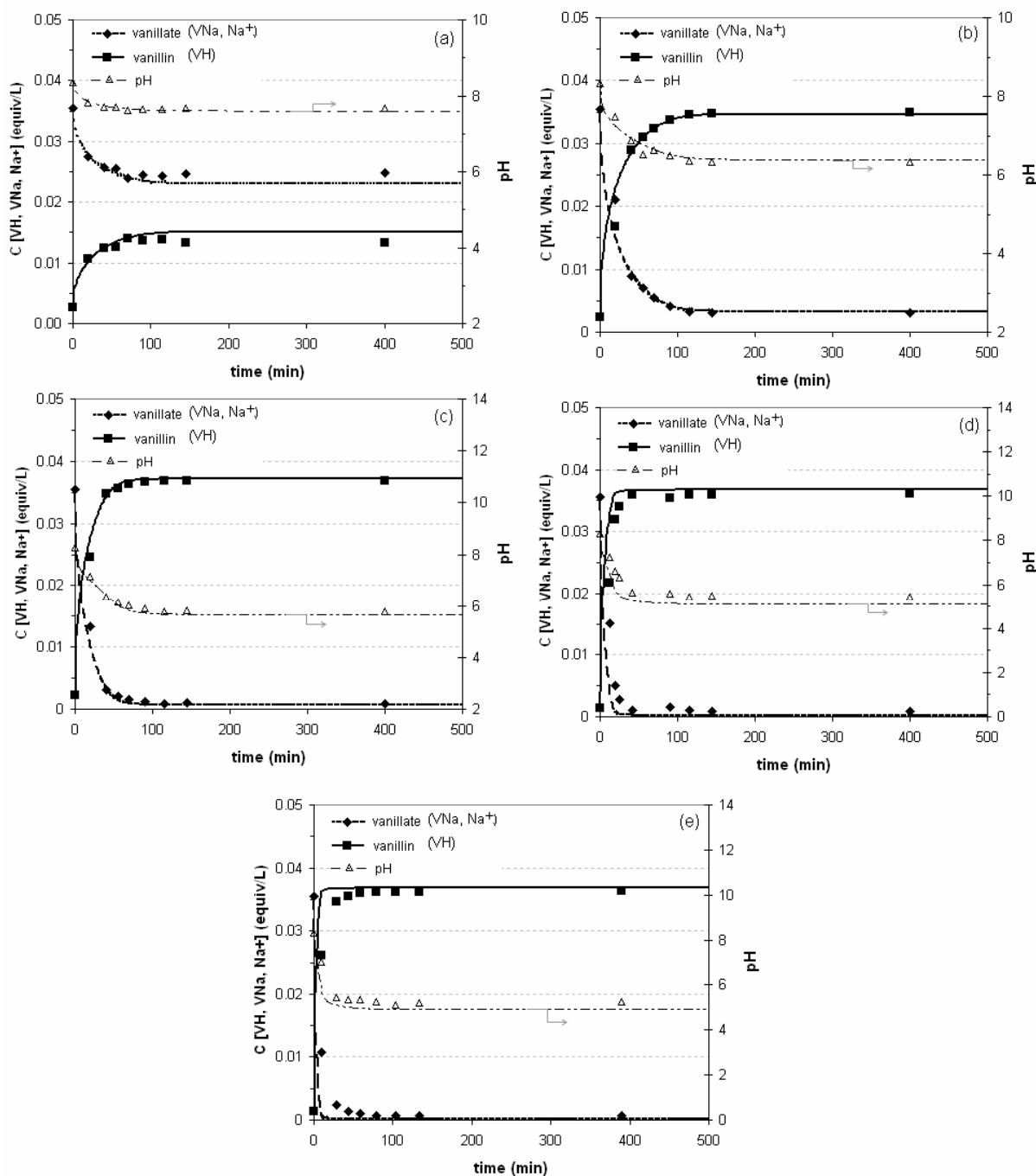


Figure 7.4 Kinetics of Na^+/H^+ ion-exchange for the system vanillin/NaOH (ion-exchanger: Amberlite IR120 in H^+ form). Mass of the wet resin added to the solution: (a) 0.3 g, (b) 0.8g, (c) 1.0g, (d) 1.5g and (e) 2.0g; (dots) – experimental points, (lines) – predicted curves by simulation

The present kinetic model of ion-exchange accompanied by reactions shown in Eqs.7.7a-b is under condition of intraparticle diffusion rate control. In this case, the observable rate when there is a contact between a resin in H^+ form and an alkaline solution in a batch (ion-exchange accompanied by neutralization reaction) is the same as for ordinary ion exchange in infinite batch (Helfferich, 1965; Blickenstaff *et al.*, 1967b; Blickenstaff *et al.*, 1967a). In both

situations, the concentration of H^+ ion is zero at the interface resin/bulk solution. Helfferich (Helfferich, 1962) has derived the fractional attainment of equilibrium – $G(t)$ function – for the ordinary ion-exchange in infinite batch. Based on the fact that ion-exchange process within the exchanger particle is the same for ordinary ion-exchange as well for ion-exchange accompanied by neutralization reaction, rate laws for this last process can be calculated depending on the relative ionic capacity of the solution and the resin phases:

1- The amount of counter-ion in the solution is sufficiently large that $q_T V_r < C_o V_s$ (where C_o is initial concentration of the counter-ion in the solution); if this condition is retained, the fractional attainment of equilibrium during neutralization is equally given by $G(t)$ (Helfferich, 1965).

2- The amount of resin is sufficiently large that $q_T V_r > C_o V_s$ that means the amount of counter-ion in the solution is not enough to convert all of the resin from its original form to counter-ion form. The critical time (t_c) is defined to represent a time required for exhaustion of the solution. While the critical time is not reached ($0 \leq t \leq t_c$), the rate law described remains valid and the fractional attainment of equilibrium is defined as $(q_T V_r / C_o V_s) G(t)$. For $t \geq t_c$, then the fractional attainment of equilibrium during neutralization is unity meaning there is no more ion-exchange.

According to our experimental results two cases can be verified considering the ion-exchange process. First, when the amount of exchangeable ion Na^+ in the solution is higher than the amount of H^+ ion in the resin ($q_T V_r < C_o V_s$); this situation can be observed when 0.3g and 0.8g (*Figure 7.4a* and *Figure 7.4b*, respectively) of resin is added to the solution.

Another case is when ($q_T V_r > C_o V_s$), that means the amount of the Na^+ ions in the solution is smaller than the exchangeable ion in the resin. Then the ion-exchanger cannot be completely converted to Na^+ form. Conversion is progressing with a finite rate until all Na^+ are used. If there is only $NaOH$ solution and exchanger in H^+ form involved in the process the equilibrium is represented by a rectangular isotherm and after reaching equilibrium there is no Na^+ ion remain in the solution. Applying this theory to studied system should result in Na^+ ions total consumption, vanillin and water formation and pH of the solution equal

pH=4.5 ($pK_d=7.4$). The dissociation constant of vanillin at the temperature 293 K is $K_d=3.98 \cdot 10^{-8} \text{ L equiv}^{-1}$ (Englis and Wollermann, 1957). As it can be observed from Figs. 4c-e, where 1.0 g, 1.5 g and 2.0 g of resin is added, the pH of the solution is always higher than pH mentioned before (pH=4.5) and still some small amount of Na^+ ion remains. This fact can be explained by the presence of weak acid (vanillin) in the solution which has an influence on equilibrium. *Figure 7.3* demonstrating equilibrium of Na^+ ions onto Amberlite IR120H for the system under consideration confirm that the isotherm is not exactly rectangular and a reversible reaction as shown in Eq.7.7b is taking place in this case. The concentration of the Na^+ ions at the surface is assumed to be at equilibrium with the interstitial liquid. Then the equilibrium shown on the *Figure 7.3* must be included in the model of the process. The mathematical model used, which involved intraparticle diffusion describes quite well the batch Na^+ / H^+ ion-exchange process accompanied by neutralization onto Amberlite IR120H at the temperature 293 K.

Figure 7.5a-b shows theoretical concentration profiles of sodium in the resin and hydrogen ions in the resin homogeneous particle at different times (for the case of 0.8 g wet resin in solution). When the ionic exchange process is running, exchanger resin is being saturated by the sodium ions and hydrogen ions diffuse to the surface and react conform to the Eq.7.7. The Na^+ concentration at the resin surface obeys an equilibrium relation – Eq.7.16 – and ion exchange is not complete such that H^+ ions still remain into the resin at the stationary state (equilibrium condition). Of course, the average resin concentration of the ion Na^+ increases until the value of resin concentration at surface, which is in equilibrium with the bulk phase. Under conditions of ion exchange accompanied by neutralization with strong bases, the concentration of the ion H^+ at surface is assumed to be zero (Helfferich, 1965; Blickenstaff *et al.*, 1967b; Blickenstaff *et al.*, 1967a; Haub and Foutch, 1986a) and consequently q_{Na^+} equal to total capacity of the resin; however, with our experimental observations, in presence of weak acid as vanillin this situation is not observed.

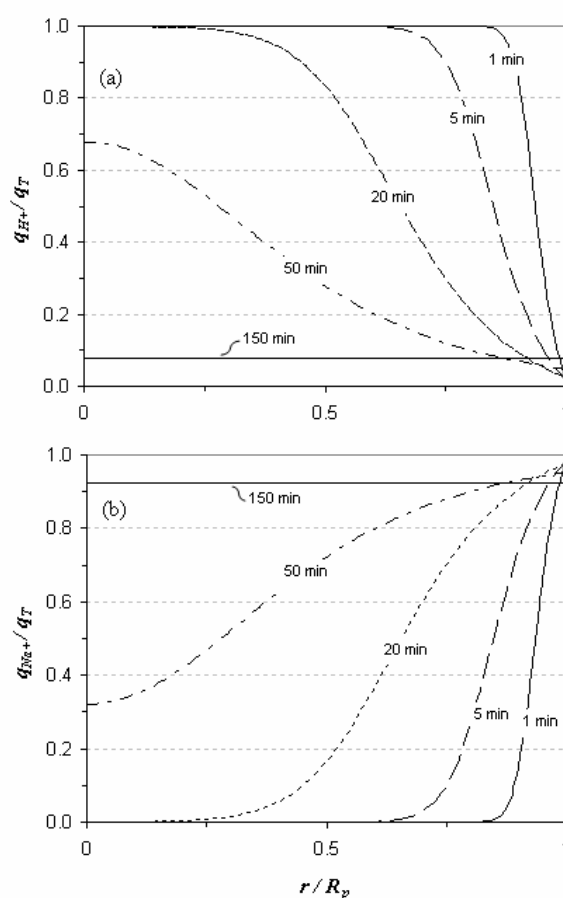


Figure 7.5 Dimensionless resin concentration profiles of hydrogen (a) and sodium (b) ions in the resin homogeneous particle at different times. Case of 0.8 g wet resin in solution.

7.4.2 Fixed-bed performance

The fixed bed ion-exchange process of Na^+ ions onto polymeric resin Amberlite IR120H ions was studied in a laboratory scale to investigate the influence pH on the ion-exchange process. The ion-exchange fixed-bed experiments were performed at the temperature 293 K and flow-rate 19 mL min^{-1} . The feed concentrations of each species in the liquid phase are reported in the Table 7.3. The different experiments were carried out at different pH 8.2, 11.4, 11.9 and 12.1. The column was initially filled with ion-exchange resin Amberlite IR120 in H^+ form and deionized water at the pH=6.1 (bed porosity is 0.4).

In Figure 7.6 and Figure 7.7, one can notice ion-exchange profiles of the Na^+ ions, vanillate (VNa), vanillin (VH) and pH at different feed solutions (mixtures of NaOH and vanillin) in the fixed bed system. Figure 7.6 shows the breakthrough curve of the vanillate in the fixed bed when a solution of vanillate and vanillin at the pH 8.2 is fed.

Table 7.3 Feed experimental concentration of vanillin (C_{VH}), vanillate (C_{VNa}), total (C_V^T) and measured pH and calculated pH^T (according to the Eq.7.4 – Fixed-bed system).

C_{OH^-} (equiv L ⁻¹)	C_{feed} (equiv L ⁻¹)				
	C_{VNa}	C_{VH}	C_V^T	pH^T	pH
0.03	0.03	0.005	0.035	8.1	8.2
0.04	0.033	0	0.033	11.9	11.4
0.05	0.033	0	0.033	12.2	11.9
0.06	0.033	0	0.033	12.4	12.1

Following the chemical reaction of the Eq.7.6 and considering the electroneutrality in bulk liquid phase, all amount of Na^+ ions is under vanillate (VNa) form. Thus, the simulated curve for Na^+ ion is equal to the experimental and simulated curve for sodium vanillate. Moreover, when the ion exchange operation starts there is no vanillin coming out from the column until its breakthrough. Therefore, vanillin history starts at zero (because the initial condition of the bed) and vanillin increases to the plateau at the space time (see also *Figure 7.7a-c*). In the model, the electroneutrality principle in the bulk phase is used to calculate the amount of vanillate and Eq.7.20 – describing the total amount of vanillin and vanillate experimentally determined C_V^T – is applied to calculate the amount of vanillin. Since we assume that the co-ion species are not interacting with the resin and the value of C_V^T must be constant, the concentration of vanillin is equal to the value of C_V^T while the Na^+ ion does not breakthrough.

Figure 7.7a-c show concentration profiles for ion sodium, vanillate, vanillin and pH versus time for cases of pH 11.4, 11.9 and 12.1. When pH of the feed solution increases, the vanillin appears in the outlet of the column earlier (even if there is the same amount of vanillate in the feed solution). The high pH value and high concentration of Na^+ ions is result of sodium hydroxide added to the vanillin solution. Of course, the resin will be converted to sodium form earlier when there are larger concentrations of Na^+ ions in the liquid phase. The pH behaviour is always decreasing from the value 6.1 (initial condition of the column) to the value around 4.5 corresponding to pH of the pure vanillin and then increases along with the saturation of the resin. The pH (and, therefore, the behavior of H^+ ions) changes according to

the buffer vanillate/vanillin formed during the ion-exchange process. A slight change in the composition of the salt and the weak acid provides a significant change in the pH value.

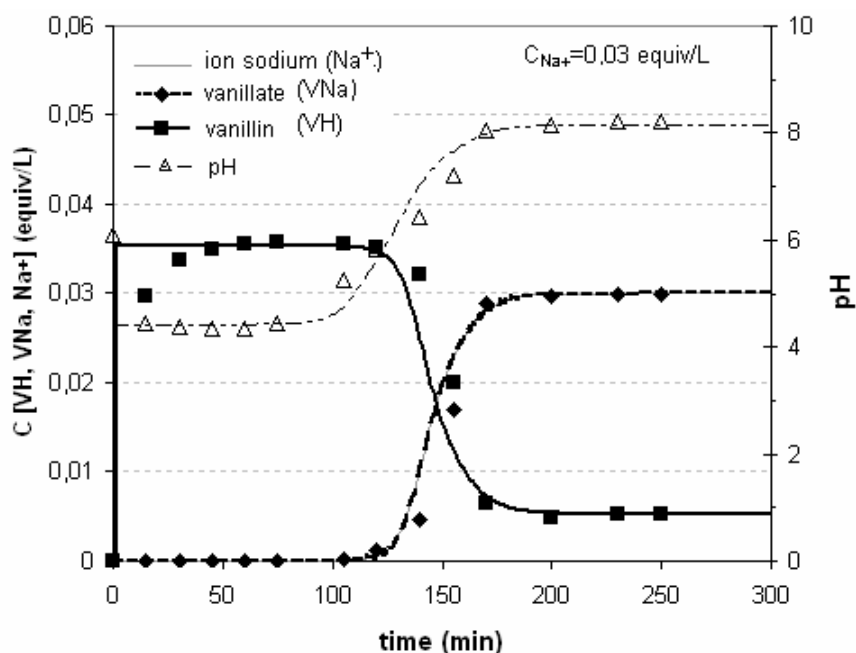


Figure 7.6 Ion-exchange profiles of the studied system Na^+ ions, vanillate (VNa), vanillin (VH) and pH. Feed solution: mixture of $0.03 \text{ equiv L}^{-1}$ NaOH and vanillin ($\text{pH}=8.2$). (dots) – experimental profile and (lines) – predicted concentration.. Conditions in column ($150 \times 20 \text{ mm}$, I.D.): $Q = 19 \text{ cm}^3 \text{ min}^{-1}$; $\text{pH}_{\text{initial}} = 6.1$; 293 K

The theoretical amount of vanillin (VH) as a weak acid and vanillate (VNa) as a salt of weak acid and strong base in the solution as a function of pH value is illustrated in Figure 7.8.

It can be observed from the figure that the $\text{pH}=4.5$ corresponds to pure vanillin in solution, $\text{pH}=7.4$, which is pKd of vanillin at the equivalence point. At $\text{pH}=10$ only vanillate is present in the solution. After pH of the solution reaches pH at the equivalence point of the system vanillin/vanillate, the pH values start to be regulated by the amount of hydroxyls anions (OH^-) in the solution.

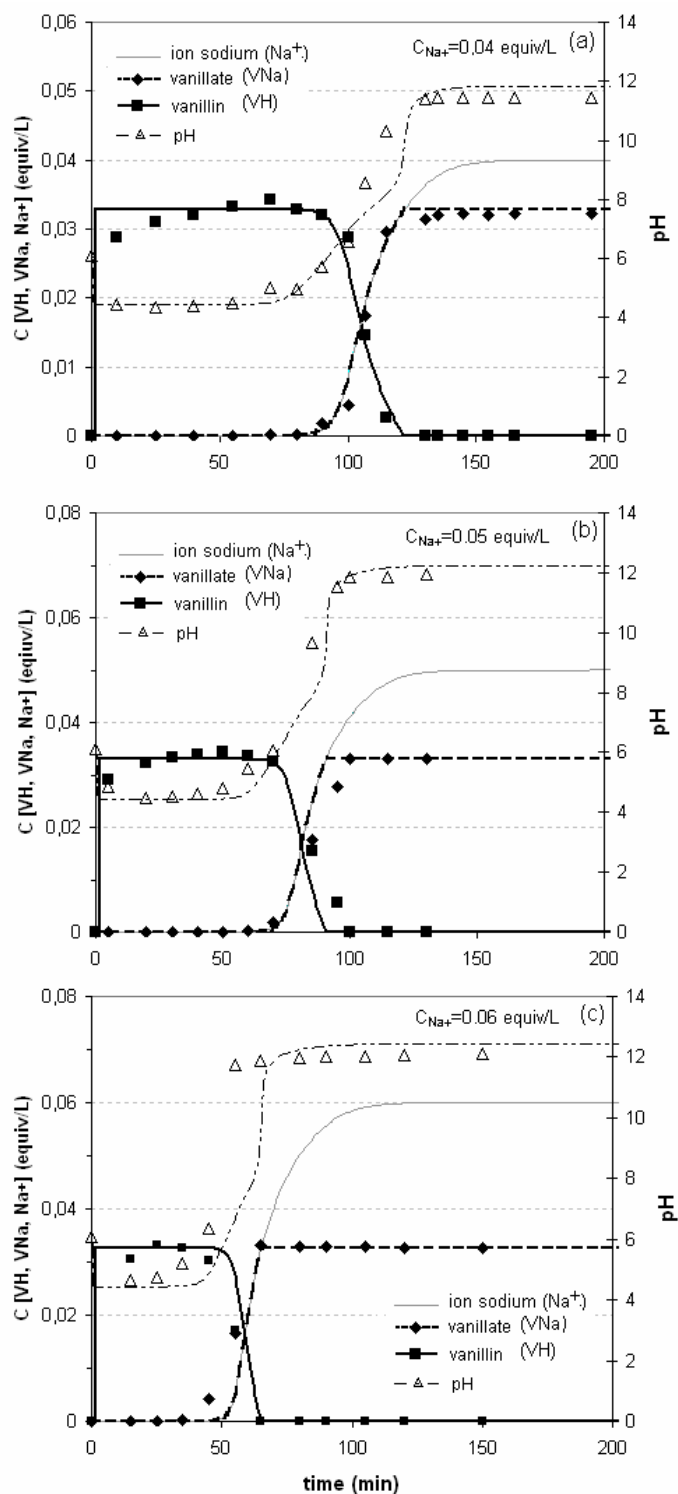


Figure 7.7 Ion-exchange profiles of the studied system Na^+ ions, vanillate (VNa), vanillin (VH) and pH. Feed solution: mixture of (a) $0.04 \text{ equiv L}^{-1}$ NaOH and vanillin ($\text{pH}=11.4$); (b) $0.05 \text{ equiv L}^{-1}$ NaOH and vanillin ($\text{pH}=11.9$); (c) $0.06 \text{ equiv L}^{-1}$ NaOH and vanillin ($\text{pH}=12.1$). (dots) – experimental profile; (lines) – predicted profile. Conditions in column ($150 \times 20 \text{ mm}$, I.D.): $Q = 19 \text{ cm}^3 \text{ min}^{-1}$; $\text{pH}_{\text{initial}} = 6.1$; 293 K

The ion-exchange equilibrium is very fast and one can expect stepped behaviour of the concentration profiles. All the experiments were performed by using glass column (150×20

mm, I.D.) and liquid was delivered by peristaltic pump. We presume that the dispersion occurs in the column and the tubes used in the experimental set-up. The axial dispersion coefficient was obtained by fitting experimental data and the value is $D_{ax} = 6.0 \cdot 10^{-4} \text{ m}^2 \text{ s}^{-1}$. Generally, in all cases our model predicts experimental data satisfactorily.

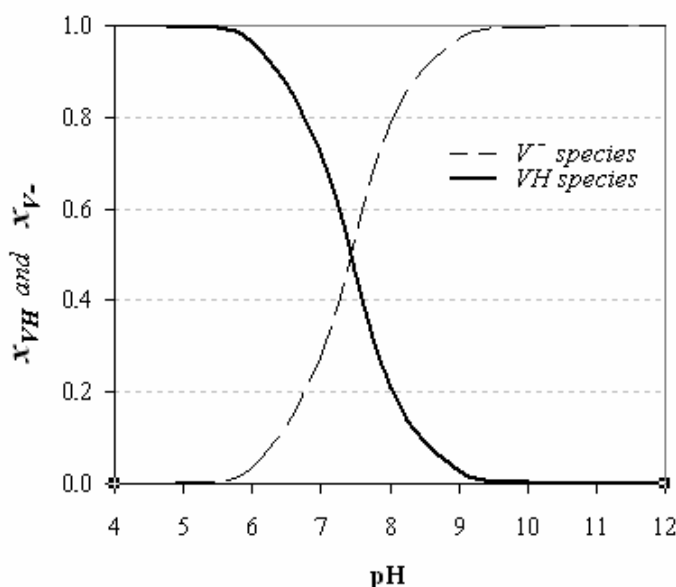


Figure 7.8 Influence of the pH values on fraction of both vanillin forms in liquid phase.

As it has been pointed out earlier, the lignin heated under reflux conditions for long time in the presence of active alkali produces vanillin under vanillate form. The Kraft process is a method for cooking wood, where a mixture of sodium hydroxide and sodium sulfite is used – see Figure 7.1. It is worth mentioning that besides producing vanillin, the lignin oxidation process can also lead to the formation of other reaction products such as oxidized lignin, acetovanillone, dehydrodivanillin, guaiacol, p-hydroxybenzaldehyde and aromatic acids. These compounds are represented as ‘others’ in Figure 7.1. It is expected that low molecular weight phenolates in the permeate stream after filtration step will be in salt form as well as vanillin (in the presence of high alkali medium). This fact will lead to a decrease on the productivity of the ion-exchange column by its faster saturation and in order to obtain high-purity vanillin, some another purification step should be necessary. The separation of vanillin from such a mixture is an important step in its production. We have found the process described in this work as a possible undemanding technique for the recovery of vanillin from Kraft process: the vanillate solution is delivered to the column packed with the ion-exchange resin in H^+ form and at the outlet the vanillin is collected for a certain time.

7.5 Conclusions

The recovery of vanillin by ion exchange involving neutralization reactions in presence of a weak acid and a strong base on ion-exchange polymeric resin Amberlite IR120H at 293 K was studied. The set of batch ion exchange experiments with different mass of ion-exchanger was carried out in order to obtain the kinetics and equilibrium of the system vanillin/vanillate on the cationic resin in H^+ form. Furthermore, the impact of pH on the ion-exchange process has been also investigated.

The mathematical model including intra-particle diffusion for system Na^+/H^+ for analyzing batch and fixed bed systems in vanillin recovery was developed and satisfactorily predicts uptake curves evaluated by batch experiments and breakthrough and elution curves evaluated by fixed bed experiments.

In batch operation, the presence of a buffer system comprising of vanillin/vanillate in the ion exchange process affects the expected rectangular behaviour of isotherm in ion exchange coupled with neutralization reaction. Thus, the Langmuir model has been used to predict experimental concentration profiles. In the fixed-bed operation, the breakthrough time of vanillate depends on the pH of the solution; it is lower when the pH of the feed is higher. The value of pH during the ion-exchange process changes according the composition of vanillin/vanillate solution passing through the column packed with ion-exchange resin in H^+ form. When the pH of the solution reaches pH at the equivalence point for the buffer vanillin/salt of vanillin, its value is regulated by the amount of hydroxyl anions (OH^-) in solution.

The final statement is that the ion exchange processed through the column filled with ion exchanger in H^+ form can therefore be useful for recovery of vanillin from the alkaline solution provided from the process of Kraft lignin oxidation.

7.6 Nomenclature

C concentration in the bulk fluid phase (equiv L^{-1})

C^* bulk liquid phase equilibrium concentration (equiv L^{-1})

C_0	initial concentration in the bulk phase (equiv L ⁻¹)
C_{feed}	feed concentration (equiv L ⁻¹)
C_V^T	total molar measured concentration of vanillate and vanillin (equiv L ⁻¹)
D	diameter of the column (m)
D_{ax}	axial dispersion coefficient (m ² s ⁻¹)
D_i^0	self diffusion coefficient of i^{th} species (m ² s ⁻¹)
d_p	diameter of the resin particle (m)
D_i^{ef}	effective homogeneous diffusivity (m ² s ⁻¹)
D_{Pi}	effective porous diffusivity (m ² s ⁻¹)
f_H	dry particle to wet particle mass ratio (g dry resin /g wet resin)
$G(t)$	tabulated conversion function [25] (-)
K_{Na-H}	equilibrium constant of the binary ion-exchange isotherm (-)
K_d	dissociation constant of vanillin (L equiv ⁻¹)
K_w	dissociation constant of water (L equiv ⁻¹)
K_L	langmuir model parameter in ion-exchange equilibrium (L equiv ⁻¹)
L	length of the bed (m)
$\overline{N}_i$	flux of the i^{th} ion (mol m ⁻² s)
Q	flow rate (m ³ s ⁻¹)
q_i	average resin phase concentration in the particle (equiv g ⁻¹ dry resin)
q_i^*	equilibrium resin phase concentration (equiv g ⁻¹ of dry resin)
q_T	total exchange capacity of the resin (equiv g ⁻¹ dry resin)

r	radius variable (m)
R_p	radius of the resin particle (m)
T	temperature (K)
t	time variable (s)
u	interstitial velocity (m s^{-1})
V_s	volume of solution (L)
V_r	volume of the resin phase (L)
W	wet weight of the resin (g)
z	axial variable (m)
z_i	valence of i th ion
x_i	ionic fraction in the liquid phase (-)
y_i	ionic fraction in the resin phase (-)

Greek letters

α	hydrogen and sodium effective homogeneous diffusivity ratio (-)
ε	bed porosity (-)
ε_p	porosity of the resin particle (-)
ρ_s	density of the wet resin ($\text{kg wet resin m}^{-3}$)
τ	bed tortuosity (-)
λ^0	limiting diffusivity ($\text{m}^2 \text{s}^{-1}$)
ϕ	electric potential (ergs coulomb^{-1})

Superscripts and subscripts

i	Species
H^+	hydrogen ion
Na^+	sodium ion

OH⁻ hydroxyl ion

V⁻ vanillate ion

VNa sodium vanillate

VH Vanillin

7.7 References

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8. Conclusion and future work

Adsorption of phenol, salicylic acid and 4-nitrophenol onto polymeric resins (Sephabeads SP206 and Sephabeads SP207, Amberlite XAD16, Duolite S861) and activated carbon (Filtrisorb F400) was investigated. Batch experiments were carried out to provide a screening of adsorbents focused on the effect of temperature on the adsorptive behavior. Langmuir isotherm model described adequately the adsorption equilibrium of phenol, salicylic acid and 4-nitrophenol on the adsorbents used.

The effect of temperature, concentration, bed length and flow rate on the fixed bed adsorption of phenolic compounds onto each polymeric adsorbents and activated carbon was studied. The effect of temperature on the fixed bed adsorption of phenol, salicylic acid and 4-nitrophenol was more important for the polymeric resins, especially for Sephabeads SP206, than for the activated carbon Filtrisorb F400. The prediction of breakthrough curves based on a linear driving force (LDF) rate model to describe the diffusional mass transfer were in good agreement with the experimental results for the adsorption of phenolic compounds studied.

Although the activated carbon (Filtrisorb F400) exhibited the highest adsorption capacity for salicylic acid ($Q = 351, 0 \text{ mg g}^{-1}$ of dry resin) and for phenol ($Q = 169, 1 \text{ mg g}^{-1}$ of dry resin) compared to polymeric adsorbents, the separation potential b as an indicator of the efficiency of thermal parametric pumping was found to be much higher for the polymeric adsorbent Sephabeads SP206 for phenol, salicylic acid and 4-nitrophenol in the range of temperature considered 293-333 K.

Thermal parametric pumping in recuperative mode was carried out using Sephabeads SP206 for purification of wastewater containing salicylic acid, phenol and 4-nitrophenol in a pilot plant. By applying a temperature for cold cycle $T_c = 293$ K and for hot cycle $T_h = 333$ K a high level of purification was obtained. Operational conditions define the degree of purification which can be obtained by thermal parametric pumping process. The concentration of all phenolic compounds in the bottom reservoir decreased significantly. The degree of separation of phenol and 4-nitrophenol was very similar, although slightly higher for phenol, which has slightly higher molecular diffusion. Under appropriate conditions, at the 10th cycle it was possible to obtain $C_{bottom}/C_F = 0.0003$ for phenol and to $C_{bottom}/C_F = 0.0013$ for 4-nitrophenol. The degree of salicylic acid purification was almost 100 times less than feed concentration. It was concluded that a high degree of purification of phenolic wastewaters may be achieved by thermal parametric pumping process using Sephabeads SP206 as adsorbent and therefore avoiding the use of any chemical regenerant.

Adsorption of vanillin onto non-ionic polymeric resins Sephabeads SP206 at different temperatures and concentration of sodium hydroxide were studied as well. The adsorption equilibrium isotherms obtained from batch experiments at the temperatures 293, 310 and 333 K were described by Langmuir isotherm model. The saturation capacity of Sephabeads SP206, $Q = 7.534 \times 10^{-4}$ mol g⁻¹ of dry resin was found to be independent of the temperature.

The impact of sodium hydroxide on the adsorption of vanillin was also investigated. It was found that at concentration of sodium hydroxide higher than 1M the adsorbed amount of the vanillin onto the polymeric adsorbent SP206 was reduced significantly. A modified Langmuir model was applied to describe the adsorption equilibrium of vanillin in presence of sodium hydroxide.

Fixed-bed adsorption of vanillin onto polymeric resin SP206 has been studied. The influence of concentration of sodium hydroxide, temperature, flowrates and feed concentration on adsorption of vanillin in fixed-bed operation has been investigated. A mathematical model including linear driving force for intraparticle mass transfer and reaction in liquid phase for the system vanillin/sodium hydroxide reasonably predicts all dynamic adsorption experiments in column.

The membrane ultrafiltration process particularly focused on the recovery of vanillin from Kraft lignin oxidation products was studied by using ceramic tubular membranes with

molecular weight cut-off of 1, 5, 15 and 50 kDa. The feed concentration of lignin and vanillin in the mixture was chosen to simulate the conditions of the mixture leaving the Kraft lignin oxidation reactor. It was found that the ultrafiltration technique can be employed in the vanillin recovery since most of the lignin is rejected during the process. The rejection of lignin is always increasing with the cut-off of the membrane.

The best results were observed by using a membrane of 1 kDa cut-off where the lignin rejection is 97% for lignin feed concentration of 60 g L^{-1} . Even higher rejection was observed (almost 99%) when the feed concentration is 2 g L^{-1} of lignin was used. Also, the formation of gel layer at the membrane surface has a significant influence on the process leading to the permeate flux decline especially at high feed concentration of lignin. Therefore it is suggested to carry out the membrane process in two steps to obtain high purity of vanillin in the permeate stream. The ceramic membranes have unique properties such as wide operating pH range, temperature resistance and can stand up several cleaning cycles. Easy and appropriate cleaning procedure can result in a rapid permeate flux recovery without significant damage of the membrane.

Apart from the use of non-ionic polymeric resin SP206, a strong cation ion-exchange resin Amberlite IR 120H was applied to the vanillin recovery from reaction media in the Kraft lignin oxidation process. The recovery of vanillin is a result of ion-exchange involving neutralization reactions in presence of a weak acid and a strong base. The kinetics and equilibrium of the system vanillin/vanillate/ cationic resin was obtained from batch ion-exchange experiments. It was found that the pH during the ion-exchange process changes according to the composition of vanillin/vanillate solution passing through the column. The breakthrough time of vanillate strongly depends on the pH of feed solution; it is shorter when the pH of the feed is higher. A mathematical model including intra-particle diffusion for system Na^+ / H^+ was developed and satisfactorily predicts the uptake curves from batch experiments and breakthrough and elution curves in fixed bed experiments. The ion-exchange process where vanillin alkaline solution is passed through a column filled with ion exchanger in H^+ form can be useful for the recovery of vanillin from Kraft lignin oxidation mixture.

Interesting results in the field of ultrafiltration and ion-exchange processes applied to the vanillin recovery from Kraft lignin oxidation were found. The integration of those processes

can lead to a suitable flowsheet applied in the vanillin production from Kraft lignin oxidation process. Future work should be focused on the integration of individual steps and construction of a prototype to illustrate the technology from raw-material to the fine product vanillin.

The integrated process will look like the scheme below combining reaction and separation steps (membrane, ion-exchange, evaporation/crystallization).

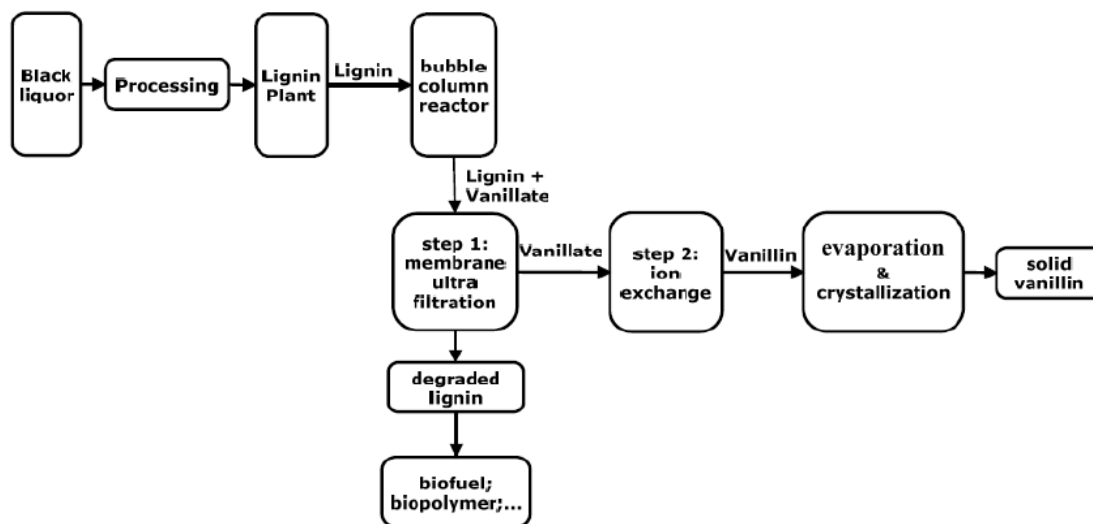


Figure 8.1 Scheme of integrated process to produce vanillin

APPENDICES

A. Safety Data

A.1 Phenol Safety Data (Sigma-Aldrich)



A.1.1 General

Synonyms: benzenol, carbolic acid, hydroxybenzene, monohydroxybenzene, monophenol, oxybenzene, phenic acid, phenylic acid, phenyl alcohol, phenyl hydrate, phenyl hydroxide, phenylic alcohol

Molecular formula: C_6H_5OH

CAS No: 108-95-2

EC No: 203-632-7

A.1.2 Physical data

Appearance: colourless crystals with a characteristic odour

Melting point: 40 - 42 °C

Boiling point: 182 °C

Vapour pressure: 0.35 mm Hg at 20 °C

Specific gravity: 1.07

Flash point: 79 °C

Explosion limits: 1.5 – 8.6 %

Autoignition temperature: 715 °C

Water solubility: soluble

A.1.3 Stability

Stable. Substances to be avoided include strong oxidizing agents, strong bases, strong acids, alkalis and calcium hypochlorite. Flammable. May discolour in light.

A.1.4 Toxicology

This material is a systemic poison and constitutes a serious health hazard. The risks of using it in the laboratory must be fully assessed before work begins. Vesicant. Typical MEL 2 ppm; typical OEL 1 ppm. Acute poisoning by ingestion, inhalation or skin contact may lead to death. Phenol is readily absorbed through the skin. Highly toxic by inhalation. Corrosive - causes burns. Severe irritant.

A.1.5 Toxicity data

Oral human lowest published lethal dose (ORL-HMN LDLO) 140 mg kg⁻¹ Oral rat lethal dose 50 percent kill (ORL-RAT LD50) 317 mg kg⁻¹ Intraperitoneal rat lethal dose 50 percent kill (IPR-RAT LD50) 127 mg kg⁻¹ Oral rabbit lowest published lethal dose (ORL-RBT LDLO) 420 mg kg⁻¹ Administration onto skin rat lethal dose 50 percent kill (SKN-RAT LD50) 669 mg kg⁻¹

A.1.6 Risk phrases

R24 Toxic in contact with skin

R25 Toxic if swallowed R34 Causes burns

R36 Irritating to eyes

R37 Irritating to respiratory system

R38 Irritating to skin

A.1.7 Transport information

UN No 1671. Hazard class 6.1. Packing group II.

A.1.8 Personal protection

Safety glasses, gloves, good ventilation.

A.2 4-Nitrophenol Safety Data (Sigma-Aldrich)



A.2.1 General

Synonyms: p-nitrophenol, 4-hydroxynitrobenzene, p-hydroxynitrobenzene, PNP, NCI-C55992, UN 1663, niphen

Use: plasticizer, insect repellent

Molecular formula: $C_6H_5NO_3$

CAS No: 100-02-7

EC No: 202-811-7

A.2.2 Physical data

Appearance: Yellow to tan crystals or powder

Melting point: 113 - 115 °C (sublimes)

Boiling point: ca. 279 °C (decomposes)

Vapour pressure: 1.0 mm Hg at 100 °C

Density: 1.48 g/ml

Flash point: 192 °C

Autoignition temperature: 282 C

A.2.3 Stability

Stable. Incompatible with strong oxidizing agents, strong bases, organics, combustible material, reducing agents. Combustible.

A.2.4 Toxicology

Possible mutagen. Toxic if swallowed, inhaled or absorbed through skin. Eye, skin and respiratory irritant. Corrosive.

A.2.5 Toxicity data

Subcutaneous rat lowest published lethal dose (SCU-RAT LDLO) 200 mg kg⁻¹ Intravenous dog lowest published lethal dose (IVN-DOG LDLO) 10 mg kg⁻¹ Intraperitoneal mouse lethal dose 50 percent kill (IPR-MUS LD50) 75 mg kg⁻¹ Unreported mammal (species unspecified) lethal dose 50 percent kill (UNR-MAM LD50) 175 mg kg⁻¹

Oral rat lethal dose 50 percent kills (ORL-RAT LD50) 202 mg kg⁻¹ A.2.6 Risk phrases

R23 Toxic by inhalation

R24 Toxic in contact with skin

R25 Toxic if swallowed

R34 Causes burns

A.2.6 Transport information

Hazard class: 6.1. Packing group: III

A.2.7 Personal protection

Safety glasses, gloves, good ventilation

A.3 Salicylic acid Safety Data (Sigma-Aldrich)



A.3.1 General

Synonyms: 2-hydroxybenzoic acid, o-hydroxybenzoic acid, retarder W, SA, SAX, Verrugon

Molecular formula: $C_7H_6O_3$

CAS No: 69-72-7

EC No: 200-712-3

A.3.2 Physical data

Appearance: white powder

Melting point: 161 °C

Boiling point: 211 °C at 20 mm Hg

Vapour density: Not available

Vapour pressure: 1 mm Hg at 114 °C

Specific gravity: Not available

Flash point: 157 °C

Explosion limits: not available

Ignition temperature: 545 °C

A.3.3 Stability

Stable. Substances to be avoided include oxidizing agents, strong bases, iodine, fluorine. Combustible. Sensitive to light.

A.3.4 Toxicology

Harmful by inhalation, ingestion and through skin absorption. Irritant. Chronic effects: laboratory experiments have shown mutagenic effects. May cause harm to the unborn child. May act as a sensitizer.

A.3.5 Toxicity data

Oral rat lethal dose 50 percent kill (ORL-RAT LD50) 891 mg kg⁻¹ Oral mouse lethal dose 50 percent kill (ORL-MUS LD50) 480 mg kg⁻¹ Inhalation mammal (species unspecified) lethal dose 50 percent kill (IHL-MAM LC50) > 300 mg m⁻³

A.3.6 Risk phrases

R22 Harmful if swallowed

R36 Irritating to eyes

R37 Irritating to respiratory system

R38 Irritating to skin

R41 Risk of serious damage to the eyes

R61 May cause harm to the unborn child

A.3.7 Transport information

Not regulated

A.3.8 Personal protection

Safety glasses. Do not breathe dust

A.4 Vanillin Safety Data (Sigma-Aldrich)



A.4.1 General

Synonyms: 4-hydroxy-m-anisaldehyde, 4-hydroxy-3-methoxybenzaldehyde, zimco, vanilline, vanillaldehyde, vanillic aldehyde, lioxin

Molecular formula: $C_8H_8O_3$

CASNo: 121-33-5

A.4.2 Physical data

Appearance: white crystals with vanilla odour

Melting point: 81 - 83 °C

Boiling point: 285 °C; 170 °C at 15 mm Hg

Vapour density: 5.3 (air = 1)

Vapour pressure: 1 mm Hg at 107 °C

Density ($g\ cm^{-3}$): 1.05

Flash point: Not available

Explosion limits: Not available

Water solubility: slight

A.4.3 Stability

Stable. May discolour on exposure to light. Moisture-sensitive. Incompatible with strong oxidizing agents, perchloric acid.

A.4.4 Toxicology

Harmful if swallowed. May be harmful by inhalation or in contact with skin. Eye irritant.

A.4.5 Toxicity data

Oral rat lethal dose 50 percent kill (ORL-RAT LD50) 1580 mg kg⁻¹ Intraperitoneal rat lethal dose 50 percent kill (IPR-RAT LD50) 1160 mg kg⁻¹ Administration onto skin rabbit lethal dose 50 percent kill (SKN-RBT LD50) >5010 mg kg⁻¹

A.4.6 Risk phrases

R22 Harmful if swallowed

R36 Irritating to eyes

A.4.7 Transport information

Non-hazardous for road, air and sea transport

A.4.8 Personal protection

Safety glasses.

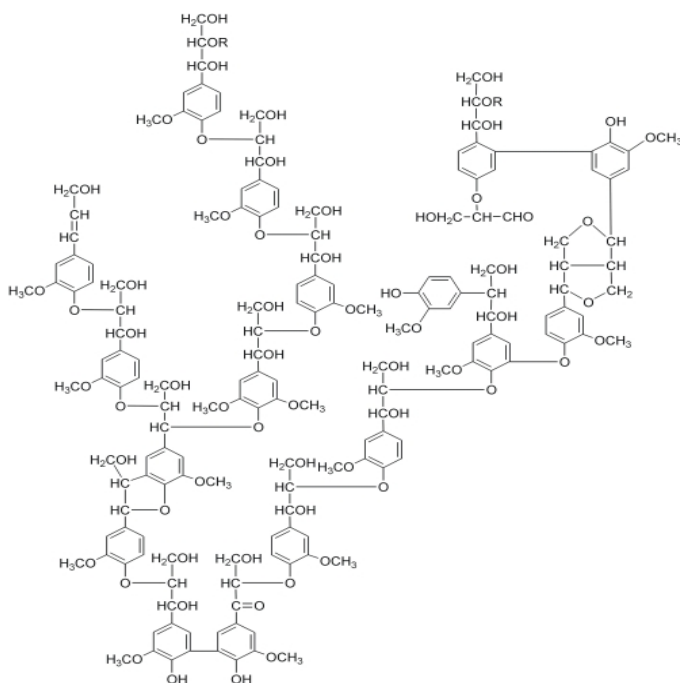
A.5 Lignin Safety Data (Sigma-Aldrich)

A.5.1 General

Synonyms: not reported

Use: extender for plastics, emulsion stabilizer

Molecular formula: macromolecule



CAS No: 9005-53-2

A.5.2 Stability

Stable. Incompatible with strong oxidizing agents.

A.5.3 Toxicology

No toxicological data available

A.5.4 Toxicity data

Not reported

A.5.5 Risk phrases

Not reported

A.5.6 Transport information

Not reported

A.5.7 Personal protection

No safety data available - treat as potentially harmful.

A.6 Sodium Hydroxide Safety Data (Sigma-Aldrich)



A.6.1 General

Synonyms: caustic soda, soda lye, lye, white caustic, aetznatron, ascarite, Collo-Grillrein, Collo-Tapetta, sodium hydrate, fotofoil etchant, NAOH, STCC 4935235, sodium hydroxide pellets, Lewis red devil lye

Molecular formula: NaOH

*CASNo:*1310-73-2

*ECNo:*215-185-5

Annex I Index No: 011-002-00-6

A.6.2 Physical data

Appearance: odourless white solid (often sold as pellets)

Melting point: 318 °C

Boiling point: 1390 °C

Vapour density: not reported

Vapour pressure: 1 mm Hg at 739 °C

Specific gravity: 2.12

Flash point: n/a

Explosion limits: n/a

Water solubility: High (Note: dissolution in water is highly exothermic)

A.6.3 Stability

Stable. Incompatible with a wide variety of materials including many metals, ammonium compounds, cyanides, acids, nitro compounds, phenols, combustible organics. Hygroscopic. Heat of solution is very high and may lead to a dangerously hot solution if small amounts of water are used. Absorbs carbon dioxide from the air.

A.6.4 Toxicology

Very corrosive. Causes severe burns. May cause serious permanent eye damage. Very harmful by ingestion. Harmful by skin contact or by inhalation of dust.

Typical TLV 2 mg m⁻¹.

A.6.5 Toxicity data

Intraperitoneal mouse lethal dose 50 percent kills (IPR-MUS LD50) 40 mg kg⁻¹
Administration into eye (irritant) monkey (EYE-MKY) 1%/24h sev administration onto skin

rabbit (SKN-RBT) 500 mg/24h sev Administration into eye (irritant) rabbit (EYE-RBT) 1% sev

A.6.6 Risk phrases

R35: Causes severe burns

A.6.7 Transport information

Hazard class 8.0. Packing group II. UN No 1823. EMS No 8.0-06

A.6.8 Personal protection

Safety glasses, adequate ventilation, Neoprene or PVC gloves

B. Adsorption of phenol and salicylic acid onto polymeric resins Amberlite XAD16 and Duolite S861^{*}

B.1 Introduction

Phenol-containing wastewater presents a serious environmental problem since biological degradation of phenol occurs too slowly or does not occur at all (Kunin, 1976). Adsorptive processes are widely used in the purification of such polluted streams and diluted wastewaters (Humphrey, 1995; Keller, 1995; Knaebel, 1995). For some target solutes, it is also interesting the fact that sorption operations are able to concentrate solutes, especially when these solutes are valuable compounds.

Phenols are probably the most extensively studied compounds in the field of wastewater treatment as they are persistent pollutants with high toxicity that are released in the wastewaters of a considerable number of industries (Morão *et al.*, 2004). Different techniques are used for the removal of phenolic compounds from wastewater (Lin *et al.*, 2002; Kujawski *et al.*, 2004). Adsorption of phenolic compounds onto different polymeric adsorbents has been studied by various groups (Crook *et al.*, 1975; Farrier *et al.*, 1979; Gusler *et al.*, 1993;

^{*} Based on the paper:

Comparative study of the adsorption of phenol and salicylic acid from aqueous solution onto nonionic polymeric resins by M. Otero, M. Zabkova, and A. E. Rodrigues, Separation and Purification Technology, 45 (2), 86-95 (2005).

Deosarkar and Pangarkar, 2004). Salicylic acid is a drug compound that nowadays is usually produced from phenol (Hanesian and Perna, 2000). The manufacture of acetylsalicylic acid (ASA) is accompanied by the production of phenolic wastewaters containing salicylic acid. Acetylsalicylic acid-ASA, the salicylate ester of acetic acid, is rapidly hydrolyzed to give salicylic acid, which is its active form.

The manufacturing of ASA is not the only use of salicylic acid; other applications of salicylic acid are cosmetics, wart-removing medicines, to externally treat fungus infections, as an acne topic treatment and to increase the cell turnover as a component of skin creams. This compound is also employed as food preservative and in plants protection against insects and pathogens and it is present in wastewaters of different industries. Salicylic acid has also been shown to be present in the so-called grey wastewaters, which are those from households, schools, hotels, business complexes as well as some types of industries where no contributions from toilets, bidets or heavily polluted process water are included (Daughton and Ternes, 1999; Eriksson *et al.*, 2003).

The performance of any adsorption-based process greatly depends on the effectiveness of design and operating conditions. Therefore, rigorous approaches to the design and operation of the adsorption system must be used to ensure efficient applications. In order to get this, the mechanism and dynamics of adsorption must be understood, as well as major variables that affect the adsorptive process.

The aim of this work is to describe and compare the adsorption of salicylic acid with that of its precursor, phenol, onto two different polymeric resins, Duolite S861 and Amberlite XAD16, both of them polystyrene resins crosslinked with DVB.

The adsorption capacity of the resins as a function of the sorbate concentration in solution, i.e., the adsorption equilibrium isotherms were measured at different temperatures and results were fitted to the Langmuir isotherm model. The effect on adsorption of the temperature variable was addressed as some purification technologies such as parametric pumping are based on a marked difference on the equilibrium dependence on temperature.

The fixed bed adsorptive performance of Duolite S861 and Amberlite XAD16 was also compared both for the removal of phenol and salicylic acid. Modeling of the fixed bed adsorption was made based on the results obtained for adsorption equilibrium isotherms.

Experiments at different temperatures were done to further determine the effect of temperature on adsorption. Also experiments at different flow rates of the feed solution were carried out.

The present study intends to be useful for evaluating the removal of phenol and salicylic acid from aqueous solutions by means of polymeric resins in view of their application to the decontamination of industrial wastewaters. For the oral treatment of poisoning activated carbon has been considered (Moore and Spector, 1986; Merigian and Blaho, 2002; Osterhoudt *et al.*, 2004).

B.2 Experimental part

B.2.1 Chemicals and adsorbents

Salicylic acid ($C_7H_6O_3$) and phenol (C_6H_5O) were both purchased from Sigma-Aldrich (Spain). Their solutions were prepared with degassed and distilled water.

Two nonionic polymeric resins were used to adsorb these phenolic compounds: Duolite S861, which was purchased from Auctel Products Ltd. India, and Amberlite XAD16, which was obtained from Rohm and Haas (France).

Nonionic polymeric resins have previously been successfully used for phenol and phenolic derivatives adsorption (Ferreira and Rodrigues, 1995b; Ferreira and Rodrigues, 1995a; Díez *et al.*, 1998; Davesac *et al.*, 2000). Table B.1 summarizes the data supplied by the manufacturers on the physical characteristics of the resins used in this work.

Table B.1 Physical properties of polymeric resins Duolite S861 and Amberlite XAD16.

Adsorbent	Duolite S861 ^a	Amberlite XAD16 ^b
Matrix	Aromatic porous resin with hydrophobic substituents	Aromatic porous resin with hydrophobic substituents
Chemistry	Polystyrene DVB	Polystyrene DVB
Physical form	White beads	White translucent
Humidity factor (f_h)	0.28	0.34
Density ($kg\ m^{-3}$)	1020	1020
Particle size (m)	5.6×10^{-4}	4.7×10^{-4}
Porosity	0.72	0.55
a) from Auctel Products Ltd. (India)		
b) from Rhom and Haas (France)		

B.2.2 Batch adsorption

Adsorption equilibrium experiments were carried out by contacting the corresponding amount of adsorbent with 100 mL of salicylic acid or phenol solution in 250 mL Erlenmeyer flasks. Initial concentration on the solution was around 100 mg L⁻¹ in all experiments. Adsorption equilibrium isotherms were measured by batch equilibration placing the volumetric flasks in a shaking mixer at 150 rpm and using a thermostatic bath for temperature control. Equilibrium experiments were carried out at 293, 310 and 333 K for each adsorbent-phenol system. After shaking for 48 h, the solution was separated from the adsorbent and the final concentration of salicylic acid and phenol in solution were determined by measuring the absorbance at 295 and 272 nm respectively by means of a UV-visible spectrophotometer Jasco (model 7800, Japan).

B.2.3 Fixed-bed adsorption

Dynamic column experiments were carried out by packing the adsorbents in lab-scale columns (0.30×0.01 m) and feeding these with the corresponding solution. A peristaltic pump (Watson-Marlow) was used to pump either the salicylic acid or the phenol solution in downward flow. The temperature of the feed was maintained by a thermostatic bath (Edmund Bühler). Salicylic acid and phenol concentration at the column outlet were both spectrophotometrically determined at 295 and 272 nm, respectively, by an UV-visible spectrophotometer Jasco (model 7800, Japan).

Fixed bed adsorption was studied at three different temperatures: 293, 310 and 333 K. Experiments at two different feed flow rates, 5.5 and 10 mL min⁻¹, were carried out. Experimental data obtained by carrying out the previously described adsorption tests were compared with the simulated results from the modeling of the different experimental conditions.

B.3 Mathematical models

B.3.1 Adsorption isotherms

The amount of salicylic acid or phenol adsorbed onto the two different adsorbents, q^* (mg g⁻¹), was calculated by a mass balance relationship (Eq. B.1).

$$q^* = (C_0 - C^*) \frac{V}{W} \quad B.1$$

where C_0 (mg L⁻¹) and C^* (mg L⁻¹) are the initial and equilibrium liquid-phase concentrations, respectively, V the volume of the solution (L) and W the dry weight (g) of the corresponding polymeric resin.

The adsorption equilibrium isotherms for phenol and salicylic acid onto each adsorbent at various temperatures, q^* (mg g⁻¹) versus the adsorbate liquid concentration at equilibrium, C^* (mg L⁻¹) were fitted with the Langmuir model.

The Langmuir equation (Eq. B.2) is based on a theoretical model which assumes that adsorption occurs onto specific sites of a uniform energetic surface, without interactions between adsorbed molecules and adsorption is confined to monolayer coverage.

$$q^* = \frac{QK_L C}{1 + K_L C} \quad B.2$$

where Q is the maximum adsorptive capacity and K_L a parameter which relates to the adsorption energy (Guiochon *et al.*, 1994).

$$K_L = K_L^\infty \exp\left(-\frac{\Delta H_L}{RT}\right) \quad B.3$$

The adsorption enthalpy in the Langmuir constant is generally a net value that includes the solvent desorption and the solute adsorption (Giles *et al.*, 1974).

The empirical parameters were calculated by MATLAB 6.1 following the optimization routine and using the Simplex direct search method.

From the equilibrium results, it may be found the separation to be expected as a function of temperature for each of the systems phenol-adsorbent. The separation parameter b , introduced by Pigford (Pigford *et al.*, 1973), is indicative of the separation potential:

$$b = \frac{a}{1 + \bar{m}} \quad B.4$$

where the average slope $\bar{m} = m(T_1) + m(T_2)/2$ and the deviation $a = m(T_1) - m(T_2)/2$, considering $T_1 < T_2$.

The capacity parameter here appearing is defined as $m(T) = \frac{(1-\varepsilon)\rho_p f_h K(T)}{\varepsilon}$ where $K(T) = QK_L$ corresponding to each temperature.

B.3.2 Fixed bed modeling

The model used to predict the fixed bed adsorption of these phenolic compounds comprises a mass balance, the adsorption equilibrium isotherm at the liquid/solid interface and a linear driving force (LDF) rate equation was used to describe the diffusional mass transfer inside adsorbent particles.

The mass balance in a bed volume element is:

$$D_{ax} \frac{\partial^2 C(z,t)}{\partial z^2} - u_i \frac{\partial C(z,t)}{\partial z} = \frac{\partial C(z,t)}{\partial t} + \frac{1-\varepsilon}{\varepsilon} \rho_p f_h \frac{\partial q(z,t)}{\partial t} \quad B.5$$

where D_{ax} is the axial dispersion coefficient, u_i is the interstitial velocity, ε is the bed porosity, z is the axial position, t is the time, ρ_p is the adsorbent particle density, f_h is the humidity factor of the corresponding adsorbent, q is the average concentration in the adsorbent particle and C is the concentration in the bulk fluid phase.

The boundary conditions are the Danckwerts boundary conditions:

$$z = 0 \quad D_{ax} \frac{\partial C(z,t)}{\partial z} \Big|_{z=0} = u_i (C(0,t) - C_0) \quad B.6$$

$$z = L \quad \frac{\partial C(z,t)}{\partial z} \Big|_{z=L} = 0 \quad B.7$$

Initial conditions are:

$$C(z,0) = 0; \quad q(z,0) = 0 \quad B.8$$

The axial dispersion to be included in the mass balance was obtained from the following expression (Guiochon *et al.*, 1994):

$$\frac{u_0 d_p}{D_{ax}} = (0.2 + 0.011 \text{Re}^{0.48}) \quad B.9$$

where $\text{Re} = u_0 \rho_f d_p / \eta$ and Péclet number is ($Pe = u_0 L / \varepsilon D_{ax}$).

The adsorption equilibrium isotherm is described by the Langmuir equation shown above (Eq. B.2 and B.3).

The adsorption rate can be represented by a Linear Driving Force approximation:

$$\frac{\partial q(z, t)}{\partial t} = k_s [q^*(z, t) - q(z, t)] \quad B.10$$

where k_s is an overall mass transfer coefficient, q^* is the adsorbed phase concentration in equilibrium with the bulk concentration C and q is the average adsorbed phase concentration in the adsorbent particle (described as homogeneous). As expressed by this model, the rate of adsorption into the particle is essentially proportional to the driving force (difference between adsorbed phase concentration in equilibrium with the bulk fluid concentration and the average adsorbed concentration in the particle) still required to reach equilibrium (Glueckauf, 1955).

The effective mass transfer coefficient (k_s) was estimated from the following correlation (Farooq and Ruthven, 1990; Silva and Rodrigues, 1997; Silva, 2001; Gorbach *et al.*, 2004):

$$\frac{1}{k_s} = \frac{r_p}{3k_f} \rho_p f_h \frac{dq^*}{dC} + \frac{r_p^2}{15D_{pe}} \rho_p f_h \frac{dq^*}{dC} = \frac{r_p}{3k_f} \rho_p f_h \frac{dq^*}{dC} + \frac{1}{k_{LDF}} \quad B.11$$

which considers macropore and film resistances to the mass transfer and where k_s is the overall mass transfer coefficient, D_{pe} is the effective pore diffusivity, r_p is the radius of the particle of the adsorbent, k_{LDF} is the coefficient accounting for macropore diffusion and adsorption, k_f is the external film mass transfer coefficient and where the derivative ($\frac{dq^*}{dC}$) represents the average slope of the Langmuir isotherm corresponding to the concentration range of the experiment.

The second term of the right hand side of (Eq. B.11) corresponds to $1/k_{LDF}$ (Glueckauf, 1955) where $k_{LDF} = \frac{15D_{pe}}{r_p^2 \rho_p f_h \frac{dq^*}{dC}}$.

The D_{pe} ($\text{m}^2 \text{s}^{-1}$) was calculated as (Reid *et al.*, 1987):

$$D_{pe} = \frac{\varepsilon_p D_m}{\tau} \quad B.12$$

where D_m is the molecular diffusivity of salicylic acid in water, τ is the tortuosity of the adsorbent and ε_p its porosity.

The molecular diffusivity of salicylic acid in water D_m ($\text{m}^2 \text{s}^{-1}$) was estimated, after the corresponding unit transformations, according to the Wilke-Chang (Wilke and Chang, 1955) method, which assigns for the D_m ($\text{cm}^2 \text{s}^{-1}$):

$$D_m = 7.4 \times 10^{-8} \frac{(\phi M)^{1/2} T}{\eta V_A^{0.6}} \quad B.13$$

where ϕ is the non-dimensional association factor corresponding to the solvent, M_B is the molecular weight of the solvent, T is the corresponding temperature, η_B the viscosity of the solvent and V_A the molar volume of the solute at the normal boiling point. In this study, the solvent was water and the solutes, phenol and salicylic acid. Wilke and Chang recommended that ϕ be chosen 2.6 if the solvent is water. The values of V_A were estimated by the Le Bas additive method (Reid *et al.*, 1987), in the case of phenol the $V_A = 108 \text{ cm}^3 \text{mol}^{-1}$ and $V_A = 146.8 \text{ cm}^3 \text{mol}^{-1}$ for salicylic acid.

Many correlations have been published for the estimation of k_f most of which are modified versions (Yang, 1987; Rexwinkel *et al.*, 1997) of the well-known Ranz-Marshall equation (Ranz and Marshall, 1952). These empirical correlations have been used for different systems and may predict quite different values of the film mass transfer (Wijffels *et al.*, 1998; Ko *et al.*, 2001). Mass transfer data in packed beds have been correlated by the Ranz-Marshall equation (Ranz and Marshall, 1952):

$$Sh = \frac{k_f d_p}{D_m} = 2.0 + 0.6 \left(\frac{\eta}{\rho_f D_m} \right)^{1/3} \left(\frac{u_0 \rho_s d_p}{\eta} \right)^{1/2} = 2.0 + 0.6 Sc^{1/3} Re^{1/2} \quad B.14$$

where Sh , Sc and Re stand for the Sherwood, Schmidt and Reynolds numbers, respectively. In the specific case of phenol adsorption from liquid phase, a correlation for the estimation of the film mass transfer coefficient k_f was developed in our laboratory (Costa and Rodrigues, 1985; Ferreira and Rodrigues, 1995a):

$$j_D = 7.32 \text{Re}'^{-0.569}$$

B.15

where the Chilton-Colburn factor $j_D = Sh/Re Sc^{1/3}$ and $\text{Re}' = \text{Re}/(1 - \varepsilon)$.

The partial differential equations for the modeling of the fixed bed adsorption were solved using the software package *gPROMS*[®] for general **PRO**cess **MO**delling **S**ystem (gPROMS, 2003). The orthogonal collocation method on finite elements (OCFE) was used with 50 finite elements and two interior collocation points in each element of the adsorption bed. No fitting parameters were used for prediction of the experimental data.

B.4 Results and discussion

B.4.1 Adsorption equilibrium isotherm

The experimental adsorbed concentrations as a function of liquid phase concentration corresponding to the phenol and salicylic acid adsorption onto each of the adsorbents at each of the temperatures considered are shown in *Figure B.1* and *Figure B.2*, respectively. The obtained fittings to the Langmuir model are shown together with the experimental points. As it may be seen, the Langmuir model well describes the equilibrium of phenol and salicylic acid onto the adsorbents used in this work.

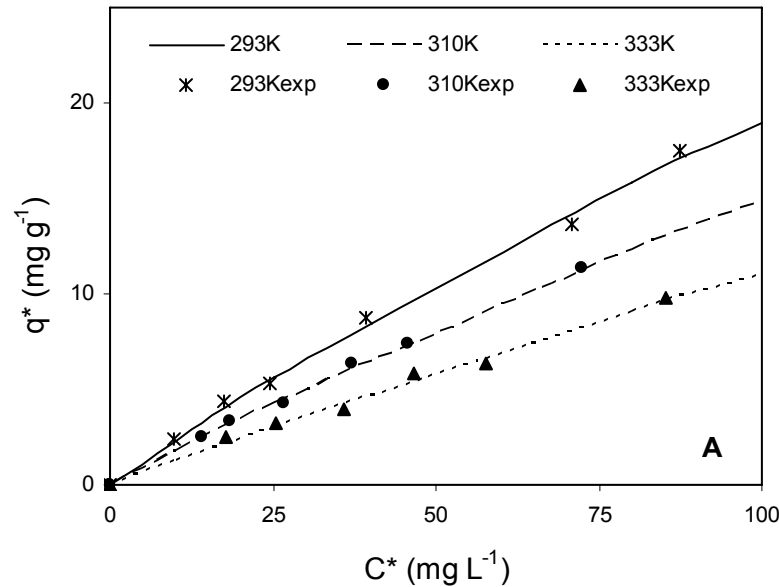


Figure B.1 Experimental adsorption equilibrium data (symbols), q^* versus C^* and fittings to Langmuir model (lines) for the adsorption of phenol onto Duolite S861 (A) at different temperatures

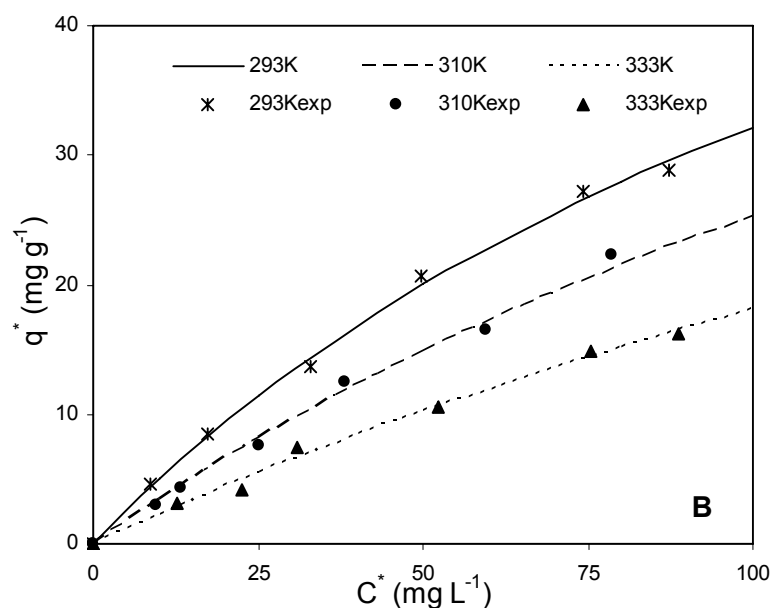


Figure B.1 (continue) Experimental adsorption equilibrium data (symbols), q^* versus C^* and fittings to Langmuir model (lines) for the adsorption of phenol onto Amberlite XAD16 (B) at different temperatures

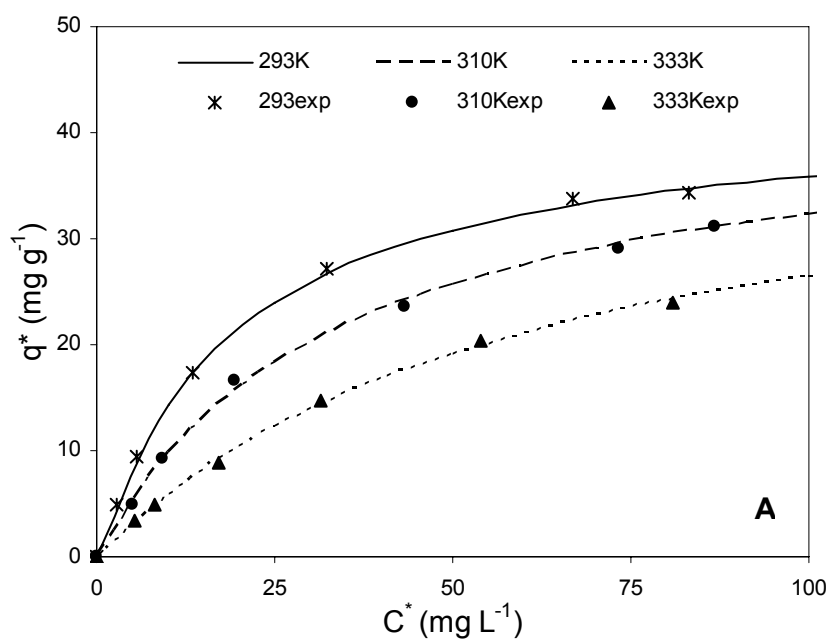


Figure B.2 Experimental adsorption equilibrium data (symbols), q^* versus C^* and fittings to Langmuir model (lines) for the adsorption of salicylic acid onto Duolite S861 (A) at different temperatures

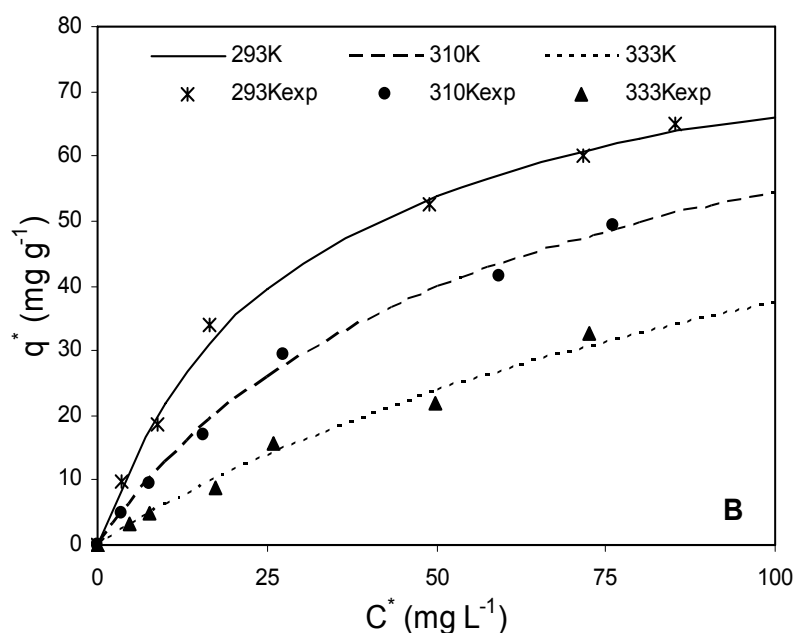


Figure B.2 (continue) Experimental adsorption equilibrium data (symbols), q^* versus C^* and fittings to Langmuir model (lines) for the adsorption of salicylic acid onto Amberlite XAD16 (B) at different temperatures.

The characteristic parameters of the Langmuir model that were obtained for the adsorption of salicylic and phenol onto Duolite S861 and Amberlite XAD16 are given in Table B.2.

The influence of temperature on the performance of each of these two adsorbents is reflected by these parameters. The value of ΔH indicates that the adsorption of salicylic acid is more exothermic than that of phenol, especially onto Amberlite XAD16. Considering that non-specific interactions dominate in the adsorption systems here considered, the fact that the net adsorption enthalpy of salicylic acid is higher than the one of phenol may be attributed to its higher molecular weight (Ruthven, 1984). The higher value of the adsorption enthalpy for the Amberlite XAD16 must be related to its structural characteristics compared to those of Duolite S861, which increases the solute-sorbent interaction on Amberlite XAD16.

The values of the separation parameter b , allow easy comparison of the feasibility of thermal parametric pumping as purification process for different solute-sorbent systems. As it may be observed in Table B.3, for both the adsorbents, the highest separation parameters occur for the whole temperature range here considered, i.e., the range 293 K-333 K.

Table B.2 Parameters obtained from fittings to the Langmuir model corresponding to the equilibrium data of the adsorption of salicylic acid and phenol onto the adsorbents used.

	Duolite S861	Amberlite XAD16
Phenol		
Q (mg g⁻¹)	96.13	81.68
K_L[∞] (m³ g⁻¹)	1.22 x10 ⁻⁵	7.02 x10 ⁻⁶
ΔH_L (J mol⁻¹)	-12.93 x10 ³	-16.65 x10 ³
Salicylic acid		
Q (mg g⁻¹)	43.01	85.06
K_L[∞] (m³ g⁻¹)	3.18 x10 ⁻⁶	1.29 x10 ⁻⁷
ΔH_L (J mol⁻¹)	-23.57 x10 ³	-30.46 x10 ³

In this temperature range, the separation parameters are larger for salicylic acid than for phenol for both adsorbents considered. On the other hand, the separation parameters are larger for Amberlite XAD16 than for Duolite S861 for both solutes considered here. The largest *b* values correspond to the adsorption of salicylic acid onto Amberlite XAD16.

*Table B.3 Separation parameters *b* corresponding to the different adsorbent-adsorbate systems here considered.*

Temperature range	293K-310K	310K-333K	293K-333K
Phenol			
Duolite S861	0.14	0.17	0.31
Amberlite XAD16	0.18	0.22	0.39
Salicylic acid			
Duolite S861	0.26	0.31	0.52
Amberlite XAD16	0.33	0.39	0.63

B.4.2 Fixed- bed adsorption

Figure B.3 shows experimental breakthrough curves results together with the simulated ones for phenol on Duolite S861 (Figure B.3a) and Amberlite XAD16 (Figure B.3b). At the same way Figure B.4 presents results for salicylic acid on both adsorbents.

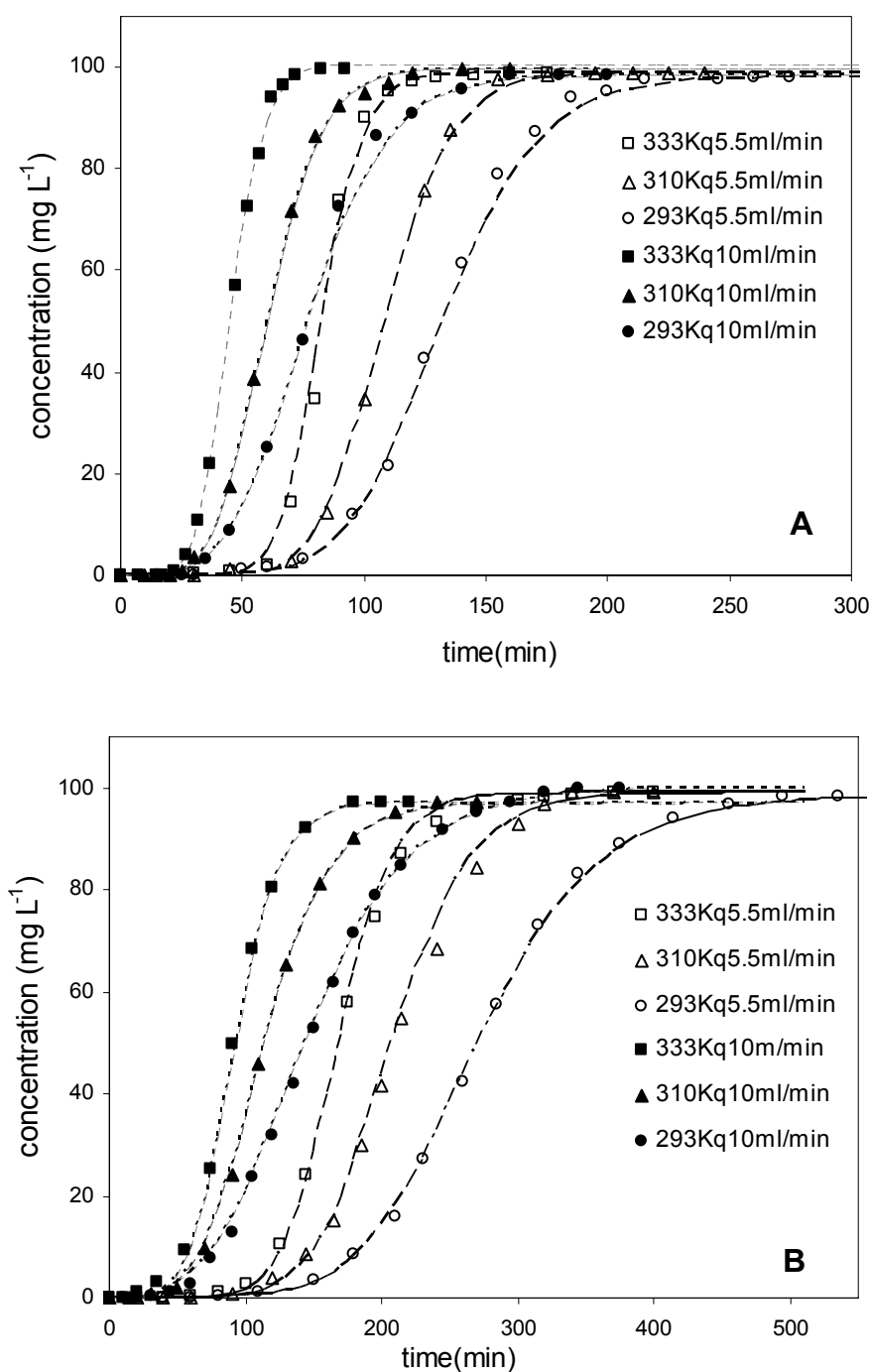


Figure B.3 Fixed bed adsorption of phenol onto Duolite S861 (A) and Amberlite XAD (B) at different temperatures and flow-rates. The bed length was 30 cm and solution was fed at three different temperatures and at two different flow-rates

The model used predicts the fixed bed adsorption of phenol and salicylic acid onto Duolite S861 and Amberlite XAD16 reasonably well. The adsorption of both phenolic compounds was kinetically more favorable onto Duolite S861, which has a higher porosity than Amberlite XAD16.

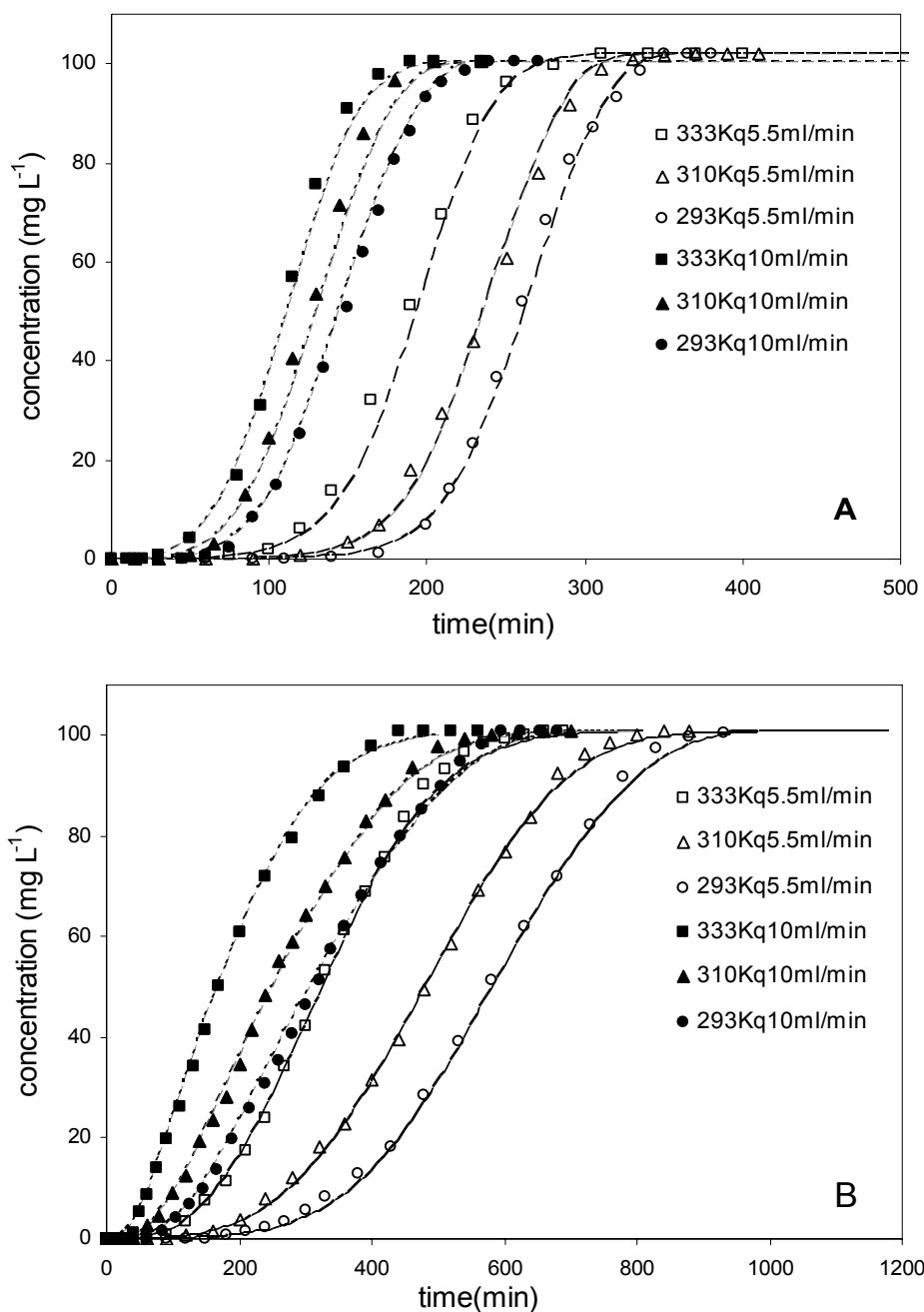


Figure B.4 Fixed bed adsorption of salicylic acid onto Duolite S861 (A) and onto Amberlite XAD (B) at different temperatures and flow-rates. The bed length was 30 cm and solution was fed at three different temperatures and at two different flow-rates.

The fixed bed adsorption capacity increases when the temperature of operation decreases and the higher the temperature, the longer it takes for the saturation of the bed for both the polymeric resins.

It may be observed that lowering the flow-rate of the feeding leads to later breakthrough times. However, for the temperatures considered, for both the flow-rates and both the adsorbents, the beds have reached a constant-pattern.

Amberlite XAD has a higher capacity than Duolite S861 for the adsorption of salicylic acid and phenol. Fixed bed saturation of salicylic acid takes longer than that of phenol for both the resins employed. On the other hand the breakthrough profiles corresponding to the adsorption of salicylic acid are more disperse than those corresponding to phenol, which is described by the model and the parameters used.

In order to further compare the obtained results, the length of unused bed (*LUB*), which is a measure of the fixed bed performance, was obtained for all cases.

The length of the unused bed, *LUB* may be calculated by:

$$LUB = L \left(1 - \frac{t_{bp}}{t_{st}} \right) \quad B.16$$

where *L* is the length of the bed (m), *t_{bp}* is the breakthrough time (s) and *t_{st}* is the stoichometric time (s), which may be determined from a single experimental breakthrough curve (Ruthven, 1984). *LUB* values together with calculated values of the Reynolds and Péclet number ($Pe = \frac{u_0 L}{\varepsilon D_{ax}}$) and axial dispersion *D_{ax}* are shown in the *Table B.4*.

In all cases, the lower the flow rate is, the smaller the corresponding *LUB* is. In the case of fixed bed adsorption of phenol adsorption, the *LUB* are smaller for its adsorption onto Amberlite XAD16 than for Duolite S861. For the adsorption of salicylic acid, the *LUB* values are similar for both resins.

The Linear Driving Force (LDF) model used in this work well predicted the experimental results obtained in the fixed bed. The mass transfer was described by an overall coefficient which groups the LDF kinetic rate constant and the estimated external film mass transfer coefficient. The calculated values of LDF kinetic rate constant are demonstrated in the *Table B.5*.

Table B.4 Parameters used for estimating the D_{ax} corresponding to the different fixed bed systems considered and values LUB (length of unused bed) for phenol.

	adsorbent	Flow-rate (mL min ⁻¹)	T (K)	Re	Pe	D_{ax} 10 ⁻⁶ (m ² s ⁻¹)	$\frac{LUB}{L}$
Phenol	Duolite S861	5.5	293	0.54	332	2.63	0.32
			310	0.85	335	2.62	0.41
			333	1.16	338	2.58	0.46
		10	293	0.98	336	4.73	0.61
			310	1.55	341	4.67	0.59
			333	2.10	344	4.62	0.49
	Amberlite XAD16	5.5	293	0.64	280	3.13	0.49
			310	1.02	283	3.10	0.48
			333	1.38	285	3.07	0.47
		10	293	1.16	284	5.62	0.64
			310	1.85	288	5.53	0.57
			333	2.50	291	5.47	0.56
Salicylic acid	Duolite S861	5.5	293	0.54	332	2.63	0.46
			310	0.85	335	2.62	0.40
			333	1.16	338	2.58	0.34
		10	293	0.98	336	4.73	0.57
			310	1.55	341	4.67	0.58
			333	2.10	344	4.62	0.61
	Amberlite XAD16	5.5	0.64	280	3.13	0.59	0.64
			1.02	283	3.10	0.64	1.02
			1.38	285	3.07	0.69	1.38
		10	293	1.16	284	5.62	0.73
			310	1.85	288	5.53	0.77
			333	2.50	291	5.47	0.78

Table B.5 Linear Driving Force kinetic rate constants (k_{LDF}) estimated for the adsorption of phenol and salicylic acid onto each adsorbent.

<i>adsorbent</i>	<i>adsorbate</i>	<i>T</i> (K)	<i>D_m</i> 10 ⁻¹⁰ (m ² s ⁻¹)	<i>D_{pe}</i> 10 ⁻¹⁰ (m ² s ⁻¹)	<i>k_{LDF}</i> 10 ⁻⁴ (s ⁻¹)
Duolite S861 (a)	Phenol	293	8.90	3.20	20.00
		310	1.48	5.33	40.17
		333	2.20	7.92	83.67
	Salicylic Acid	293	7.43	2.67	7.33
		310	7.87	2.83	8.50
		333	8.45	3.05	11.17
Amberlite XAD16 (b)	Phenol	293	8.90	2.45	6.83
		310	1.48	4.07	12.83
		333	2.20	6.05	23.67
	Salicylic Acid	293	7.43	2.05	1.67
		310	7.87	2.17	2.17
		333	8.45	2.32	3.50
(a) $\epsilon_p = 0.72$ $\tau = 2$; (b) $\epsilon_p = 0.55$ $\tau = 2$					

Table B.6 shows the values of the k_f coefficients predicted by the Ranz-Marshall correlation and correlation from our laboratory.

Table B.6 Parameters used for estimating the external film mass transfer coefficients (k_f) corresponding to the adsorption of phenol and salicylic acid onto Duolite S861 and Amberlite XAD16.

<i>adsorbent</i>	<i>adsorbate</i>	<i>T</i> (K)	<i>Flow-rate</i> (mL min ⁻¹)	<i>Sc</i>	<i>Sh</i>	k_f^a 10 ⁻⁵ (m s ⁻¹)	<i>j_D</i>	k_f^b 10 ⁻⁵ (m s ⁻¹)
Duolite S861	Phenol	293	5.5	1149.2	6.6	1.25	7.8	8.30
		310		434.3	6.2	1.95	6.0	12.22
		333		215.7	5.9	2.75	5.0	16.35
		293	10	1149.2	8.2	1.55	5.5	10.73
		310		434.3	7.7	2.42	4.3	15.77
		333		215.7	7.2	3.38	3.6	21.17
Duolite S861	Salicylic Acid	293	5.5	1376.6	6.9	1.08	7.8	7.37
		310		816.8	7.2	1.20	6.0	8.00
		333		561.5	7.3	1.32	5.0	8.65
		293	10	1376.6	8.6	1.35	5.5	9.52
		310		816.8	9.0	1.50	4.3	10.35
		333		561.5	9.2	1.65	3.6	11.18
Amberlite XAD16	Phenol	293	5.5	1149.2	7.0	1.12	7.1	7.52
		310		434.3	6.6	1.73	5.4	11.03
		333		215.7	6.2	2.45	4.6	14.80
		293	10	1149.2	8.8	1.40	5.0	9.72
		310		434.3	8.2	2.17	3.9	14.28
		333		215.7	7.7	3.02	3.2	19.15
Amberlite XAD16	Salicylic Acid	293	5.5	1376.6	7.3	9.67	7.1	6.67
		310		816.8	7.6	1.08	5.4	7.25
		333		561.5	7.8	1.18	4.6	7.82
		293	10	1376.6	9.2	1.22	5.0	8.62
		310		816.8	9.6	1.35	3.9	9.37
		333		561.5	9.8	1.48	3.2	10.12
k_f^a estimated by the Ranz-Marshall empirical correlation (Ranz and Marshall, 1952).								
k_f^b estimated by the Costa-Rodrigues empirical correlation (Costa and Rodrigues, 1985).								

Table B.7 shows the overall mass transfer coefficient k_s used in (Eq. B.5) for the simulations of the experimental breakthrough curves in each case. In the case of salicylic acid adsorption onto Duolite S861 and onto Amberlite XAD16, the k_s that better fits the experimental results used a film mass transfer coefficient k_f estimated from the Ranz-Marshall correlation. For phenol adsorption in fixed bed packed with these polymeric resins, better fittings were obtained if in the calculation of the k_s parameter, the estimation of the film mass transfer

coefficient k_f is based on the correlation developed by Costa and Rodrigues (Costa and Rodrigues, 1985).

Table B.7 Overall mass transfer coefficients used for the simulations of the fixed bed adsorption of phenol and salicylic acid onto Duolite S861 and Amberlite XAD16

adsorbent	adsorbate	T (K)	Flow-rate (mL min ⁻¹)	$1/k_{LDF}$ 10 ² (s)	$\frac{r_p}{3k_f} \rho_p f_h \frac{dq^*}{dC}$ (s)	$1/k_s$ (s)
Duolite S861	Phenol	293	5.5	5.00	40.98	540.00
		310		2.48	23.10	271.80
		333		1.19	12.30	132.00
		293	10	5.00	31.68	531.60
		310		2.48	17.88	266.40
		333		1.19	9.54	129.00
Duolite S861	Salicylic Acid	293	5.5	13.76	719.10	2095.20
		310		11.87	595.38	1783.20
		333		8.99	441.84	1340.40
		293	10	13.76	576.54	1952.40
		310		11.87	475.80	1663.20
		333		8.99	352.56	1251.00
Amberlite XAD16	Phenol	293	5.5	14.51	84.42	1536.00
		310		7.79	51.36	830.40
		333		4.22	30.84	453.00
		293	10	14.51	65.28	1516.80
		310		7.79	39.66	819.00
		333		4.22	23.82	446.40
Amberlite XAD16	Salicylic Acid	293	5.5	58.55	2194.98	8050.20
		310		45.23	1624.62	6147.00
		333		28.86	1016.28	3902.40
		293	10	58.55	1751.22	7606.20
		310		45.23	1292.10	5814.60
		333		28.86	807.12	3693.00

The adsorption onto the two resins used showed a larger overall mass transfer coefficient for phenol than salicylic acid. Comparing the polymeric resins from a kinetic point of view, it may be concluded that the adsorption of both phenolic compounds was kinetically more favorable onto Duolite S861, which has a higher porosity than onto Amberlite XAD16.

B.5 Conclusions

Phenol being the precursor of salicylic acid, the adsorption of both compounds onto two different polymeric resins (Duolite S861 and Amberlite XAD16) was compared.

The equilibrium of adsorption of phenol and salicylic acid was described by the Langmuir isotherm model. In the range of concentration under study, isotherms corresponding to phenol do not show a clear plateau as they do for the salicylic acid. From the equilibrium results it may be seen that the capacity of Duolite S861 for phenol adsorption ($Q = 96.13 \text{ mg g}^{-1}$) is slightly higher than for Amberlite XAD ($Q = 81.68 \text{ mg g}^{-1}$). On the contrary, Amberlite XAD salicylic acid adsorptive capacity ($Q = 85.06 \text{ mg g}^{-1}$) was nearly double than that of Duolite S861 ($Q = 43.01 \text{ mg g}^{-1}$). Differences on the equilibrium of the two solutes are more evident when considering their adsorption onto Duolite S861 than onto Amberlite XAD16. The maximum adsorptive capacity Q of phenol onto Duolite S861 is double than that of salicylic acid. Similar results have been reported on the adsorption of phenol and salicylic acid onto polymeric resins (Deosarkar and Pangarkar, 2004). Nevertheless, the separation parameter b based on temperature is higher for salicylic acid than for phenol, especially onto Amberlite XAD16, which indicates that purification by parametric pumping would be easier for salicylic acid in comparison with phenol and using Amberlite XAD16 rather than Duolite S861 as adsorbent. This separation potential was further confirmed by the results obtained from the dynamic experiences, the effect of temperature on breakthrough curves being more noticeable for salicylic acid. In terms of a temperature based purification of salicylic acid, such as thermal parametric pumping, Amberlite XAD16 would be a better option than Duolite S861, which may be worth to be studied in future.

The Linear Driving Force (LDF) model used in this work well predicted the experimental results obtained in the fixed bed. The mass transfer was described by an overall coefficient which groups the LDF kinetic rate constant and the estimated external film mass transfer coefficient. The adsorption onto the two resins used showed a larger overall mass transfer coefficient for phenol than salicylic acid. Comparing the polymeric resins from a kinetic point of view, it may be concluded that the adsorption of both phenolic compounds was kinetically more favorable onto Duolite S861, which has a higher porosity than onto Amberlite XAD16.

B.6 Nomenclature

- a deviation in the separation parameter
- b separation parameter
- C concentration in the bulk fluid phase (mg L^{-1})

C_0	initial liquid-phase concentration of phenol (mg L^{-1})
d_p	diameter of the particle of the adsorbent (cm)
D_{ax}	axial dispersion ($\text{m}^2 \text{s}^{-1}$)
D_{pe}	the effective pore diffusivity ($\text{m}^2 \text{s}^{-1}$)
D_m	the molecular diffusivity ($\text{m}^2 \text{s}^{-1}$)
f_h	humidity factor (g dry adsorbent/g adsorbent)
$K(T)$	equilibrium constant dependent on temperature ($\text{m}^3 \text{g}^{-1}$)
K_L	parameter in the Langmuir isotherm model ($\text{m}^3 \text{g}^{-1}$)
K_L^∞	equilibrium constant corresponding to the Langmuir model ($\text{m}^3 \text{g}^{-1}$)
k_{LDF}	Linear Driving Force (LDF) kinetic rate constant (s^{-1})
k_f	external film mass transfer coefficient (m s^{-1})
k_s	overall mass transfer coefficient (s^{-1})
L	total bed length (m)
LUB	length of unused bed (m)
L_t	length of the transference zone (m)
m	mass of adsorbent (g)
MW	molecular weight (g mol^{-1})
M_B	molecular weight of solvent B (g mol^{-1})
$\overline{m}(T)$	capacity parameter in the separation parameter b (-)
m	average slope in the separation parameter b (-)
Pe	Péclet number $= u_0 L / \varepsilon D_{ax}$ (-)

Q	constant in the Langmuir isotherm model (mg g^{-1}) related to the adsorptive capacity
q	solute adsorbed per dry mass of adsorbent at a certain time (mg g^{-1})
q^*	solute adsorbed per dry mass of adsorbent in equilibrium with the phenol concentration in solution (mg g^{-1})
Re	Reynolds number $= u_0 \rho_f d_p / \eta$
r_p	radius of the particle of the adsorbent (m)
Sc	Schmidt number $= \eta / \rho_f D_m$
Sh	Sherwood number $= k_f d_p / D_m$
t	time (s)
t_{bp}	breakthrough time at 2% outlet concentration (s)
t_{st}	stoichiometric time (s)
T	absolute temperature (K)
U	feed flow rate ($\text{m}^3 \text{s}^{-1}$)
u_0	superficial velocity (m s^{-1})
u_i	(u_0 / ε) - interstitial velocity (m s^{-1})
V	volume of the solution (L)
V_A	molar volume of solute a at its normal boiling temperature ($\text{cm}^3 \text{mol}^{-1}$)
W	dry weight (g) of the corresponding adsorbent
z	axial coordinate in the bed (m)
ΔH_L	adsorption enthalpy (Jmol^{-1})

Greek Letters

ε	bed porosity

ε_p	porosity of the adsorbent
ϕ	dimensionless association factor of solvent B
η	viscosity of the solution (Pa.s)
η_B	viscosity of solvent B (cp)
Ω	LDF factor, which is equal to 3, 8 or 15 for slab, cylindrical or spherical geometry
ρ_p	density of the adsorbent (kg m ⁻³)
ρ_f	density of the solution (kg m ⁻³)
τ	tortuosity of the adsorbent

Indexes

A	sub index for the solute
B	sub index for the solvent

B.7 References

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C. Ion-exchange equilibrium experimental data

C.1 Ordinary binary Na^+/H^+ ion-exchange isotherm

Contacting different wet mass (0.005-1.6g) of strong cationic resin Amberlite IR120H with a given volume of solution at the same initial concentration the batch ion exchange experiments were carried out. The moisture content of the resin Amberlite IR120 in H^+ form was determined for each experiment as a difference between the weight of wet resin and after drying at 423 K. The initial solution was prepared as a mixture of 0.1 equiv/L sodium chloride (NaCl) and pH was 5.34. The volume of the solution was 50 mL. The excess of H^+ ion was determined by measuring the pH after equilibrium was established. In order to obtain the data and parameters of ion-exchange equilibrium isotherm, the following mass balance is used

$$q_i^* = \frac{V}{W f_H} (C_{0i} - C_i^*) \quad C.1$$

where q_i^* represents the resin-phase equilibrium concentration, C_{0i} and C_i^* are the initial and equilibrium concentrations in the bulk fluid phase, V is the volume of bulk solution, W is the wet mass of resin and f_H is dry particle to wet particle mass ratio.

Table C.1 Experimental measured values of the ion-exchange isotherm

dry resin (g)	dry resin $10^{-4}(\text{L})$	pH	$C (H^+)$ $10^{-3}(\text{equiv/L})$	$C (Na^+)$ $10^{-2}(\text{equiv/L})$	$q^* (Na^+)$ (equiv/L)	X_{Na^+}	Y_{Na^+}
0.08	1.43	2.09	8.10	9.19	2.843	0.919	0.948
0.16	2.86	1.81	15.5	8.45	2.710	0.845	0.903
0.20	3.57	1.71	19.5	8.05	2.729	0.805	0.910
0.24	4.29	1.64	22.9	7.71	2.672	0.771	0.891
0.28	5.00	1.58	26.3	73.7	2.630	0.737	0.877
0.32	5.71	1.52	30.2	69.8	2.642	0.698	0.881
0.40	7.14	1.44	36.3	63.7	2.541	0.637	0.847
0.48	8.57	1.38	41.7	58.3	2.431	0.583	0.810
0.56	10.0	1.32	47.9	52.1	2.393	0.521	0.798
0.72	12.9	1.26	55.0	45.1	2.137	0.451	0.712
1.04	18.6	1.17	67.6	32.4	1.820	0.320	0.607

C.2 Ion-exchange equilibrium of the system vanillin/NaOH-Amberlite IR120H

Contacting different wet mass of strong cationic resin Amberlite IR120H with a given volume of solution at the same initial concentration the batch ion exchange experiments were carried out. The moisture content of the resin Amberlite IR120 in H^+ form was determined for each experiment as a difference between the weight of wet resin and after drying at 423 K. The solution was prepared by dissolving 0.033 equiv (≈ 5 g) of vanillin in 1L of sodium hydroxide solution with the concentration $0.03 \text{ equiv L}^{-1}$. Immediately after dissolution, according to the chemical reaction between sodium hydroxide and vanillin, the vanillate is formed and equilibrium is characterized by the equilibrium constant of the reaction. The batch experiment has been performed in 250 mL Erlenmeyer flasks where 70 mL of prepared solution with the same concentration and an amount of the wet resin have been added. The weight of wet resin was in the range 0.005 g to 1.6 g. The temperature (293 K) was controlled by a thermostatic bath. The volumetric flasks were placed in a shaking mixer at constant speed 150 rpm. The equilibrium in the resin-liquid mixture has been reached approximately within 24 hours. The solution was separated from the ion-exchanger and the final concentration of vanillin was

determined by measuring the absorbance using UV-VIS spectrophotometer. The total concentration of vanillin and vanillate species was determined by measuring the absorbance at the wavelength 259 nm, which is the isobestic point. Additionally, the concentration of vanillate was determined at the wavelength of 376 nm.

Table C.2 Measured and calculated values of the ion-exchange isotherm with initial concentration of Na^+ cations in solution C_{0i} was 0.027 equiv/L

Dry resin (g)	pH	$C (\text{Na}^+)$ $10^{-3}(\text{equiv/L})$	$q^*(\text{Na}^+)$ $10^{-3}(\text{equiv/g dry resin})$
0.21	7.19	11.8	5.13
0.25	7.01	9.10	5.04
0.29	6.79	6.49	4.95
0.34	6.57	4.32	4.78
0.42	5.66	1.00	4.37
0.50	5.38	0.32	3.74
0.59	4.88	0.11	3.23

D.Experimental data obtained during ultrafiltration experiments

In this appendix additional experimental results obtained on the membrane experimental setup are described. It focus mainly the variation of the volume in the tank and gel resistance as a function of the time ($R_g = f(t)$) obtained by linear regression of experimental data are presented. Moreover, the experimental results obtained using membrane of 50 kDa cut-off are presented. Chemicals and experimental setup were already described elsewhere (see Chapter 6).

D.1 Experimental data obtained with membrane of 1 KDa cut-off

The variation of feed volume in the tank (points) measured for all feed concentrations during experiments using membrane of 1kDa cut-off is shown in *Figure D.1*. Lines in *Figure D.1* represent predicted volume reduction of feed solution in the tank using the mathematical model assuming gel layer resistance for the case of lignin/vanillin concentration in the feed 60/6 g L⁻¹ at pH=12.5 and pH=8.5 and model assuming concentration polarization with osmotic pressure for lignin/vanillin concentration in the feed 2/6 g L⁻¹ of at pH=12.5.

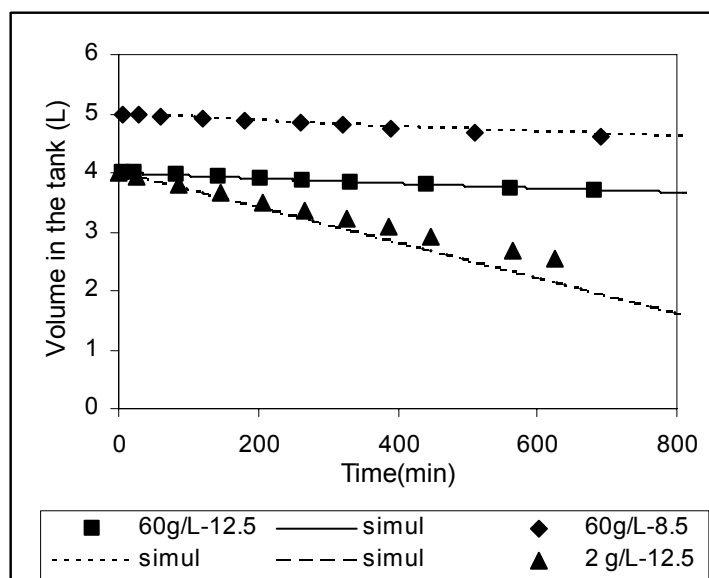


Figure D.1 Volume in the tank as a function of the time for membrane of 1 kDa cut-off. The concentrations of lignin/vanillin mixture were $2/6 \text{ g L}^{-1}$, $60/6 \text{ g L}^{-1}$, $\text{pH}=12.5$ and 8.5 . The initial volume was 5 and 4 L. The predicted curves are shown along with the experimental data.

The variation of permeate volume as a function of the time is shown in Figure D.2. The experimental data (points) are reported with the simulated results (lines).

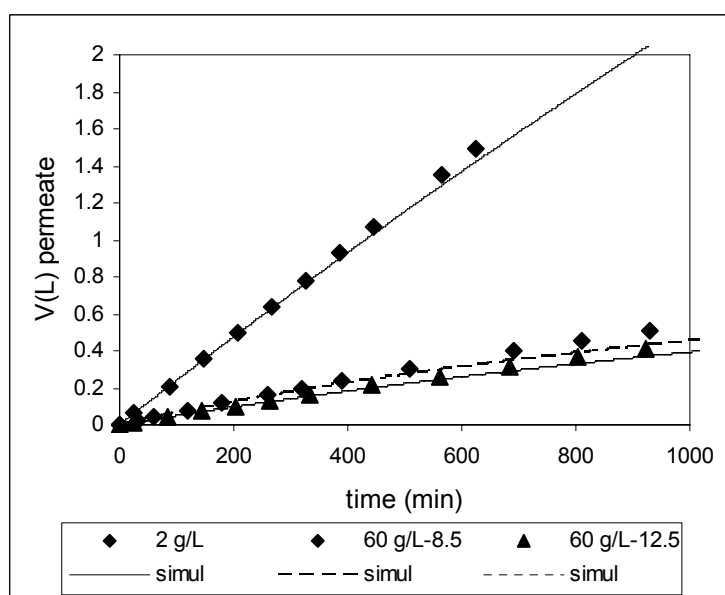


Figure D.2 Permeate volumes as a function of time for membrane of 1 kDa cut-off. The concentration of the lignin/vanillin mixture: $2-6 \text{ g L}^{-1}$, $60-6 \text{ g L}^{-1}$, $\text{pH}=8.5$ and 12.5 .

The gel resistance (R_g) was calculated from the experimental data and plotted as function of the time. Then the data were analyzed by linear regression and the function $R_g = f(t)$ was obtained. The equations of gel resistance as a function of the time ($R_g = f(t)$) for the case of concentration of lignin/vanillin 60/6 g L⁻¹ in the feed and pH = 8.5 and 12.5 are reported in Table D.1.

Table D.1 Gel resistance versus time $R_g = f(t)$ obtained by linear regression for each experimental run

Run	pH	$R_g = f(t)$
1	8.5	$R_g = 7.52 \times 10^{-8} \times (t) + 6.59 \times 10^{13}$; $R^2 = 0.971$
2	12.5	$R_g = 6.17 \times 10^{-8} \times (t) + 9.44 \times 10^{13}$; $R^2 = 0.988$

Linear regression of experimental values of the gel layer resistance (R_g) are shown in Figure D.3.

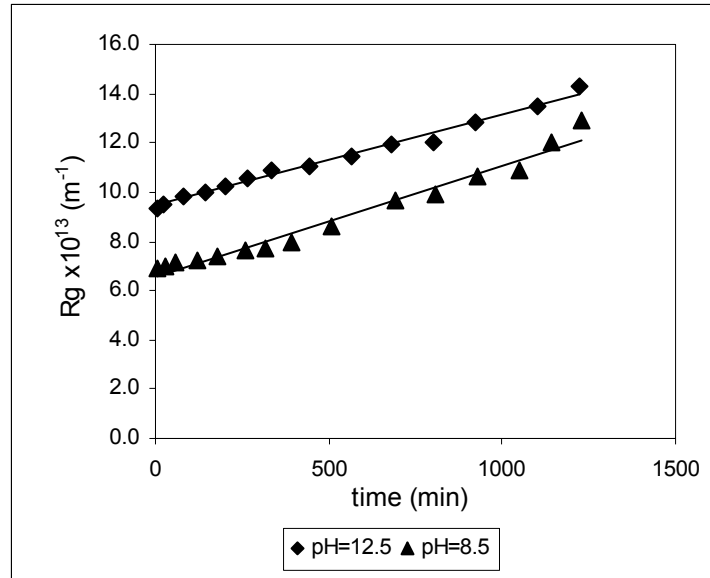


Figure D.3 The gel layer resistance (R_g) as the function of time obtained from experimental permeate flux results and linear regression of the data. Lignin and vanillin concentration were 60 g L⁻¹ and 6 g L⁻¹, the pH=8.5 and 12.5

D.2 Experimental data obtained with membrane of 5 KDa cut-off

The volume change in the tank during experiment using membrane of 5 kDa cut-off is shown in Figure D.4. The initial volume was 4 L and the initial feed concentration was 60/5g L⁻¹ lignin/vanillin mixture at the pH=12.5.

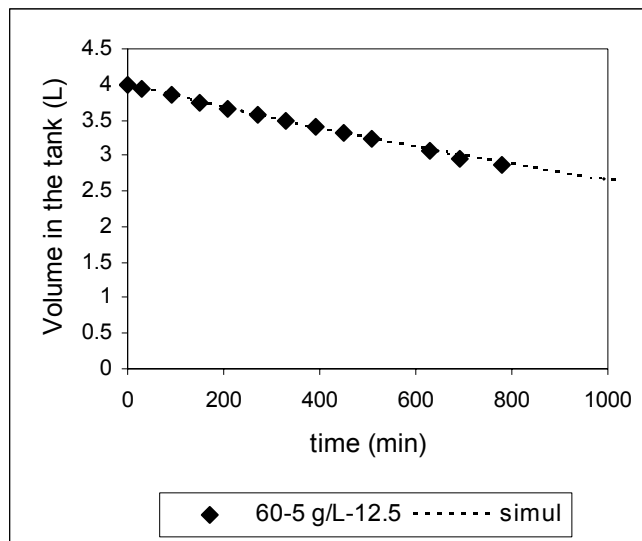


Figure D.4 Volume in the tank as a function of time for the membrane of 5 KDa cut-off and at a concentration of lignin/vanillin mixture 60-5 g/L and pH=12.5

The volume change in the permeate as a function of time using 5 kDa membrane is shown in Figure D.5.

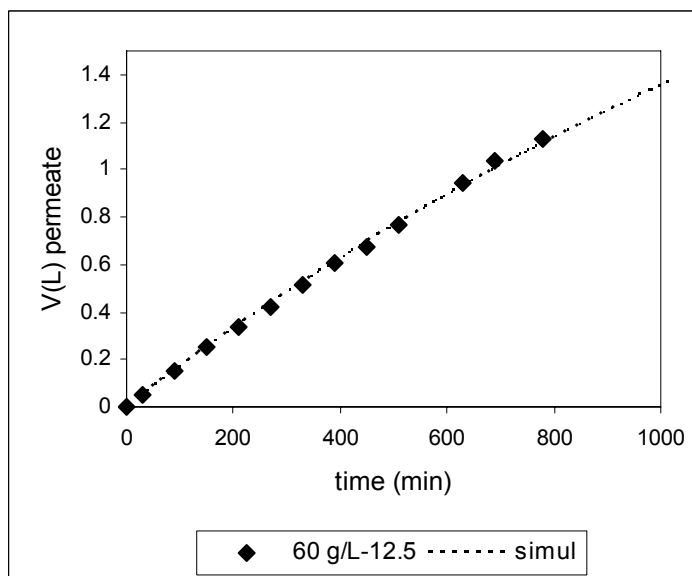


Figure D.5 Permeate volume as a function of time for membrane of 5 kDa cut-off

Table D.2 reports the gel layer resistance (R_g) as a function of time.

Table D.2 Gel resistance versus time $R_g = f(t)$ obtained by linear regression for experimental run 1.

Run	$R_g = f(t)$
1	$R_g = 1.59 \times 10^{-8} t + 2.41 \times 10^{-13}$; $R^2 = 0.890$

Linear regression of experimental values of the gel layer resistance (R_g) is shown in *Figure D.6*.

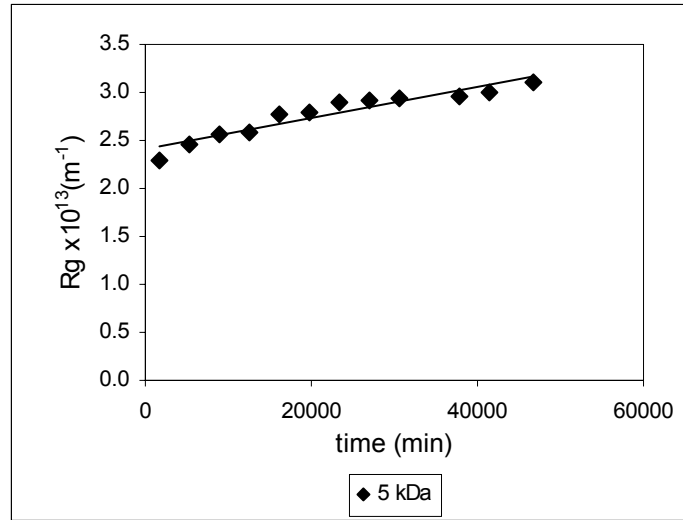


Figure D.6 The gel layer resistance (R_g) as the function of the time obtained from experimental permeate flux results and linear regression of the data. The lignin and vanillin concentration was 60 g L^{-1} and 5 g L^{-1} , the $\text{pH}=12.5$

D.3 Experimental data obtained with membrane of 15 kDa cut-off

The variation of volume in the tank and in the permeate measured for the feed concentration of lignin/vanillin $20/2 \text{ g L}^{-1}$ at $\text{pH}=8.5$ and 12.5 during the experiments using membrane of 15 kDa cut-off are shown in *Figure D.7* and *Figure D.8*, respectively. The lines represent predicted volume reduction using the mathematical model assuming the gel layer resistance.

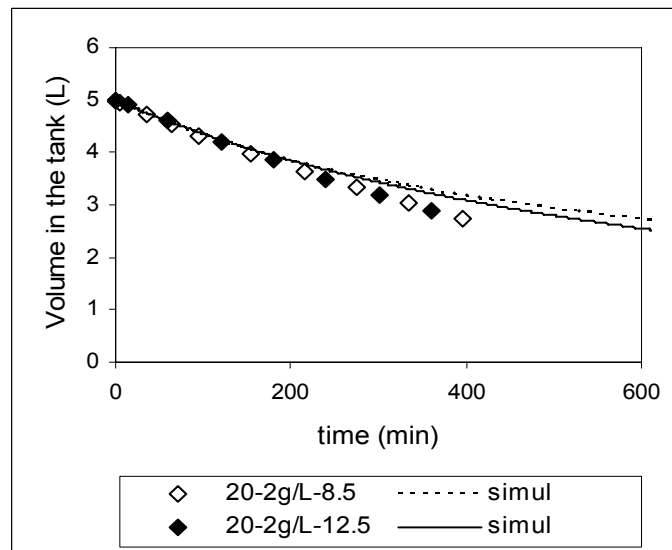


Figure D.7 Volume in the tank as a function of time for the membrane of 15 kDa cut-off; lignin/vanillin mixture at concentration of $20/2 \text{ g L}^{-1}$ and $\text{pH}=8.5$ and $\text{pH}=12.5$

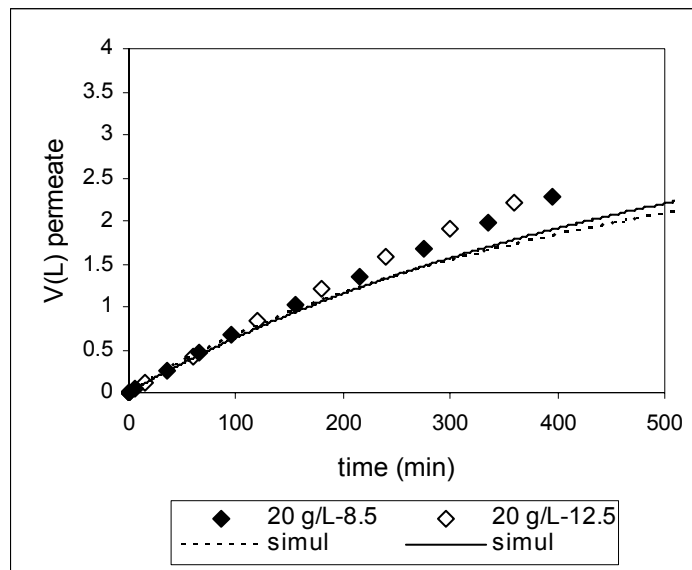


Figure D.8 Permeate volume as a function of time for membrane of 15 kDa cut-off for lignin/vanillin concentration of 20/2 g L⁻¹ at pH=8.5 and 12.5.

The variation of volume in the tank and in the permeate measured for the feed concentrations of 60/6 g L⁻¹ and 5/0.5 g L⁻¹ of lignin/vanillin and at pH=8.5 and 12.5 during the experiments using membrane of 15 kDa cut-off are shown in *Figure D.7* and *Figure D.8*, respectively. The experimental points are fitted with predicted lines using the mathematical model assuming the gel layer resistance.

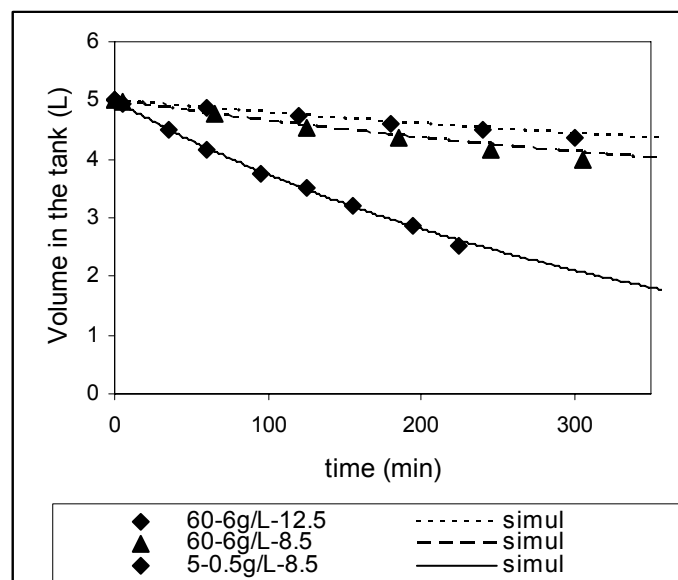


Figure D.9 Volume in the tank as a function of time for the membrane of 15 KDa cut-off at concentrations of lignin/vanillin mixture 5/0.5 g L⁻¹ pH=8.5 and 60/6 g L⁻¹ pH=12.5 and 60/6 g L⁻¹ pH=8.5.

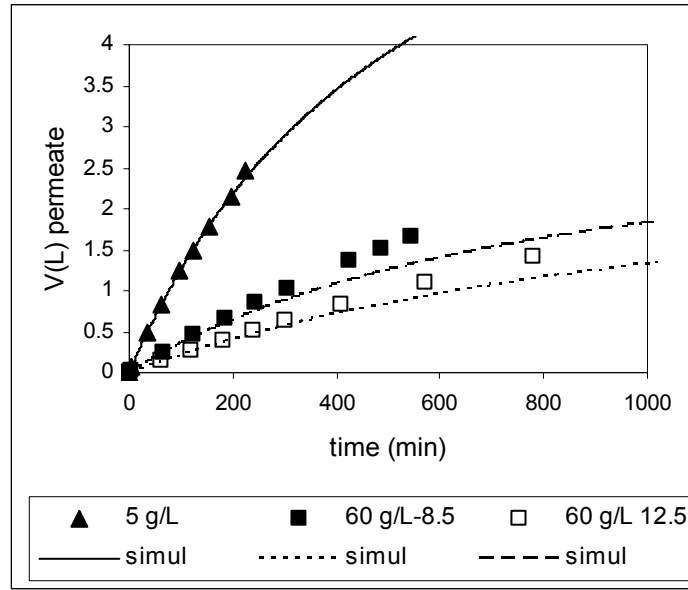


Figure D.10 Permeate volume as a function of time for membrane of 15 kDa cut-off for the concentration of lignin/vanillin mixture $5/0.5 \text{ g L}^{-1}$ $\text{pH}=8.5$ and $60/6 \text{ g L}^{-1}$ $\text{pH}=12.5$ and $60/6 \text{ g L}^{-1}$ $\text{pH}=8.5$.

The variation of the gel layer resistance (R_g) with time obtained from experimental data together with linear regression is showed in Figure D.11.

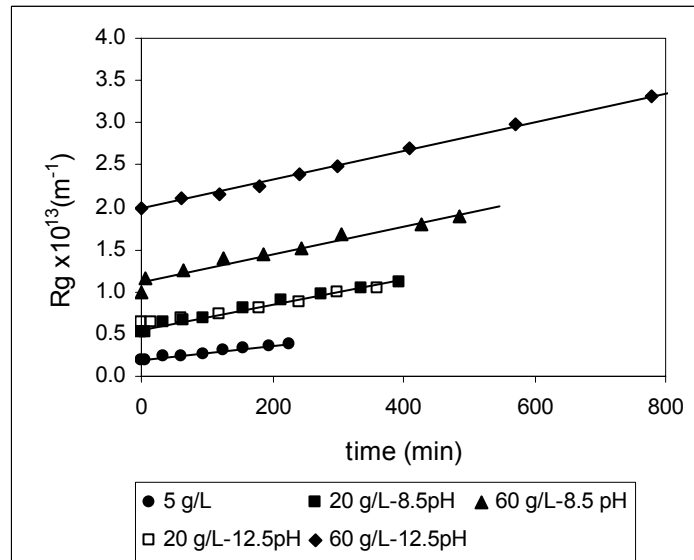


Figure D.11 The gel layer resistance (R_g) as a function of time obtained from experimental permeate flux results and linear regression of the data. The lignin and vanillin concentration were $60/6 \text{ g L}^{-1}$, $20/2 \text{ g L}^{-1}$ and $5/0.5 \text{ g L}^{-1}$ at $\text{pH}=12.5$ and 8.5

The gel layer resistance as a function of the time ($R_g = f(t)$) for each experimental run performed using membrane 15 kDa cut-off is reported in Table D.3.

Table D.3 Gel resistance versus time $R_g = f(t)$ obtained by using linear regression for each experimental run

Run	$R_g = f(t)$
1	$R_g = 1.43 \times 10^8 t + 1.92 \times 10^{12}; R^2 = 0.998$
2	$R_g = 2.49 \times 10^8 t + 5.51 \times 10^{12}; R^2 = 0.983$
3	$R_g = 1.95 \times 10^8 t + 6.19 \times 10^{12}; R^2 = 0.987$
4	$R_g = 2.59 \times 10^8 t + 1.05 \times 10^{13}; R^2 = 0.990$
5	$R_g = 2.84 \times 10^8 t + 1.98 \times 10^{13}; R^2 = 0.998$

D.4 Experimental data obtained with membrane of 50 KDa cut-off

The membrane permeability which was obtained from the water flux measurement for the membrane of 50 kDa cut-off was lower than that of 15 kDa membrane. The value of corrected water flow rate measured with completely new membrane at the pressure 4 bar and 25 °C was 410 L h⁻¹m². This value of corrected water flow rate is in disagreement with the one given by supplier Orelis France which is 1100+-300 L h⁻¹m² (Kersep, 2005). The supplier did not offer any explanation of the mentioned membrane performance. However, there is already published work (Rojas *et al.*, 2006) where disagreement with the expected performance could be found using tubular ceramic membrane.

The viscosity of water at 25 °C is 0.891 ×10⁻³ kg m⁻¹ s⁻¹) and the value of the membrane resistance (R_m) obtained from experimental results was 3.741×10¹² m⁻¹ for 50 kDa membrane which was higher than for membrane 15 kDa (2.805 ×10¹²m⁻¹). The pure water flowrate measured at different transmembrane pressure (ΔP) using membrane of 50 kDa cut-off is shown in *Figure D.12*.

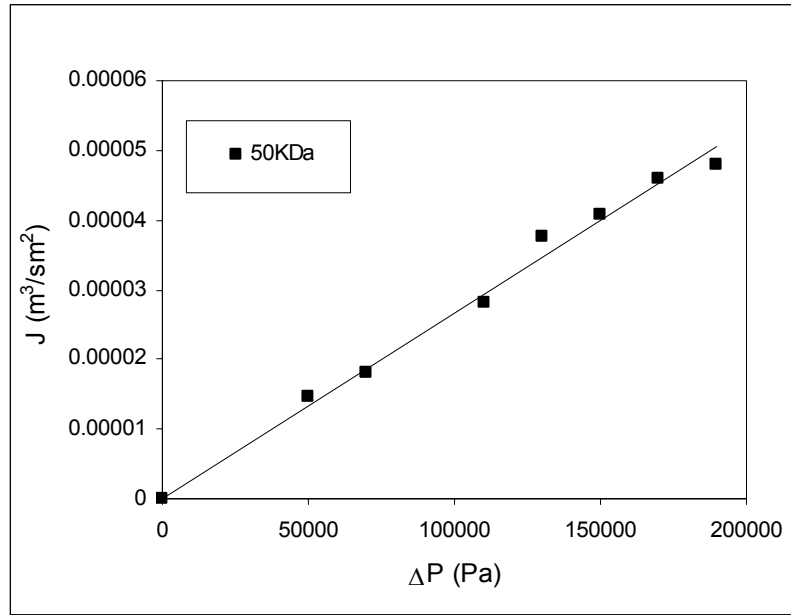


Figure D.12 The pure water permeate flux obtained at different transmembrane pressures for the membrane 50 kDa cut-off.

Permeate fluxes measured during the experiments for each tested concentrations of lignin/vanillin (0.5/5, 20/2 and 60/6 g L⁻¹, pH=8.5) solution are compared in Figure D.13. The mathematical model which involves gel-layer resistance was used to predict experimental results of permeate flux. The predicted lines are reported together with experimental points in Figure D.15.

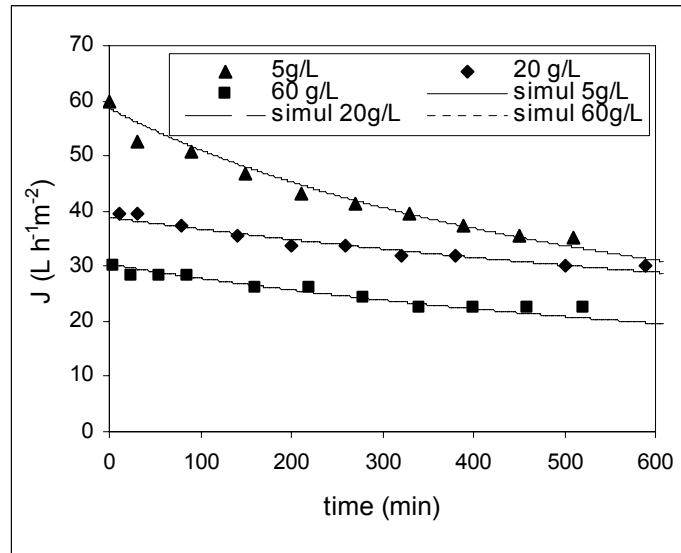


Figure D.13 Permeate fluxes in membrane of 50 kDa cut-off at pH = 8.5. The concentration of lignin was 5, 20 and 60 g L⁻¹ and vanillin 0.5, 2 and 6 g L⁻¹. Transmembrane pressure $\Delta P = 1.3$ bar. Feed flow-rate: $Q_{feed} \approx 56, 100$ and 120 L h⁻¹

The model parameters used in simulations are reported in Table D.4.

Table D.4 The model parameters used in simulations considering the gel layer resistance.

C_{feed}^0 (Lignin) (g L ⁻¹)	C_{feed}^0 (Vanillin) (g L ⁻¹)	pH	R_m (m ⁻¹)	η (kg m ⁻¹ s ⁻¹)	Q_{feed} (L h ⁻¹)	ΔP (bar)
5	0.5	8.5	3.741×10^{12}	0.887×10^{-3}	56	1.3
20	2	8.5	3.741×10^{12}	0.954×10^{-3}	100	1.3
60	6	8.5	3.741×10^{12}	1.190×10^{-3}	120	1.3

Gel layer resistance (R_g) obtained from experimental results was analysed using linear regression is shown in Figure D.14. The gel layer resistance as a function of time ($R_g = f(t)$) for each concentration performed using membrane of 50 kDa cut-off is reported in Table D.5.

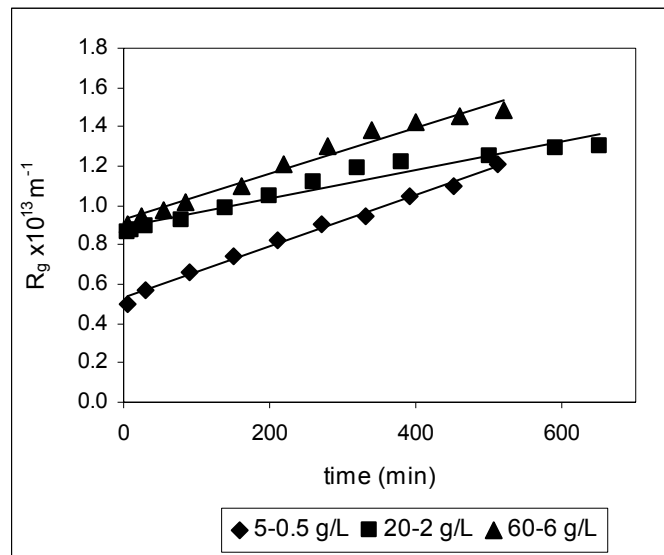


Figure D.14 The gel layer resistance (R_g) as the function of the time obtained from experimental permeate flux results and linear regression of the data. The lignin and vanillin concentration was 60/6, 20/2 and 5/0.5 g L⁻¹; pH= 8.5

Table D.5 Gel resistance versus time $R_g = f(t)$ obtained by using linear regression for each studied concentration.

C_{feed}^0 (Lignin) (g L ⁻¹)	C_{feed}^0 (Vanillin) (g L ⁻¹)	pH	$R_g = f(t)$
5	0.5	8.5	$R_g = 2.21 \times 10^8 t + 5.28 \times 10^{12}$; $R^2 = 0.993$
20	2		$R_g = 1.21 \times 10^8 t + 8.89 \times 10^{12}$; $R^2 = 0.950$
60	6		$R_g = 1.97 \times 10^8 t + 9.27 \times 10^{13}$; $R^2 = 0.977$

After each experiment the volume of permeate and retentate was measured as well as the concentration of vanillin and lignin in each stream. The values of volume reduction, and observed retention of lignin and vanillin are summarized in *Table D.6*.

Table D.6 The values of volume reduction and retention for vanillin and lignin obtained from experiments onto 50 kD membrane.

$C(L)$ [g L ⁻¹]	$C(VH)$ [g L ⁻¹]	VR	$R_{obs} (L)$	$R_{obs} (VH)$
5	0.5	0.410	0.891	0.34
20	2	0.371	0.95	≈ 0
60	6	0.312	0.93	≈ 0

The concentration of vanillin and lignin was determined also in the each sample of the retentate and the permeate taken during the time of the experiment. The concentration histories of vanillin and lignin in retentate and permeate using membrane of cut-off 50 kDa are presented in *Figure D.15 a, b* and *Figure D.16 a, b* respectively. The experiment was performed at constant transmembrane pressure $\Delta P = 1.3$ bar. Feed flow rate was adjusted to 56, 100 and 119 L h⁻¹ for each feed concentration, respectively.

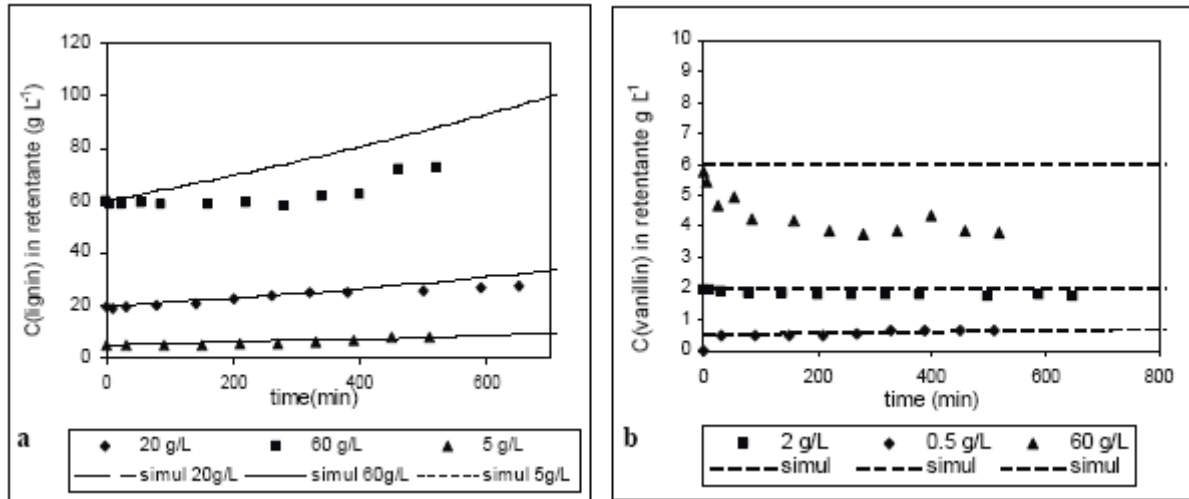


Figure D.15 Variations of lignin (a) and vanillin (b) concentration in retentate stream with time using membrane of 50 kDa cut-off. The initial concentration of lignin was 5, 20 and 60 g L⁻¹ and initial concentration of vanillin was 0.5, 2 and 6 g L⁻¹ and pH=8.5. Transmembrane pressure $\Delta P = 1.3$ bar. Feed flowrate: $Q_{feed} \approx 56, 100$ and 119 L h⁻¹

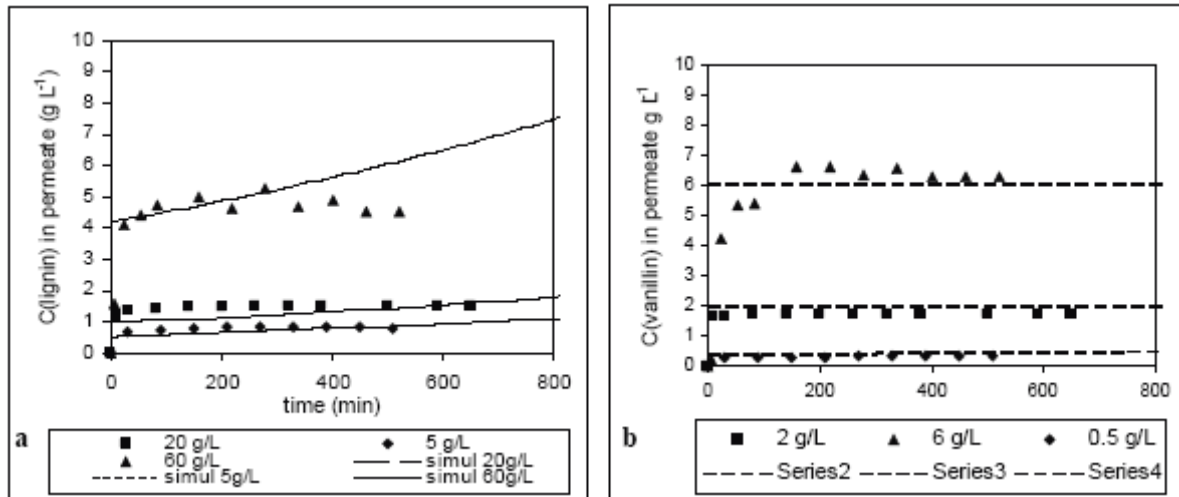


Figure D.16 Variations of lignin (a) and vanillin (b) concentration in permeate stream with time using membrane of 50 kDa cut-off. The initial concentration of lignin was 5, 20 and 60 g L⁻¹ and initial concentration of vanillin was 0.5, 2 and 6 g L⁻¹ and pH=8.5. Transmembrane pressure $\Delta P = 1.3$ bar. Feed flowrate: $Q_{feed} \approx 56, 100$ and 119 L h⁻¹

The variation of the volume in the tank measured for all feed concentrations during experiments using membrane of 50kDa cut-off is shown in Figure D.17. The full lines represents the predicted volume reduction using the mathematical model assuming gel layer resistance for concentrations of lignin/vanillin 60/6 g L⁻¹, 20/2 g L⁻¹ and 5/0.5 g L⁻¹, pH=8.5

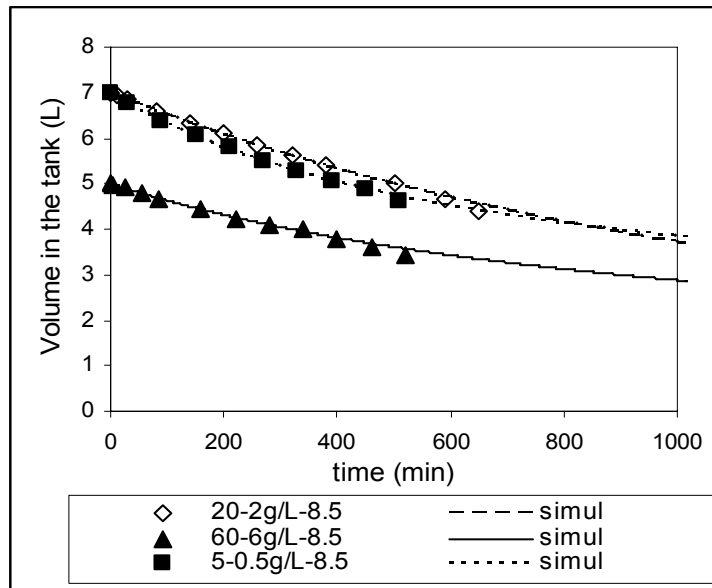


Figure D.17 Volume in the tank as a function of time for the membrane of 50 KDa cut-off and at concentrations of lignin/vanillin mixture 5/0.5 g L⁻¹ pH=8.5 and 20/2 g L⁻¹ pH=8.5 and 60/6 g L⁻¹ pH=8.5

The variation of permeate volume as a function of the time is shown in Figure D.18. The experimental data are reported together with the simulated results.

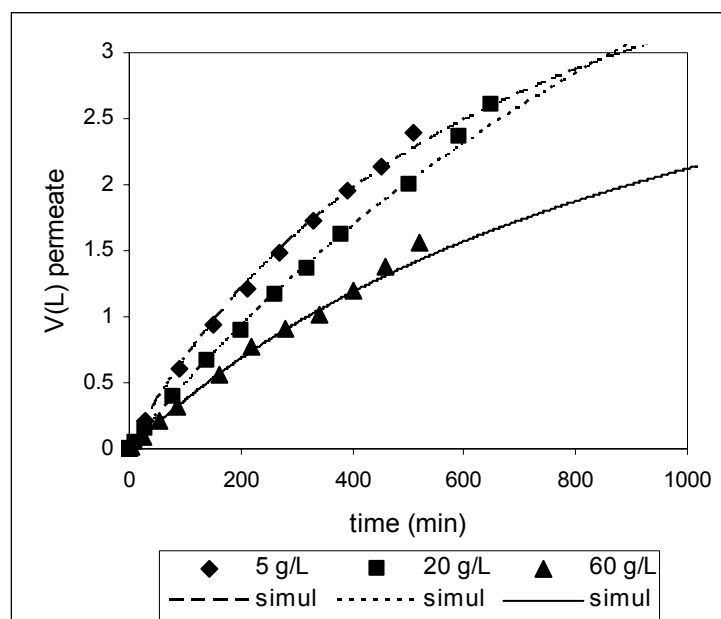


Figure D.18 Permeate volume as a function of time for membrane of 50 kDa cut-off for different lignin/vanillin concentrations $5/0.5 \text{ g L}^{-1}$ $\text{pH}=8.5$ and $20/2 \text{ g L}^{-1}$ $\text{pH}=8.5$ and $60/6 \text{ g L}^{-1}$ $\text{pH}=8.5$

D.5 References

Kerasep, *Operating manual Microcarbosep*, Rhodia group, Orelis, France, 2005.

Rojas, O. J., Song, J. and Argyropoulos, D. S., Lignin separation from kraft black liquors by tangential ultrafiltration. *Ind. La Chimica e l'Industria*, **88** (1), 88 - 95 (2006).