

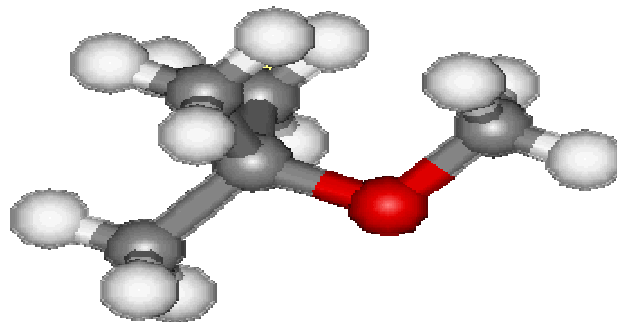


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Removal of MTBE from Groundwater with Solvent Impregnated Resins



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Abstract.

The performance of Solvent Impregnated Resins (SIRs) for extraction of MTBE from aqueous solutions has been investigated. The extraction capability of two extractants, 3-iodophenol (IPhOH) and 3,5-dimethyl-4-iodophenol (DMIP), was studied and compared. IPhOH showed a better affinity for MTBE. As these extractants are solid at room temperature, a diluent screening was performed. The diluents used were nonane, phenyldodecane, 1-decanol, nonanoic acid, heptyl cyanide, toluene and propylbenzene. Toluene and propylbenzene were determined to have the highest capacity to solubilize IPhOH and the highest overall distribution coefficients for the distribution of MTBE between the aqueous and organic phases. As the solid support is an important feature in SIR technology, four adsorbents were tested for the extraction of MTBE: the carbonaceous resin Ambersorb XE-348F, the polymeric resins Amberlite XAD-7 and macro-porous polypropylene MPP and granular activated carbon Aquasorb 202. The carbonaceous resin presents the best affinity for MTBE. In order to test the impregnated resins, Ambersorb XE-348F, Amberlite XAD-7 and MPP were impregnated. The extraction of ETBE with SIR was also tested. Three models for the prediction of the extraction with SIR were tested. Two models consider the adsorption on the surface of the beads, and the other model does not. A selectivity analysis was performed for impregnated MPP between humic acid and MTBE. The results yield good prospects for the use of SIR in contaminated groundwater treatment. The dynamic behavior was examined in column experiments. Separation is favoured at low flow rates.

Resumo.

Neste projecto foi estudada a extracção de MTBE de soluções aquosas com resinas impregnadas. Para tal fez-se uma análise de extractantes, o 3-iodofenol (IPhOH) e o 3,5-dimetil-4-iodofenol (DMIP). Notou-se que o IPhOH apresenta uma maior capacidade na extracção do MTBE. Dado que os extractantes se apresentam sólidos em condições atmosférico, foi necessário fazer uma análise de diluentes. Para tal, foram testados sete diluentes, nonano, fenildodecano, heptil cianeto, 1-decanol, ácido nonanóico, tolueneo e propilbenzeno. De entre os diluentes testados o tolueno e o propilbenzeno apresentaram maiores capacidades para solubilizar o IPhOH assim como os maiores valores para os coeficientes totais de distribuição entre as fases aquosa e orgânica.

Uma vez que a matriz sólida tem alguma influência na extracção com resinas impregnadas, quatro adsorventes foram testados, as resinas Amborsorb XE-348F, Amberlite XAD-7 e o polipropileno macroporoso MPPe o carvão activado Aquasorb 202. O adsorvente que apresentou maior afinidade pelo MTBE foi a resina Amborsorb XE-348F. Com o intuito de estudar a extracção de MTBE com resinas impregnadas, impregnaram-se as três resinas. De modo a traduzir a extracção de MTBE com resinas impregnadas testaram-se três modelos, um que não considera a adsorção do soluto na superfície das partículas e dois que o fazem. Visto que o ETBE é um possível substituto do MTBE nas gasolinas, a extracção deste composto também foi testada. Uma vez que o ácido húmico está muitas vezes presente nas águas contaminadas com MTBE uma análise à selectividade do MPP impregnado foi realizada e foi determinada sempre maior que um, o que traz uma boa indicação para o uso destas resinas para o tratamento de águas contaminadas com MTBE e ácido húmico. Finalmente, para perceber o comportamento dinâmico da extracção do MTBE em colunas foram realizadas experiências em colunas. Com estes resultados é possível dizer que a extracção de MTBE por resinas impregnadas é favorecida a baixos caudais.

Key Words: MTBE, Extraction, Solvent impregnated resins, Groundwater.

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A todos vocês OBRIGADO.

Nomenclature

V	volume
C_{MTBE}	concentration of MTBE after equilibrium
K_{D}	overall distribution coefficient
K_{ph}	physical distribution coefficient
K_{C}	chemical distribution coefficient
$C_{\text{s},0}$	initial concentration of solute
C_{s}	concentration of solute after equilibrium
C_{c}	concentration of complexes after equilibrium
$C_{\text{E},0}$	initial concentration of extractant
x_{IPhOH}	massic composition of 3-iodophenol
x_{DMIP}	massic composition of 3,5-dimethyl-4-iodophenol
$\Delta H_{\text{m,IPhOH}}^{\text{S-L}}$	melting enthalpy of 3-iodophenol
$\Delta H_{\text{m,DMIP}}^{\text{S-L}}$	melting enthalpy of 3,5-dimethyl-4-iodophenol
C_{E}	concentration of extractant after equilibrium
C_{total}	total concentration of MTBE after equilibrium
R (chap 3.1.3)	gas constant
T	temperature
$T_{\text{m,IPhOH}}$	melting temperature of 3-iodophenol
$T_{\text{m,DMIP}}$	melting temperature of 3,5-dimethyl-4-iodophenol
q	concentration of MTBE after equilibrium
K	Freundlich constant
n	Freundlich constant
r^2	correlation coefficient
q_{max}	maximum concentration of MTBE on the sorbent after equilibrium
C_{max}	maximum concentration of MTBE in the aqueous phase after equilibrium
R (chap 3.2)	constant of adsorption
$K_{\text{ph}}^{\text{ads}}$	physical distribution coefficient of adsorption
$C_{\text{s,max}}$	maximum concentration of solute after equilibrium
$q_{\text{s,max}}$	maximum concentration of solute after equilibrium on the sorbent
m_{SIR}	mass of solvent impregnated resin
V_{p}	pore volume
t_{st}	stoichiometric time
V^{column}	Volume of the column
Q_0	initial flow rate

Greek letters

ϵ_p	particle porosity
α	selectivity
ϵ_b	bulk porosity
ρ_{SIR}	density of the solvent impregnated resin

Subscripts and superscripts

SIR	respect to the solvent impregnated resin
aq	respect to the aqueous phase
org	respect to the organic phase

List of Acronyms

MTBE	methyl tert-butyl ether
ETBE	ethyl tert butyl ether
TBA	tert-butyl alcohol
NOMs	natural organic matter
GAC	granular activated carbon
AOPs	advanced oxidation process
TBF	Tert-butyl formate
SIR	solvent impregnated resin
I _{Ph} OH	3-iodophenol
DMIP	3,5-dimethyl-4-iodophenol
LLE	liquid-liquid extraction
HSGC	headspace gas chromatography
BTEX	Benzene, toluene, ethylbenzene and xylene

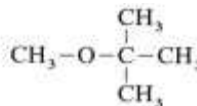
Table of Contents

1. Introduction	2
1.1. Background on MTBE	2
1.2. State – of – the – art MTBE removal techniques	3
1.3. Alternative approach MTBE removal technique	6
1.4. Objective	9
2. Materials and Methods	10
2.1. Substances	10
2.2. Liquid-liquid extraction	10
2.3. Isotherm experiments	11
2.4. Impregnation method	11
2.5. Selectivity experiments	11
2.6. Column experiments	12
2.7. MTBE analysis	13
3. Results and Discussion	14
3.1. Liquid-liquid extraction	14
3.1.1. Effect of the diluents	14
3.1.2. Extractant comparison	17
3.1.3. Eutectic point	18
3.2. Adsorption on unimpregnated sorbents	19
3.3. Adsorption on solvent impregnated resin	23
3.3.1. MTBE extraction with SIR	23
3.3.2. Sensitivity test	35
3.3.3. ETBE extraction with SIR	38
3.4. Selectivity	40
3.5. Column experiments	41
3.6. Cost evaluation	42
4. Conclusions	43
5. Evaluation of the presented work	45
5.1. Accomplished objectives	45
5.2. Other accomplished work	45
5.3. Recommendations for future work	45
5.4. Final evaluation	47
References	48
Appendix	I

1. Introduction

1.1. Background on MTBE

Methyl tert-butyl ether or 2-methoxy-2-methylpropane (MTBE) is an ether that was first synthesized and characterized in 1904 (Peters, U. *et al*, 2005) and its formula is:



[1]

MTBE's physical properties are presented in table 1.1. Besides those properties one can mention the density of 740,5 kg/m³ and the Henry's law coefficient between 0,018 and 0,026 (Peters, U. *et al*, 2005). MTBE is colorless and has a terpene-like odor. MTBE is very soluble in water (48 g/L at 25°C) (Melin, G., 2000) and in any organic liquids. When MTBE is present in the soil as the result of a petroleum release, it tends to separate from the rest of the petroleum components, reaching the groundwater first and dissolving rapidly. MTBE travels at the same speed as the water, while the other components will start to biodegrade (B. Ray, A. *et al*, 2003). It forms azeotropes with water and methanol. In the basic phase, as well as in neutral or weakly acidic solutions, this component is very stable. In strong acidic solutions, it cleaves to methanol and isobutene, depending on the reaction conditions.

Table 1.1 – Physical properties of MTBE (Peters, U. *et al*, 2005).

Melting point	- 108,6°C
Boiling point	55,3°C
n_D^{20}	1,3692
Dielectric constant (20°C)	4,5
Viscosity (20°C)	0,36 mPa s
Surface tension (20°C)	20 mN m ⁻¹
Flash point (Abel - Pensky)	- 28°C
Ignition temperature (DIN 51794)	460°C
Explosion limits in air	1,65-8,4 vol%
Critical data	
T _{cr}	224,0°C
P _{cr}	3,43 MPa

MTBE is produced by the reaction between methanol and isobutene contained in the C₄ fraction from dehydrogenation of butane, steam crackers or fluid catalytic crackers (Peters, U. *et al*, 2005). MTBE is used mainly as an additive compound in gasoline. It is used since the 1970s in gasoline as an octane enhancer, in order to prevent engine knocking, to increase the oxygen level, and to reduce carbon monoxide emissions (US Environmental Protection Agency, 1998).

Nowadays, 95% of the world's production is used for that purpose. MTBE is also used to produce methanol or isobutene by the reverse reaction of its production, and as a dewaxing solvent for hydrocarbon oils (Peters, U. *et al*, 2005).

Because MTBE is very soluble in water, any leakage, either from a storage facility or from the incomplete combustion in car engines or during fuel transfer at gas stations, may present a risk of contamination of groundwater. Although this contamination is not dangerous, neither for public health nor for aquatic life (Peters, U. *et al*, 2005), MTBE removal is important, because it has a strong taste and odor. The MTBE concentration in drinking water should not exceed 20 µg/L (US Environmental Protection Agency, 1998), as the average of the taste threshold (40 µg/L) and the odor threshold (15 µg/L) (Peters, U. *et al*, 2005). Among the most important MTBE removal methods, there are air stripping, adsorption with granular activated carbon, chemical and biological treatments and adsorption with synthetic resins.

1.2. State – of – the – art MTBE removal techniques.

1.2.1. Air stripping.

MTBE removal by air stripping is a physical process that separates it from water by evaporation. This process strongly depends on the Henry's constant and on the air/water ratio. Due to the very low Henry's constant (0,018-0,026), the air/water ratio must be high (100-250) (Peters, U. *et al*, 2005). This method has been widely studied, presenting recovery rates of at least 90%. The main disadvantage of using air stripping for MTBE removal is that the off-gas stream needs to be treated before the release into the atmosphere (Peters, U. *et al*, 2005). This is due to the fact that after the stripping stage MTBE is contained in the gas phase. Such a process including off-gas treatment may involve high costs (US Environmental Protection Agency, 1998).

1.2.2. Granular activated carbon.

Adsorption in granular activated carbon (GAC) is also a widely studied process. This method is very efficient for small concentrations (200 µg/L) of MTBE (Peters, U. *et al*, 2005). However, when MTBE is present in large concentrations (over 2000 µg/L) (Melin, G., 2000), this process can only be used as a polishing step, followed by biological or chemical treatment or air stripping (Peters, U. *et al*, 2005). This is because of the low affinity of MTBE for sorption on solids. MTBE adsorption on GAC strongly depends on the presence of other components due to competitive adsorption. These components are natural organic matters (NOMs), humic acid for instance, and other gasoline additives, such as ETBE or benzene, toluene, ethylbenzene and xylenes (BTEX). Products of MTBE decomposition, tert-butyl alcohol (TBA), and MTBE cleaved products, methanol or isobutene also compete in the adsorption on GAC. This causes

selectivity problems when using GAC technology. Thus, a high amount of GAC is needed, which can increase the costs significantly (Melin, G., 2000). A second disadvantage is the low affinity of MTBE for adsorbing when the concentration in the liquid phase is lower than the concentration in the solid phase (Melin, G., 2000). In this case, MTBE will start desorbing, hence contaminating the water because it is very water soluble. Consequently a tight control of the process is required. A third problem arises from the difficulty to regenerate GAC, which usually is incinerated after its saturation, thus reducing its life-time to typically 10 – 20 cycles (B. Ray, A. *et al*, 2003).

1.2.3. Advanced Oxidation Processes.

Advanced oxidation processes (AOPs) decompose MTBE and a large spectra of other organic compounds (Melin, G., 2000). These processes involve the oxidation of MTBE by Fenton's reagent (B. Ray, A. *et al*, 2003), UV-peroxide (R. Cater, A. *et al*, 2000), UV-ozone (L. Acero, J., 2001), high-energy electron beam irradiation (E-beam) or sonication-hydrodynamic cavitation (Peters, U. *et al*, 2005). All these techniques produce hydroxyl radicals to oxidate the compounds to be treated. In the case of ozonation, in particular, an advantage is that the presence of NOMs enhances the formation of hydroxyl radicals. Although in the Fenton's reagent and the UV-peroxide techniques few studies have been performed, the existing studies suggest that these could be feasible techniques. Nevertheless, one significant drawback of AOPs is the production of lateral compounds, such as TBA, tert-butyl formate (TBF) and acetone. The removal of these components from water is also problematic (Xu, Z. *et al*, 2003).

1.2.4. Biological treatments.

The biological treatments can be separated into two processes. One degrades the MTBE at aerobic conditions and the other at anaerobic conditions. At anaerobic conditions MTBE is used as a carbon and energy source for bacterial cultures (J. Stocking, A. *et al*, 2000). This is only possible when there is a low amount of organic carbon content. The degradation of MTBE can be enhanced by the addition of iron (III) and humic substances, such as humic acid. Nevertheless, in the presence of TBA, a high concentration of iron (III) and of humic substances is necessary to ensure the degradation of both components, MTBE and TBA (T. Finneran, K. and R. Lovley, D., 2001).

In the aerobic treatment MTBE also serves as a substrate for bacterial cultures (A. Deeb, R. *et al*, 2000). It is possible to totally degradate MTBE into CO₂ by a direct metabolism (A. Deeb, R. *et al*, 2000). However, this can only be done at MTBE concentrations around 200 mg/L, low flows and with high residence times (A. Deeb, R. *et al*, 2000). Intermediate products of the MTBE degradation, such as TBA or TBF, show even slower degradation times than MTBE. In figure 1.1 the different pathways for the degradation of MTBE can be identified. One

hydrophilic and has a lower Henry's coefficient than MTBE. It can hardly be removed by GAC sorption or air stripping. Furthermore, the separation by an adsorption process does not produce lateral compounds. The only compounds that can cause a decrease in selectivity during MTBE removal are those which already exist in the groundwater, such as humic acid. The main disadvantages of the use of synthetic resins are fouling and their price, because they are not widely used (Melin, G., 2000).

1.3. Alternative approach MTBE removal technique.

1.3.1. Solvent impregnated resin.

Solvent impregnated resins (SIR) are porous synthetic resins, in which an extractant is immobilized inside the pores, see figure 1.2.

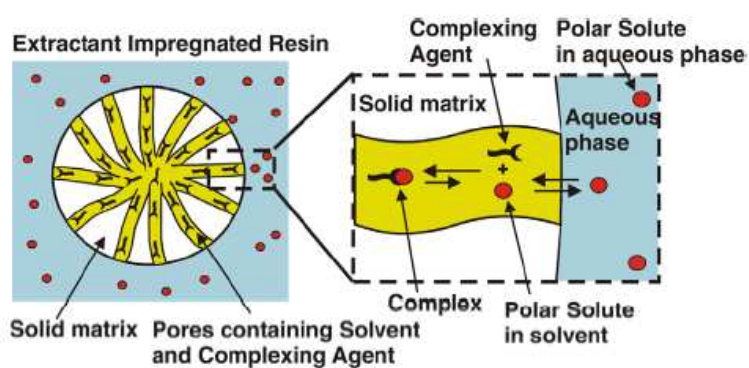


Figure 1.2 – Extractant impregnated resins (Bábic, K. *et al*, 2006).

It is desirable to use an extractant which is able to form complexes with the solute to shift the extraction equilibrium to the organic phase. When contacted with an aqueous phase containing a polar contaminant, the contaminant will diffuse into the pores and form complexes with the extractant. The reaction should be reversible to assure regenerability of the resin, but should still be strong enough to increase the affinity of the contaminant towards the organic phase.

SIRs are a synergy between adsorption and reactive extraction combining high capacity and high selectivity with simple equipment and operation (Bábic, K. *et al*, 2006). This technique avoids emulsification and can decrease the solvent loss, problems which are frequently encountered in liquid-liquid extraction. Another advantage of SIRs lies in the possibility of choosing an optimum extractant. This way, SIRs can be tailor-made to solve a specific contamination problem obtaining high removal efficiencies (MPPSystems,2004).

SIRs have a very large spectrum of uses, such as removal of dissolved and dispersed hydrocarbons from water (MPPSystems,2004) or removal of metals, such as copper or zinc, from contaminated solutions (S. Juang, R. and C. Lin, H., 1995; Saha, B: *et al*, 2004; G.

Strikovskiy, A. *et al*, 1996; Kabay, N, *et al*, 2004). However, many of these applications are just performed on a bench-scale. So far, the only large-scale applications of SIRs are the removal of aliphatic, aromatic and halogenated hydrocarbons from waste water. An example for the macroporous particles used as solid support for a SIR is MPP (MPPSystems, 2001). MPP is used for the removal of hydrocarbons from water in offshore oil platforms. A very high removal efficiency can be achieved with MPP (99,9999%) in the removal of hydrocarbons with lower polarities than water (MPPSystems, 2004). In figure 1.3, a scanning electron microscopic picture of the surface structure of an MPP particle is shown.

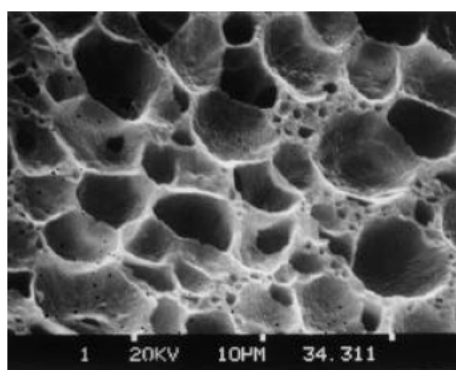


Figure 1.3 – Internal structure of MPP (MPPSystems, 2001).

The key component of a SIR is the extractant. It should be chosen according to the purpose of the remediation. Depending on the contaminant, the extractant should be highly selective in order to prevent co-extraction of other components, which can decrease the capacity of SIR. Other requirements for the extractant, the polymeric matrix, and the impregnation method are the following (Bábic, K., 2006):

- The extractant must either be a liquid or be retained as one by the addition of a diluent;
- Extractant and diluent should have minimal solubility in the aqueous phase, as mentioned before;
- The polymeric matrix should be fully expanded during impregnation and it should remain so;
- The impregnation method should not destroy the properties of the extractant or the polymer.

There are several methods to perform the impregnation of a resin (S. Juang, R., 1999). Among these methods, the dry method and the wet method, see figure 1.4, are the most usual. The dry method requires the extractant to be dissolved in a diluent and contacted with the resin. The diluent is then removed by slow evaporation under vacuum. This method is particularly suitable for hydrophilic extractants (S. Juang, R., 1999). The wet method involves the extractant to be dissolved in a pre-calculated amount of diluent, and contacted with the resin until the

liquid phase is completely absorbed by the solid phase (L. Cortina, J. and Warshawsky, A., 1997). In the removal of metals from aqueous solutions with a SIR further treatment can be necessary (S. Juang, R., 1999).

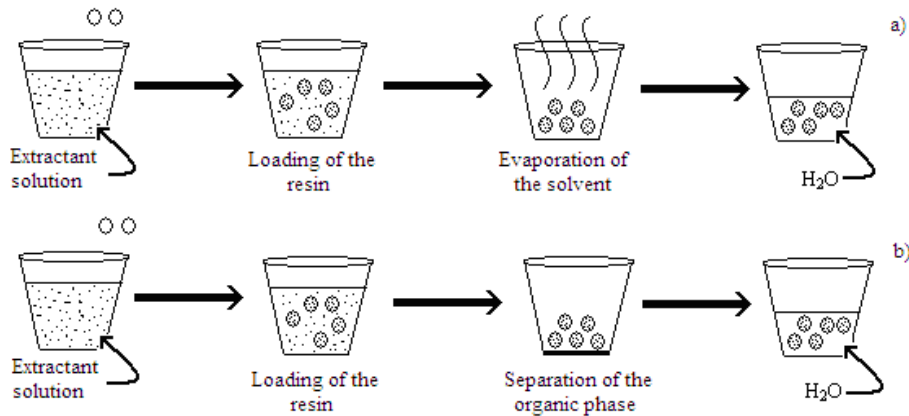


Figure 1.4 – Description of the different impregnation methods. a) Dry method; b) Wet method (L. Cortina, J. and Warshawsky, A., 1997).

The solute removal process with SIRs can be interpreted as follows: (1) the contaminated groundwater passes through a column packed with SIR; (2) the contaminant will react with the extractant and will be extracted from the groundwater; (3) when the saturation of the SIR is reached, its regeneration starts. This regeneration can be performed with steam. The extraction can restart once the SIR is regenerated, see figure 1.5.

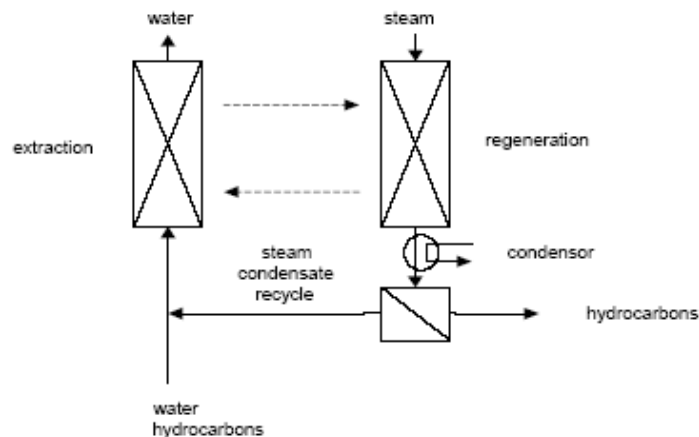


Figure 1.5 – Schematic overview of macro porous polymer extraction process (MPPSystems, 2004).

Recent studies indicate that this kind of extraction has good perspectives in the near future (MPPSystems, 2004; S. Juang, R. and C. Lin, H., 1995; Saha, B. *et al*, 2004; G. Strikovskiy, A. *et al*, 1996; Kabay, N. *et al*, 2004).

1.4. Objective

The main goal of this research project is to investigate the most suitable system in order to remove MTBE from contaminated groundwater with solvent impregnated resins. MTBE has to be removed from groundwater either to avoid further contamination or to obtain high purity streams. To achieve the objective the following topics are studied:

- Extractant screening;
- Diluent screening;
- Adsorbent screening;

Two extractants are tested 3-iodophenol (IPhOH) and 3,5-dimethyl-4-iodophenol (DMIP). These compounds are solid at room temperature, thus they have to be solubilized. In order to achieve the best possible extraction six diluents are tested: toluene, nonane, nonanoic acid, decanol, propylbenzene, phenyldodecane and octanonitrile. The best pair extractant/diluent is used for impregnation.

Because the SIR implies adsorption on solids, an important feature is the solid matrix of the resins. Based on literature four adsorbents are investigated. These are macroporous polypropylene particles MPP, polyacrylate Amberlite XAD-7, carbonaceous resin Amborsorb XE-348F and granular activated carbon AquaSorb 202.

The best resin is then impregnated and the isotherm of extraction of MTBE is determined. The isotherm of ETBE is also studied. Additionally the selectivity of the SIR for MTBE, TBA and humic acid is investigated for the best system.

In order to determine the breakthrough for the best system tested, column experiments were performed.

2. Materials and Methods.

2.1. Substances.

The chemicals used in this project are 3-iodophenol (> 98%, Sigma-Aldrich Chemie GmbH, Germany), toluene (> 99%, Sigma-Aldrich Chemie GmbH, Switzerland), nonane (> 99%, Sigma-Aldrich Chemie GmbH, Germany), 1-decanol (> 99%, Merck Schuchardt, Germany), methyl tert-butyl ether (> 99%, Merck KGaA, Germany), nonanoic acid (>98%, TCI Europe, Netherlands), heptyl cyanide (> 97%, Sigma-Aldrich Chemie GmbH, Germany), 3,5-Dimethyl-4-iodophenol (> 98%, ABCR GmbH & Co. KG, Germany), phenyldodecane (>99%, Merck Schuchardt, Germany), propylbenzene (> 98%, Sigma-Aldrich Chemie GmbH, Germany), tert-butyl alcohol (>99,7%, Sigma-Aldrich GmbH, Germany), humic acid (Sigma-Aldrich GmbH, Switzerland). The reagents were used without further purification.

The polymeric resins that were used are the MPP (Akzo MPP Systems, Netherlands), Amberlite XAD-7 (Rohm and Haas Company, France) and Amborsorb XE-348F (Sigma Aldrich Chemie GmbH, USA). The resins were used without further treatment. The granular activated carbon used is AquaSorb 202 (Jacobi Carbons, Germany).

2.2. Liquid-liquid Extraction.

Liquid-liquid extraction experiments with 3-iodophenol (IPhOH) were conducted for different concentrations of the extractant. As IPhOH is solid at standard conditions, it was diluted with different diluents, namely phenyldodecane, decanol, nonanoic acid, heptyl cyanide to give concentrations of 0,5, 1,5 and 2,5 mol/L_{diluent}. For toluene and propylbenzene IPhOH was solubilized up to 10 and 6 mol/L_{diluent}. Pure diluent was also used in each case. The ratio between the aqueous phase and the organic phase was 5:1. The initial concentration of MTBE was 5000 ppm in the aqueous phase. The two phases were then stirred for 16h at 500 rpm in a closed 50ml Erlenmeyer flask to ensure that the equilibrium was reached. After this the stirring was stopped and the solutions were left on the work-bench for 2h for gravimetric phase separation. The experiments were performed at room temperature (20 °C) and atmospheric pressure. The liquid-liquid extraction was also performed for constant concentration of IPhOH (2,5 mol/L_{diluent}) in propylbenzene changing the concentration of MTBE in the aqueous phase between 500 and 45000ppm

3,5-dimethyl-4-iodophenol (DMIP) also is a solid at standard conditions. Due to its low solubility in toluene (<0,3g/mL), phenyldodecane, nonanoic acid and heptyl cyanide the DMIP was diluted in decanol (maximum concentration 1,5 mol/L_{diluent}). Therefore experiments were performed at 0,5 and 1,5mol/L_{diluent}. Pure diluent was also tested. The liquid-liquid extraction experiments with DMIP were performed as mentioned above.

2.3. Isotherm experiments.

Isotherm experiments were conducted in 10 mL glass bottles. In each bottle 0,3 g of adsorbent were introduced. The bottles were then filled with solutions of different concentrations of MTBE, see below. The two phases were then magnetically stirred for 24h in case of Amberlite XAD-7 and MPP resins to ensure that equilibrium was reached (Hung, Hsu-W. and Lin, Tsair-F., 2006). For the Ambersorb XE-348F and the Aquasorb 202 the phases were stirred for 5 days according to literature (Melin, G., 2000; Hung, Hsu-W. and Lin, Tsair-F., 2006) , to ensure that equilibrium was reached. The samples were stirred at 500 rpm. The resins were used without further treatment.

The SIR extraction experiments were performed with Ambersorb XE-348F fully impregnated with toluene/IPhOH and propylbenzene/IPhOH. Amberlite XAD-7 and MPP were impregnated with propylbenzene/IPhOH. In order to avoid extractant loss in the experiments with toluene/IPhOH, the aqueous phase was saturated with these components prior to use. To ensure equilibrium the phases were stirred for 5 days for impregnated Ambersorb XE-348F and 24h for impregnated Amberlite XAD-7 and impregnated MPP. The stirrer speed used was 750rpm. Isotherm experiments were performed at room temperature (20 °C) and atmospheric pressure.

For all experiments the aqueous concentration of MTBE ranged from 500 to 45000 mg/L. Regarding the extraction of ETBE with a SIR the concentrations were set in the range of 500 to 20000 mg/L, as ETBE has a lower water solubility than MTBE.

2.4. Impregnation method.

Ambersorb XE-348F was impregnated with toluene/IPhOH and propylbenzene/IPhOH, respectively, with a concentration of 2,5 mol/L_{diluent}. The resin was put in a solution of extractant and left for 48h in a 50 ml Erlenmeyer. Due to the existence of micropores in Ambersorb XE-348F the flasks were then put in an ultrasonic bath to ensure full impregnation. Resin was assumed fully impregnated when no air bubbles were noticed for at least 30 minutes. For impregnation of Amberlite XAD-7 and MPP the beads were put in the extractant solution and left for 24h. Due to the lack of micropores in these particles, no ultrasound needed to be applied during impregnation. The solvent impregnated resins were then separated from the solution, washed with water saturated with toluene and IPhOH or propylbenzene and IPhOH and left to dry. The SIR was considered dry when it did not form clusters.

2.5. Selectivity experiments.

The selectivity experiments were carried out in 20mL amber bottles. The mass of impregnated resin was 0,3g. The resin used was MPP impregnated with propylbenzene and IPhOH (2,5mol_{IPhOH}/L_{diluent}). The selectivity of the SIR was studied between MTBE and humic

acid and MTBE and TBA. The concentrations of MTBE and of humic acid used are depicted in table 2.1 (Melin, G.,2000).

Table 2.1 – Concentrations of MTBE and humic acid used for different experiments.

	Exp. 1	Exp. 2	Exp.3	Exp.4
Initial concentration of MTBE (mg/L)	92	14	7	1
Initial concentration of humic acid (mg/L)	3	1,5	1	0,5

In case of TBA, its concentrations ranged between 0,5 and 32mg/L and the concentrations of MTBE were in the same range as for the study of the selectivity with humic acid. Nevertheless, severe problems were encountered during TBA analysis, such as varying peak area of the same sample and insufficient peak separation between MTBE and TBA. Since the development of a suitable analysis method is a longsome process, these experiments could not be analyzed within the timeframe of this project.

2.6. Column experiments.

The column experiments were carried out in a stainless steel column with a length of 118 mm and internal diameter of 8 mm. Besides the column, the set-up consisted of a HPLC pump K1001 Wellchrom and a 2142 differential refractometer, LKB Bromma connected via a Penlab module to a PC for online detection, see figure 2.1. The feed stream used had an MTBE concentration of 5000ppm. Different flows were used in a range of 5 to 15mL/min. The SIR used was MPP impregnated with a solution of $2,5\text{mol}_{\text{IPhOH}}/\text{L}_{\text{diluent}}$.

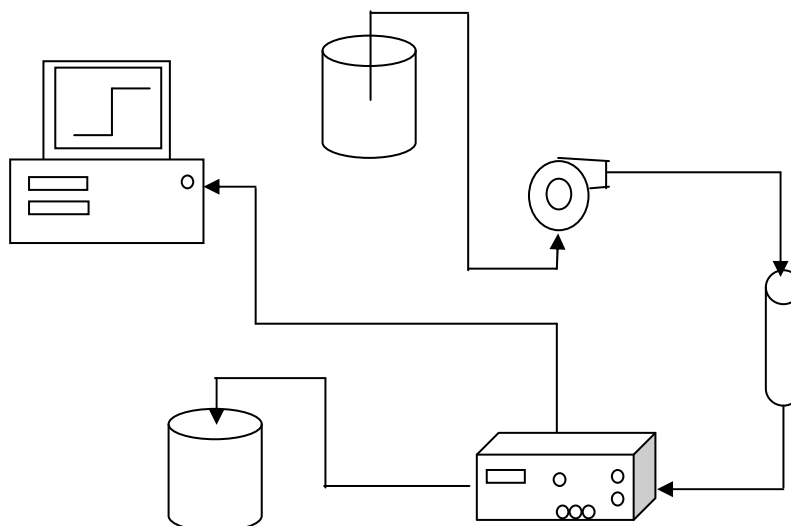


Figure 2.1 – Set-up used for the column experiments.

2.7. MTBE analysis.

Two different methods were evaluated for the analysis of MTBE in the aqueous phase. These are direct aqueous injection and headspace gas chromatography (HSGC). The advantages of direct aqueous injection are the simplicity and speed of analysis (C. Schmidt, T *et al*, 2001). Very low sample volume is needed and duplicate or triplicate analyses are easily carried out (C. Schmidt, T *et al*, 2001). However, serious problems were encountered during the analysis. On the one hand, a lack of reproducibility occurred and the retention times changed in each analysis. On the other hand, column bleeding was observed in the chromatograms. These problems exist because gas chromatography analyses are usually conducted in silica columns. These kinds of columns are very sensitive to water. The analysis of MTBE is then affected by the elution of the stationary phase from the column. Due to these problems HSGC was eventually preferred. This technique uses the partitioning of compounds from the aqueous phase to the gas phase in a closed system. The transfer of MTBE to the gas phase is enhanced by thermostatic control of the samples at 70 °C (C. Shmidt, T *et al*, 2001). In this investigation the vials were heated up to 70 °C. To ensure that phase equilibrium was reached each vial was agitated for 10 minutes before the injection. Calibration was done using an external standard. The concentration of MTBE in organic and solid phases was calculated by a simple mass balance (Bábic, K., 2006).

Samples for analysis were prepared in 20 ml vials. In each vial an equal amount of aqueous phase was added, in order to have the same distribution between aqueous and vapor phase. A headspace was left in the vials. To measure the concentration of MTBE at equilibrium, the aqueous phase was analyzed by HSGC in a CombiPal Atas Focus (Atas GL International B.V., Netherlands) with a Varian CP-3800, gas chromatograph including an 11/70 injector. The column used was a capillary column CP 8945, factor four, VF-5ms, with 30m length, 0,25mm internal diameter and 0,50 µm of film thickness connected to a FID.

3. Results and Discussion

3.1. Liquid-liquid extraction.

3.1.1 Effect of the diluents.

The main objective of performing the liquid-liquid extraction is to determine the best suitable diluent for the extractant 3-iodophenol (IPhOH). The diluents which were investigated were toluene, 1-decanol, nonanoic acid, heptyl cyanide, nonane, phenyldodecane and propylbenzene. It was observed that the diluents nonane and phenyldodecane did not solubilize the extractant IPhOH to a sufficient degree to conduct LLE experiments. Solubility of IPhOH in decanol and nonanoic acid was sufficient, but stirring was needed to facilitate solubilization. Toluene, heptyl cyanide and propylbenzene were the diluents that solubilized the extractant best in this study.

To quantify the extraction of MTBE from the aqueous phase, the distribution coefficient K_D was determined for each pair diluent/extractant, its definition will be presented next. As mentioned before, the aqueous concentration was determined by HSGC and the concentration of MTBE in the organic phase was determined by a simple mass balance as given in equation 3.1.1.

$$V^{aq}(C_{MTBE,i}^{aq} - C_{MTBE,f}^{aq}) = V^{org} C_{MTBE,f}^{org} \quad (3.1.1)$$

By plotting the distribution coefficients for the different experiments as a function of the concentrations of the extractant it is possible to determine which diluent is most suitable for the MTBE removal, see figure 3.1.1. As can be seen in figure 3.1.1 for all the different diluents the distribution coefficients increase with the increasing concentration of IPhOH. Toluene and propylbenzene are the diluents that result in the highest distribution coefficients. For 1-decanol, nonanoic acid and heptyl cyanide it can be seen that this increase is significantly less pronounced than for the pairs toluene/IPhOH and propylbenzene/IPhOH. This suggests that the diluent plays an important role in the extraction. The fact that the diluents 1-decanol, nonanoic acid and heptyl cyanide give lower K_D 's with IPhOH than toluene with IPhOH or propylbenzene with IPhOH may imply hydrogen bonding between these diluents and IPhOH. In case of toluene and propylbenzene this hydrogen bond is not possible. Hydrogen bonding between extractant and diluent will reduce the capacity of the extractant for MTBE, as MTBE also forms complexes with the extractant by hydrogen bonding.

The approximate maximum concentrations of IPhOH in 1-decanol, nonanoic acid and heptyl cyanide only go up to 2,5 mol/L_{diluent} due to the low solubility of the extractant in these diluents at room temperature (20 °C). In toluene the solubility of IPhOH is around 12 mol/L_{diluent}. For the pair propylbenzene/ IPhOH the K_D increases with the increase of the

concentration of the extractant (M. Lankvelt, B., 2008). The LLE performance with this pair diluent/extractant is similar to the LLE performance with the pair toluene/ IPhOH.

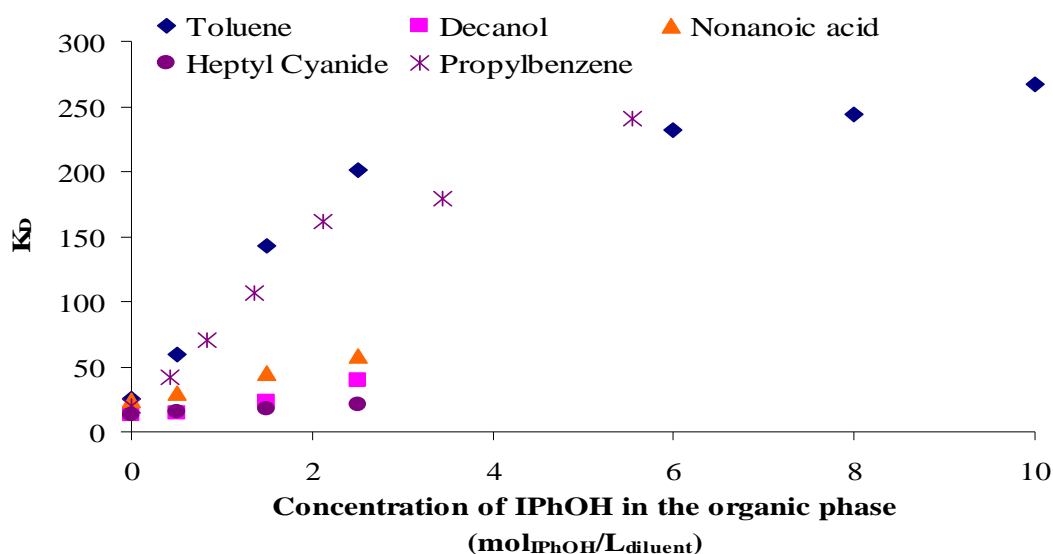


Figure 3.1.1 – Graphical representation of the distribution coefficient K_D versus the concentration of the IPhOH in the diluent (initial MTBE concentration = 5000ppm).

With the pair toluene/ IPhOH a significantly lower increase of the slope can be seen after an extractant concentration of 2,5 mol/L_{diluent}. Apparently, a high degree of MTBE removal is already reached at extractant concentrations of approximately 6 mol/L_{diluent}. An additional increase of extractant concentration in the organic phase does not provide a significantly better extraction. This fact might be caused by extractant and diluent loss to the aqueous phase. Also co-extraction of water might play a role. Another possibility for such a *plateau* may be dimerization of the extractant. In table 3.1.1 the physical distribution coefficients K_{ph} for the five diluents are depicted. However, the physical distribution coefficients for decanol, nonanoic acid and heptyl cyanide may also involve chemical distribution, as hydrogen bonds occur between these diluents and MTBE.

Table 3.1.1 – Physical distribution coefficients for the different pairs diluent/extractant.

Diluent	K_{ph}
Decanol	12,996
Nonanoic acid	24,618
Heptyl cyanide	12,903
Toluene	25,246
Propylbenzene	19,617

In order to determine the complexation distribution coefficient K_c a model for the overall distribution is necessary. This model is based on the mass balance of the solute and the extractant as well as the equilibrium constants see eq 3.1.2 – 3.1.6.

$$V^{aq} \cdot (C_{s,0}^{aq} - C_s^{aq}) = V^{org} \cdot (C_s^{org} + C_c^{org}) \quad (3.1.2)$$

$$C_{E,0}^{org} = C_E^{org} + C_c^{org} \quad (3.1.3)$$

In previous equations, $C_{s,0}$ and C_s represent the initial concentration and the concentration after equilibrium of the solute MTBE, respectively. C_c represents the concentration of complex formed by MTBE and IPhOH in the organic phase. $C_{E,0}$ stands for the initial concentration of IPhOH and C_E for the concentration of uncomplexed extractant after equilibrium. The superscript *aq* and *org* represent the aqueous and the organic phases, respectively.

Regarding the distribution coefficients one can define the physical distribution coefficient K_{ph} as:

$$K_{ph} = \frac{C_s^{org}}{C_s^{aq}} \quad (3.1.4)$$

The chemical complexation coefficient K_c can be defined as:

$$K_c = \frac{C_c^{org}}{C_s^{org} \cdot C_E^{org}} \quad (3.1.5)$$

The overall distribution coefficient K_D is defined as described in equation 3.1.6., where C_{total}^{org} stands for the overall MTBE concentration in the organic phase as described in equation 3.1.7.

$$K_D = \frac{C_{Total}^{org}}{C_s^{aq}} \quad (3.1.6)$$

$$C_{Total}^{org} = C_s^{org} + C_c^{org} \quad (3.1.7)$$

Rearranging equations 3.1.2 – 3.1.5 and equation 3.1.7 it is possible to define C_{total}^{org} as a function of K_{ph} , K_c and the concentration of MTBE in the aqueous phase after equilibrium:

$$C_{Total}^{org} = K_{ph} \cdot C_s^{aq} \left(1 + \frac{K_c \cdot C_{E,0}^{org}}{1 + K_{ph} \cdot K_c \cdot C_s^{aq}} \right) \quad (3.1.8)$$

With equations 3.1.6 and 3.1.8, the overall distribution coefficient K_D can be described as follows.

$$K_D = K_{ph} \cdot \left(1 + \frac{K_c \cdot C_{E,0}^{org}}{1 + K_{ph} \cdot K_c \cdot C_s^{aq}} \right) \quad (3.1.9)$$

This model will be referred as MLL in the future. For determination of the complexation distribution constant the fitting of the experimental data has to be done, see figure 3.1.2.

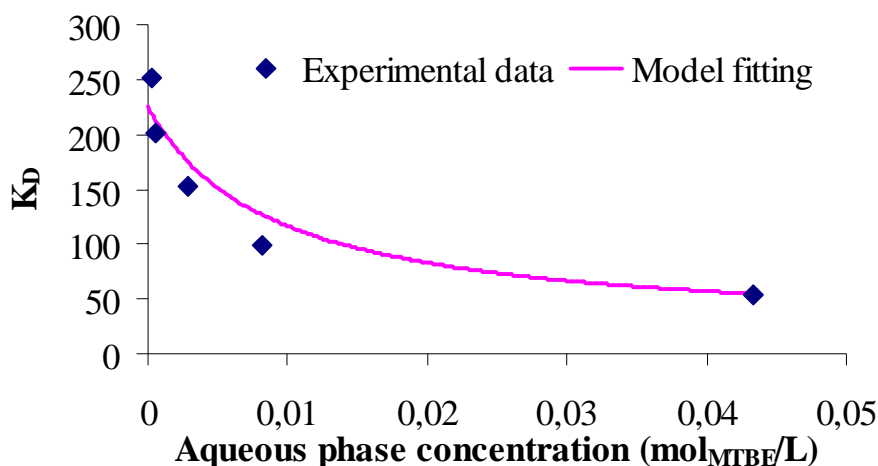


Figure 3.1.2 – Graphical representation of the overall distribution coefficient K_D versus the concentration of MTBE in the aqueous phase, for the experimental data and the model.

Figure 3.1.2 shows the relation between K_D and the MTBE concentration in the aqueous phase for the system propylbenzene/IPhOH. After the fitting the K_C was determined as 5,72. The correlation coefficient of this fitting was 0,991.

3.1.2 Extractant comparison.

The comparison between IPhOH and 3,5-dimethyl-4-iodophenol (DMIP) had to be done with decanol as diluent. This is, because DMIP does not dissolve in the other tested diluents. It also has a low solubility in decanol, which is why DMIP could only be dissolved up to a concentration of 1,5 mol/L_{diluent}. The results are presented in figure 3.1.3, where the determined K_D values are depicted over the concentration of the extractant in the diluent.

It can be seen in figure 3.1.3 that the K_D increases with the increase in the concentration of IPhOH and DMIP, respectively. However, the overall increase of the K_D is less pronounced for DMIP than for IPhOH. The reason for this could be an inductive effect created by the two methyl groups of the DMIP. Inductive effects are caused by the transmission of charge through a chain of atoms by electrostatic induction (Schröter, W. *et al*, 1990). In case of IPhOH, the iodine causes a $-I$ effect, which lowers the electron density of the hydrogen of the OH group. This way, the respective hydrogen atom has a slightly higher partial positive charge than it would have in an ordinary phenol molecule. In case of DMIP, the two additional CH_3 groups cause a $+I$ effect, which weakens the $-I$ effect of the iodine. Thus, the hydrogen of the OH

group in DMIP has a slightly lower partial positive charge than IPhOH. This can be a reason why hydrogen bonding between IPhOH and MTBE is more effective than between DMIP and MTBE.

The lower capacity of DMIP compared to IPhOH and the lack of a suitable diluent suggests that this component is less suitable for MTBE extraction than IPhOH.

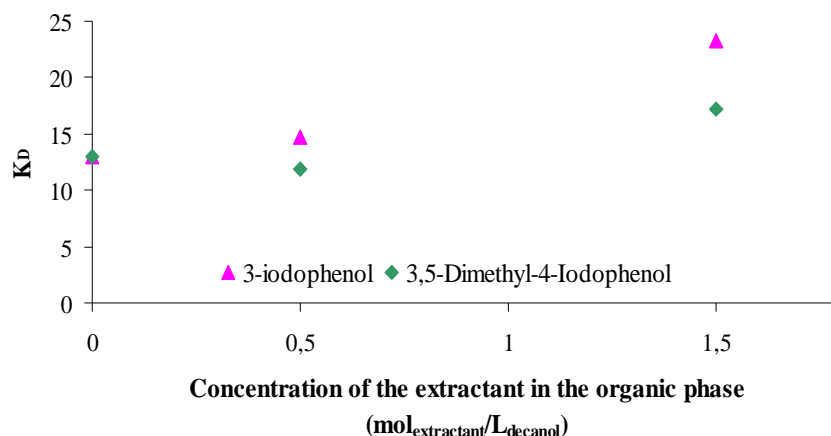


Figure 3.1.3 – Graphical representation of the distribution coefficient K_D versus the concentration of IPhOH and DMIP.

3.1.3. Eutectic point.

In order to avoid the problems encountered with the diluents, such as low solubility of the extractant and hydrogen bonding between extractant and diluent, the eutectic point between the two possible extractants, IPhOH ($T_m = 44$ °C) and DMIP ($T_m = 130$ °C) is calculated. Mixing these two components could provide an extractant blend, which is liquid at room temperature. Thus, there would be no need for a diluent any more. The eutectic point was calculated assuming that the solids are immiscible when they are in the solid phase and that they can form an ideal liquid solution when liquefied. The calculations were made using the Clausius – Clapeyron equation 3.1.10 for IPhOH and equation 3.1.11 for DMIP (M. Smith, J and C. Van Hess, H., 1975). This equation relates the melting enthalpy, the temperature and the composition in the liquid phase. In fact, the melting enthalpy can be found by the slope of a plot $\ln(x)$ vs $1/T$ (A. Gokcen, N., 1996).

$$x_{IPhOH} = e^{\left[\frac{\Delta H_{m,IPhOH}^{S-L}}{R \cdot T_{m,IPhOH}} \left(\frac{T - T_{m,IPhOH}}{T} \right) \right]} \quad (3.1.10)$$

$$x_{DMIP} = 1 - e^{-\left[\frac{\Delta H_{m,DMIP}^{S-L}}{R \cdot T_{m,DMIP}} \left(\frac{T - T_{m,DMIP}}{T} \right) \right]} \quad (3.1.11)$$

Since the melting enthalpies of the components are unknown, equation 3.1.12 was used (De Haan, A., 2008).

$$\Delta H_m = \frac{R}{2} T_m^{4/3} \quad (3.1.12)$$

R is the gas constant and T_m is the melting temperature in Kelvin. Figure 3.1.4 shows the eutectic point of the system IPhOH/DMIP.

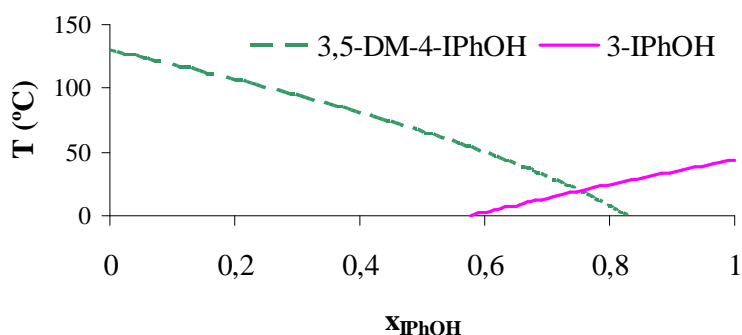


Figure 3.1.4 – Eutectic point of the system IPhOH/DMIP.

As can be seen in figure 3.1.4, the calculated eutectic point for this system is 19 °C. However, when tested, the mixture started to melt at 27 °C. This is too high for an application of this system at standard conditions. The deviation of the calculated eutectic point from the experimentally determined one is due to the assumptions in the calculations. The equations given above assume that the mixture is an ideal one. That is not the case. An error is also introduced by equation 3.1.12, as it is just an empirical estimation of the melting enthalpy.

3.2. Adsorption on unimpregnated sorbents.

The main objective of performing adsorption experiments was to determine which adsorbent has the best affinity for MTBE. For this purpose four different adsorbents are tested, namely polypropylene MPP, non-ionic aliphatic acrylic Amberlite XAD 7, carbonaceous resin Amborsorb XE-348F and activated carbon Aquasorb 202. The best adsorbent of the tested ones is then used as a solid support for the extractant in order to combine its adsorptive capacity with the capacity of the immobilized extractant. In figure 3.2.1 the isotherms of the MTBE adsorption experiments are given.

Figure 3.2.1 shows that amongst the adsorbents tested the Ambersorb XE-348F has the highest adsorption capacity, while the MPP has the lowest adsorption capacity. The adsorption capacity of XAD-7 is only slightly higher than the adsorption capacity of MPP. The MTBE adsorption capacity of Aquasorb 202 is higher than the capacity of MPP and of XAD-7. The reason why Ambersorb XE-348F is the best MTBE adsorbent may be the presence of micropores in the carbonaceous resin. These micropores, formed by the pyrolysis of the ion-exchange resin, are the reason for its high efficiency during water treatment (Melin, G., 2000).

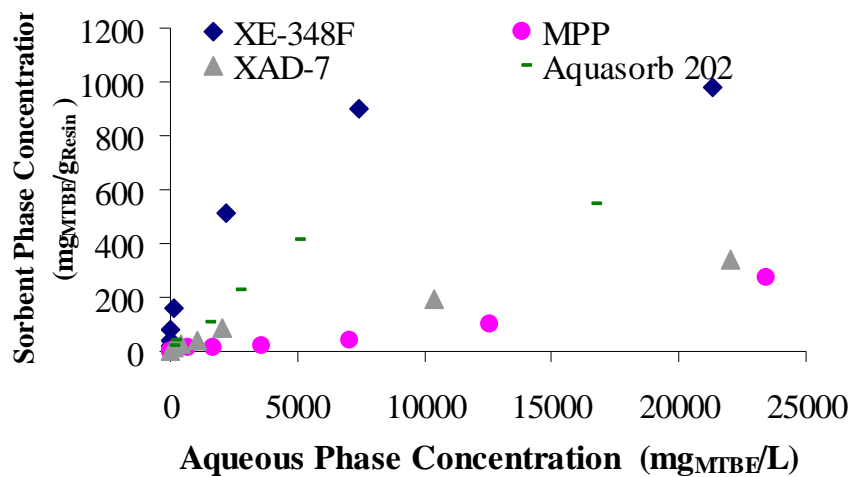


Figure 3.2.1 – Representation of the isotherms of MTBE on the different adsorbents at 20 °C.

When the isotherms are plotted in a log-log coordinate system they are linear with the exception of the MPP isotherm, see figure 3.2.2.

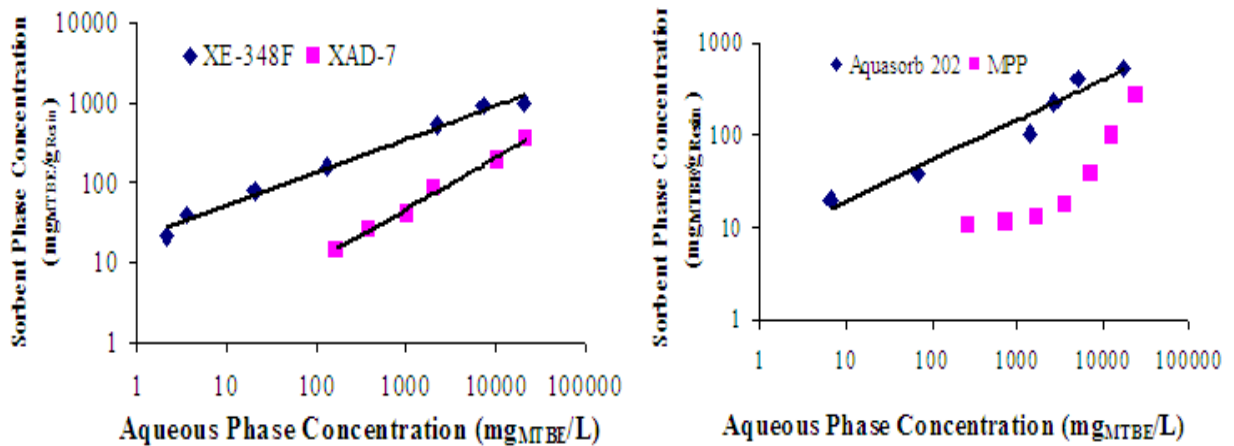


Figure 3.2.2 – Representation of the isotherms of adsorption for different adsorbents in a log-log coordinates system. a) Ambersorb XE-348F and Amberlite XAD-7; b) Aquasorb 202 and MPP.

Therefore, the Freundlich equation is adequate for describing the isotherms of MTBE on the different adsorbents with the exception of MPP. The Freundlich isotherm stands for

heterogeneous adsorbents (K. R. Hall, C. *et al*, 1966), i.e. adsorbents with a porous surface. The Freundlich isotherm also assumes that the adsorbate is polar and the adsorbent is polar or strongly polar (K. R. Hall, C. *et al*, 1966).

$$q = KC^n \quad (3.2.1)$$

The K value represents the sorption capacity and the n value is related to the energy of sorption and to site heterogeneity (Melin, G., 2000). The Freundlich parameters were determined by the least squares method and are given in table 3.2.1. The curve fittings are depicted in figure 3.2.3.

Table 3.2.1 - Freundlich isotherm parameters of the tested adsorbents

Sorbent	K (mg/g)/(mg/L) ⁿ	n	r ²
XE-348F	43,78	0,3201	0,968
XAD-7	0,4809	0,6554	0,995
Aquasorb 202	5,482	0,4783	0,939

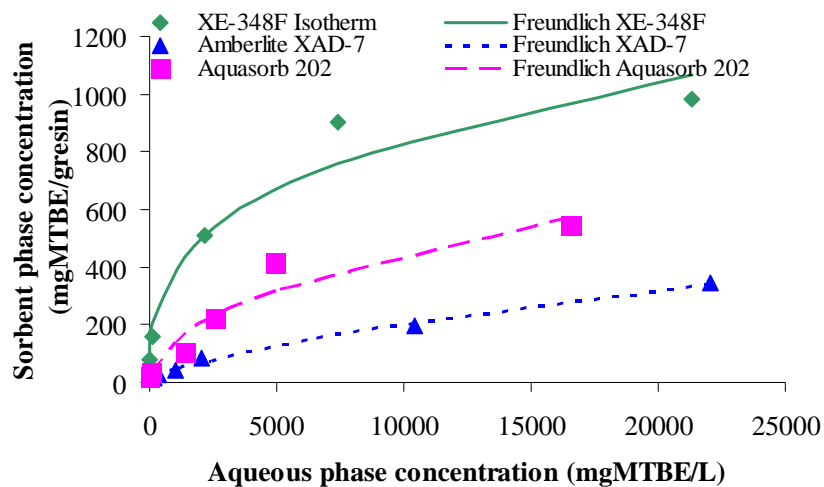


Figure 3.2.3 – Representation of the fitting isotherms for Ambersorb XE-348F, Amberlite XAD-7 and Aquasorb 202.

As can be seen in figure 3.2.3, the Freundlich isotherm describes the experimental data rather well with correlation coefficients of more than 0.9.

For the adsorption of MTBE on MPP the constant separation factor isotherm (K. R. Hall, C. *et al*, 1966), as given in eq. 3.2.2. fits the experimental data very well, see figure 3.2.4.

$$\frac{q}{q_{\max}} = \frac{C/C_{\max}}{R + (1-R)C/C_{\max}} \quad (3.2.2)$$

In equation 3.2.2 R is the constant separation factor equilibrium constant, q_{\max} is the highest experimental concentration at equilibrium in the solid phase and C_{\max} is the highest concentration at equilibrium in the aqueous phase. This isotherm is based on the mass action law. It is a simple mathematical model, which is a sub-set of the Langmuir equation (Arévalo, E. *et al*, 2000). With this isotherm many experimental systems can be represented, such as irreversible equilibrium, favourable equilibrium, linear equilibrium or unfavourable equilibrium. The constant separation factor will be different for the four different systems. $R=0$ if the system is irreversible, $R<1$ for a favourable system, $R=1$ when there is a linear system or $R>1$ for unfavourable systems (K. R. Hall, C. *et al*, 1966).

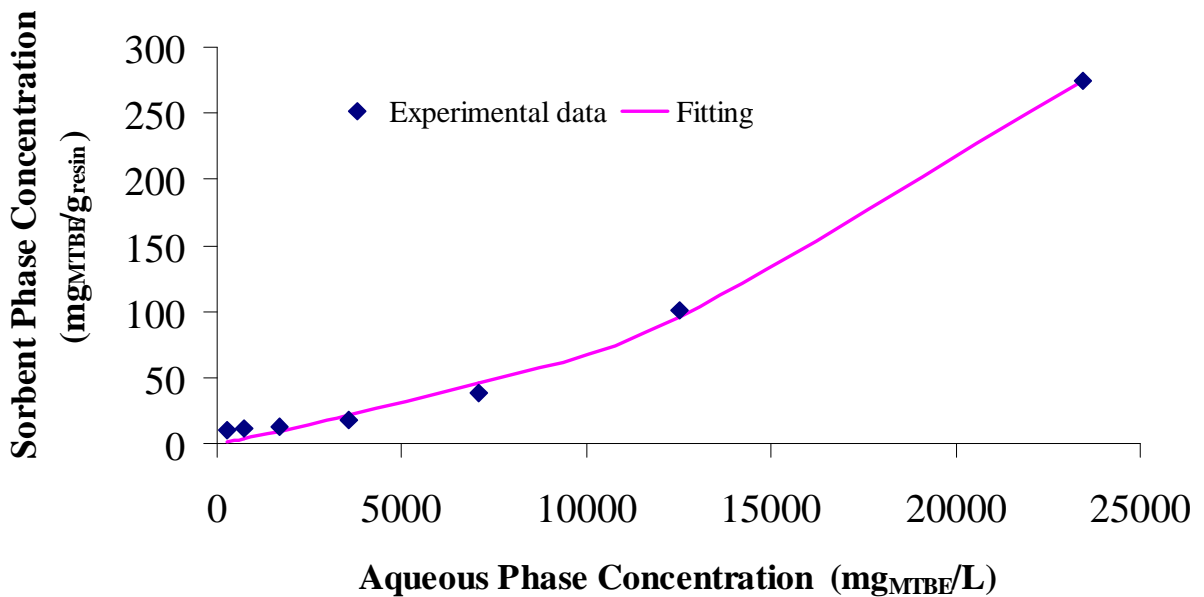


Figure 3.2.4 – Graphical representation of the experimental data for the adsorption isotherm of MTBE on MPP and the constant separation factor fit.

The constant separation factor R for this system is 2,1446 and the correlation coefficient is 0,9970.

Apparently, this is an unfavourable isotherm ($R > 1$) which will lead to a dispersive wave in an adsorption column (Guiochon, G. *et al*, 1994). The adsorbents with this type of isotherm are not often used in industry, as the breakthrough time will be different than the stoichiometric time due to the low bed length used in packed bed processes.

3.3. Adsorption on solvent impregnated resins.

3.3.1. MTBE extraction with SIR.

The first part of this sub-chapter will focus on the extraction of MTBE with impregnated Ambersorb XE-348F. In order to evaluate the removal capacity of solvent impregnated resins, Ambersorb XE-348F was impregnated with two pairs of diluent/extractant, namely toluene/IPhOH and propylbenzene/IPhOH. In figure 3.3.1 the extraction isotherms of MTBE on Ambersorb XE-348F impregnated with the pairs toluene/IPhOH and propylbenzene/IPhOH are given. The concentration of the extractant was of 2,5 mol/L_{diluent}.

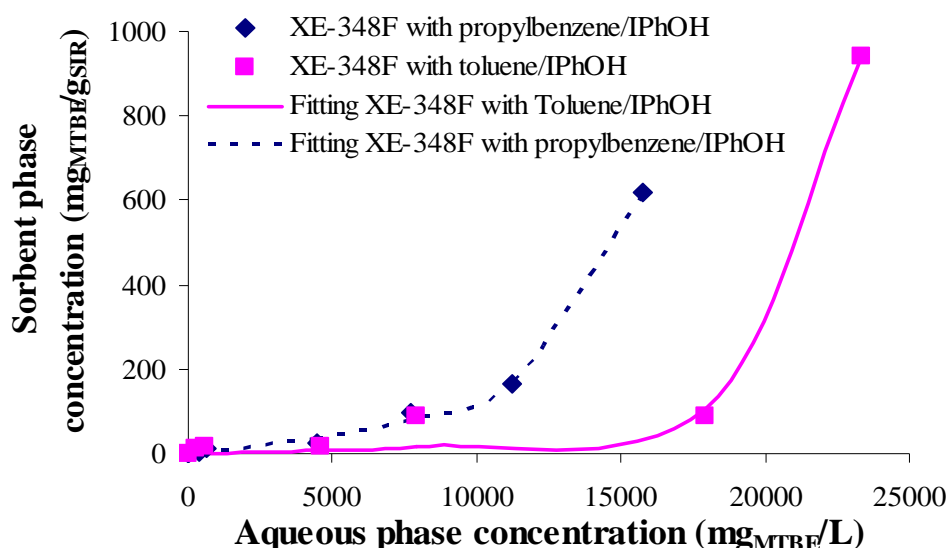


Figure 3.3.1 – Graphical representation of the experimental data for the adsorption isotherm of MTBE on solvent impregnated Ambersorb XE-348F and the constant separation factor fit.

As can be seen in figure 3.3.1, the impregnation of the carbonaceous resin Ambersorb XE-348F causes a significant decrease of MTBE capacity at concentrations below 20 000 mg_{MTBE}/L. Furthermore, the isotherms of impregnated Ambersorb XE-348F are now unfavourable. Before, the unimpregnated resin had a favourable isotherm. Such effect may be caused by the fact that this type of resin has micropores, which are crucial for their high solute capacity in water treatment as they have relatively non-polar surfaces (Melin, G., 2000). The micropores might be filled or blocked by the impregnated extractant. The adsorption of extractant by the resin, which decreases the number of active sites, may also be an explanation

for these results. Another reason may be a too low extractant capacity inside the pores of the resin, as the particles are relatively small.

The fitting of the isotherms presented above were done using the constant separation factor, as in the previous case of the adsorption of MTBE with unimpregnated MPP. The constant separation factor isotherm parameters were determined by the least squares method and are stated in table 3.3.1. The curve fittings are depicted in figure 3.3.1. Apparently, the fitting is describing the experimental data well, which means that this isotherm can be reliably used in this case.

Table 3.3.1 – Constant separation factor isotherm parameters for the adsorption of MTBE in the different SIR.

System	R	r ²
Amborsorb XE-348F impregnated with toluene/IPhOH	26,3708	0,991
Amborsorb XE-348F impregnated with propylbenzene/IPhOH	6,3339	0,998

Since impregnated Amborsorb XE-348F did not have the expected high MTBE capacity, two other resins were evaluated for impregnation. These two resins are MPP and Amberlite XAD-7. The impregnation of these resins was done with propylbenzene/IPhOH. The concentration of IPhOH was 2,5 mol/L_{diluent}. The activated carbon Aquasorb 202 was not considered for impregnation as its life time is about 10 to 20 cycles after which the activated carbon must be incinerated (B. Ray, A. *et al*, 2003).

The extraction of MTBE on fully impregnated Amberlite XAD-7 and fully impregnated MPP resulted in two linear isotherms, see figure 3.3.2. The fitting of these isotherms was made using the Freundlich isotherm. In figure 3.3.2 the fitted isotherms are also depicted.

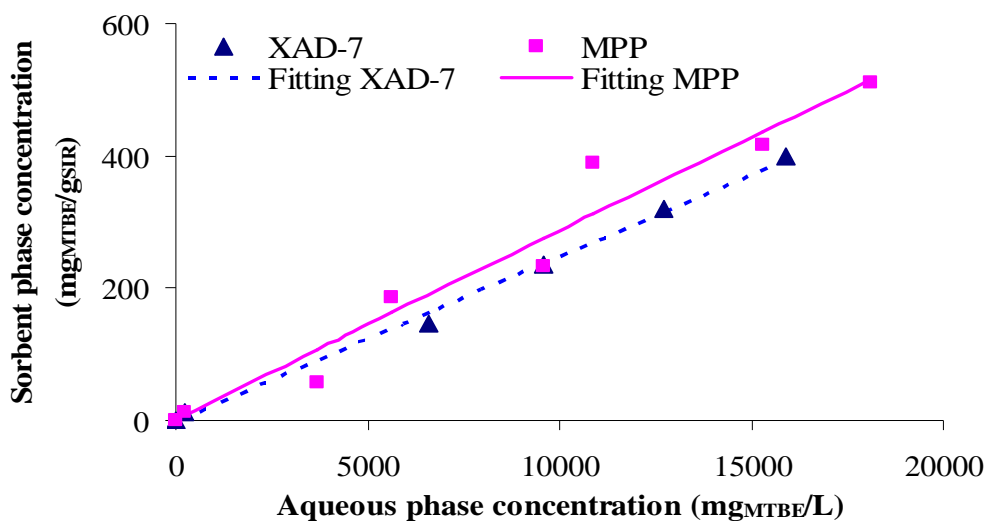


Figure 3.3.2 – Representation of the isotherms and the fitting isotherms for the adsorption of MTBE on fully impregnated Amberlite XAD-7 and fully impregnated MPP.

In table 3.3.2 the corresponding fitted parameters and the correlation coefficients are stated.

Table 3.3.2 – Freundlich isotherm parameters for the adsorption of MTBE on the fully impregnated Amberlite XAD-7 and fully impregnated MPP.

Solvent impregnated resin	K ($\text{mg}_{\text{MTBE}}/\text{g}_{\text{SIR}})/(\text{mg}_{\text{MTBE}}/\text{L})^n$	n	r^2
Amberlite XAD-7 SIR	0,02443	1	0,9800
MPP SIR	0,03235	0,9870	0,9586

Comparing the two isotherms it is possible to say that the MTBE extraction with fully impregnated MPP is better than the one with fully impregnated XAD-7. This is probably due to the higher porosity of MPP. This means that the MPP particles will have a higher amount of extractant inside the beads. Nevertheless, both fully impregnated XAD-7 and fully impregnated MPP have a better affinity for MTBE than impregnated Ambersorb XE-348F. This observation is contrary to the affinity during the adsorption of MTBE on the unimpregnated adsorbents.

When comparing the results for the adsorption on fully impregnated XAD-7 and the adsorption on unimpregnated XAD-7 it is possible to say that for lower concentration ($C_{\text{MTBE,aq}} < 5000$ ppm) the adsorption on unimpregnated XAD-7 is better than for the fully impregnated XAD-7. However, for high concentration of MTBE in water ($C_{\text{MTBE,aq}} > 5000$ ppm) the SIR has a higher MTBE capacity for it, see figure 3.33–a). In case of MPP the isotherm of unimpregnated MPP is unfavourable and when the MPP particles are impregnated it presents a linear isotherm, thus favourable, see figure 3.3.3–b).

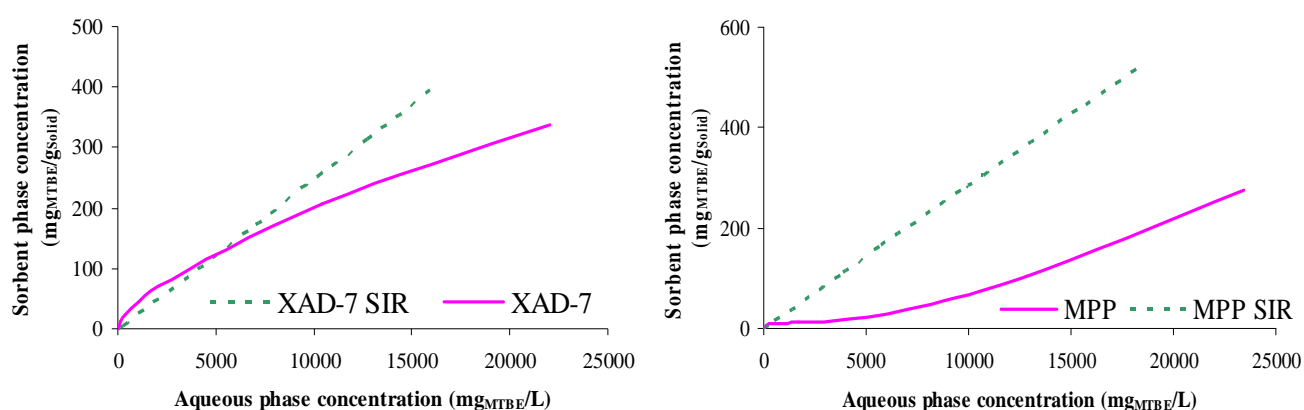


Figure 3.3.3 – Graphical representation of the isotherms of MTBE on: a) fully impregnated Amberlite XAD-7 and unimpregnated Amberlite XAD-7; b) fully impregnated MPP and unimpregnated MPP.

Such fact can occur due to the addition of a chemical complexation in the system. This chemical complexation may contribute to the linearization of the isotherms. When the resins are

unimpregnated the MTBE is recovered by its distribution between the aqueous phase and the solid phase, i.e. by a physical adsorption distribution, K_{ph}^{ads} , see figure 3.3.5–a). When the resin is impregnated, the distribution of MTBE between the phases can additionally be influenced by the solubility in the extractant phase and by a chemical complexation reaction. MTBE will physically dissolve in the mixture of propylbenzene and IPhOH, which can be described by the physical equilibrium constant K_{ph} . Then, MTBE will form complexes with IPhOH which can be described with the chemical equilibrium constant K_C , see figure 3.3.5–b). The overall distribution coefficient, K_D , will then be a function of K_{ph}^{ads} , K_C and K_{ph} . This relation between the distribution coefficients and equilibrium constants is valid for Amberlite XAD-7, as it has a certain capacity for MTBE. For MPP the relation between the equilibrium constants is also assumed valid, but the affinity of MPP for MTBE can be neglected up to a concentration of MTBE of 10000mg/L.

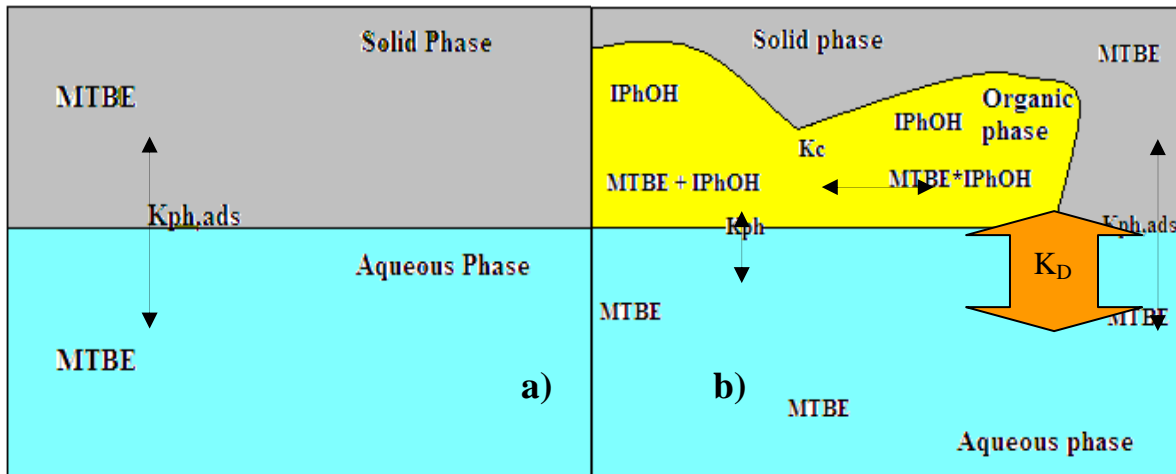


Figure 3.3.5 – Distribution of MTBE from an aqueous phase to: a) Unimpregnated resin; b) Impregnated resin.

To determine these coefficients a model is necessary. Three models were tested. The first one neglects the adsorption of the solute on the surface of the particles. This model (MLL) was derived previously in chapter 3.1.1. The other models were determined by the use of the mass balance to the system, see equation 3.3.1 – 3.3.2, the mass balance for the extractant, see equation 3.3.3 and the definition of the different distribution coefficients and equilibrium constants such as K_{ph} , K_C and the overall distribution coefficient K_D , see equation 3.3.3-3.3.5. In the two models the adsorption is considered, as said before. These equilibrium constants are different according to the porous matrix used. This will be discussed later for each case impregnated MPP and Amberlite XAD-7.

The mass balances for the two systems will be:

$$V^{aq} \cdot (C_{s,0}^{aq} - C_s^{aq}) = V^{SIR} \cdot (\epsilon_p \cdot (C_s^{SIR} + C_c^{SIR}) + (1 - \epsilon_p) \cdot C_s^{solid}) \quad (3.3.1)$$

In these equations, V^{aq} represents the volume of the aqueous phase, $C_{s,0}^{aq}$ the initial concentration of MTBE in the aqueous phase, C_s^{aq} the concentration of MTBE in equilibrium, V^{SIR} the volume of the solvent impregnated resin, C_s^{SIR} and C_c^{SIR} the concentration of physically bound MTBE in the solvent impregnated resin and the concentration of the complexes formed between MTBE and the extractant after equilibrium, respectively. ε_p stands for the porosity of the particles and C_s^{solid} for the concentration of MTBE adsorbed on the surface of the solid matrix.

The mass balance for the extractant can be written as:

$$C_{E,0}^{SIR} = C_E^{SIR} + C_c^{SIR} \quad (3.3.2)$$

In equation 3.3.2, $C_{E,0}^{SIR}$ stands for the initial concentration of IPhOH in the SIR and C_E^{SIR} for the concentration of uncomplexed extractant after equilibrium.

Regarding the distribution coefficients one can define K_{ph} as:

$$K_{ph} = \frac{C_s^{SIR}}{C_s^{aq}} \quad (3.3.3)$$

K_c as:

$$K_c = \frac{C_c^{SIR}}{C_s^{SIR} \cdot C_E^{SIR}} \quad (3.3.4)$$

K_D is defined as:

$$K_D = \frac{C_{Total}^{SIR}}{C_s^{aq}} \quad (3.3.5)$$

The value for C_{Total}^{SIR} in equation 3.3.5 is defined by equation 3.3.6 for MPP and for Amberlite XAD-7.

$$C_{Total}^{SIR} = \varepsilon_p \cdot (C_s^{SIR} + C_c^{SIR}) + (1 - \varepsilon_p) \cdot C_s^{solid} \quad (3.3.6)$$

These models state that the existence of adsorption is a fact in the extraction of the solute. The model for MPP (MMPP) will be discussed next. As it was previously said, an adsorption equilibrium constant K_{ph}^{ads} must be defined. This constant comes from the isotherm equation stated in sub-chapter 3.2 the constant separation factor isotherm. Thus for MPP this constant will be defined as:

$$K_{ph}^{ads} = \frac{x \cdot (1 - y)}{y \cdot (1 - x)} \quad (3.3.7)$$

In this equation x and y represent the mole fraction of MTBE in the aqueous and the solid phases, respectively.

Rearranging equations 3.3.1 – 3.3.4 and equations 3.3.6 and 3.3.7 it is possible to define C_{total}^{SIR} as a function of the concentration of MTBE in the aqueous phase after equilibrium as:

$$C_{Total}^{SIR} = \frac{\varepsilon_p \cdot K_{ph} \cdot C_s^{aq} \cdot \left(1 + K_c \cdot C_{E,0}^{SIR} + K_c \cdot \left(\frac{1 - \varepsilon_p}{\varepsilon_p} \cdot q^* + K_{ph} \cdot C_s^{aq} \right) \right)}{B} + (1 - \varepsilon_p) \cdot \frac{q^*}{B} \quad (3.3.8)$$

In this equation q^* is defined by equation 3.2.2, where R takes the form of K_{ph}^{ads} and B is defined such as:

$$B = 1 + K_{ph} \cdot K_c \cdot C_s^{aq} \quad (3.3.9)$$

By equation 3.3.5 it is then possible to define the overall distribution coefficient as:

$$K_D = \frac{\varepsilon_p \cdot K_{ph} \cdot \left(1 + K_c \cdot C_{E,0}^{SIR} + K_c \cdot \left(\frac{1 - \varepsilon_p}{\varepsilon_p} \cdot q^* + K_{ph} \cdot C_s^{aq} \right) \right)}{B} + (1 - \varepsilon_p) \cdot \frac{q^*}{B} \quad (3.3.10)$$

This is the final equation of the MMPP.

In order to determine K_{ph}^{ads} and K_c for the complexation of MTBE with the extractant impregnated MPP the plot of K_D vs. C_s^{aq} is essential. The fit of the experimental data was made with MLL, model defined in sub-chapter 3.1.1 and with MMPP, see figures 3.3.6 and 3.3.7. The least squares method was used to determine the fitting parameters. The fitted parameters and the correlation coefficients are depicted in table 3.3.3.

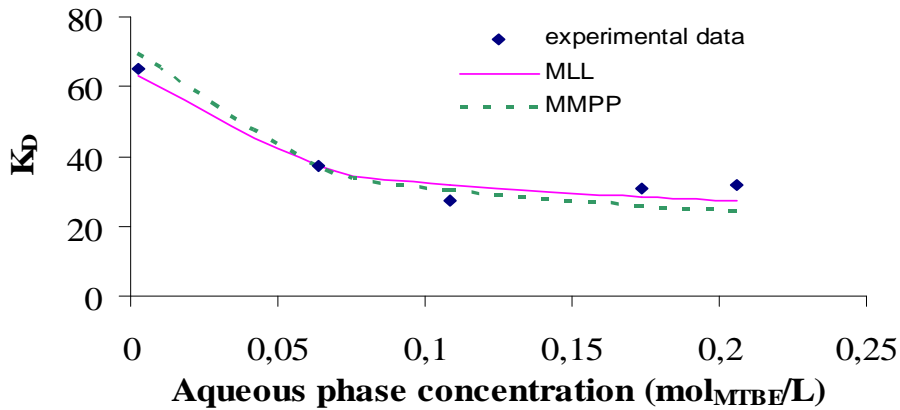


Figure 3.3.6 – Graphical representation of the overall distribution coefficient as a function of the concentration of MTBE in the aqueous phase for the experimental data and the MLL and MMPP models for the extraction of MTBE by impregnated MPP.

Table 3.3.3 – Fitted parameters for the two models and respective correlation coefficients.

System	Model	K_{ph}	K_c	K_{ph}^{ads}	$C_{s,max}^{aq}$	$C_{s,max}^{solid}$	r^2
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Impregnated MPP	MLL	19,61	1,287	-	-	-	0,9966
Impregnated MPP	MMPP	19,61	1,878	0,4864	0,2056	3,580	0,9940

The physical distribution coefficients K_{ph} were fixed as the values of K_{ph} for propylbenzene obtained from the liquid-liquid extraction experiments. The reason for such fact will be explained later. The $C_{s,max}^{aq}$ was fixed with the value of the concentration of MTBE in the aqueous phase after equilibrium for the experiment with the higher initial concentration of MTBE. $C_{s,max}^{solid}$ was fixed with the value of the concentration of MTBE on MPP after equilibrium for the experiment of adsorption of MTBE on unimpregnated MPP with the higher initial concentration. As it can be noticed the chemical complexation constant decreased relatively to the determined by the liquid-liquid extraction. Such fact can be explained by a decrease of active sites after the impregnation of the propylbenzene/IPhOH solution inside the beads. Another explanation may be a decrease in the surface area where the mass transfer occurs. In fact assuming that the beads have cylindrical shape then the area over the volume will be $\frac{2}{r}$. However in the liquid-liquid extraction a strong emulsion is created. Assuming the droplets of organic phase as spheres its ratio area:volume will be $\frac{3}{r}$. Thus, even if the beads were as many as the droplets in a liquid-liquid extraction experiment the contact area between the technique used to extract and the aqueous solution would always be smaller for the beads.

The MMPP model for the system of impregnated MPP depicted in table 3.3.3 fits the extraction well. However the model defined by MLL model gives a better fit of the extraction of MTBE on impregnated MPP. For further validation of the models the isotherms of the extraction of MTBE by SIR were fitted. These isotherms take into account the distribution of the solute between the aqueous and organic phases in the case of the MLL model and the three phases, aqueous, organic and solid for the extraction of MTBE described by the MMPP model.

The isotherm for the extraction of MTBE by SIR can be defined as:

$$q = \frac{V^{SIR} \cdot C_{Total}^{SIR}}{m_{SIR}} \quad (3.3.11)$$

For the case represented by MLL model the concentration of MTBE in the SIR can be rewritten introducing equation 3.1.8 in equation 3.3.11.

$$q = \frac{K_{ph} \cdot V_p \cdot C_s^{aq} \left(1 + \frac{K_c \cdot C_{E,0}^{SIR}}{1 + K_{ph} \cdot K_c \cdot C_s^{aq}} \right)}{m_{SIR}} \quad (3.3.12)$$

The V^{SIR} was substituted by the V_p , as this model assumes that the extraction is made only by the distribution between the organic phase that is immobilized inside the pores of the resin and the aqueous phase. This will be referred as IMLL.

For the case of the extraction of MTBE on impregnated MPP the isotherm will be represented by:

$$q = \frac{V_p}{m_{SIR}} \left(\frac{K_{ph} \cdot C_s^{aq} \cdot \left(1 + K_c \cdot C_{E,0}^{SIR} + K_c \cdot \left(\frac{1 - \epsilon_p}{\epsilon_p} \cdot q^* + K_{ph} \cdot C_s^{aq} \right) \right)}{B} + \frac{(1 - \epsilon_p) \cdot q^*}{\epsilon_p \cdot B} \right) \quad (3.3.13)$$

This isotherm will be presented as IMMPP in the future.

The curve fitting for both models are plotted in figures 3.3.7.

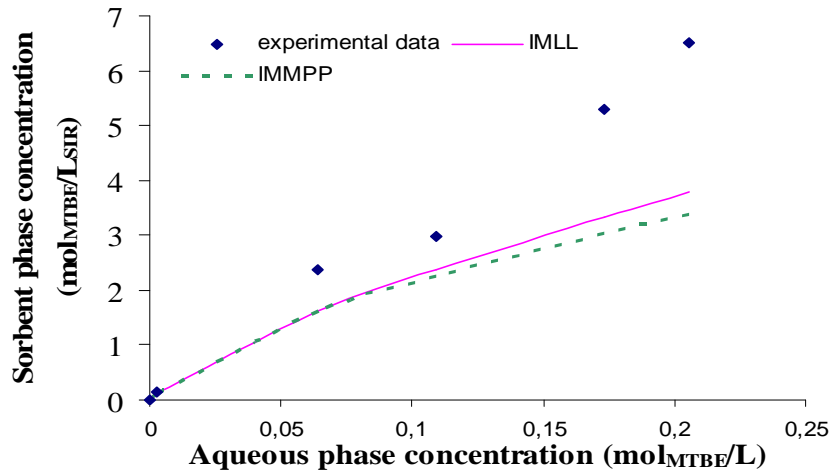


Figure 3.3.7 – Isotherm of the extraction of MTBE with impregnated MPP for the two models and the experimental data at 20°C.

As can be noticed, the fitting of the experimental data of the extraction of MTBE with impregnated MPP with both models is similar. The correlation coefficients are 0,8842 for the IMLL and 0,8499 for the IMMPP. This can be due to some extra extraction on the surface of the beads that is not taken into account.

In order to have a clear view of the differences between the fitting and the experimental data, parity graphs are presented. In figure 3.3.8 the parity graphs for MLL for impregnated MPP are shown. The parity graphs were plotted for the model and for an error in the model of $\pm 15\%$. The errors encountered may be due to the analysis method, to small errors in the laboratorial settings, or because the model is not valid for the system.

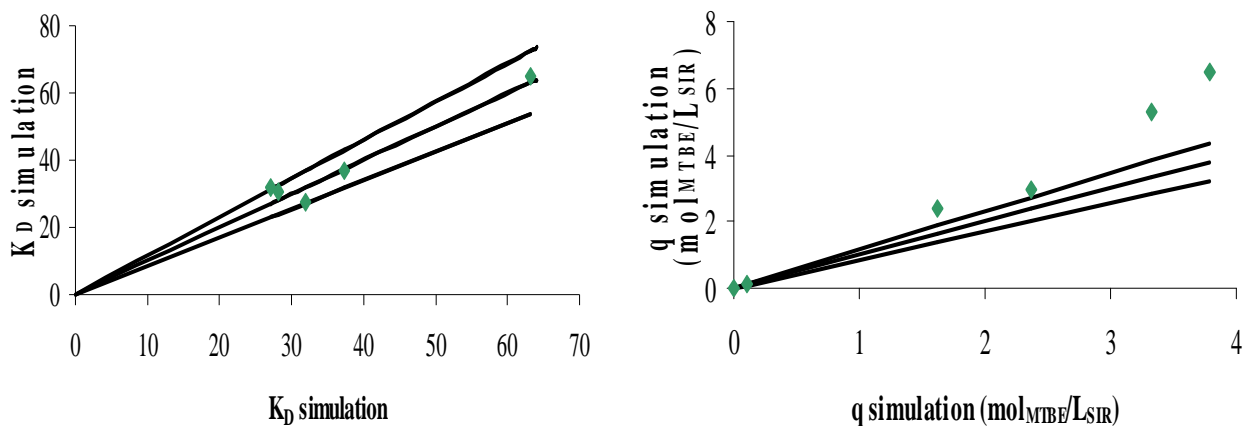


Figure 3.3.8 – Parity graphs for the overall distribution coefficient K_D and for the isotherm of extraction of MTBE with impregnated MPP by MLL and IMLL, respectively.

As it can be noticed, this model does not represent the data well. For small concentration of MTBE in the aqueous phase, and consequently in the SIR, the model represents quite well the experiments. However, when higher concentrations are used the model has a big deviation relative to the experimental data.

Next, the parity graphs for the IMLL and IMMPP are depicted, see figure 3.3.9.

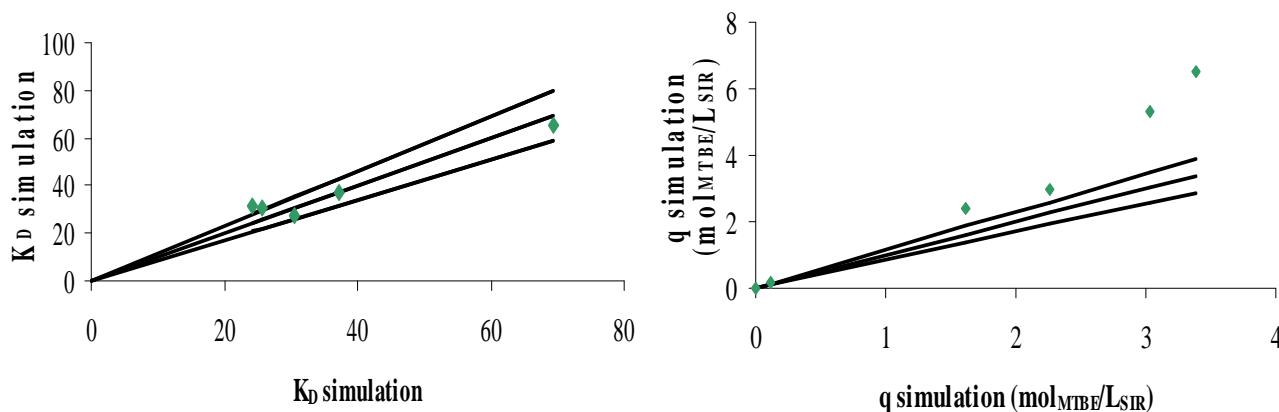


Figure 3.3.9 – Parity graphs for the overall distribution coefficient K_D and for the isotherm of extraction of MTBE with impregnated MPP by MMPP and IMMPP, respectively.

As can be noticed in figure 3.3.9 for the model that relates K_D with the concentration of MTBE in the aqueous phase the experimental data are inside the range of the error defined ($\pm 15\%$). However for the isotherm of extraction of MTBE the same is not noticed. For high concentration in the SIR ($>1,5M$) the model does not fit the experimental data well.

Next the emphasis goes to the model for the extraction with impregnated Amberlite XAD-7. For this model equations 3.3.1–3.3.6 and equation 3.3.11 are also valid. As it was said

before, an adsorption constant term was defined. Since the isotherm of adsorption of MTBE on unimpregnated Amberlite XAD-7 is assumed to follow the Freundlich isotherm, K_{ph}^{ads} can be defined as:

$$K_{ph}^{ads} = \frac{C_s^{Solid}}{C_s^{aq^n}} \quad (3.3.14)$$

Combining this last equation with equations 3.3.1 – 3.3.6 it is possible to define C_{Total}^{SIR} as:

$$C_{Total}^{SIR} = \frac{C_s^{aq} \cdot K_{ph} \cdot \varepsilon_p \left(1 + K_c \cdot C_{E,0}^{SIR} + \frac{K_c}{\varepsilon_p} \cdot \left((1 - \varepsilon_p) \cdot K_{ph}^{ads} \cdot C_s^{aq^n} + \varepsilon_p \cdot K_{ph} \cdot C_s^{aq} \right) \right) + (1 - \varepsilon_p) \cdot K_{ph}^{ads} \cdot C_s^{aq}}{(1 + K_{ph} \cdot C_s^{aq} \cdot K_c)} \quad (3.3.15)$$

The overall distribution coefficient, including adsorption for impregnated Amberlite XAD-7 will then be defined as:

$$K_D = \frac{K_{ph} \cdot \varepsilon_p \left(1 + K_c \cdot C_{E,0}^{SIR} + \frac{K_c}{\varepsilon_p} \cdot \left((1 - \varepsilon_p) \cdot K_{ph}^{ads} \cdot C_s^{aq^n} + \varepsilon_p \cdot K_{ph} \cdot C_s^{aq} \right) \right) + (1 - \varepsilon_p) \cdot K_{ph}^{ads} \cdot C_s^{aq}}{(1 + K_{ph} \cdot C_s^{aq} \cdot K_c)} \quad (3.3.16)$$

This model will be referred as MXAD.

In order to determine K_{ph}^{ads} , n for the adsorption on the surface of the beads and K_c for the complexation of MTBE with the extractant impregnated Amberlite XAD-7 the plot of K_D vs. C_s^{aq} is again essential. The fit of the experimental data was made with MLL and MXAD, see figures 3.3.10. The least squares method was used to determine the fitting parameters. The fitted parameters and the correlation coefficient are depicted in table 3.3.4.

Table 3.3.4 – Fitted parameters for the two models and respective correlation coefficients.

System	Model	K_{ph}	K_c	K_{ph}^{ads}	n	r^2
Impregnated Amberlite XAD-7	MLL	19,61	0,2617	–	–	0,9913
Impregnated Amberlite XAD-7	MXAD	19,61	0,00589	25,7	0,9035	0,9928

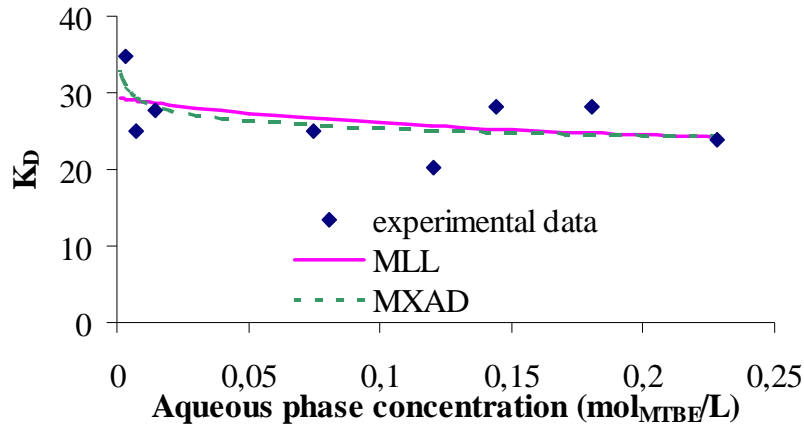


Figure 3.3.10 – Graphical representation of the overall distribution coefficient as a function of the concentration of MTBE in the aqueous phase for the experimental data and the models MLL and IMLL for the extraction of MTBE by impregnated Amberlite XAD-7.

As it is possible to notice, model MXAD fits the experimental data better than the model MLL for the extraction of MTBE on impregnated Amberlite XAD-7. As it can be noticed, again, the chemical complexation constant is less than the same constant for liquid-liquid extraction. The same explanation as the one given for the extraction with impregnated MPP can be used in this case. But, here the contact area for both droplets and beads will be calculated by the same ratio as mentioned before for the droplets. So for this system one has to notice that the number of droplets is higher than the number of beads. Nevertheless, the results for this model suggest that the complexation between MTBE and IPhOH does not have a very important role in the extraction or is taken into account in the adsorption distribution constant. Thus, the extraction would be due mainly to the physical solubility of MTBE in propylbenzene and to the adsorption on the surface of the beads. For further validation of the model the isotherms of extraction of MTBE on impregnated Amberlite XAD-7 were plotted. As it was said equation 3.3.11 is also valid in this case. The two models fitted were the IMLL and the IMXAD that will be defined next. Rearranging equation 3.3.11 and equation 3.3.15, the IMXAD will be defined as:

$$q = \frac{C_s^{aq} \cdot V_p \cdot \left(K_{ph} \left(1 + K_c \cdot C_{E,0}^{SIR} + K_c \cdot \left((1 - \varepsilon_p) \cdot K_{ph}^{ads} \cdot C_s^{aq} + K_{ph} \cdot C_s^{aq} \right) \right) + \frac{(1 - \varepsilon_p)}{\varepsilon_p} \cdot K_{ph}^{ads} \cdot C_s^{aq} \right)}{\left(1 + K_{ph} \cdot C_s^{aq} \cdot K_c \right) \cdot m_{SIR}} \quad (3.3.17)$$

The result of the fitting is depicted in figure 3.3.10. In this case of the extraction of MTBE with impregnated Amberlite XAD-7 the IMXAD ($r^2 = 0,9919$) fits the experimental data better than the IMLL ($r^2 = 0,8431$). These results were expected, as the MLL assumes that the solute does not adsorb on the surface of the resin. In fact, for small concentrations this effect is not important, as the organic phase does not saturate. However for higher concentrations of

MTBE ($C_{\text{MTBE}}^{\text{aq}} > 0,07 \text{ mol/L}$) the organic phase saturates with MTBE and the adsorption on the surface of the beads becomes more important. These results also validate MXAD

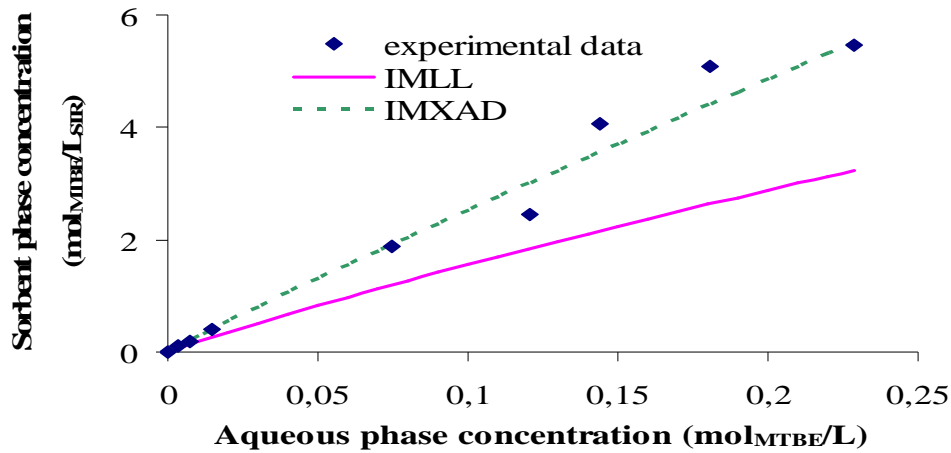


Figure 3.3.11 – Isotherm of the extraction of MTBE with impregnated Amberlite XAD-7 for the two models and the experimental data at 20°C.

To have a clear view of the differences between the fitting and the experimental data, parity graphs were plotted. In figure 3.3.11 the parity graphs for the MLL and IMLL for impregnated Amberlite XAD-7 are depicted. The parity graphs were plotted for the model and for an error in the model of $\pm 15\%$. The errors encountered may be due to the analysis method, to small errors in the laboratorial settings, or because the model is not valid for the system.

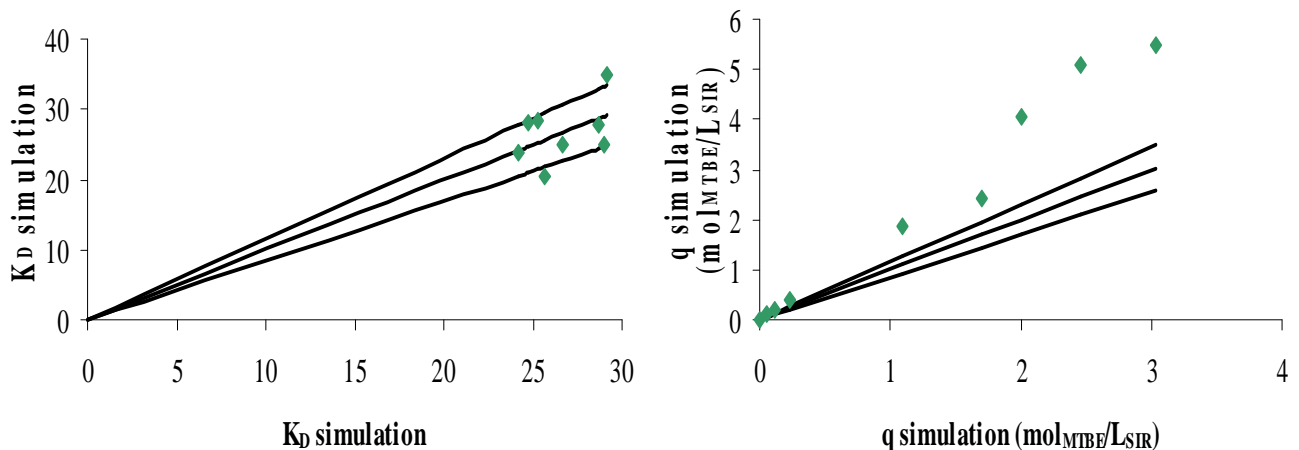


Figure 3.3.12 – Parity graphs for the overall distribution coefficient K_D and for the isotherm of extraction of MTBE with impregnated Amberlite XAD-7 by MLL and IMLL, respectively.

For this model the values of K_D are situated inside the errors allowed. However, when the parity graph is plotted for the isotherm of extraction, the results are dispersed for higher

aqueous concentration ($<0,05M$). This model does not represent the data well. For small concentration of MTBE in the aqueous phase, and consequently in the SIR, the model represents quite well the experiments. However, when higher concentrations are used the model has a big deviation relative to the experimental data.

For the case of models MXAD and IMXAD it is possible to say that this is the model that gives better results for the overall distribution coefficient and for the isotherm of extraction of MTBE. All the experimental data are in the range of errors allowed, see figure 3.3.12.

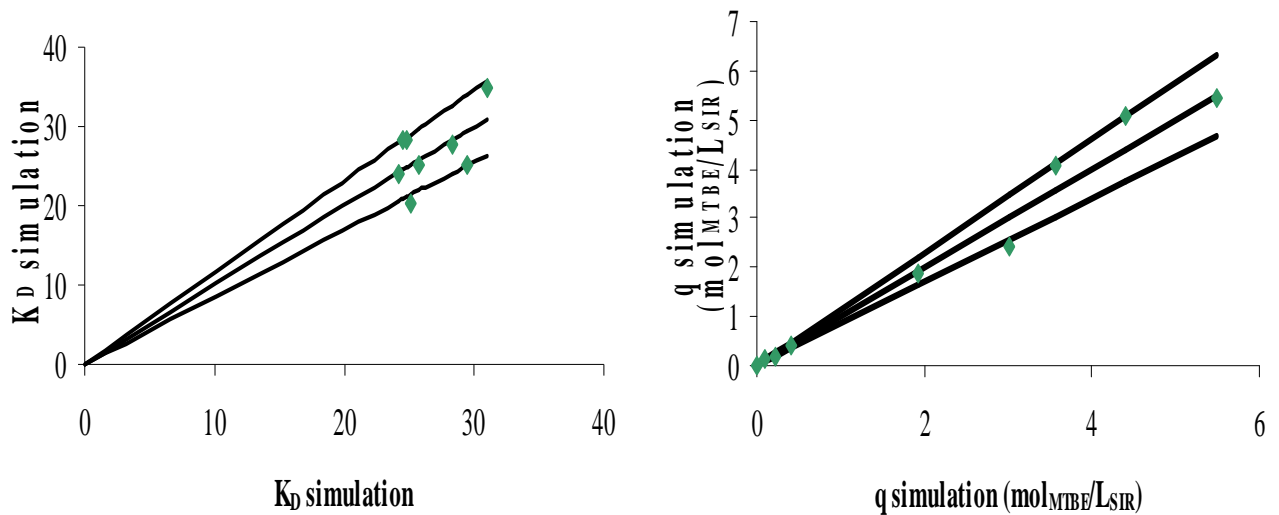


Figure 3.3.13 – Parity graphs for the overall distribution coefficient, K_D , and for the isotherm of extraction of MTBE with impregnated Amberlite XAD-7 for MXAD and IMXAD.

3.3.2. Sensitivity analysis.

The main goal performing a sensitivity analysis is to see which parameters have a high impact on a model. In this case the sensitivity analyses were made for the six models. Models MLL, MMPP, MXAD, IMLL, IMMPP and IMXAD. In the case of MLL and IMLL for the extraction of MTBE with impregnated MPP the only fitting parameter is K_C . However, for this sensitivity test K_C and K_{ph} were increased by 10%, see figure 3.3.14.

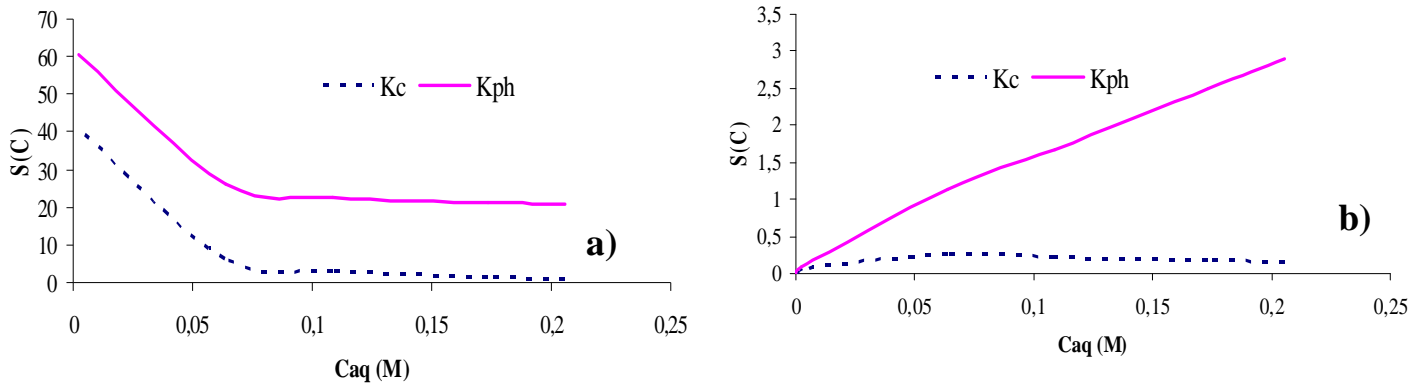


Figure 3.3.14 – Sensitivity test changing the values of K_C and K_{ph} for the extraction of MTBE with impregnated MPP; a) for MLL; b) for IMLL.

As it can be noticed in figure 3.3.14, for MLL an increase in K_C or K_{ph} have a similar behaviour. At low concentrations of MTBE ($<0,05M$) these constant have a high impact in the fitting. After $0,05M$ the effect is still significant for K_{ph} but not for K_C . This suggests that for high concentration of MTBE K_C can be fixed. For IMLL the effect of K_C is even less important. Nonetheless, K_{ph} maintain its influence over the fitting. The sensitivity analysis for MMPP and IMMP is presented in figure 3.3.15.

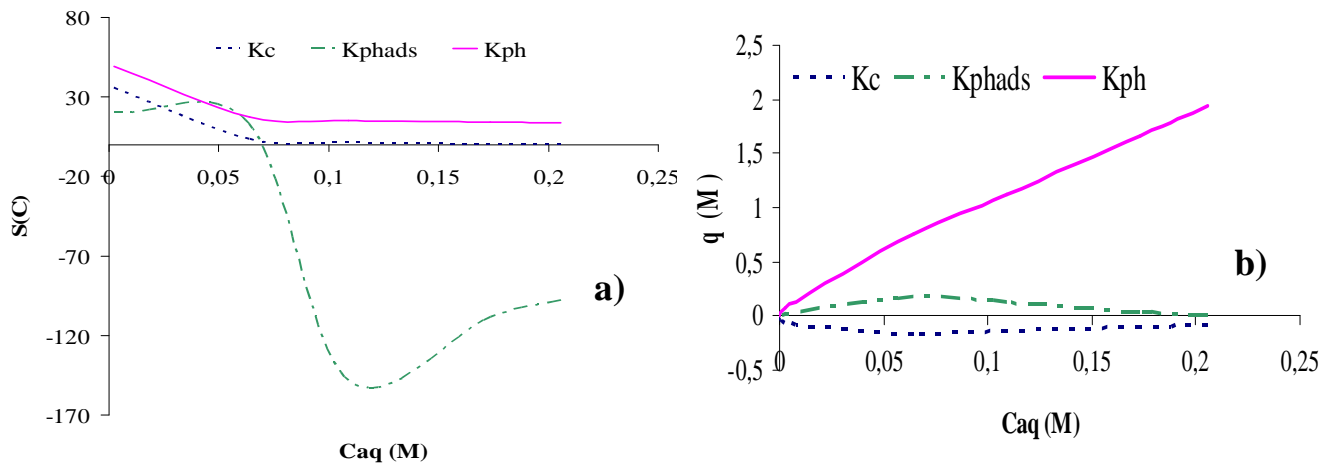


Figure 3.3.15 – Sensitivity test changing the values of K_C and K_{ph} for the extraction of MTBE with impregnated MPP; a) for MMPP; b) for IMMPP.

In this case it is possible to notice a similar effect with MMPP and for IMMPP as with MLL and IMLL when K_{ph} and K_C are changed. However, the sensitivity is lower in this case. Regarding K_{ph}^{ads} the sensitivity is high in the case of MMPP but not so high for IMMPP.

For the extraction of MTBE with impregnated Amberlite XAD-7 the sensitivity tests were performed for MLL, MXAD, IMLL and IMXAD. Again for MLL and IMLL K_C and K_{ph} were varied increasing 10% of the fitted value, see figure 3.3.16.

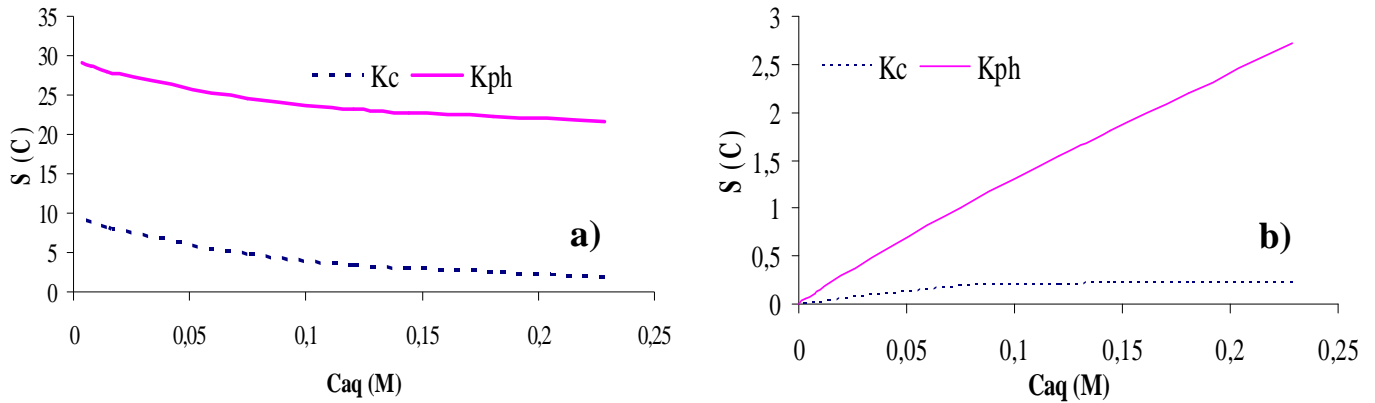


Figure 3.3.16 – Sensitivity test changing the values of K_C and K_{ph} for the extraction of MTBE with impregnated Amberlite XAD-7; a) for MLL; b) for IMLL.

As it was expected the sensitivity is similar to the one calculated for the same model and impregnated MPP, i.e. for low MTBE concentrations ($<0,1M$) the sensitivity of the model for the two constant is higher than for concentrations above that range. And as previously, for the IMLL the model is not sensible to changes in the value of K_C . However, a slight change in the value of K_{ph} is felt by the response of the model.

Regarding MXAD and IMXAD the parameters that can be changed are K_{ph} , K_C , K_{ph}^{ads} and n . The sensitivity tests for these models are depicted in figure 3.3.17.

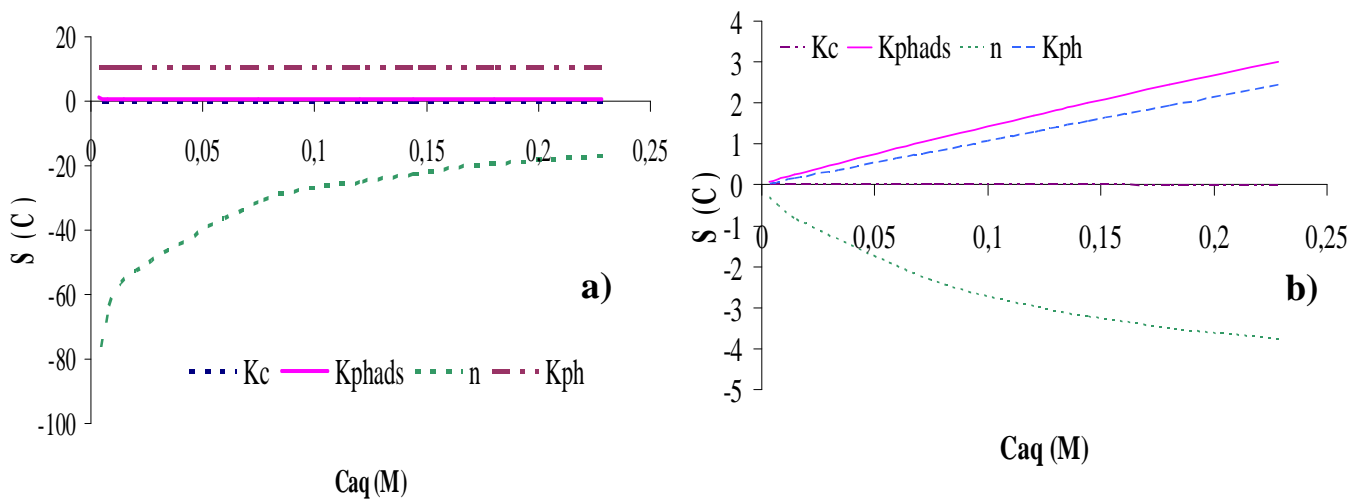


Figure 3.3.17 – Sensitivity test changing the values of K_{ph} , K_C , K_{ph}^{ads} and n for the extraction of MTBE with impregnated Amberlite XAD-7; a) for MXAD; b) for IMXAD.

3.3.2. ETBE extraction with SIR.

The extraction equilibrium of ethyl tert-butyl ether (ETBE) was also studied as ETBE is a possible substitute for MTBE gasoline. The extraction of ETBE was performed by two systems impregnated Ambersorb XE-348F with toluene/3-iodophenol (IPhOH) and propylbenzene/IPhOH. In figure 3.3.18 are depicted the two isotherm and the fitting by the Freundlich isotherm.

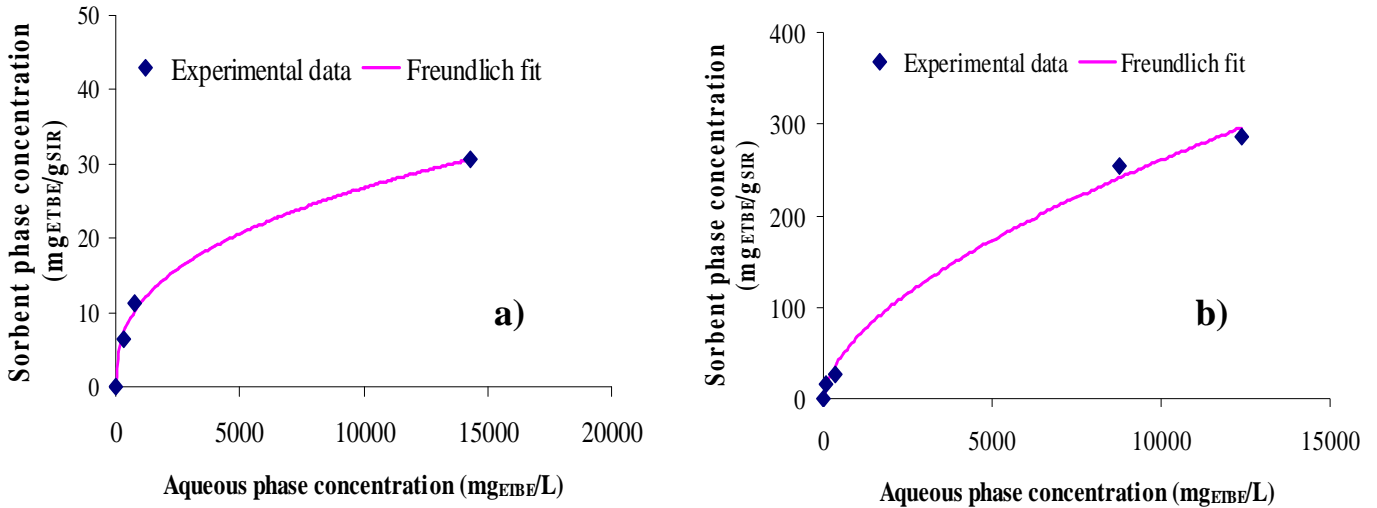


Figure 3.3.18 – Extraction isotherm of ETBE with Freundlich fit for the systems a) impregnated Ambersorb XE-348F with Toluene/IPhOH; b) impregnated Ambersorb XE-348F with propylbenzene/IPhOH.

The Freundlich parameters are depicted in table 3.3.5.

Table 3.3.5 – Freundlich isotherm parameters for the adsorption of ETBE on fully impregnated Ambersorb XE-348F with toluene/IPhOH and propylbenzene/IPhOH and their correlation coefficients..

System	K (mg/g)/(mg/L) ⁿ	n	r ²
Impregnated Ambersorb XE-348F with toluene/IPhOH	0.8252	0.3776	0.994
Impregnated Ambersorb XE-348F with propylbenzene/IPhOH	1.118	0.5918	0.999

As it is possible to see in figure 3.3.18, the isotherm of extraction of ETBE on the different systems present a shape typical of a favourable isotherm. It is also possible to notice that the extraction with impregnated Ambersorb XE-348F with propylbenzene is better than with impregnated Ambersorb XE-348F with toluene. Such fact might be due to a higher solubility of ETBE into propylbenzene than into toluene. When comparing this isotherm and the isotherm of MTBE on impregnated Ambersorb XE-348F with toluene/IPhOH, figure 3.3.1, it is possible to see that the isotherms have different shapes. The different shapes of the isotherm may be due to

the difference of solubilities of the two compounds in the organic phase. A reason for such fact may be the higher polarity of MTBE when compared with ETBE, once ETBE has a larger carbon chain that MTBE. As for the extraction of MTBE the plot of K_D vs. C_s^{aq} is necessary for determine the fitting parameters K_{ph} and K_c , see figure 3.3.19. K_{ph} was fitted as it has a large influence over the fit as was shown in sub-chapter 3.3.2. However, this constant should be measured experimentally. The fitting was made using MLL and MXAD.

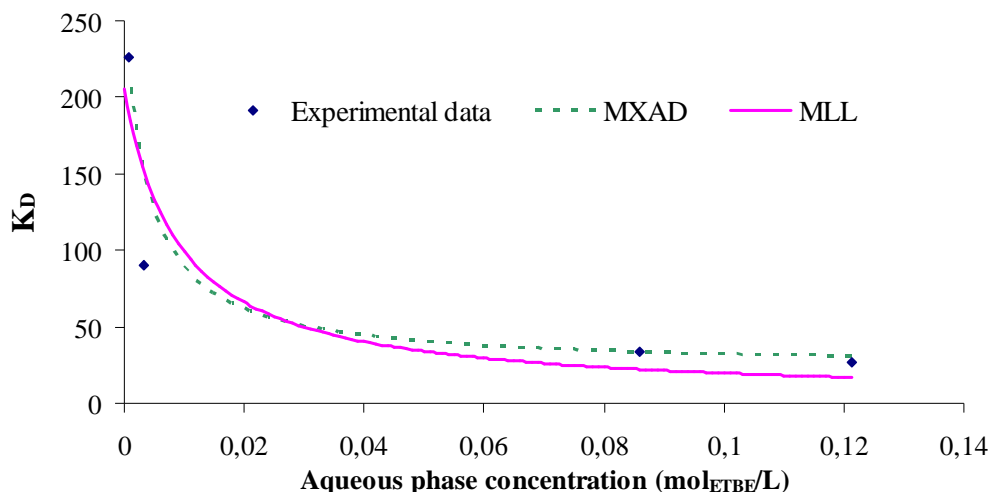


Figure 3.3.19 – Graphical representation of the overall distribution coefficient as a function of the concentration of ETBE in the aqueous phase for the experimental data and the models MLL and IMML for the extraction of ETBE by impregnated Amborsorb XE-348F with propylbenzene/IPhOH.

As it can be noticed the IMXAD model, i.e. the model that consider some adsorption on the surface of the beads fits better the experimental data than the MLL model. The parameters fitted are depicted in table 3.3.6, along with the correlation coefficients.

Table 3.3.6 – Fitted parameters for the two models and respective correlation coefficients.

Model	K_{ph}	K_c	K_{phads}	n	r^2
MLL	2,925	37,68	–	–	0,9454
MXAD	40,01	6,516	7,618	0,8923	0,9879

For further validation of the model the isotherms of extraction were represented graphically by IMML and IMXAD, see figure 3.3.20.

As it is possible to see the IMML model represents the experimental data well for small concentrations. However, for higher concentration (0,01M) it diverges from the experimental data. With the IMXAD model the experimental data is well represented in the whole range of tested concentrations. Once again these results validate the IMXAD model.

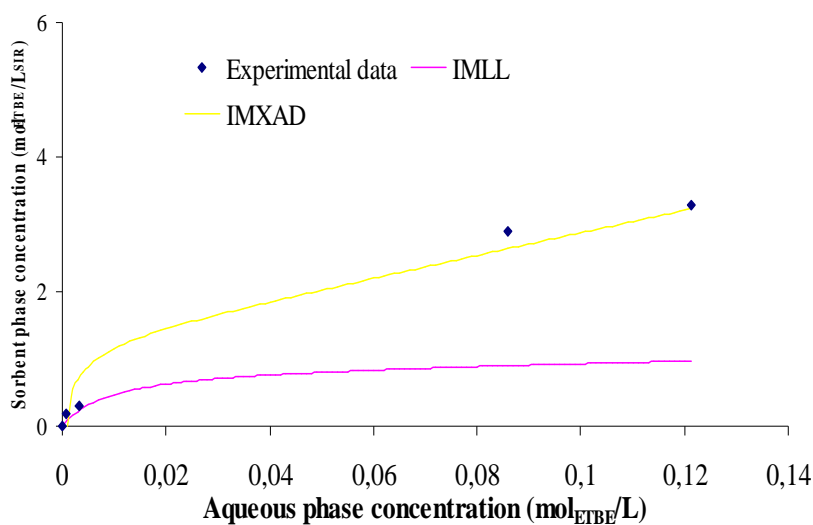


Figure 3.3.20 – Isotherm of the extraction of ETBE with impregnated Ambersorb XE-348F for the two models and the experimental data at 20°C.

3.4. Selectivity.

The selectivity of impregnated MPP between MTBE and humic acid and MTBE and TBA were studied. In the case of the selectivity between MTBE and humic acid it is possible to say that the selectivity is dependent of the concentration, see figure 3.3.26. The selectivity was calculated as:

$$\alpha_{A/B} = \frac{K_{D,A}}{K_{D,B}} \quad (3.3.18)$$

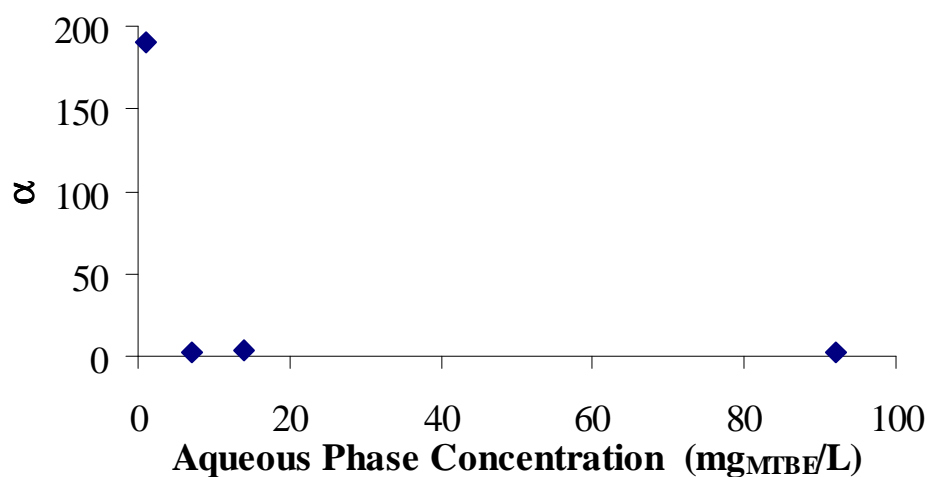


Figure 3.3.21 – Graphical representation of the selectivity of impregnated MPP relative to MTBE and humic acid, at 20°C.

As it can be noticed, for concentrations lower than 10mg/L the selectivity of the SIR for MTBE increases drastically. The selectivity of the SIR for MTBE is around 3 for concentrations higher than 10mg/L. But for small concentrations it has values near 200. This may be due to the fact that when the concentration of humic acid increases it can block the pores of the resin as it is a large molecule. Nevertheless, this is a good indication of the selectivity of the SIR, as the selectivity of the SIR is always greater than one. Thus the SIR has a better selectivity for MTBE than for humic acid.

For the case of TBA, the method of analysis was not suitable, as there was no separation between the peaks of the two compounds, see figure 3.3.27.

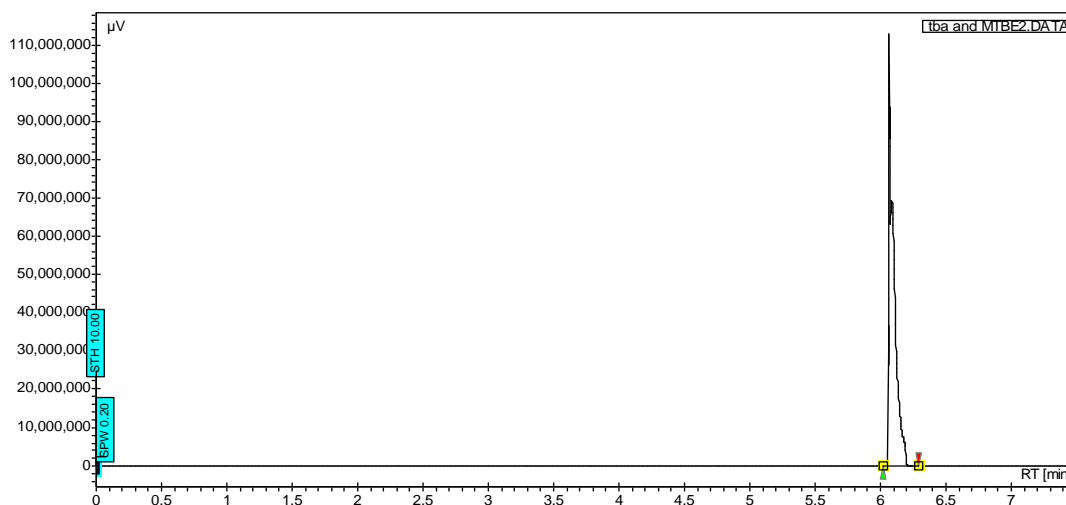


Figure 3.3.22 – Chromatogram of the analysis of the mixture MTBE / TBA.

3.5. Column experiments.

Column experiments were performed in order to determine the breakthrough curves. The curves were determined for three different flows 15, 10 and 5ml/min. The initial concentration of MTBE was kept constant, 5000ppm. For this purpose, the water used in these experiments had to be saturated with propylbenzene and 3-iodophenol (IPhOH) in order to avoid a leak of these compounds from the SIR.

As it was expected, when the flow increases the breakthrough time decreases. The breakthrough time is the time for which the solute starts to leave the column. At that time the beads start to saturate and some solute is not extracted from the stream. It is also possible to see that when the flow decreases the shape of the breakthrough curve becomes smoother. That means that when the flow rate is lower the contact time between the liquid stream and the beads is longer, thus more MTBE is extracted. Therefore, it is possible to say that the extraction of MTBE with impregnated MPP is better at lower flow rates. However if the desired is a fast

process, the high flows will be more suitable for that purpose as the shape of the curve is more steep.

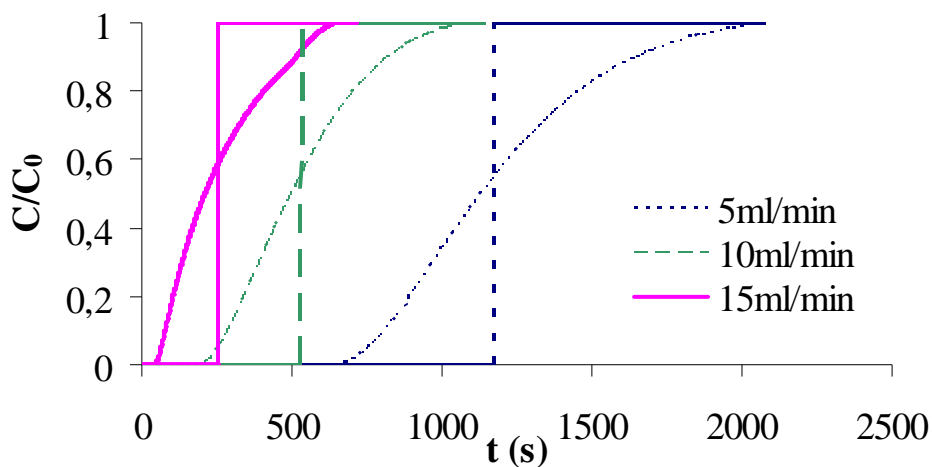


Figure 3.3.23 – Breakthrough curves for the different flows and their stoichiometric times.

3.6. Cost evaluation.

As the extraction of MTBE with unimpregnated Ambersorb XE-348F has shown to be better than with impregnated MPP, a small cost evaluation was performed. This cost evaluation was made for a volume of resin of 10L. The concentration of extractant used was 2,5M. The cost of the resins, propylbenzene and 3-iodophenol (IPhOH) per kilogram are depicted in table 3.6.1. In order to present the prices in kg/€ the volumes were multiplied by the density of the pure compounds.

Table 3.6.1. – Prices per kilogram of the different chemicals used.

Chemicals	Price (€/kg)
MPP	10
Ambersorb XE-348F	3230
3-IPhOH	3800
Propylbenzene	104,41

Performing the calculations it is possible to say that for 10L of unimpregnated Ambersorb XE-348F costs 39729€. However, when performing the cost analysis for MPP impregnated with propylbenzene/IPhOH the cost for the same volume with the previously mentioned concentration is 11000,52€. Nevertheless, this price may decrease if the extractant was sold in big amounts as for this analysis the extractant is bought in flasks of 25g. Therefore, it is possible to say that the impregnated MPP is more cost effective, as its price for the same amount of resin is about three times lower than that of Ambersorb XE-348F.

4. Conclusions.

The main goal of this project was the extraction of MTBE from groundwater. It was shown that this is possible but with some limitations.

In order to perform the extraction of MTBE two extractants were tested 3-iodophenol (IPhOH) and 3,5-dimethyl-4-iodophenol (DMIP). The two extractants are solids at room temperature, thus the use of a diluent is required to solubilize them. The diluent used was 1-decanol. Amongst these two extractant 3-iodophenol presented the best extraction. In order to avoid the use of a diluent the eutectic point of the mixture of the two solids was calculated. Nevertheless, the experimental result did not go towards the theoretical result. So a diluent was needed.

For such purpose a diluent screening was made. Seven different diluents were tested nonane, phenyldodecane, 1-decanol, nonanoic acid, heptyl cyanide, toluene and propylbenzene. Nonane and phenyldodecane did not solubilize either of the extractants. 1-decanol, nonanoic acid and heptyl cyanide solubilized IPhOH but due to a possible hydrogen bond between extractant and diluent the overall distribution coefficient were low. Amongst the diluents propylbenzene and toluene presented the highest distribution coefficients. Thus the diluent plays an important role in the extraction. However, due to the high solubility of toluene in water, propylbenzene was used for the rest of the project.

Because the solid support in the solvent impregnated resin is an important feature an adsorbent screening was also performed. Four different adsorbents were tested Ambersorb XE-348F, Amberlite XAD-7, macro-porous polypropylene MPP and the activated carbon Aquasorb 202. From these adsorbents Ambersorb XE-348F presents the best extraction followed by the activated carbon, Amberlite XAD-7 and MPP.

Also, because the Ambersorb XE-348F presents the best extraction it was impregnated with toluene/IPhOH and propylbenzene/IPhOH. Contrary to expectations this SIR presented an unfavourable isotherm shape, thus not useful for industrial application. In order to find the best system Amberlite XAD-7 and MPP were impregnated with propylbenzene/IPhOH. The impregnated MPP presented the best extraction as a SIR. Nevertheless, the extraction of MTBE with unimpregnated Ambersorb XE-348F was proved to be better than with any impregnated resin. However, impregnated MPP has the advantages of being less costly and takes less time to attain equilibrium, turning the process faster.

In order to model the extraction of MTBE with the SIR, three models were tested. One such model has been presented in the literature (Bábic, K., 2006), model MLL. The two other models were derived in this work. These two models take into account the fact that some MTBE can adsorb on the surface. One of these models, MXAD, was derived for the extraction of MTBE with a SIR whose resin, when unimpregnated, follows a Freundlich isotherm. The other

model, MMPP, assumes that the adsorption of the solute on the unimpregnated resin follows a constant separation factor isotherm. The MXAD was validated. However, the MMPP model needs some refinement.

The extraction of ETBE with SIR was also tested. In this case the Amborsorb XE-348F presented a favourable isotherm either when impregnated with toluene/IPhOH and propylbenzene/IPhOH. It was also determined that the extraction of ETBE with a SIR impregnated with propylbenzene/IPhOH has a better extraction than with toluene/IPhOH.

A sensitivity test was performed to the fitting parameters. In such test was determined that K_{ph} has a big influence over the fitting. However, since it is a measurable constant it was determined by the LLE experiments and fixed when fitting. Against the expectations K_C does not have significant importance in the model. K_{ph}^{ads} and n both significantly affect the fit of experimental data.

A selectivity analysis was performed for impregnated MPP between humic acid and MTBE and TBA and MTBE. The selectivity between MTBE and humic acid was determined to be quite high and to increase when the concentrations of both compounds in the aqueous phase are low ($C_{MTBE}^{aq}=1\text{ppm}$ and $C_{HA}=0,5\text{ppm}$). This is a good indication of the selectivity of SIR for water treatment. A suitable analysis method was not found for the selectivity between MTBE and TBA. Thus the selectivity could not be determined.

Column experiments were also performed in order to determine the breakthrough curve. At low flow rates (5ml/min), the extraction was shown to be better, as the shape of the breakthrough curve is less sharp than at higher flow rates. Thus, the extraction is favoured by using low feed flow rates.

To conclude, it can be said that the extraction of MTBE with solvent impregnated resins is possible, although it still presents a number of limitations, namely the lack of an extractant, of a diluent, and of a better solid support. However, the cost analysis provided good prospects for the use of SIR in water treatment.

5. Evaluation of the presented work.

5.1. Accomplished objectives.

The objectives presented in chapter 1.4 were accomplished, with the exception of the measurement of the selectivity of impregnated MPP between MTBE and TBA. This was due to the lack of a suitable method of analysis, as mentioned before. It was not possible to set up such method in the timeframe of this project.

5.2. Other accomplished work.

As other accomplished work, one may point out the determination of a suitable method for the analyses of MTBE through headspace gas chromatography. That method is presented in chapter 2 – *MTBE Analysis*. Another extractant was tested as an alternative to 3-iodophenol (IPhOH), namely 3,5-dimethyl-4-iodophenol (DMIP). However, this extractant did not perform as well as IPhOH. The eutectic point of the mixture between DMIP and IPhOH was calculated and tested in order to yield an extractant blend with a low melting point. The melting point of the mixture of IPhOH and DMIP proved to be too high for an application at room temperature. Three resins were impregnated and tested instead of the best resin, as referred in the objectives. Two models for the extraction of MTBE with SIR taking into account some adsorption on the surface of the beads were derived and tested. One of them was validated. These results are presented in chapter 3.

5.3. Recommendations for future work.

This work provides an insight about the recovery of MTBE with Solvent Impregnated Resins (SIR) and presents a new model for the extraction of solutes with solvent impregnated resins (SIR), where the adsorption on the surface of the beads is also taken into account. However, several key issues need further attention:

- Extractant used for the extraction;
- Diluent used to solubilize the extractant;
- Concentration of the extractant in the organic phase;
- Effect of the porous support;
- Temperature effect on the extraction of MTBE with SIR;
- Multicomponent sorption behavior;
- Kinetic studies;
- Column studies;
- Regeneration of SIR.

The extractant used in this work, 3-iodophenol (IPhOH), is solid at room temperature. This fact represents a big drawback in the extraction, as it has to be solubilized. Also, its comparatively high solubility in water (411,7mg/L) is an important issue. Another extractant

was tested in this work is 3,5-dimethyl-4-iodophenol (DMIP). This extractant was very difficult to solubilize, and could only be tested with decanol as a diluent. However, the results obtained by the LLE experiments did not yield a better extraction of MTBE than with IPhOH. In order to overcome problems associated with using a diluent, an extractant blend might be used. In such a blend, the melting point of the mixture is lower than the melting points of the pure components. In this way, the use of a diluent can be avoided. Also, the capacity of such an undiluted extractant will be higher than when a diluent is used. Thus, the extractant investigated in this study should be optimized in terms of water solubility, melting point and overall distribution coefficient K_D .

If the investigated extractant can not be optimized, a diluent might still be needed. The effect of the diluent was studied in this work. As was shown, the diluent plays an important role in the extraction, as it can inhibit the extraction by bonding with the extractant. Thus, other diluents should be tested, for example Butylbenzene. Butylbenzene should not bond with IPhOH once it does not have any group that could bond and it has a lower solubility in water (11,8mg/L @ 25°C) than propylbenzene (~50mg/L @ 25°C). Its vapour pressure is also lower (141Pa @ 25°C) than the vapour pressure of propylbenzene (412 Pa @ 25°C). Another possibility is to impregnate the resin with an ionic liquid. These compounds can be tailor made as the SIR, what represent a big advantage. Another advantage of these liquids is their low vapor pressure (~0 kPa), thus turning possible the use of thermo regeneration at high temperatures. Nevertheless, some caution should be taken into account when choosing the ionic liquid. It has to be insoluble in water to guarantee the non-leakage of the liquid from the beads. It should be acidic in order to remove MTBE since this last compound has basic characteristics but not so acid that it would destroy the solid support. This can be achieved performing a ionic liquid screening.

The concentration of extractant in the organic phase used in this study was 2,5 mol_{IPhOH}/L_{diluent}. Other concentrations above 2,5 mol_{IPhOH}/L_{diluent} should be tested in order to verify the behavior of the extraction at higher concentrations of extractant. It might be seen at higher extractant concentrations that the sorption of the solute on the surface of the beads has no effect, as the organic phase may not be saturated.

The effect of the porous support was studied. As was shown, the effect of the sorption is more evident at higher concentration of MTBE (>4500 ppm). These concentrations are hardly found in water treatment. However, also other porous matrices should be tested in order to validate the model presented in this work. Another model was tried for the extraction of MTBE with impregnated MPP. This model did not bring a significant improvement in the prediction of the extraction. Refinement of the model by also considering the adsorption of solute on the outer particle surface could give better results.

The influence of the temperature should be tested in order to define the limitations and optimal conditions of the process. Such limitations can occur due to a significant increase of leakage of the extractant/diluent from the porous matrix, as the solubility of these components in water increases with increasing temperature. However, at higher temperature a higher solubility of the extractant in the diluent can be reached. This can increase the capacity of extraction of the SIR.

Multicomponent adsorption should be considered. This work showed that SIRs have a good selectivity for MTBE in the presence of humic acid. Selectivity between MTBE and TBA should be studied. It was tried to perform such studies but a suitable method of analysis was not found within the timeframe of this project. A suitable analysis method should be found in order to analyze such systems, as TBA is an important contaminant of water and a product of the oxidation of MTBE.

In order to understand which step is controlling the extraction and to determine constants such as film diffusion or pore diffusion, kinetic experiments should be done. However, this study is already being done in another master's project. This will bring further information in order to implement this technique in an industrial scale. For this last objective, column experiments should also be performed. These experiments will bring a better insight about the cycles of adsorption and regeneration. This would allow a better prediction of the behavior of the extraction process, such as breakthrough time, mass transfer zone, length of unused column and dynamic behavior of the process.

Regarding the regeneration of the SIR, column experiments should be investigated in order to detect if there is a hysteresis phenomenon. By hysteresis one means a different breakthrough time or even a different shape in the solute wave between extraction and regeneration. The breakthrough curves must be the same in case of the absence of a hysteresis phenomenon. However, a change in the shape of the breakthrough curve is expected, as the isotherm of adsorption is favorable. Thus the regeneration of the SIR in a column should result in a dispersive wave of the solute. One way to regenerate the column would be through thermal regeneration with nitrogen. Nevertheless, one should be cautious, because there is also a diluent inside the solid matrix. At high temperatures this diluent may evaporate together with the MTBE, as mentioned before.

5.4. Final evaluation.

This project served to get in contact with a new technology in the process separation field. The use of solvent impregnated resins as a method for the extraction of groundwater contaminants was proven to be possible, although with some limitations. A diluent and a solid screening were done in order to discover the best possible system for the extraction in the timeframe of this project. Two models that take into account the adsorption on the surface of the beads were introduced. A selectivity analysis was done and led to good perspectives of the use

of SIRs for remediation in contaminated water. Column experiments were also performed and the dynamics of the extraction could be understood a bit better.

As a conclusion, one may consider that the project went well in spite of some small challenges that emerged along the road.

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Appendix A

Removal of MTBE from Groundwater with Solvent Impregnated Resins

This part regards the effect of the thermal regeneration over MTBE. The vapour pressure of this compound was calculated by the Antoine equation, see equation A.1. This empirical equation relates the vapour pressure of pure compounds with the temperature and takes, usually the form (M. Smith, J. and C. Van Hess, H., 1975).

$$P^{vapour} = A - \frac{B}{C + T} \quad (A.1)$$

In the Antoine's equation A, B and C are constants, P^{vapour} stands for the vapour pressure in kPa and T for the temperature in Kelvin. The Antoine's constants are depicted in table A.1

Table A.1 – Antoine's constants for MTBE (H. J.-HyekOh, Kyu-J. and P. D.-B. Won, So-J., 2003)

Antoine constants	
A	6,25487
B	1265,4
C	242,571

In order to check the validity of the theoretical equation some literature research was made. The values encountered for the vapour pressure at different temperatures are depicted in table A.2.

Table A.2 – Vapour pressures of MTBE at different temperatures (B. Belaribia, G. *et al*, 2006).

T (K)	263,15	273,15	283,15	293,15	298,15	303,15	313,15	323,15	333,15	343,15
P^{vapour} (kPa)	6,252	10,641	17,31	27,064	33,392	40,862	59,808	85,152	118,271	160,66

The results of the Antoine equation correlation and the plot of the data collected are depicted in figure A.1.

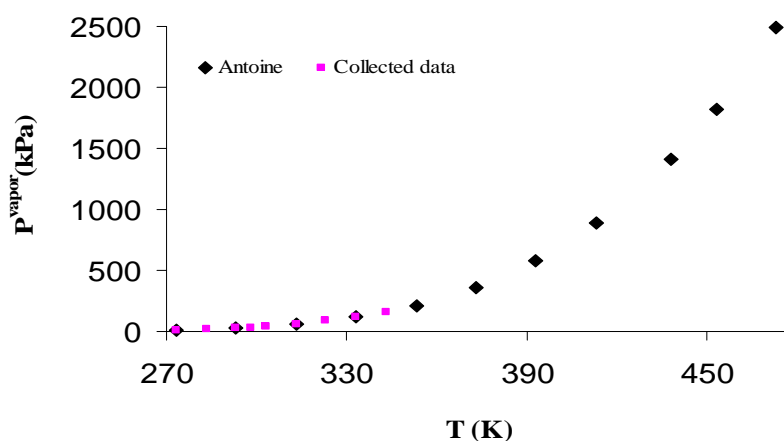


Figure A.1 – Vapour pressure as a function of the temperature by the Antoine equation and by the collected data (B. Belaribia, G. *et al*, 2006).

Removal of MTBE from Groundwater with Solvent Impregnated Resins

As it can be noticed the empirical correlation is valid for MTBE.

The thermal regeneration of the column would be done at 120°C. At this temperature the vapour pressure of MTBE is 581,8kPa. Thus the regeneration would be possible by this method if it would depend only of MTBE. Nevertheless, the diluent plays an important role as a possible limitation once it can vaporize with MTBE and be carried by the nitrogen stream.

The same study is done for propylbenzene. However for this compound the Antoine equation takes the form:

$$\text{Log}(P^{\text{vapour}}) = B - \frac{A}{T} \quad (\text{A.2})$$

The Antoine constants for propylbenzene are depicted in table A.3.

Table A.3 – Antoine’s constants for propylbenzene (Busch, A. *et al*, 1960).

Antoine constants	
A	2367
B	8,479

In order to check the validity of the Antoine equation for this compound literature research was made. The values encountered for propylbenzene are shown in table A.4.

Table A.4 – Vapour pressures of propylbenzene at different temperatures (Busch, A. *et al*, 1960).

T (K)	279.5	316.6	367.2	432.4
P ^{vapor} (kPa)	2096.42	2374.70	2754.23	3243.27

The representation of the vapour pressure as a function of the temperature and the collected experimental data are depicted in figure A.2.

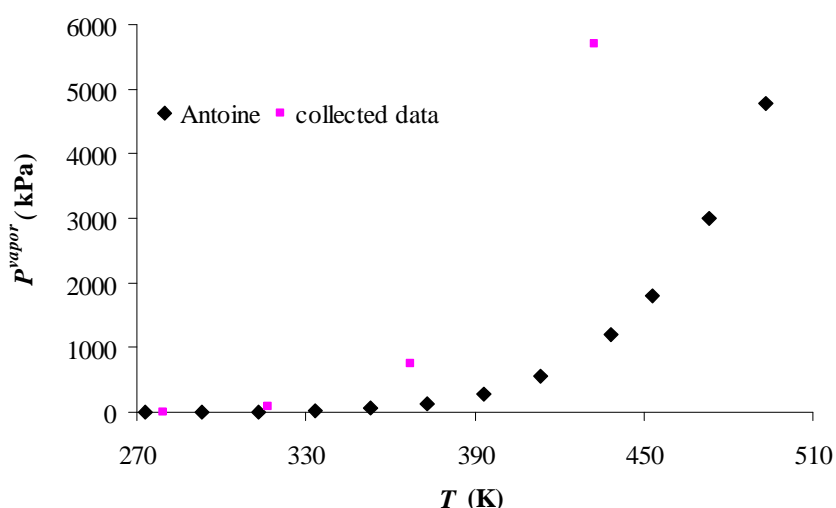


Figure A.2 – Vapour pressure as a function of the temperature by the Antoine equation and by the collected data (Busch, A. *et al*, 1960).

Removal of MTBE from Groundwater with Solvent Impregnated Resins

As can be seen the Antoine equation is only valid up to approximately 330K. After that temperature the experimental vapour pressure increases more than the empirical vapour pressure.

By the comparison between the vapour pressure of the two compounds, MTBE and propylbenzene it is possible to say if the thermo regeneration with N₂ at 120°C is possible, see figure A.3.

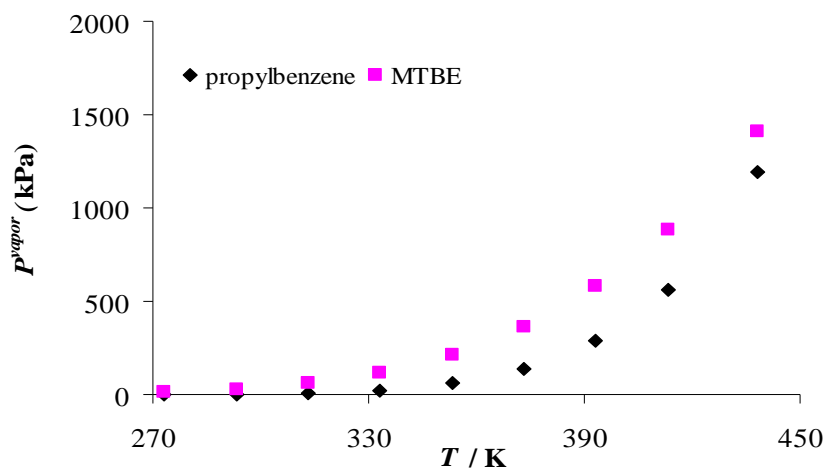


Figure A.3 – Vapour pressure as a function of the temperature by the Antoine equation for MTBE and propylbenzene.

As it can be noticed at 120°C (393K) the vapour pressure of propylbenzene is half of the vapour pressure of MTBE. That brings a problem for the thermo regeneration once the propylbenzene would vaporize with MTBE and be carried by the N₂ stream. It is then possible to conclude that or the propylbenzene is not a suitable diluent for the extraction of MTBE with SIR or that for this system, MTBE/IPhOH/propylbenzene, the thermo regeneration is not a suitable method for the regeneration of the SIR.

As it was mentioned in the recommendations for future work, butylbenzene could be a suitable diluent for the extraction of MTBE with SIR. In order to assure the non vaporization of this compound the same analysis was made for it. Its Antoine constants for butylbenzene and the range of temperature where the constants are valid are depicted in table A.5.

Table A.5 – Antoine’s constants for propylbenzene and their range of application (Busch, A. *et al*, 1960).

A	B	ΔT (K)
2476	8,389	273,15 - 335,5
2385	8,140	335,5 - 456,4
2238	7,780	456,4 - 753,15

In order to verify the validity of the Antoine equation for butylbenzene, literature research was made. The values found in the literature are depicted in table A.6.

Removal of MTBE from Groundwater with Solvent Impregnated Resins

Table A.6 – Vapour pressures of propylbenzene at different temperatures (Busch, A. *et al*, 1960).

T (K)	295.9	335.5	388.4	456.4
P ^{vapour} (kPa)	2219.43	2516.46	2913.24	3423.28

The representation of the vapour pressure as a function of the temperature is depicted in figure A.4.

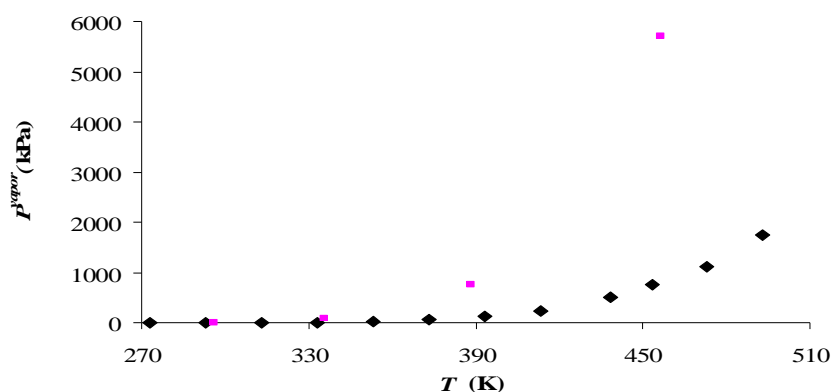


Figure A.4 – Vapour pressure as a function of the temperature by the Antoine equation and by the collected data (Busch, A. *et al*, 1960).

As it can be noticed the vapour pressure of butylbenzene follows the Antoine equation until 380K, approximately. However, its vapour pressure when compared to propylbenzene is lower, thus it gives a good indication of its possible use as a diluent regarding the thermo regeneration. The comparison between butylbenzene and MTBE is given in figure A.5.

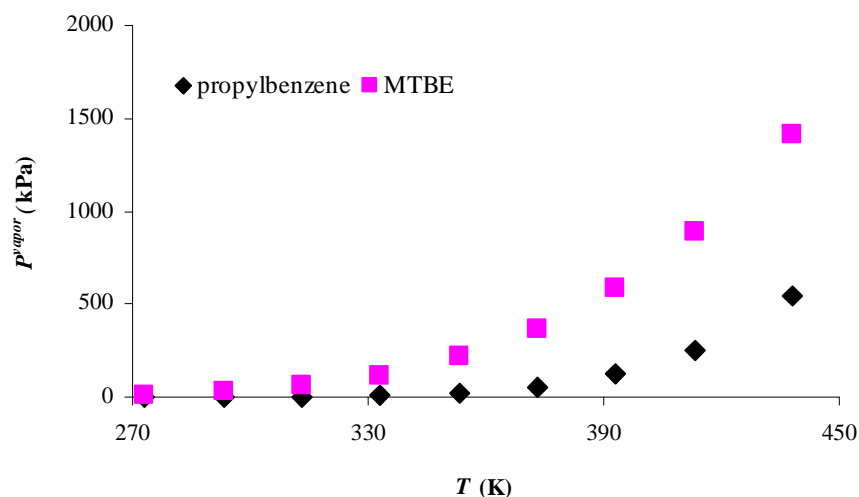


Figure A.5 – Vapour pressure as a function of the temperature by the Antoine equation for MTBE and butylbenzene.