

HOMOGENEOUS AND HETEROGENEOUS OXIDATION OF THE AZO DYE ORANGE II WITH FENTON'S REAGENT-BASED PROCESSES

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PREFACE

This PhD thesis structure results from different papers published and/or submitted for publication in international journals, during the work carried out at LEPAE (Laboratório de Engenharia de Processos, Ambiente e Energia) in the Chemical Engineering Department of FEUP (Faculty of Engineering - University of Porto), throughout the period between November 2003 and April 2008.

The main goal of this dissertation was to try understanding the basis of the homogeneous and heterogeneous Fenton system, and to determine the factors that control the decomposition of organic compounds present in wastewaters by hydrogen peroxide, in the presence of iron and iron-based catalysts. As model compound, a non-biodegradable azo dye was selected: Orange II (OII). This knowledge can help to increase the efficiency of Fenton's-based treatment processes when applied to textile wastewaters.

The dissertation is organized in 8 chapters. The first one (part I) considers a general introduction and review of the state of the art focused in the Fenton's system, an advanced oxidation process (AOP) often employed for wastewater treatment. Emphasis is put in the treatment of textile dyeing wastewaters, and alternative AOPs to the Fenton's process are briefly described. The basics of the oxidation with Fenton's reagent are remarked, which is based on ferrous or ferric ion and hydrogen peroxide and exploits the very high reactivity of the hydroxyl radical produced in acidic solution by the catalytic decomposition of H_2O_2 .

The experimental set-up is described in chapter 2 (part II); in particular, the specifications of the batch and continuous reactors employed are presented, along with the analytical techniques used. Finally, it is provided a short description of the solid catalysts synthesis and characterization techniques employed.

The use of a statistical tool (design of experiments – DOE), using JMP software, for the optimization of the homogeneous process was examined in chapter 3. Herein it is studied with detail the importance of the variables that affect the homogeneous Fenton process, such as temperature, H_2O_2 concentration and $\text{Fe}^{2+}:\text{H}_2\text{O}_2$ ratio. With this tool a statistical model was obtained that represents well the experimental data of orange II degradation under different experimental conditions.

In chapter 4, the experimental work regarding the homogeneous process is finished (part III). Now, a more phenomenological approach is used, with the objective of analyzing the kinetics of the OII degradation and establishing a reaction rate, to be further validated in a continuous stirred tank reactor.

Part IV of the thesis is dedicated to the heterogeneous Fenton's process, being composed by chapters 5 to 7. In chapter 5, several catalysts based on Al-pillared saponite impregnated with iron salts were prepared. The effectiveness of these catalysts in the oxidation of the dye in a batch reactor, as well as the influence of the variables of the synthesis and of the reaction conditions on the catalytic activity is discussed.

Chapter 6 is mostly addressed to the used of activated carbons as iron supports, but a comparison between clay- and carbon-like supports was also made. Two different types of carbon materials were used: i) an activated carbon prepared from agricultural by-products (olive stone) and ii) a carbon aerogel prepared by sol-gel technology. Both types of materials can be considered as examples of the classical and new carbon materials form. The performance of both materials was compared and the effect of the most relevant operating conditions in Fenton's oxidation evaluated.

In chapter 7 a design of experiments (DOE) approach is employed for optimization of the heterogeneous process using a pillared clay impregnated with iron (III) acetylacetonate. The optimum conditions to maximize both color and total organic carbon removal, while minimizing the iron loss from the support, were found using the DOE tool.

Finally, in chapter 8, the main conclusions are summarized and future work is proposed.

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ABSTRACT

In this dissertation the factors that influence the Fenton's reagent oxidation of the azo dye Orange II (OII) in homogeneous and heterogeneous systems were investigated. This compound was selected as model molecule to represent the concerned dye group because it is inexpensive and very used in the textile, pulp and paper industries.

The first part of the thesis experimental work is dedicated to the homogeneous process, wherein the catalyst (Fe^{2+}) is dissolved in the original solution. Firstly, an experimental design methodology was applied having in mind the optimization of the Orange II degradation in a batch reactor, at fixed dye concentration. The variables considered were the temperature, H_2O_2 concentration and the $\text{Fe}^{2+}:\text{H}_2\text{O}_2$ ratio, at optimum pH of 3. It was found that both H_2O_2 concentration and temperature have an important effect in the organic matter degradation efficiency, being possible, under the optimum conditions, to reach color removals of 99.7% and mineralization degrees as high as 70.7% in only 2 hours of operation.

After this statistical approach, a more phenomenological modelling technique was employed. For this, a simple kinetic model was used to study the degradation of the dye using Fenton's reagent in the Fenton-like stage. The effect of pH, temperature, Cl^- concentration and initial concentration of OII, hydrogen peroxide and ferrous ion on the degradation rate were investigated in a batch reactor. A pseudo-first-order reaction rate with respect to OII concentration was found to be adequate to fit the experimental data, in which the apparent kinetic constant depends on the initial conditions following a power-law dependency. This equation, without further fitting parameters, was then used to validate experiments performed in a continuous stirred tank reactor, also carried out in a wide range of experimental conditions.

In a second stage, the degradation and mineralization of Orange II solutions was studied using catalysts in which the iron was incorporated into different solid supports (pillared clays and activated carbons). All the catalysts were characterized through commonly used techniques and the experiments were performed in a slurry batch reactor. Firstly, several runs were performed using a pillared saponite that was impregnated with different iron salts (Fe(II) acetate, Fe(II) oxalate, Fe(II) acetylacetonate and Fe(III) acetylacetonate) and three iron loads (7.5, 13.0 and 17.0

wt.%). For the most promising catalysts, a preliminary analysis of the main operating conditions effects during OII degradation was carried out. It is worth mentioning that these solids present good catalytic properties (above 99% dye degradation and 90% total organic carbon – TOC – removal in 4 hours), using less than 0.1 g_{catalyst}/L, with simultaneous low leaching degrees (final concentration of iron < 1 ppm).

As above-mentioned, a heterogeneous Fenton-like oxidation process was also tested using two carbon-based supports, impregnated with 7.0 wt.% iron. The carbon supports employed are quite different, being one of them an activated carbon prepared from agricultural by-products, while the other one is a carbon aerogel. In this catalyst, characterization data point for a very good iron dispersion on the carbon surface, which is related with the better catalytic performances exhibited by this sample. However, iron leaching from the support is considerable, leading to a progressive deactivation in consecutive reaction cycles.

Finally, an experimental design methodology was applied to further analyze and optimize the Fenton-like process of Orange II degradation while minimizing also the leaching of iron. The independent variables considered were the temperature, H₂O₂ concentration and catalyst (iron-impregnated pillared saponite clay) load. The multivariate experimental design allowed developing empiric quadratic models for dye degradation, TOC removal and iron leaching after 1, 2, 3 and 4 h of reaction, which were adequate to predict responses in all the range of experimental conditions used. Data obtained revealed that the optimal conditions depend on the response factor considered, being advisable to use less-aggressive conditions if responses are taken at longer reaction times. Particularly temperature, but also catalyst concentration, were found out to be the main parameters affecting all the responses, while the effect of initial H₂O₂ concentration was found out to be negligible. It is remarkable the low leaching values attained (in the range 0.7-5.0%), pointing for a good stability of the catalyst.

SUMÁRIO

Nesta dissertação estudou-se o efeito dos factores que influenciam a oxidação do corante azo Orange II (OII) usando o reagente de Fenton, em sistemas homogéneos e heterogéneos. Este composto foi seleccionado como molécula modelo para representar o grupo de corantes em estudo por ser barato e muito utilizado nas indústrias têxtil e do papel.

A primeira parte do trabalho experimental reportado na tese diz respeito ao processo homogéneo, onde o catalisador (Fe^{2+}) é dissolvido na solução original. Inicialmente, foi usada uma metodologia de planeamento de experiências tendo como objectivo a optimização da degradação do corante Orange II num reactor fechado, com uma concentração constante de corante. As variáveis consideradas foram a temperatura, a concentração de H_2O_2 e a razão $\text{Fe}^{2+}:\text{H}_2\text{O}_2$, ao pH óptimo de 3. Verificou-se que tanto a concentração de H_2O_2 como a temperatura têm uma influência significativa na eficiência da degradação da matéria orgânica, sendo possível, nas condições óptimas, atingir remoções de cor de 99,7 % e um grau de mineralização de 70,7 %, em apenas 2 horas de operação.

Depois desta abordagem estatística, recorreu-se a um modelo mais fenomenológico. Para tal, utilizou-se um modelo cinético simples para se estudar a degradação do corante com reagente de Fenton, na fase tipo-Fenton (segunda fase deste processo). Avaliou-se o efeito do pH, temperatura, concentração de Cl^- e concentração inicial de OII, peróxido de hidrogénio e ião ferroso na velocidade de degradação, em reactor fechado. Verificou-se que uma cinética reaccional de pseudo-primeira ordem, relativamente à concentração de OII, era adequada e se ajustava aos resultados experimentais, na qual a constante cinética aparente depende das condições iniciais com um comportamento tipo lei de potência. Esta equação, sem nenhum parâmetro de ajuste adicional, foi usada para validar ensaios efectuados num reactor contínuo perfeitamente agitado, também realizados numa vasta gama de condições experimentais.

Na segunda parte, estudou-se a degradação e mineralização de soluções de Orange II usando catalisadores nos quais o ferro foi incorporado em diferentes suportes sólidos (argilas pilareadas e carvões activados). Todos os catalisadores foram caracterizados usando técnicas vulgarmente empregues e os ensaios foram novamente conduzidos num reactor fechado, agora tipo *slurry*. Primeiramente, realizaram-se

algumas experiências usando uma argila saponita pilareada, a qual foi impregnada com diferentes sais de ferro (acetato de Fe(II), oxalato de Fe(II), acetilacetato de Fe(II) e acetilacetato de Fe(III)) e três teores de ferro (7,5, 13,0 e 17,0 % em peso). Para os catalisadores mais promissores, realizou-se uma análise preliminar dos efeitos das principais condições operatórias na degradação do OII. Importa mencionar que estes sólidos apresentam boas propriedades catalíticas (degradação do corante superior a 99 % e remoções de 90 % do carbono orgânico total – COT – em 4 horas), usando-se concentrações inferiores a 0,1 g_{catalisador}/L, com baixos níveis de lixiviação (concentração final de ferro < 1 ppm).

Como foi referido anteriormente, testou-se igualmente um processo de oxidação heterogéneo tipo-Fenton usando-se dois suportes de carbono, impregnados com 7,0 % (p/p) de ferro. Os suportes de carbono utilizados são bastante diferentes, sendo um deles um carvão activado preparado a partir de sub-produtos agrícolas e o outro um aerogel de carbono. Neste catalisador, os dados da caracterização apontam para uma muito boa dispersão do ferro na superfície do carbono, o que está relacionado com o melhor desempenho catalítico exibido por esta amostra. No entanto, a lixiviação do ferro do suporte é considerável, conduzindo à progressiva desactivação do catalisador quando usado em ciclos de reacção consecutivos.

Finalmente, aplicou-se uma metodologia de planeamento de experiências foi para se analisar mais em detalhe e otimizar o processo tipo-Fenton da degradação do Orange II, minimizando-se também a lixiviação do ferro. As variáveis independentes consideradas foram a temperatura, a concentração de H₂O₂ e o teor do catalisador (argila saponita, pilareada e impregnada com ferro). O planeamento de experiências multivariável permitiu desenvolver modelos quadráticos empíricos para a degradação do corante, para a remoção do COT e para a lixiviação do ferro após 1, 2, 3 e 4 horas de reacção, os quais se revelaram serem adequados para preverem as respostas em todo o domínio de condições experimentais utilizado. Os resultados obtidos revelaram que as condições óptimas dependem do factor de resposta considerado, sendo recomendável o uso de condições menos agressivas se as respostas forem consideradas a tempos de reacção longos. Em particular a temperatura, mas também a concentração de catalisador, revelaram ser os parâmetros que mais afectam todas as respostas, ao passo que o efeito da concentração inicial de H₂O₂ pode ser considerado desprezável. São notórios os baixos valores de lixiviação atingidos (entre 0,7-5,0 %), sugerindo uma boa estabilidade do catalisador.

RÉSUMÉ

Dans cette thèse, les facteurs qui affectent l'oxydation du colorant azo Orange II (OII) par réaction de Fenton dans des systèmes homogènes et hétérogènes ont été étudiés. Ce composé a été sélectionné comme molécule modèle représentative du groupe de colorant concerné puisqu'il est bon marché et très utilisé dans les industries du textile et du papier.

La première partie de la thèse est consacrée à une étude expérimentale du procédé homogène où le catalyseur (Fe^{2+}) est dissout dans la solution originelle. Premièrement, une méthode de design expérimental a été appliquée avec comme objectif l'optimisation de la dégradation de l'Orange II dans un réacteur de type batch, à concentration fixe en colorant. Les variables considérées furent la température, la concentration de H_2O_2 et le rapport $\text{Fe}^{2+}:\text{H}_2\text{O}_2$, à un pH optimum de 3. Il s'est avéré que la concentration de H_2O_2 et la température ont toutes les deux un effet important sur l'efficacité de la dégradation de la matière organique, rendant possible, dans les conditions optimales, l'élimination de 99.7% de la couleur avec des degrés de minéralisation allant jusqu'à 70.7 % en seulement 2 heures d'opération.

A la suite de cette approche statistique, une technique de modélisation plus phénoménologique a été employée. Un simple modèle cinétique a été utilisé pour étudier la dégradation du colorant au moyen du réactif Fenton (dans la seconde phase du procédé de type Fenton). Les effets du pH, de la température, de la concentration en Cl^- et de la concentration initiale de OII, de peroxyde d'hydrogène et d'ion ferrique sur le taux de dégradation ont été étudiés dans un réacteur de type batch. Une vitesse de réaction de type pseudo premier ordre s'est avérée adéquate afin d'ajuster les données expérimentales de la concentration en OII. La constante apparente de la cinétique est fonction des conditions initiales avec une dépendance en loi de puissance. Cette équation, qui ne contient pas d'autres paramètres additionnels pour l'ajustement, a alors été utilisée pour valider les expériences menées dans un réacteur tank à agitation continue avec également une gamme élargie de conditions expérimentales.

Dans une deuxième partie, la dégradation et la minéralisation des solutions d'Orange II ont été étudiées en utilisant des catalyseurs dans lesquels le fer a été incorporé dans différents supports solides (charbons activés et argiles). Tous les catalyseurs ont été caractérisés au moyen de techniques courantes et les expériences ont

été menées en réacteur clos. D'abord, plusieurs essais ont été entrepris avec de la saponite imprégnée de différents sels de fer (acétate de Fe(II), oxalate de Fe(III), acétyl acétonate de Fe(II) et de Fe(III)) et trois teneurs en fer (7.5, 13.0 et 17.0 % en poids). Pour les catalyseurs les plus prometteurs, une analyse préliminaire des principales conditions d'opération durant la dégradation de OII a été entreprise. Il est intéressant de souligner que tous ces solides présentent de bonnes propriétés catalytiques (une dégradation du colorant supérieure à 99% et une élimination de 90% du carbone organique total - COT – en 4 heures), obtenues en utilisant une concentration en catalyseur inférieure à 0.1 g/L, et présentant simultanément un taux de lessivage bas (la concentration finale en fer est inférieure à 1 ppm).

Comme mentionné ci-dessus, un procédé d'oxydation hétérogène de type Fenton a également été essayé où deux supports de carbone imprégnés de 0.7 % en poids de fer ont été utilisés. Les supports de carbone utilisés sont assez différents puisque l'un d'eux est un charbon activé préparé à partir de résidus de l'agriculture, tandis que l'autre est un aérogel de carbone. Pour ce dernier, les résultats de la caractérisation indiquent une bonne dispersion du fer sur la surface de carbone, ce qui est associé avec de meilleures performances catalytiques. Cependant, la perte de fer dans le support est importante et entraîne une désactivation progressive lors de cycles successifs de réaction.

Finalement, une méthodologie de design expérimental a été appliquée afin d'analyser et d'optimiser le procédé de type Fenton de dégradation de l'Orange II tout en minimisant le lessivage du fer. Les variables indépendantes considérées furent la température, la concentration en H_2O_2 et la charge de catalyseur (argile de saponite imprégnée de fer). Le design expérimental à variables multiples a permis de développer des modèles quadratiques empiriques pour décrire la dégradation du colorant, l'élimination du COT et le lessivage du fer après 1, 2, 3 et 4 heures de réaction. Ces modèles se sont avérés être adaptés à la prédiction des réponses dans toute la gamme de conditions expérimentales utilisée. Les données obtenues ont révélé que les conditions optimales dépendent du facteur de réponse considéré, et qu'il est conseillé d'utiliser les conditions les moins agressives si les réponses à obtenir le sont pour des temps de réaction plus longs. En particulier, la température ainsi que la concentration en catalyseur se sont avérées être les principaux paramètres affectant toutes les réponses, tandis que l'effet de la concentration initiale en H_2O_2 s'est avéré être négligeable. Il est

à noter que les basses valeurs de lessivage atteintes (dans la gamme de 0.7-5%) suggèrent une bonne stabilité du catalyseur.

NOMENCLATURE

Latin characters

A	Pre-exponential coefficient of the kinetic law (s^{-1})
C_i	Concentration of species i (M)
$C(t)$	Danckwerts' C curve (dimensionless)
$E(t)$	Residence-time distribution function (s^{-1})
E_a	Apparent activation energy ($kJ\ mol^{-1}$)
F_i	Molar flow rate of species i ($mol\ s^{-1}$)
k_{ap}	Apparent kinetic rate constant (s^{-1})
k_i	Rate constant for elementary Fenton reaction step i ($M^{-1}s^{-1}$ or s^{-1})
Q	Volumetric flow rate ($L\ s^{-1}$)
$(-r_{OII})$	Reaction rate for orange II consumption ($mol\ L^{-1}\ s^{-1}$)
R	Ideal gas constant ($J\ mol^{-1}\ K^{-1}$)
t	Time (s)
T	Temperature (K)
V	Volume of reactor (L)
X	Orange II conversion (%)

Greek symbols

λ	Wavelength
τ	Space-time (s)

Subscripts

batch	Refers to batch reactor;
Cl^-	Refers to chloride ion
exp	Refers to experimental conditions
Fe^{2+}	Refers to ferrous ion
Fe^{3+}	Refers to ferric ion
H_2O_2	Refers to hydrogen peroxide

in	Refers to inlet conditions (continuous reactor)
mod	Refers to model prediction
o	Refers to initial conditions (batch reactor)
OII	Refers to Orange II
out	Refers to outlet conditions (continuous reactor)

Superscripts

a	Reaction order with respect to Orange II concentration
b	Reaction order with respect to H ₂ O ₂ concentration
c	Reaction order with respect to Fe ²⁺ concentration
o	refers to initial conditions (continuous reactor – tracer experiments)

Abbreviations

OII	Orange II dye
TOC	Total Organic Carbon
AOPs	Advanced Oxidation Processes
DOE	Design of Experiments
<i>HO•</i>	Hydroxyl Radical
PILCs	Pillared clays
Al-PILCs	Al-pillared saponite impregnated with iron salts

PART I

INTRODUCTION

CHAPTER 1 – INTRODUCTION

1.1 Water and Environmental Problems

Everyone needs water everyday to cover the daily demand in food, domestic use, etc. Water is used in agriculture, construction, transport, chemical industry, and numerous other activities of human beings. According to the United Nations, the first priority of poor countries, especially in Africa, should be not financial support or technological knowledge but clean water supply to the population [1].

Unfortunately, despite the fact that most of the planet is covered by water, only a small amount of this water is available as fresh water. Almost 97.5% of the total is in oceans and it is not suitable for drinking, watering, or industrial use. The remaining 2.5% is fresh water. According to the European Commission, less than 1% of the planet's water is available for human consumption and more than 1.2 billion people in the world have no access to safe drinking water [1].

On the other hand, the domestic use and industrial activity, of especially impact among the developed countries, generate high amounts of residual wastewater, whose direct disposal to natural courses causes a considerable effect in the environment. This fact, together with the need to restore this water for new uses, makes practically essential the purification of wastewater to achieve the desired degree of quality. Recently, reflecting a new environmental conscience, the European Directive 2000/60/CE [2] stresses the need to adopt measures against water pollution in order to achieve a progressive reduction of pollutants.

1.2 The Textile Industry in Portugal

The textile industry is an example of the industrial sector where large quantities of water are used, basically as a solvent. This industry plays a part in the economy of several countries around the world. China is the largest exporter of textile products around the world, and the European Union (mainly Italy, Germany, France and United Kingdom), USA, Japan, Pakistan, Turkey, Taiwan and Korea are the top ten of world exporters [3]. Dyeing is a fundamental operation during textile fibre processing, which causes the production of more or less colored wastewaters [4]. On this way, use and

disposal of wastewater from textile industries are important considerations when assessing environmental impact of textiles.

At the beginning of the 20th century, the importance of the textile industry in the Portuguese economy increased until representing up to 50% of the national exportations [5]. Nowadays, Portuguese textiles and clothes have permitted to Portugal having a relevant position in the ranking of exporters from the European Union. Since 2000, Portugal has been ranked in the first ten highest exporters of textiles in the European Union, corresponding to 4.3% of the total exportations and 18.5% of national exportations [6].

In Portugal the textile industry is concentrated in three regions: North, Centre and Lisbon. Being evident, in the last years (1999-2002), a little increase of this industry in the north and even centre of the country when compared with the Lisbon zone (see Figure 1.1) [7].

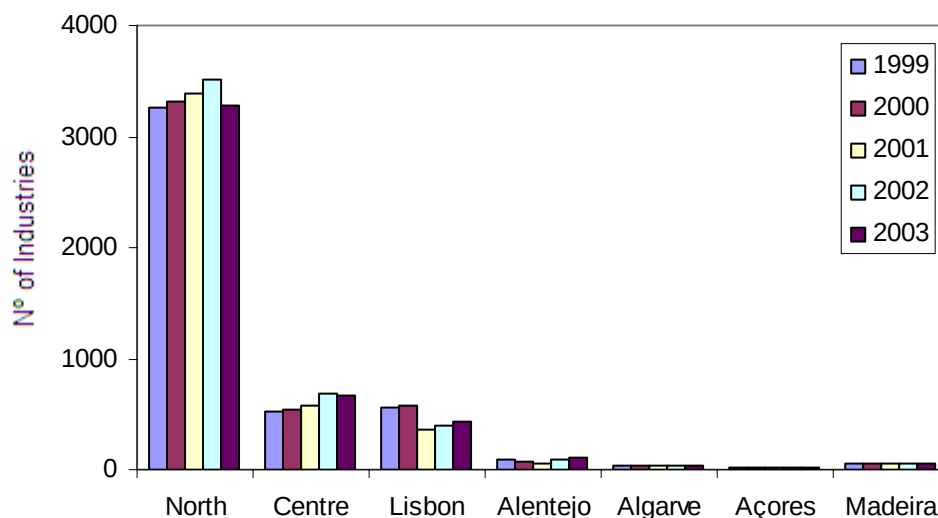


Fig. 1.1 – Localization of textile industries in Portugal. Adapted from [7].

In particular the Ave hydrographic bay is characterized by a strong industrialization, spreading through Porto and Braga districts, where the biggest factories of most important industries in the textile sector are found. The highly polluted effluents of the textile industries, even more of concern than the high flow rates, significantly contribute to pollute the hydric reserves of the country. Actually, it is observed a significant potential pollution by dangerous substances associated to industrial effluents, namely textile industries, in middle and low Ave and Este and

Vizela rivers, due to the nature of the industrial park settled and the insufficient installations of adequate treatment systems [8].

The high number of pollution risk points in the Ave river, as well as, the high human occupation and the significant number of pollute industrial unities, are causes of the extreme situation of pollution in the Ave hydrographic bay. In 1985, the “Comissão de Gestão Integrada da Bacia Hidrográfica do Ave” prepared a general plan of depollution in this region, which was approved in 1990 [6]. This commission proposed the construction of three stations of residual water treatment (ETARs from the name in Portuguese): the ETARs of Gondar, Rabada and Agra in Porto and Braga, which are working up to now.

Nowadays, the textile activity is regularized by the portaria sectorial nº 423/97 of June 25th and by Annex XVIII of decree law no 236/98 of August 1st, with the objective to obligate for an efficient treatment of textile effluents [6].

1.3 Dyes

Kirk-Othmer defines dyes as intensely colored or fluorescent organic substances which impart color to a substrate by selective absorption of light [9]. Dyes are used to color fabrics, leather, paper, ink, lacquers, varnishes, plastics, cosmetics, and some food items. Several thousands of individual dyes of various colors and types are manufactured worldwide. This large number is attributable to the many different types of materials to which dyes are applied and the different conditions of service for which dyes are required [10]. Commercial dyes are sold in several physical forms including granular, powders, liquid solutions, and pastes [11].

Organic dyes are classified in several ways, including according to their chemical structure or class, general dye chemistry, and application process. In particular, the chemical structure classifications divides them into azo dyes, triaryl-methanes, diphenyl-methanes, anthraquinones, stilbenes, methines, polymethines, xanthenes, phthalocyanines, sulfurs and so on. Kirk-Othmer [9] describes the common application process classes of dyestuffs to include acid dyes, mordant dyes, metal complex dyes, direct dyes, fiber reactive dyes, basic dyes, vat dyes, sulfur dyes, disperse dyes, ingrain dyes, azoic dyes, and other dyes. Using the general dye chemistry approach, textile dyes typically are grouped into the following categories: acid dyes, direct (substantive dyes), azoic dyes, disperse dyes, sulphur dyes, fiber reactive dyes,

basic dyes, oxidation dyes, mordant (chrome) dyes, developed dyes, vat dyes, pigments, optical/fluorescent brighteners, and solvent dyes [12].

In the Federal Food, Drug, and Cosmetic Act (FD&C) colorants are dyes and pigments that have been certified or provisionally certified by the Food and Drug Administration (FDA) for use in food items, drugs, and/or cosmetics. The International Association of Color Manufacturers (IACM) represents certain FD&C colorant manufacturing facilities. Typically, FD&C colorants are azo, anthraquinone, or triarylmethane dyes with azo representing the largest category. Actually, azo dyes make up 60-70% of all textile dyestuffs and are not removed from wastewaters via conventional biological treatments [13].

Of the dyes available on the market today, up to 70% are azo compounds [14]. Azo dyes can be divided into monoazo, diazo and triazo classes, according to the presence of one or more azo bonds ($-N=N-$). Nevertheless, according to the classifications above mentioned, they are found in various other categories, i.e. acid, basic, direct, disperse, azoic and pigments [15,16]. Some azo dyes and their dye precursors have been shown to be or are suspected to be human carcinogens as they form toxic aromatic amines [17-19].

Unfortunately, the exact amount of dyes produced in the world is not known. Exact data on the quantity of dyes discharged into the environment are also not available. It is assumed that a loss of 1–2% in production and 1–10% loss in use are a fair estimate [20]. Because of their commercial importance, the impact and toxicity of dyes that are released in the environment have been extensively studied. As several thousand different synthetic dyes that are employed exhibit various biological activities, it is understandable that our knowledge concerning their behaviour in the environment and health hazards involved in their use is still incomplete [20].

1.4 Orange II Azo Dye

Orange II (OII), also called acid orange 7, is a molecule that has O–H... N and N=N bonds (see Figure 1.2). It is widely used in the dyeing of textiles, food, and cosmetics and thus is found in the wastewaters of the related industries [21]. For these reasons, OII degradation has been studied widely [22].

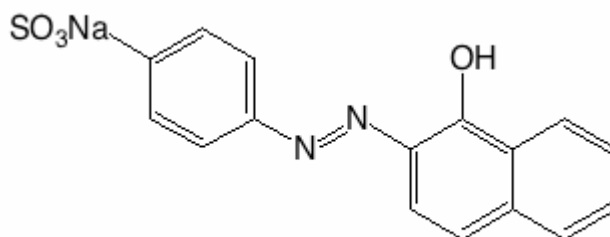


Fig. 1.2 – Azo dye Orange II structure.

OII is possibly the most studied compound among the azo dyes as far as its catalytic degradation under several experimental conditions is concerned. The degradation pathways and the formation of by-products is also fully described [23-34]; thus, OII could be used as a model compound for oxidative degradation studies of azo dyes. The oxidative attack of an azo dye from the phenyl azonaphthol family as OII leads to benzene sulfonate and naphthoquinone as primary degradation products. Vinodgopal *et al.* [25] reported the formation of four by-products (benzene sulphonic acid, sulphanilic acid, 1,4-naphthoquinone and phthalic acid) and Bauer *et al.* [26] have identified in addition quinone and 4-hydroxybenzene sulphonic acid during the first steps of Vis/TiO₂ photosensitized degradation of OII. The former products were also identified by Styliadi *et al.* [17], which studied the complete degradation of OII under solar light irradiation. Twenty-two transformation products were identified in total, including 2-naphthol, 2-hydroxy-1,4-naphthoquinone, smaller aromatic intermediates such as phthalic acid and phthalimide and aliphatic acids such as fumaric, succinic, maleic and malonic acids. The lowest molecular weight compounds detected in that study are oxalic, acetic and formic acids.

1.5 Wastewater Treatment Processes

The waste management is a very broad area, and therefore only wastewater treatment will be briefly focused in this section, which will in concrete be applied on the removal of an organic non-biodegradable dye (Orange II), because it is toxic, frequently encountered in today's industrial effluents, and can not be efficiently treated by the conventional methods. However, to give a more complete picture of the situation, the main types of pollutants and treatment methods are briefly mentioned.

There is a big variety of water pollutants from diverse sources. Physically, wastewater is usually characterised by its colour (e.g. grey), odour (e.g. musty), and solids content, which can be suspended (e.g. about 30%) as well as dissolved (e.g. about 70%) [27]. Chemically, wastewater might be composed of organic and inorganic compounds, as well as various dissolved gases. Organic components may consist of carbohydrates, proteins, fats and greases, surfactants, oils, pesticides, phenols, etc. Inorganic components may consist of heavy metals, nitrogen, phosphorus, sulphur, chlorides, among others. Gases commonly dissolved in wastewater are hydrogen sulphide, methane, ammonia, oxygen, carbon dioxide and nitrogen. The first three gases result from the decomposition of organic matter present in the wastewater. Biologically, wastewater may contain many pathogenic organisms, which generally originate from human beings [27].

The typical processes used to decontaminate wastewaters are physical, biological and chemical treatments. Flocculation, sedimentation, flotation, filtration, extraction and adsorption, for instance on activated carbon, are typical physical or physicochemical operations.

On the other hand, the biological treatment usually refers to the use of microorganisms (bacteria) in engineered reactor systems for effecting the removal of certain constituents, such as organic compounds, trace elements and nutrients. In aerobic systems, oxygen is provided and used by the bacteria to bio-chemically oxidise organic matter to carbon dioxide and water. In an anaerobic system, oxygen is excluded and the microorganisms utilise compounds other than molecular oxygen for the completion of metabolic processes [28].

Finally, chemical treatment processes “manipulate” the chemical properties of the contaminants to facilitate their removal from the bulk wastewater or to decompose them within the waste stream. Chemical precipitation, for instance, is used for removal of phosphorus and enhancement of suspended solids removal. Disinfection is a selective destruction of disease-causing organisms. Chemical oxidation/reduction is applied basically for treatment of hazardous organic wastes, but also inorganic.

All above-mentioned treatments can be used separately or combined with other processes to enhance the treatment efficiency of the process [29,30]. For example, a flocculation stage may be often followed by a secondary biological process. The choice of the correct system must be carried out considering several factors, both technical

(treatment efficiency, plant simplicity, etc.) and economical (investment and operating costs).

Generally, in the case of high organic pollutant concentrations and high flow rates, classic incineration is most widely used for liquid (and solid) waste destruction [31]. For wastes with only low to moderate concentration of organic material, the process is not self sustainable and auxiliary fuel has to be added. Due to the high temperature required, incineration needs an extremely high energetic input. The implant of air pollution control devices is even raising the cost of this process. Another alternative is separation and reuse of organics, but it requires additional energy costs for the facilities construction and operation [31].

For low to mediate concentration of dissolved organics, there are several ways/possibilities to treat liquid waste streams. One option is the adsorption, namely on activated carbon [32], but the saturated carbon is a hazardous waste, requiring either regeneration or transportation to a hazardous waste landfill [33]. An apparent low cost option is offered by the biological oxidation, but the organic pollutant has to be biodegradable, dilute and of low toxicity. However, the process usually proceeds at low rates and generates a huge amount of sludges [34]. This high sludge generation requires physical treatments for sludge volume reduction, and the subsequent landfilled leading to a potential secondary pollution source [30].

Summarising, the actual conventional methods are clearly not suitable to treat toxic, non-biodegradable organic pollutants, and new improved treatment methods have to be developed and tested. Recent progress in the removal of such type of compounds and particularly dyes has led to the development of advanced oxidation processes (AOPs), described in detail in the following section. Due to increasing amounts and complex composition of real organic effluents, advanced oxidation technologies will probably constitute the best option in the near future, as they can treat wastes with high total organic carbon (TOC) and chemical oxygen demand (COD) contents [35].

1.6 Advanced Oxidation Processes (AOPs)

To overcome the inconveniences of conventional treatment methods such as biological treatment, physical adsorption or incineration, various chemical oxidation techniques have emerged in the last decades, in particular for the treatment of industrial wastewaters. Among these techniques, the so-called advanced oxidation processes

appear to be a promising field of study, which have been reported to be effective for the degradation of soluble organic contaminants from waters and soils, because they can often provide an almost total degradation, under reasonably mild conditions of temperature and pressure [36-48].

AOPs utilise chemical reactions, electron beams, UV light or ultrasound pulses to obtain high oxidation rates through the generation of free radicals (mainly hydroxyl radicals). Indeed, highly reactive hydroxyl radicals ($HO^\bullet$) are traditionally thought to be the main active species responsible for the destruction of pollutants [36, 49-52]. Thanks to its high standard reduction potential of 2.8 V in acidic media (see Table 1.1), these radicals would be able to oxidize almost all organic compounds to carbon dioxide and water, except for some of the simplest organic compounds, such as acetic, maleic and oxalic acids, acetone or simple chloride derivatives as chloroform [53]. These species are however of a very interesting kind because they are typical oxidation products of larger molecules after fragmentation, being continuously generated by chemical, photochemical or electrochemical reactions. Depending on the nature of the parent organic species, two types of initial attack might be possible by that radical: it might abstract a hydrogen atom in the case of alkanes and alcohols, or it might attach itself to a molecule in the case of aromatic compounds, such as dyes.

Table 1.1 – Standard reduction potential of some oxidants in acidic media. Adapted from [53].

Oxidant	Standard Reduction Potential (V)
Fluorine (F_2)	3.03
Hydroxyl Radical ($HO^\bullet$)	2.80
Atomic Oxygen	2.42
Ozone (O_3)	2.07
Hydrogen Peroxide (H_2O_2)	1.77
Potassium Permanganate ($KMnO_4$)	1.67
Hypobromous Acid ($HBrO$)	1.59
Chlorine Dioxide (ClO_2)	1.50
Hypochlorous Acid ($HClO$)	1.49
Chlorine (Cl_2)	1.36
Bromine (Br_2)	1.09

This work is specially focused in homogeneous and heterogeneous advanced oxidation process based on hydrogen peroxide, which is supposed to mainly give rise to hydroxyl radicals after catalytic decomposition, and for this reason a brief review of these processes is treated here. Hydrogen peroxide is a safe, efficient and easy to use chemical oxidant, suitable for wide usage on contamination prevention. Discovered by Thenard in 1818, it was first used to reduce odor in wastewater treatment plants, and from then on, it became widely employed in wastewater treatment [54]. However, since hydrogen peroxide itself is not an excellent oxidant for many organic pollutants (*cf.* Table 1.1), it must be combined with UV light, salts (particularly metals) or ozone to produce the desired degradation results.

1.6.1 Fenton's Reagent ($H_2O_2/Fe^{2+}/Fe^{3+}$)

More than 110 years ago Fenton (1894) reported that ferrous ions strongly promote the oxidation of tartaric acid by hydrogen peroxide [55]. Forty years later, Haber and Weiss (1934) discovered that the hydroxyl radical is the actual oxidant in such systems [56]. In reality, the Fenton catalyst (Fe^{2+}/Fe^{3+} system) causes the dissociation of hydrogen peroxide and the formation of highly reactive HO radicals that attack and destroy the organic compounds. This reaction is a widely used and studied catalytic process based on an electron transfer between H_2O_2 and a metal (usually transition metal) acting as a homogeneous catalyst [57,58]. By far, the most common of these ones is iron [53, 59].

Oxidation with Fenton's reagent is based on ferrous or ferric ion and hydrogen peroxide and exploits the very high reactivity of the hydroxyl radical produced in acidic solution by the catalytic decomposition of H_2O_2 [59]. The mechanism of Fenton's oxidation involves basically the following steps (Eqs. (1.1) to (1.6)), wherein the kinetic constants are given in $M^{-1}s^{-1}$ (with the exception of k_5) and were taken from the literature:





The $HO^\bullet$ species produced through reaction given by Eq. (1.1) will then attack the organic matter present in the reaction medium, because the hydroxyl radical is a powerful inorganic oxidant that reacts non-selectively with numerous compounds (rate constants in the range 10^7 - $10^{10} \text{ M}^{-1}\text{s}^{-1}$) [59]. In the case under study in this dissertation, such process is initiated by the following reaction:



Fenton's reagent can be employed to treat a variety of industrial wastes containing a broad range of organic compounds like phenols, formaldehyde, pesticides, wood preservatives, plastic additives, dyes and rubber chemicals, for instance [60-70].

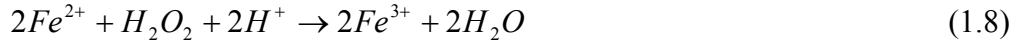
A large quantity of information exists regarding the mechanism and kinetics of $HO^\bullet$ production during the decomposition of H_2O_2 by Fe^{2+} and Fe^{3+} [56,71-77]. For example, the generally accepted mechanism of the decomposition of H_2O_2 by Fe^{3+} consists of a chain reaction with the iron cycles between Fe^{3+} and Fe^{2+} as H_2O_2 is consumed [56,73,77]. This can be simplified into the above mentioned equations, but many other are found in the literature. Nevertheless, the rate constants vary from author to author, and the activation energies are not well documented.

The main factors that influence the Fenton's processes are the medium pH, the contaminant nature/character and its concentration, the concentration of iron species and their nature, the hydrogen peroxide quantity required for oxidation, and finally the temperature [78]. Below the influence of some of these parameters on Fenton's oxidation performance is shortly described.

Regarding the last parameter mentioned, it is worth of noting that the Fenton's reagent has been often used at room temperature, but rarely at higher temperatures [79]. The main reason for this is the accelerated thermal decomposition of H_2O_2 into oxygen and water at higher temperatures, such non-productive decomposition affecting obviously the process performance.

In what concerns the pH of the reaction medium, a range of 2 to 4 has been repeatedly described as optimum for free radicals generation [80-83]. The explanation

of why acidic pH values are optimum for Fenton's process was given by Walling (1975), among others, who simplified the overall Fenton chemistry by accounting for the following reaction [59]:



This equation suggests that the presence of H^+ is required in the decomposition of H_2O_2 , indicating the need for an acid environment to produce the maximum amount of hydroxyl radicals. A dependence of the reaction performance with the pH is normally observed in homogeneous reaction, and the decreased performance at lower pHs is usually attributed to the inhibition of the reaction between Fe^{3+} and hydrogen peroxide, because the formation of the iron(III) peroxocomplexes (as intermediates) decreases when pH decreases [69]. Above pH 4, the rapid H_2O_2 decomposition produces molecular oxygen without formation of appreciable amounts of hydroxyl radicals [84].

Many times the quantity of hydrogen peroxide used is bigger than the stoichiometric quantity, because the consumption of H_2O_2 is not equal to the formation rate of hydroxyl radicals, once a part of the hydrogen peroxide decomposes into water and oxygen via non-radical pathways [85]. Even if the increase in the H_2O_2 load improves significantly the conversion of COD, for instance, there is a maximal peroxide dose, above which the process performance does not improve anymore [76]. The main reason for this is due to the well-known hydroxyl radicals scavenging effect [59,86]:



The use of high ferrous ion concentrations is believed to be appropriate for producing large quantities of $HO^\bullet$ within a short period of time [87]. Precisely the increase in the iron (catalyst) concentration seems to increase the oxidation rate [82] and COD reduction [88]. However, this is not always the case. Yoon *et al.* [87] observed that ferrous ions disappeared very rapidly in the absence of organic, but not in its presence. On the other hand hydrogen peroxide is consumed within seconds, independently on the presence or absence of organics. So, the presence of organics affects the behaviour of ferrous ions, because both compete for HO radicals. This is because as hydrogen peroxide decomposes to yield HO radicals, they mainly react with

ferrous ion and not with hydrogen peroxide (in absence of organic matter), due to the fact that the reaction between HO radicals and ferrous ions is ten times faster than between HO radicals and hydrogen peroxide (*cf.* rate constants for Eqs. (1.2) Vs. (1.4)).

In the industrial applications of Fenton's oxidation the Fe^{2+}/H_2O_2 ratio is usually high. The initial ferrous ion and hydrogen peroxide are consumed in a few seconds, and consequently the use of high concentrations of ferrous ion produces the sufficient quantity of HO radicals in a short period of time. However, such a high Fe^{2+} concentration can cause three problems. First, the high ratios of ferrous ion to hydrogen peroxide can decrease the efficiency of HO radicals for degradation of organics as ferrous ion itself can be HO radicals scavenger, as above-mentioned. Second, very rapid production of organic radical may cause depletion of dissolved oxygen and in that way decrease the mineralization grade. Third, such a quantity of iron will result in big amount of iron sludge [87]. Therefore, the doses employed have to be carefully analysed, varying according to the application intended and type of wastewater to be handled.

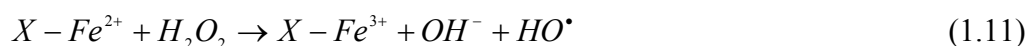
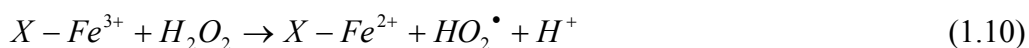
1.6.2 Heterogeneous Fenton Reagent's (H_2O_2/Fe^{2+} -solid)

The Fenton's process can be conducted homogeneously, when iron is dissolved into the reaction solution, or heterogeneously. However, homogeneously catalyzed reactions need up to 50-80 ppm of Fe ions in solution, which is well above the European Union directives that allow only 2 ppm of Fe ions in treated water to dump directly into the environment [89]. In addition, the removal/treatment of the sludge-containing Fe ions at the end of the wastewater treatment is expensive and needs large amount of chemicals and manpower.

To overcome the disadvantages of the homogeneous Fenton process, and also considering the possibility of recovering the catalyst, some attempts have been made to develop heterogeneous catalysts, prepared by incorporating Fe ions or Fe oxides into porous supports [90-93]. Other transition metal complexes supported on several surfaces such as metal oxides, resins, and mixed (Al-Cu) pillared clay have also been used as potentially active catalysts for the decomposition of H_2O_2 and for the oxidative degradation of organics [94]. Among the porous solids used as supports for the iron phases, it is worth mentioning the use of silica, alumina, silica-alumina and cation-exchanged resins, which have been used in the degradation and mineralization of dyes

[90]. More complex systems have been prepared by modifying a polyacrylonitrile (PAN) fibre by treatment with a mixture of hydrazine and hydroxylamine to introduce chelating functional groups onto the fibre surface. These functional groups are used to coordinate the transition metal cations Fe^{3+} , Co^{2+} , Ni^{2+} and Cu^{2+} to the fibre to act as the active catalytic sites for decomposition of the hydrogen peroxide [91]. Using an alternative strategy, other catalytic systems have been prepared by co-intercalation of two natural smectites (Wyoming SWy-1 and Tunisia-Gafsa VI) with Fe-Al polycations, obtained by polymerisation of a mixture of FeCl_3 and chlorhydrol [92]. Tachiev *et al.* [93] have reported other catalysts, in which Fe(II) and Fe(III) cations are complexed by the ligands DTPA, EDTA, EGTA, and NTA. The use of zeolites [95,96] and carbons [97,98] to support iron catalysts is also worth mentioning.

The mechanism of H_2O_2 decomposition by homogeneous Fenton's oxidation is not well (or at least unambiguously) established, where several oxidising agents have been suggested to be involved in the oxidation reactions, in addition to the $\text{HO}^\bullet$ radicals. For the heterogeneous systems this is still less clear, being a matter of controversy. Some authors suggest an initial step of fast adsorption of the H_2O_2 molecule on ($\equiv\text{Fe(III)}$) sites [98] and others the adsorption of the organics [99]. Nevertheless, the involvement of the following steps has been suggested in most of the works found in the literature, which correspond to Fe^{3+} reduction with generation of less oxidative $\text{HO}_2^\bullet$ radicals, followed by Fe^{3+} regeneration with formation of the hydroxyl radicals:



where X represents the surface of the catalyst. However, it must be remarked that the radicals can also be generated in the surface of the solid so they are actually "caged" in the solid structure, subsequently reacting with the adsorbed reagent(s) without radicals generation. Obviously, besides the indicated steps many other radical reactions occur, including those involving the reaction intermediates.

Among the above-mentioned catalyst supports, some will be briefly mentioned, as they are used in later chapters of this work. Is the case of pillared clays (PILCs in short), which is one of the families of microporous solids developed by Molecular Engineering that have been more studied in recent years, because of their particular

properties and structures (with tunable pore size), as well as the abundance and low cost of natural clay minerals. Besides, they lead to active and stable solids in aqueous media, usually being very stable against leaching [100]. The PILCs synthesis procedure can be divided into three main steps: i) preparation of polyoxocations by careful hydrolysis of certain multivalent cations, which under appropriate conditions give rise to cationic polymeric species, ii) ionic exchange of the original charge-compensating cations of swellable smectite clays by the polyoxocations before synthesized, this exchange giving rise to the so called “intercalated clays”, and iii) stabilisation of the intercalated clays by calcination at relatively high temperatures, which transform the metastable polyoxocations into “pillars”, stable metallic clusters, close to oxi-hydroxidic phases, which maintain the layers of the clays separated to a long distance [101], thus able to accommodate large molecules susceptible to undergo chemical transformations. These solids are called “pillared clays”, showing a bidimensional microporous network of molecular dimensions, with the pillars occupying the interlayer space defined by the clay layers. The number and size of the pillars in the interlayer region are responsible for the pore parameters of the pillared clay structure (see Figure 1.3) [102].

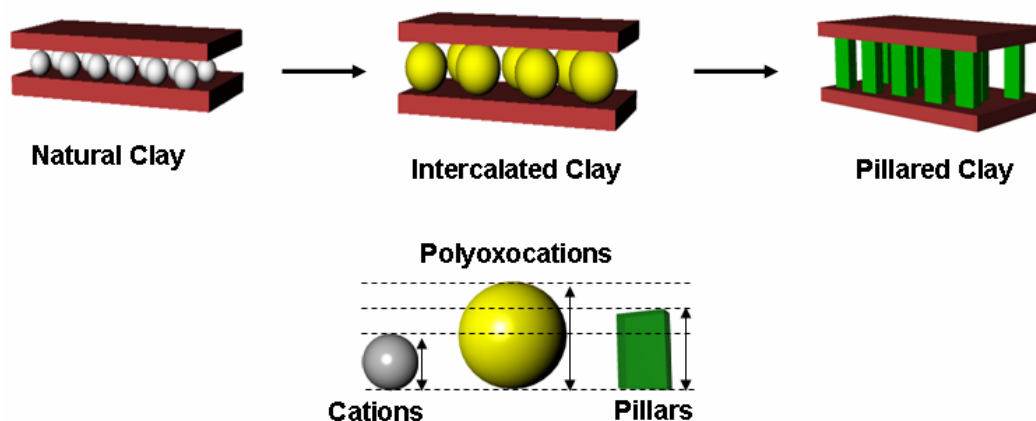


Fig. 1.3 – Pillared clays synthesis.

Recently, Feng and co-workers [99,103] synthesized clay-based Fe nanocomposites by the so-called pillaring technique and used them as heterogeneous catalysts for the photo-Fenton discoloration and mineralization of azo-dyes. Their results clearly indicate that the solids are promising photo catalysts, but the use of light increases the costs of the overall process as compared to dark Fenton oxidation.

However, in their conditions the oxidation is much faster, which is also important to be taken into account in economical analysis.

On the other hand, activated carbon is a member of a family of carbons ranging from carbon blacks to nuclear graphite, from carbon fibers and composites to electrode graphite, and many more [104]. Classical activated carbons are cheap materials prepared from very different raw precursors, but are heterogeneous solids with variable composition, depending on the raw material used. On the contrary, carbon aerogels (also used in this work, chapter 6) offer purity, homogeneity and controlled porosity, but are however more expensive because the synthesis method needs very specific equipment, such as the supercritical drying. Carbon aerogels have two main advantages over other carbon supports: i) their structure and pore texture can be designed at nanometer scale and ii) they can be prepared in the form of monoliths, beads, powders or thin films [105].

1.6.3 Photo-Fenton's Reagent ($H_2O_2/Fe^{2+}/UV$)

The photo-Fenton reaction is also well-known in the literature [58,106,107], which is an efficient and inexpensive method for wastewater and soil treatment [108-112]. Photo-Fenton is known to be able to improve the efficiency of dark Fenton or Fenton-like reagents, respectively, by means of the interaction of radiation (UV or Vis) with Fenton's reagent [69,70,113,114]. With light, the rate of $HO^\bullet$ formation is increased by photoreactions involving H_2O_2 ($\lambda < 360$ nm) and/or Fe(III) (Eqs. (1.12)-(1.14)) that produce $HO^\bullet$ directly or regenerate Fe(II), which can in turn yield more radicals through reaction (1.1) [115]:



This process has been suggested to be feasible and promising to remove pollutants from natural and industrial waters and increase the biodegradability of wastewaters, being used as a pre-treatment method to decrease the toxicity of water [47,116-118]. However, artificial UV/UV-vis light source was employed in most

studies, which is uneconomical for practical applications. Indeed, the solar irradiation offers an inexpensive and environmental friendly source of energy, and therefore will be particularly advantageous if applied to wastewater treatment processes, particularly in countries like Portugal where an important part of the year has a large quantity of hours of sun. Some innovative applications dealing with photo-Fenton's reagent include oxalate as a ligand of iron ions [119].

1.6.4 H_2O_2/UV Reagent

This AOP is based on the formation of $HO^\bullet$ radicals by means of the photolysis of hydrogen peroxide and the subsequent propagation reactions:



The molar absorptivity of hydrogen peroxide at 253.7 nm is low, about $20 \text{ M}^{-1} \text{ cm}^{-1}$, and $HO^\bullet$ radicals are formed per incident photon absorbed [36]. At this wavelength, the rate of photolysis of aqueous hydrogen peroxide is about 50 times slower than ozone. This technique requires therefore a relatively high dose of H_2O_2 and/or a much longer UV-exposure time than, for example, the UV/ O_3 process. On the other hand, the rate of photolysis of hydrogen peroxide has been found to be pH dependent and increases when more alkaline conditions are used, because, at 253.7 nm, peroxide anions HO_2^- may be formed, which display a higher molar absorptivity than hydrogen peroxide, $240 \text{ M}^{-1} \text{ cm}^{-1}$ [36].

References

1. Inglezakis, V. J.; Pouloupoulos. S. G. Adsorption, ion exchange and catalysis - Design of operations and environmental applications. Elsevier B. V. **2006**.
2. EC Directive 2000/60/EC of the European parliament and of the council of october 23. Establishing a framework for community action in the field of water policy **2000**.
3. Rocha, E. O.; Sousa, M. J.; Ferreira. M. L. Como evoluíram os clusters do têxtil e vestuário em portugal durante o período de desmantelamento do acordo multi-fibras (1995-2005)?. Universidade Católica Portuguesa **2006**.

4. Orfão, J. J. M.; Silva, A. I. M.; Pereira, J. C. V.; Barata, S. A.; Fonseca, I. M.; Faria, P. C. C.; Pereira, M. F. R. Adsorption of a reactive dye on chemically modified activated carbons-Influence of pH. *Journal of Colloid and Interface Science* **2006**, 296, 480.
5. Indústria Têxtil e do Vestuário em Portugal - Informe Universidade do Minho – **2008**. (<https://repositorium.sdum.uminho.pt/bitstream/1822/943/8/AnexosIV.pdf>)
6. Ribeiro da Cunha Figueiredo, S. A. Remoção de corantes têxteis em solução aquosa usando materiais naturais contendo quitina. PhD Dissertation, FEUP **2002**.
7. Vasconcelos, E. Análise da indústria têxtil e do vestuário Estudo EDIT VALUE Empresa Júnior N.º 02 **2006**.
8. Hidrorumo, Hidro4, ProceSl, Prosistemas, (Rev. 1 – 00/01/15). Plano de Bacia Hidrográfica do Rio Ave, 1ª Fase e diagnóstico da situação de referência, vol. III.
9. Othmer, K. Dyes and dye intermediates. *Encyclopedia of chemical technology*. 4th Edition. New York: John Wiley & Sons, Inc, **1993**, V. 8.
10. Synthetic organic chemicals United States production and sales, 1991,” USITC Publication 2607, **1993**.
11. Chemical economic handbook marketing research report—dyes,” SRI International, **2000**.
12. Kulkarni, S. V.; Blackwell, C. D.; Blackard, A. L.; Stackhouse, C. W.; Alexander, M. W. U.S. Environmental protection agency, Air and energy engineering research laboratory, “Project summary textile dyes and dyeing equipment: classification, properties, and environmental aspects” EPA/600/S2–85/010 **1985**.
13. Carliell, C. M.; Barclay, S. J.; Naidoo, N.; Buckley, C. A.; Mulholland, D. A.; Senior, E. Microbial decolourisation of reactive azo dye under anaerobic conditions. *Water S.A.* **1995**, 21, 61.
14. Carliell, C. M.; Barclay, S. J.; Shaw, C.; Wheatley, A. D.; Buckley, C. A. The effect of salts used in textile dyeing on microbial decolourisation of a reactive azo dye. *Environmental Technology* **1998**, 19, 1133.
15. Rafols, C.; Barcelo, D. Determination of mono- and disulphonated azo dyes by liquid chromatography–atmospheric pressure ionization mass spectrometry. *Journal of Chromatography A* **1997**, 777, 177.
16. Vandevivere, P. C.; Bianchi, R.; Verstraete, W. Treatment and reuse of wastewater from the textile wet-processing industry: review of emerging technologies. *Journal of Chemical Technology and Biotechnology* **1998**, 72, 289.
17. Styliadi, M.; Kondarides, D. I.; Verykios, X. E. Pathways of solar light-induced photocatalytic degradation of azo dyes in aqueous TiO₂ suspensions. *Applied Catalysis B: Environmental* **2003**, 40, 271.

18. Gomes da Silva, C.; Faria, J. L. Degradation of an azo dye in aqueous solution by UV irradiation. *Journal of Photochemistry and Photobiology A: Chemistry* **2003**, 155, 133.
19. Brown, M. S.; De Vito, S. C. Predicting azo dye toxicity. *Critical Reviews in Environmental Science and Technology* **1993**, 23, 249.
20. Forgacs, E.; Cserhati, T.; Oros, G. Removal of synthetic dyes from wastewaters: a review. *Environment International* **2004**, 30, 953.
21. Méndez-Paz, D.; Omil, F.; Lema, J. M. Anaerobic treatment of azo dye Acid Orange 7 under fed-batch and continuous conditions. *Water Research* **2005**, 39, 771.
22. Oakes, J.; Gratton, P. J. Kinetic investigations of azo dye oxidation in aqueous media. *Chemical Society Perkin Transactions* **1998**, 2, 1857.
23. Chen, F.; Xie, Y.; Zhao, J.; Lu, G. Photocatalytic degradation of dyes on a magnetically separated photocatalyst under visible and UV irradiation. *Chemosphere* **2001**, 44, 1159.
24. Gonçalves, M. S. T.; Oliveira-Campos, A. M. F.; Pinto, M. M. S.; Plasencia, P. M. S.; Queiroz, M. J. R. P. Photochemical treatment of solutions of azo dyes containing TiO₂. *Chemosphere* **1999**, 39, 781.
25. Vinodgopal, K.; Wynkoop, D.; Kamat, P. Environmental photochemistry on semiconductor surfaces: photosensitized degradation of a textile azo dye, acid orange 7, on TiO₂ particles using visible light. *Environmental Science and Technology* **1996**, 30, 1660.
26. Bauer, C.; Jacques, P.; Kalt, A. Photooxidation of an azo dye induced by visible light incident on the surface of TiO₂. *Journal of Photochemistry and Photobiology A: Chemistry* **2001**, 140, 87.
27. Paradowska, M. A. Tailored chemical oxidation techniques for the abatement of bio-toxic organic wastewater pollutants: An experimental study. Dissertation Escola Tècnica Superior d'Enginyeria Química Departament d'Enginyeria Química Universitat Rovira i Virgili Tarragona. **2004**.
28. Brock, T. D.; Madigan, M. T. *Biology of microorganisms*. Prentice Hall: Englewood Cliffs, NJ **1988**.
29. Abderrazik, N. B.; Al-Momani, F.; Sans, C.; Esplugas, S. Combined Photo-Fenton with biological treatment. *Afinidad* **2002**, 59, 498.
30. Bertanza, G.; Collivignarelli, C.; Pedrazzani, R. The role of chemical oxidation in combined chemical-physical and biological processes: experiences of industrial wastewater treatment. *Water Science and Technology* **2001**, 44, 109.
31. Santolieri, J. J. Liquid-injection incinerators, *Standard Handbook of Hazardous Waste Treatment and Disposal*, H.M. Freeman (ed.), McGraw-Hill, New York, **1988**.
32. Matatov, M. Y. I.; Sheintuch, M. Catalytic abatement of water pollutants. *Industrial and Engineering Chemistry Research* **1998**, 37, 309.

33. Voice, T. C. Activated carbon adsorption, Standard Handbook of Hazardous Waste Treatment and Disposal, H.M. Freeman (ed), McGraw-Hill, New York, **1988**.
34. Irvine, R. L.; Wilderer, P. A. Aerobic processes, Standard Handbook of Hazardous Waste Treatment and Disposal, H.M. Freeman (ed), McGraw-Hill, New York, **1988**.
35. Yue, P.L. Oxidation reactors for water and wastewater treatment. *Water Science and Technology* **1997**, 35, 189.
36. Glaze, W. H.; Kang, J. W.; Chapin, D. H. The chemistry of water treatment processes involving ozone, hydrogen peroxide and ultraviolet radiation, *Ozone Science and Engineering* **1987**, 9, 335.
37. Andreozzi, R.; Caprio, V.; Insola, A.; Martota, R. Advanced oxidation processes (AOP) for water purification and recovery. *Catalysis Today* **1999**, 53, 51.
38. Benítez, F. J.; Beltrán-Heredia, J.; Acero, J. L.; Pinilla, M. L. Ozonation kinetics of phenolic acids present in industrial wastewaters from olive oil mills. *Industrial and Engineering Chemistry Research* **1997**, 36, 638.
39. Benítez, F. J.; Beltrán-Heredia, J.; González, T.; Real, F. Photooxidation of carbofuran by a polychromatic UV irradiation without and with hydrogen peroxide. *Industrial and Engineering Chemistry Research* **1995**, 34, 4099.
40. Casero, I.; Sicilia, D.; Rubio, S.; Perez-Bendito, D. Chemical degradation of aromatic amines by Fenton's reagent. *Water Research* **1997**, 31, 1985.
41. Guittoneau, S. ; De Laat, J. ; Dore, M.; Duguet, J. P.; Bonnel, C. Comparative study of the photodegradation of aromatic compounds in water by UV and H₂O₂/UV. *Environmental Technology Letters* **1988**, 9, 1115.
42. Hoigne, J.; Bader, H. Rate constants of reactions of ozone with organic and inorganic compounds in water—I. *Water Research* **1983**, 17, 173.
43. Hoigne, J.; Bader, H. Rate constants of reactions of ozone with organic and inorganic compounds in water—II. *Water Research* **1983**, 17, 185.
44. Legrini, O.; Oliveros, E.; Braun, A. M. Photochemical processes for water treatment. *Chemical Reviews* **1993**, 93, 671.
45. Masten, S. J.; Davies, S. H. The use of ozonation to degrade organic contaminants in wastewaters. *Environmental Science and Technology* **1994**, 28, 180.
46. Meunier, B.; Sorokin, A. Oxidation of pollutants catalyzed by metallophthalocyanines. *Accounts of Chemical Research* **1997**, 30, 470.
47. Miller, R. M.; Singer, G. M.; Rosen, J. D.; Bartha, R. Sequential degradation of chlorophenols by photolytic and microbial treatment, *Environmental Science and Technology* **1988**, 22, 1215.
48. Ullmann's Encyclopedia of Industrial Chemistry, 6th ed., Wiley, New York, **1998**.

49. Braun, A. M.; Jacob, L.; Oliveros, E.; Do Nascimento, C. A. O. Up-scaling photochemical reactions, in: D. Volman, G.S. Hammond, D.C. Neckers (Eds.), *Advances in Photochemistry*, vol. 18, Wiley, New York, **1993**.
50. Glaze, W. H.; Kang, J. W. Advanced oxidation processes. Description of a kinetic model for the oxidation of hazardous materials in aqueous media with ozone and hydrogen peroxide in a semi-batch reactor. *Industrial and Engineering Chemistry Research* **1989**, 28, 1573.
51. Haag, W. R.; Yao, C. C. D. Rate constants for reaction of hydroxyl radicals with several drinking water contaminants. *Environmental Science and Technology* **1992**, 26, 1005.
52. Peyton, G. R.; Huang, F. R.; Burleson, J. L.; Glaze, W. H. Destruction of pollutants in water with ozone in combination with ultraviolet radiation. 1. General principles and oxidation of tetrachloroethylene. *Environmental Science and Technology* **1982**, 16, 448.
53. Bigda, R. J. Consider Fenton chemistry for wastewater treatment. *Chemical Engineering and Processing* **1995**, 91, 62.
54. Elizardo, K. Fighting pollution with hydrogen peroxide. *Pollution Engineering* **1991**, 106.
55. Fenton, H. J. H. Oxidation of tartaric acid in presence of iron. *Journal of the Chemical Society* **1894**, 65, 899.
56. Haber F.; Weiss J. The catalytic decomposition of hydrogen peroxide by iron salts. *Proceedings of the Royal Society London* **1934**, 147, 332.
57. Lücking, F.; Köser, H.; Jank, M.; Ritter, A. Iron powder, graphite and activated carbon as catalysts for the oxidation of 4-chlorophenol with hydrogen peroxide in aqueous solution. *Water Research* **1998**, 32, 2607.
58. Safarzadeh-Amiri, A.; Bolten, J.R.; Cater, S.R. The use of iron in advanced oxidation processes. *Journal of Advanced Oxidation Technologies* **1996**, 1, 18.
59. Walling, C. Fenton's reagent revisited. *Accounts of Chemical Research* **1975**, 8, 125.
60. Barbeni, M.; Minero, C.; Pelizzetti, E.; Borgarello, E.; Serpone, N. Chemical degradation of chlorophenols with Fenton's reagent. *Chemosphere* **1987**, 16, 2225.
61. Bishop, D. F.; Stern, G.; Fleishman, M.; Marshall, L. S. Hydrogen peroxide catalytic oxidation of refractory organics in municipal waste waters. *Journal of the American Chemical Society Division Waste Water Chemical* **1964**, 4, 85.
62. Gau, S. H.; Chang, F. H. Improved Fenton method to remove recalcitrant organics in landfill leachate. *Water Science and Technology* **1996**, 34, 455.
63. Lipczynska-Kochany, E.; Sprah, G.; Harms, S. Influence of some groundwater and surface waters constituents on the degradation of 4-chlorophenol by the Fenton reaction. *Chemosphere* **1995**, 30, 9.
64. Lipczynska-Kochany, E.; Bolton, J. R. Flash photolysis/HPLC applications. 2. Direct photolysis vs hydrogen peroxide mediated photodegradation of 4-chlorophenol as studied

- by a flash photolysis/HPLC technique. *Environmental Science and Technology* **1992**, 26, 259.
65. Lipczynska-Kochany, E. Degradation of aqueous nitrophenols and nitrobenzene by means of Fenton reaction, *Chemosphere* **1991**, 22, 529.
66. Miller, C. M.; Valentine, R. L.; Roehl, M. E.; Alvarez, P. P. J. Chemical and microbiological assessment of pendimethalin-contaminated soil after treatment with Fenton's reagent. *Water Research* **1996**, 30, 2579.
67. Moza, P. N.; Fytianos, K.; Samanidou, V.; Korte, F. Photodecomposition of chlorophenols in aqueous medium in the presence of hydrogen peroxide. *Bulletin of environmental contamination and toxicology* **1988**, 41, 678.
68. Murphy, A. P.; Boegli, W. J.; Price, M. K.; Moody, C. D. A Fenton-like reaction to neutralize formaldehyde waste solutions. *Environmental Science and Technology* **1989**, 23, 166.
69. Pignatello, J. J. Dark and photoassisted Fe^{3+} -catalyzed degradation of chlorophenoxy herbicides by hydrogen peroxide. *Environmental Science and Technology* **1992**, 26, 944.
70. Spacek, W.; Bauer, R.; Heisler, G. Heterogeneous and homogeneous wastewater treatment—comparison between photodegradation with TiO_2 and the photo-Fenton reaction. *Chemosphere* **1995**, 30, 477.
71. Barb, W. G.; Baxendale, J. H.; George, P.; Hargrave, K. R. Reactions of ferrous and ferric ions with hydrogen peroxide. Part I.—The ferrous ion reaction. *Transactions of the Faraday Society* **1951**, 97, 462.
72. Barb, W. G.; Baxendale, J. H.; George, P.; Hargrave, K. R. Reactions of ferrous and ferric ions with hydrogen peroxide. Part II.—The ferric ion reaction. *Transactions of the Faraday Society* **1951**, 97, 591.
73. Walling, C.; Goosen, A. Mechanism of the ferric ion catalyzed decomposition of hydrogen peroxide. Effect of organic substrates. *Journal of the American Chemical Society* **1973**, 95, 2987.
74. Abbot, J.; Brown, D. G. Kinetics of Iron-catalyzed decomposition of hydrogen peroxide in alkaline solution. *International Journal of Chemical Kinetics* **1990**, 22, 963.
75. Millero, F. J.; Sotolongo, S.; Stade, D. J.; Vega, C. A. Effect of ionic interactions on the oxidation of Fe(II) with H_2O_2 in aqueous solutions. *Journal of Solution Chemistry* **1991**, 20, 1079.
76. Voelker, B. M.; Sulzberger, B. Effects of Fulvic Acid on Fe(II) Oxidation by hydrogen peroxide. *Environmental Science and Technology* **1996**, 30, 1106.
77. De Laat, J.; Gallard, H. Catalytic Decomposition of hydrogen peroxide by Fe(III) in homogeneous aqueous solution: Mechanism and kinetic modeling. *Environmental Science and Technology* **1999**, 33, 2726.

78. Kakarla, P. K.; Andrews, T.; Greenberg, R. S.; Zervas, D. S. Modified Fenton's processes for effective in-situ chemical oxidation - Laboratory and field evaluation. *Remediation Journal* **2002**, 12, 23.
79. Koubek, E. Photochemically induced oxidation of refractory organics with hydrogen peroxide. *Industrial and Engineering Chemistry Process Design and Development* **1975**, 14, 348.
80. Watts, R. J.; Bottenberg, B. C.; Hess, T. F.; Jensen, M. D.; Teel, A. L. Role of reductants in the enhanced desorption and transformation of chloroaliphatic compounds by modified Fenton's reactions. *Environmental Science and Technology* **1999**, 33, 3432.
81. Rivas, F. J.; Navarrete, V.; Beltran, F. J.; Garcia-Araya, J. F. Simazine Fenton's oxidation in a continuous reactor. *Applied Catalysis B: Environmental* **2004**, 48, 249.
82. Neyens, E.; Baeyens, J. A review of classic Fenton's peroxidation as an advanced oxidation technique. *Journal of Hazardous Materials* **2003**, 98, 33.
83. Neyens, E.; Baeyens, J.; Weemaes, M.; de Heyder, B. Pilot-scale peroxidation (H₂O₂) of sewage sludge. *Journal of Hazardous Materials* **2003**, 98, 91.
84. Guo, J.; Al-Dahhan, M. Catalytic wet oxidation of phenol by hydrogen peroxide over pillared clay catalyst. *Industrial and Engineering Chemistry Research* **2003**, 42, 2450.
85. Southworth, B. A.; Voelker, B. M. Hydroxyl radical production via the Photo-Fenton reaction in the presence of fulvic acid. *Environmental Science and Technology* **2003**, 37, 1130.
86. De Laat, J.; Le, T. G. Effects of chloride ions on the iron(III)-catalyzed decomposition of hydrogen peroxide and on the efficiency of the Fenton-like oxidation process. *Applied Catalysis B: Environmental* **2006**, 66, 137.
87. Yoon, J.; Lee, Y.; Kim, S. Technol. Investigation of the reaction pathway of OH radicals produced by Fenton oxidation in the conditions of wastewater treatment. *Water Science and Technology* **2001**, 44, 15.
88. Rivas, F. J.; Beltran, F. J.; Gimeno, O.; Frades, J. Treatment of olive oil mill wastewater by Fenton's reagent. *Journal of Agricultural and Food Chemistry* **2001**, 49, 1873.
89. EEC List of Council Directives 76/4647. European Economic Community. Brussels, Belgium, **1982**.
90. Gemeay, A. H.; Mansour, I. A.; El-Sharkawy, R. G.; Zaki, A. B. Kinetics and mechanism of the heterogeneous catalyzed oxidative degradation of indigo carmine *Journal of Molecular Catalysis A: Chemical* **2003**, 193, 109.
91. Ishtchenko, V. V.; Huddersman, K. D.; Vitkovskaya, R. F. Part 1. Production of a modified PAN fibrous catalyst and its optimization towards the decomposition of hydrogen peroxide. *Applied Catalysis A: General* **2003**, 242, 123.

92. Letaief, S.; Casal, B.; Aranda, P.; Martín-Luengo, M. A.; Ruiz-Hitzky, E. Fe-containing pillared clays as catalysts for phenol hydroxylation. *Applied Clay Science* **2003**, 22, 263.
93. Tachiev, G.; Roth, J. A.; Bowers, A. R. Kinetics of hydrogen peroxide decomposition with complexed and free iron catalysts. *International Journal of Chemical Kinetics* **2000**, 32, 24.
94. Carriazo, J. G.; Guelou, E.; Barrault, J.; Tatibouët, J. M.; Moreno, S. Catalytic wet peroxide oxidation of phenol over Al–Cu or Al–Fe modified clays *Applied Clay Science* **2003**, 22, 303.
95. Neamtu, M.; Zaharia, C.; Catrinescu, C.; Yediler, A.; Macoveanu, M.; Kettrup, A. Fe-exchanged Y zeolite as catalyst for wet peroxide oxidation of reactive azo dye Procion Marine H-EXL. *Applied Catalysis B: Environmental* **2004**, 48, 287.
96. Maurya, M. R.; Titinchi, S. J. J.; Chand, S. Oxidation of phenol with H₂O₂ catalysed by Cr(III), Fe(III) or Bi(III) N,N'-bis(salicylidene) diethylenetriamine (H₂saldien) complexes Encapsulated in zeolite-Y. *Journal of Molecular Catalysis A Chemical* **2003**, 193, 165.
97. Zazo, J. A.; Casas, J. A.; Mohedano, A. F.; Rodriguez, J. J. Catalytic wet peroxide oxidation of phenol with a Fe/Active carbon catalyst. *Applied Catalysis B: Environmental* **2006**, 65, 261.
98. Dantas, T. L. .P.; Mendonça, V. P.; Jose, H. J.; Rodrigues, A. E.; Moreira. R. F. P. M. Treatment of textile wastewater by heterogeneous Fenton process using a new composite Fe₂O₃/carbon. *Chemical Engineering Journal* **2006**, 118, 77.
99. Feng, J.; Hu, X.; Yue, P. L.; Zhu, H. Y.; Lu. G. Q. A novel laponite clay-based Fe nanocomposite and its photo-catalytic activity in photo-assisted degradation of Orange II. *Chemical Engineering Science* **2003**, 58, 679.
100. Catrinescu, C.; Neamtu, M.; Miehe-Brendle, J.; Garcia, M. G.; Kettrup, A. Catalytic wet oxidation of reactive azo dyes over iron-containing pillared beidellite catalyst. In: M.A. Vicente, M. Suarez, V. Rives, M. J. Sanchez (Eds.), *Materiales Arcillosos: de la Geologia a las Nuevas Aplicaciones*, Salamanca, **2006**, 87.
101. Belver, C.; Banares-Munoz, M. A.; Vicente, M. A. Fe-saponite pillared and impregnated catalysts: I. Preparation and characterization. *Applied Catalysis B: Environmental* **2004**, 50, 101.
102. Gil, A.; Gandia, L. M.; Vicente, M. A. Recent advances in the synthesis and catalytic applications of pillared clays. *Catalysis Reviews - Science and Engineering* **2000**, 42, 145.
103. Sum, O. S. N.; Feng, J.; Hu, X.; Yue, P.L. Pillared laponite clay-based Fe nanocomposites as heterogeneous catalysts for photo-Fenton degradation of acid black 1. *Chemical Engineering Science* **2004**, 59, 5269.
104. Marsh, H.; Rodriguez-Reinoso, F. Activated carbon. Elsevier B. V. **2006**.

105. Padilla-Serrano, M. N.; Maldonado-Hodar, F. J.; Moreno-Castilla, C. Influence of Pt particle size on catalytic combustion of xylenes on carbon aerogel-supported Pt catalysts. *Applied Catalysis B: Environmental* **2005**, 61, 253.
106. Kiwi, J.; Pulgarin, C.; Peringer, P. Beneficial effects of homogeneous photo-Fenton pre-treatment upon the biodegradation of anthraquinone sulfonate in wastewater treatment. *Applied Catalysis B: Environmental* **1993**, 3, 85.
107. Ruppert, G.; Bauer, R.; Heisler, G. J. The photo-Fenton reaction - an effective photochemical wastewater treatment process. *Journal of Photochemistry and Photobiology A: Chemistry* **1993**, 73, 75.
108. Bauer, R.; Fallmann, H. The photo-Fenton oxidation - a cheap and efficient wastewater treatment method. *Research on Chemical Intermediates* **1997**, 23, 341.
109. Chen, R.; Pignatello, J. J. Role of quinone intermediates as electron shuttles in Fenton and photoassisted Fenton oxidations of aromatic compounds. *Environmental Science and Technology* **1997**, 31, 2399.
110. Krutzler, T.; Fallmann, H.; Maletzky, P.; Bauer, R.; Malato, S.; Blanco, J. Solar driven degradation of 4-chlorophenol. *Catalysis Today* **1999**, 54, 321.
111. Ruppert, G.; Bauer, R.; Heisler, G. J. UV-O₃, UV-H₂O₂, UV-TiO₂ and the photo-Fenton reaction - comparison of AOP's for wastewater treatment. *Chemosphere* **1994**, 28, 1447.
112. Sauleda, R.; Brillas, E. Mineralization of aniline and 4-chlorophenol in acidic solution by ozonation catalysed with Fe²⁺ and UVA light. *Applied Catalysis B: Environmental* **2001**, 29, 135.
113. Hislop, K. A.; Bolton, J. R. The photochemical generation of hydroxyl radicals in the UV-Vis/ferrioxalate/H₂O₂ system. *Environmental Science and Technology* **1999**, 33, 3119.
114. Sundstrom, D. W.; Weir, B. A.; Klei, H. A. Destruction of aromatic pollutants by UV light catalysed oxidation with hydrogen peroxide. *Environmental Progress* **1989**, 8, 6.
115. Pignatello, J. J.; Liu, D.; Huston, P. Evidence for an additional oxidant in the photoassisted fenton reaction. *Environmental Science and Technology* **1999**, 33, 1832.
116. Fallmann, H.; Krutzler, T.; Bauer, R.; Malato, S.; Blanco, J. Applicability of the photo-Fenton method for treating water containing pesticides, *Catalysis Today* **1999**, 54, 309.
117. Fallmann, H.; Krutzler, T.; Bauer, R.; Malato, S.; Blanco, J. Detoxification of pesticide containing effluents by solar driven Fenton process. *Z. Phys. Chem.* **1999**, 213, 67.
118. Maletzky, P.; Bauer, R. The photo-Fenton method—degradation of nitrogen containing organic compounds. *Chemosphere* **1998**, 37, 899.
119. Aplin, R.; Freitz, A. J. Effect of Fe(II)-ligand properties on effectiveness of modified photo-Fenton processes. *Water Science and Technology* **2001**, 44, 23.

PART II

EXPERIMENTAL SECTION

CHAPTER 2 – EXPERIMENTAL SECTION

2.1 Materials

The dye used in all the experiments was Orange II (OII - $C_{16}H_{11}N_2NaO_4S$), also known as acid orange 7, from Fluka p.a. For oxidation runs in homogeneous phase, solid iron sulphate ($FeSO_4 \cdot 7H_2O$, from Panreac) was used. As oxidant, hydrogen peroxide solution (30% w/w, from Merck) was always employed (i.e., in either homogeneous or heterogeneous Fenton process).

The initial pH of the solutions was adjusted through addition of 1 M NaOH (prepared with NaOH p.a. from Merck, 99 %) or 0.1 M H_2SO_4 (prepared with H_2SO_4 95-97 % from p.a. Merck) solutions.

For the total organic carbon (TOC) analysis of samples taken along reaction time in batch experiments, the Fenton reaction was stopped by adding excess Na_2SO_3 p.a. from Riedel-de Haen, 96 %.

2.2 Oxidation Experiments

Oxidations experiments were performed either in a batch or in a continuous mode, both using stirred reactors, as described below.

2.2.1 Batch Reactor

Chemical oxidation of an aqueous solution of the azo dye Orange II was conducted in a stirred jacketed glass batch reactor, being the temperature controlled through a Huber thermostatic bath (Polystat CC1 unit) – *cf.* Fig. 2.1. The reactor (0.3 or 1.5 L capacity) was equipped with a Falc F30ST magnetic stirrer for continuous stirring of the reaction mixture (230 rpm), and a thermocouple was used to assess the temperature in the liquid phase. The absorbance and the pH were continuously monitored, using a Philips PU8625 UV/VIS spectrophotometer and a pH-meter from EDT instruments (RE 357 TX electrode), respectively. For on-line absorbance measurements (at $\lambda_{max} = 486$ nm – *cf.* section 2.3), a flow-through cell was used, being the recirculation of the solution made with the help of a Watson-Marlow 5055

peristaltic pump, at very high flow rate. Data acquisition (at a frequency of 0.3 s^{-1}), with displaying and saving capabilities in a PC, was performed using a home-designed interface with the software Labview 5.0, from National Instruments.

The assembly shown in Fig. 2.1 allows an almost in-situ monitoring of the dye concentration in the reaction mixture, which, coupled with a high data frequency acquisition, provided a good perspective of the concentration history. However, in most figures not all the data are included, for a better visualization.

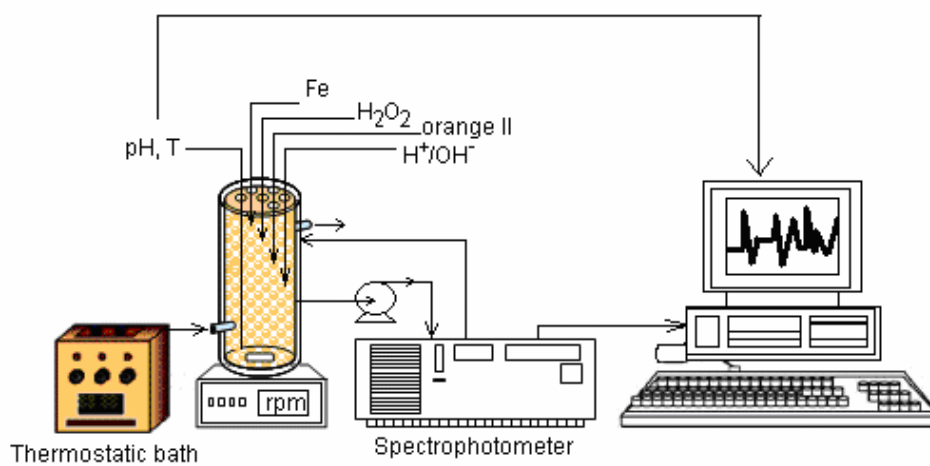


Fig. 2.1 – Experimental set-up used in the batch reactor runs.

In the experiments, the dye solution was first prepared, and the required volume put in the reactor. The dye was used as received. In all the runs the initial pH was adjusted through addition of NaOH or H_2SO_4 solutions. Then, and depending if the runs concern homogenous (chapters 3 and 4) or heterogeneous (chapters 5-7) catalysis, iron sulphate or powder solid catalyst was added, respectively. This was followed by the hydrogen peroxide solution addition (initial instant of the runs – $t = 0$), with intermediate pH adjustment when necessary.

2.2.2 Continuous Reactor

Experiments were also conducted in a jacketed continuous stirred tank reactor (CSTR), with 0.92 L capacity. The reactor is provided with the same magnetic stirrer and thermostatic bath as the batch one, and the pH and temperature were also

continuously monitored, as above. Figure 2.2 shows a sketch of the experimental set-up.

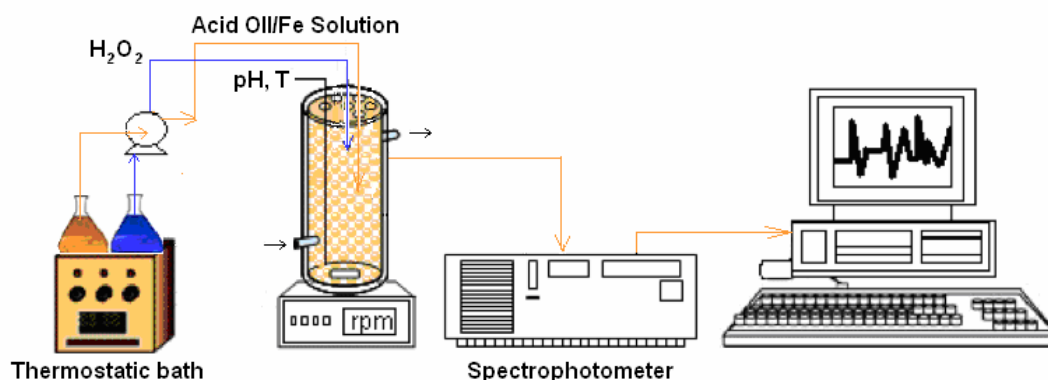


Fig. 2.2 – Experimental set-up used in the CSTR runs.

For operation of the CSTR, the Watson-Marlow 5055 peristaltic pump was used to feed two streams: one acidic containing the dye solution with the iron catalyst, and another with the H_2O_2 solution. Both flasks are placed within the thermostatic bath and the corresponding tubes thermally isolated, for a better control of temperature. The flow rates were carefully measured so that the concentration of each species, at the reactor inlet, was known. The exit stream was flowed through the spectrophotometer until a steady dye concentration was measured.

2.3 Analytical Techniques

The oxidation degree of the Fenton's process was evaluated in terms of: i) decrease of dye concentration (or simply color), and ii) mineralization degree, as described in this section.

Figure 2.3 illustrates the azo dye Orange II structure, which is basically consisted by an azo ($\text{N}=\text{N}$) linkage, a benzene ring and a naphthalene ring. Its concentration was obtained from a calibration curve (Fig. 2.4) at the characteristic dye wavelength (486 nm, as shown in Fig. 2.5), because this corresponds to the absorption maximum and in this range interference by oxidation products does not exist (*cf.* chapter 5, section 5.3.2.1). For this reason, in most chapters the terms discolorisation or OII removal will be indifferently used.

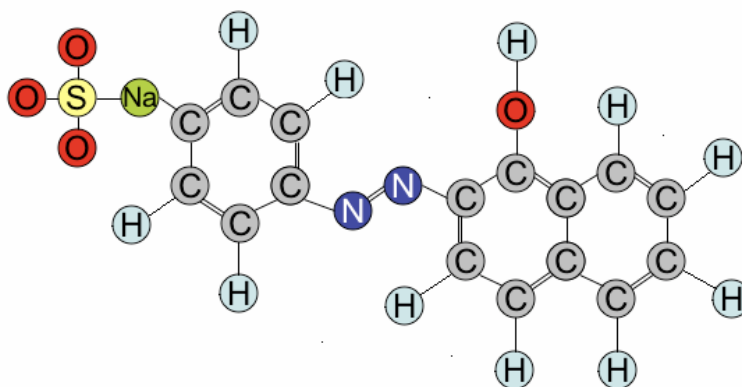


Fig. 2.3 – Chemical structure of the OII molecule.

The calibration curve shown in Fig. 2.4 is a typical one, which was up-dated whenever necessary (usually each 2 months). A good linear relationship between dye concentration (C_{OII}) and absorbance at 486 nm is noticed, for C_{OII} values up to 1×10^{-4} M. Absorbances were monitored in a Philips PU8625 UV/VIS spectrophotometer.

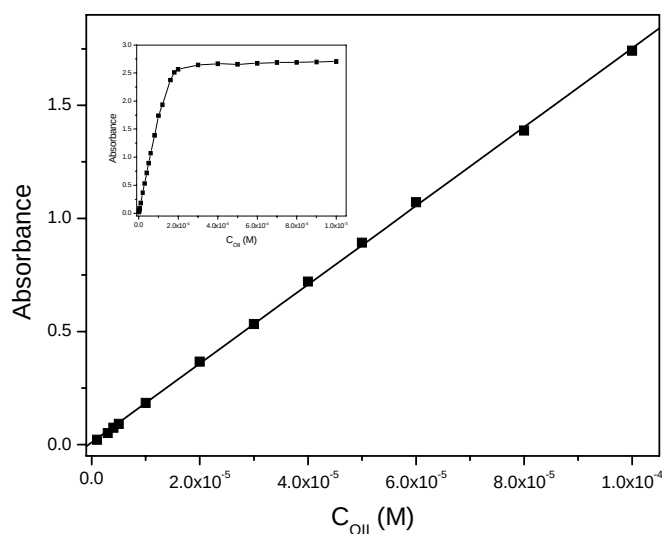


Fig. 2.4 – Typical calibration curve for OII quantification at 486 nm. Using plastic cell.

Figure 2.5 shows the UV-Vis spectrum recorded for the original dye solution, which is the expected one [1,2], with the characteristic absorbance peaks at around 235, 315 and 486 nm.

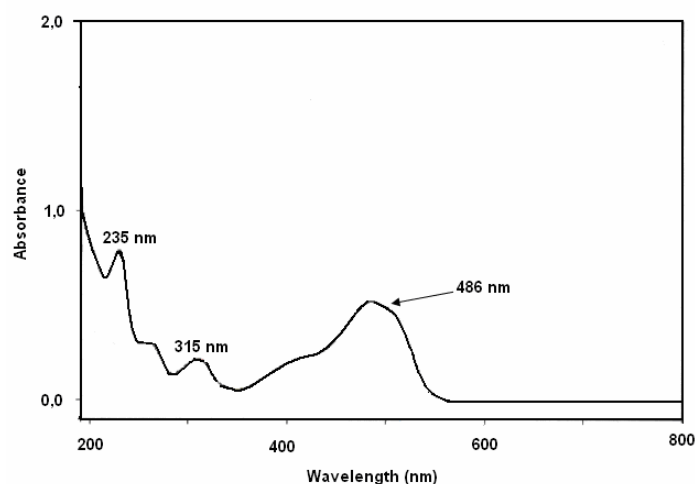


Fig. 2.5 – UV-Vis spectrum of an OII solution (concentration 5×10^{-5} M). Using quartz cell.

Degradation of OII (or discoloration of the dye solution) does not mean that it has been completely oxidized into CO_2 and H_2O , as reaction intermediates can be formed during oxidation. Therefore, it is important to evaluate the mineralization degree. So, total organic carbon (TOC) was measured by catalytic oxidation followed by IR spectrometry for CO_2 quantification using a Shimadzu 5000A instrument, model TOC-5000 CE, equipped with an automatic sample injector. TOC was calculated as the difference between the total carbon (TC) and inorganic carbon (IC) in the liquid sample. TOC values represent the average of at least two measurements; in most cases each sample was injected three times, which is validated by the apparatus only if the standard deviation is less than 3%. For such analysis samples were withdrawn from the reactor at several times, and reaction was stopped by adding excess Na_2SO_3 , which instantaneously consumes the remaining hydrogen peroxide. When using heterogeneous catalysts, the sample was previously submitted to filtration (by means of $0.8 \mu\text{m}$ glass fibre paper) for separation of the catalyst from the liquid phase.

When performing heterogeneous experiments, it is important to evaluate the amount of metal (iron) lost from the support. For that reason, the total Fe in the solution was determined in the same samples taken along the batch process using a UNICAM 939/959 atomic absorption spectrophotometer.

2.4 Synthesis of Solid Catalysts

In this work two main types of heterogeneous catalysts were employed: i) pillared clay-based (*cf.* chapters 5 and 7) and carbon-based (*cf.* chapter 6), which synthesis is described below.

2.4.1 Pillared Clay-Based Catalysts

Saponite clay (catalyst support) from Yuncillos (Toledo, Spain) was kindly supplied by TOLSA (Madrid, Spain). The fraction with particle size smaller than 2 μm , obtained by dispersion in water and controlled decantation of the natural clay, was used for intercalation/pillaring. Its chemical composition is given in Table 2.1. It is a well ordered smectite with basal spacing of 14.4 Å, a BET specific area of 152 m^2/g and a cation exchange capacity of 0.9 meq/g.

Table 2.1 – Chemical composition of the natural clay, expressed in oxides form, and referred to water-free solid.

Element	SiO ₂	MgO	Al ₂ O ₃	Fe ₂ O ₃	TiO ₂	Na ₂ O	K ₂ O	CaO
wt. %	62.21	29.45	5.21	1.46	0.30	0.54	0.30	0.53

Saponite was intercalated with $[\text{Al}_{13}\text{O}_4(\text{OH})_{24}(\text{H}_2\text{O})_{12}]^{7+}$ polycations (in short, Al_{13}), by using a standard procedure [3,4]. First, the Al_{13} solution to be intercalated was obtained by careful hydrolysis of an Al^{3+} solution, derived from $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ (Panreac, *purissimum*), with 1M NaOH (Panreac, *purissimum*), using a ratio $\text{OH}^-/\text{Al}^{3+}=2.2$, stirring vigorously to avoid local increases of pH that may lead to the precipitation of aluminum hydroxide, and aging 24 h (final pH = 4.1). After that, the solution was added to the saponite, employing an Al/clay ratio of 5 mmol/g clay. In order to favor intercalation, the clay had been swollen by preparing an aqueous suspension 12 hours before the addition of the intercalating solution. The new suspension was stirred for 24 h, and then washed by centrifugation and dialysis until absence of chloride (evaluated by the Ag^+ test). The solid obtained was dried at 70 °C for 16 h, and then heated to 500 °C at a heating rate of 1 °C/min under air atmosphere and maintained at this temperature for four hours. The solid obtained, designated as Al_{13} -500, was used as support for the preparation of the supported catalysts.

Impregnation of the support was carried out by means of the incipient wet impregnation method, by using four Fe-salts as precursors, namely Fe(II) acetate, Fe(II) oxalate, Fe(II) acetylacetonate and Fe(III) acetylacetonate. For each precursor, the amounts needed for obtaining a given amount (wt. %) of iron in the final catalysts were dissolved in the minimum amount of the appropriate solvent, water for the acetate and the oxalate, and acetone for both acetylacetonates. The first two salts were very soluble and a single impregnation step was needed, while five cycles were needed for both acetylacetonates because of their low solubility. After completing the impregnation, the solid was dried at 70 °C for 16 h and then calcined at 500 °C following the calcination procedure described for Al₁₃-500, thus obtaining the final catalysts.

2.4.2 Carbon-Based Catalysts

Two different carbon materials were used as Fe-supports: an activated carbon and a carbon aerogel. The activated carbon was prepared from olive stones by carbonization of the raw material at 1123 K for 15 min in N₂ flow (300 cm³/min), and activation at 1123 K in CO₂ flow (300 cm³/min) to 22% of burn-off. The synthesis of the carbon aerogel involves the synthesis and carbonization of an organic aerogel prepared from resorcinol (R) – formaldehyde (F) polymerization in aqueous solution [5]. The polymerization and, therefore, the textural characteristics of the final aerogel strongly depend on the synthesis conditions [6]. In this case, the molar ratios employed for water (W), R, F and Na₂CO₃ used as polymerization catalyst (C) were as follows: R/F = 0.5, R/W = 0.07 and R/C = 300. The obtained pH was 6.5. Polymerization was allowed to proceed during 7 days, controlling the temperature (25 °C in the first day, 50 °C in the second one, and 80 °C afterwards). After this period, the polymer was removed from the moulds and introduced in acetone for 2 days before the supercritical drying in CO₂. The obtained aerogel was carbonized in N₂ atmosphere (100 cm³/min) at 500 °C for 5h, increasing the temperature at a rate of 1.5 °C/min. Then, the oven is turned-off and the sample allowed cooling down in the same N₂ stream.

Finally, both supports were milled and screened and the fraction with a particle size smaller than 200 µm impregnated by means of the classical impregnation method with aqueous solution, using ferrous acetate (FeAc₂) as precursor. Thus, the amount of FeAc₂ needed for obtaining 7 wt. % of iron in the final catalyst was dissolved in the minimum amount of water and added drop by drop on the corresponding carbon

support. After impregnation, the samples were dried over night at 100°C and finally treated in N₂ flow at 200 °C for 2 h. TG and FTIR analyses showed that this thermal treatment is enough for the acetate decomposition.

2.5 Techniques used for Characterization of Solid Catalysts

In the following sections the physical-chemical techniques used to characterize the above-mentioned heterogeneous catalysts are described.

2.5.1 Pillared Clay-Based Catalysts

Elemental chemical analyses were performed to determine the composition of the original clay (support) and the exact amount of iron in the final catalysts, by using scanning electronic microscopy (SEM-JEOL-JSM6301-F) with an Oxford INCA/ENERGY-350 microanalysis system. The samples were covered with carbon by vaporization.

Powder X-ray diffraction (XRD) patterns of the solids were recorded in the 2 θ range of 2-65° by a Siemens D-500 diffractometer at 40 kV and 30 mA using filtered Cu K α radiation (λ = 1.5418 Å).

FT-Infrared spectra were recorded in the 4000-350 cm⁻¹ region with a Perkin-Elmer 1730 FT-IR spectrometer, using a He-Ne laser source (λ = 632.8 nm), in KBr pellet (0.001 g sample with 0.3 g KBr), and 15 scan per minute to improve the signal-to-noise ratio.

BET specific surface areas were determined by adsorption of nitrogen at 77K, measuring five adsorption points by using a Micromeritics Gemini apparatus and measuring five adsorption points between 0.01 and 0.2 of relative pressure. The samples were previously outgassed by treatment at 110 °C for 2 h, under flow of nitrogen.

Simultaneous thermal gravimetric (TG) and differential scanning calorimetric (DSC) analyses of samples were carried out using a TA-SDT Q600 Instrument. Samples of about 40 mg were heated in air (flow rate = 100 mL/min) from room temperature up to 900 °C, with a heating rate of 10 °C/min.

2.5.2 Carbon-Based Catalysts

Textural characterization was carried out by N₂ and CO₂ adsorption at -196 and 0 °C respectively, and mercury porosimetry. The BET surface areas (S_{BET}) were calculated from the corresponding nitrogen adsorption isotherms. The micropore volume (W_0) and mean micropore width (L_0) were calculated by the application of the Dubinin-Raduskevich equation to CO₂ adsorption isotherms [7]. Mercury porosimetry was obtained up to a pressure of 4200 kg cm⁻² using a Quantachrome Autoscan 60 equipment. With this technique, the following parameters were obtained: pore size distribution of pores with a diameter greater than 3.7 nm; surface area of these pores, which will be referred to as external surface area, S_{ext} ; pore volume corresponding to pores with a diameter between 3.7 and 50 nm, V_2 , referred to as “mesopore” volume (one should note that the mesopore volume range is defined as 2-50 nm); pore volume of pores with a diameter greater than 50 nm, or macropore volume, V_3 ; and particle density, ρ .

The morphology of the supports and catalysts was analyzed by scanning electron microscopy. Experiments were carried out with a ZEISS DSM 950 (30 kV) microscope. Metal dispersion and nature were followed by high-resolution transmission electron microscopy (HRTEM) using a Phillips CM-20 electron microscope and XRD using a Bruker D8 Advance diffractometer. Finally, X-ray photoelectron spectroscopy (XPS) measurements were performed using an ESCALAB 200A, VG Scientific (UK) system, with PISCES software for data acquisition and analysis. An achromatic Al (K α) X-ray source operating at 15kV (300 W) was used, and the spectrometer, calibrated with reference to Ag 3d5/2 (368.27 eV), was operated in CAE mode with 20 eV pass energy. Data acquisition was performed with a pressure lower than 10⁻⁶ Pa. Spectra analysis was performed using peak fitting with Gaussian-Lorentzian peak shape and Shirley type background subtraction.

References

1. Mielgo, I.; Moreira, M. T.; Feijoo, G.; Lema, J. M. A packed-bed fungal bioreactor for the continuous decolourisation of azo-dyes (Orange II). *Journal of Biotechnology* **2001**, 89, 99.

2. Mu, Y.; Yu, H. Q.; Zheng, J. C.; Zhang, S. J. TiO₂-mediated photocatalytic degradation of Orange II with the presence of Mn²⁺ in solution. *Journal of Photochemistry and Photobiology A: Chemistry* **2004**, 163, 311.
3. Lahav, N.; Shani, V.; Shabtai, J. Cross-Linked Smectites. I. Synthesis and Properties of Hydroxy-Aluminum-Montmorillonite. *Clays and Clay Minerals* **1978**, 26, 107.
4. Bottero, J. Y.; Cases, J. M.; Flessinger, F.; Porlier, J. E. Studies of hydrolyzed aluminum chloride solutions. 1. Nature of aluminum species and composition of aqueous solutions. *Journal of Physical Chemistry* **1980**, 84, 2933.
5. Pekala, R. W. Organic aerogels from the polycondensation of resorcinol with formaldehyde. *Journal of Materials Science* **1989**, 24, 3221.
6. Maldonado-Hódar, F. J.; Ferro-García, M. A.; Rivera-Utrilla, J.; Moreno-Castilla, C. Synthesis and textural characteristics of organic aerogels, transition-metal-containing organic aerogels and their carbonized derivatives. *Carbon* **1999**, 37, 1199.
7. Bansal, R. C.; Donnet, J. B.; Stoeckli, F. *Active Carbon*, Dekker, New York, **1998**.

PART III

HOMOGENEOUS SYSTEM

CHAPTER 3 – EXPERIMENTAL DESIGN TO OPTIMIZE THE DEGRADATION OF THE SYNTHETIC DYE ORANGE II USING FENTON'S REAGENT *

Abstract

The experimental design methodology was applied having in mind the optimization of the azo dye Orange II degradation using the Fenton's reagent (mixture of H_2O_2 and Fe^{2+}). The variables considered were the temperature, H_2O_2 concentration and $\text{Fe}^{2+}:\text{H}_2\text{O}_2$ ratio, for a dye concentration of 3×10^{-4} M and $\text{pH} = 3$. The multivariate experimental design allowed to develop quadratic models for: i) colour removal and ii) total organic carbon (TOC) reduction (both after 2 hours of reaction), which were adequate to predict responses in all the range of experimental conditions used. Under the optimum conditions, performances of 99.7% and 70.7% for colour and TOC removal, respectively, were experimentally reached. It was found that both H_2O_2 concentration and temperature have an important effect in the organic matter degradation efficiency.

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3.1 Introduction

To achieve high performances in the Fenton's process, the experimental conditions must be optimised. And this is not an easy task since in Fenton oxidation several parameters affect the oxidation efficiency, like the pH of the reaction medium, the temperature, the hydrogen peroxide concentration and the amount of catalyst used, usually expressed as the $\text{Fe}^{2+}/\text{H}_2\text{O}_2$ ratio. Although many researchers have usually only focussed on the single-factor-at-a-time approach, studying the effect of each experimental parameter on the process performance while keeping all other conditions constant, this approach does not take into account cross effects from the factors considered and leads to a poor optimization result. When a multifactor system is present, it is more appropriate to employ statistically-based optimization strategies to achieve such goal, with the minimum number of experiments [1,2]. Indeed, an alternative to the above-mentioned univariate strategy is the experimental design approach, which implies the use of statistical tools that allow the simultaneous change of several variables (multivariate analysis) [1]. The experimental design methodology is a modern approach which has been widely used in several applications [e.g., 3-5], also allowing the modelling of the process. In fact, the design of experiments (DOE) is used to identify or screen the important factors affecting a process or product and to develop statistically significant empirical models.

This study concerns the degradation of the non-biodegradable azo dye Orange II by Fenton's reagent. As azo dyes are extensively used in textile dyeing and finishing processes [6], orange II was selected as the test chemical to represent the concerned dye group because it is inexpensive and very used in the textile, pulp and paper industries. It is also a main goal of the present work to find the optimum conditions to maximize both colour and total organic carbon (TOC) removal, and so a DOE tool will be used.

3.2 Materials and Methods

The batch reactor, with 0.3 L capacity, the chemical reagents, the experimental set-up and the analytical techniques used in this chapter are described with more detail in chapter 2.

In all experiments a reaction volume of 0.2 L was used, with a 3×10^{-4} M dye concentration (to which corresponds a total organic carbon content of 58.6 mg/L) and

the runs were carried out at $\text{pH} = 3$. This pH value was set based on previous experimental results [7] and agrees with literature findings, as it is usually accepted that acidic pH levels near 3 are usually optimum for Fenton oxidation [8,9,10]. All experiments were run up to 120 min and replicates of some of them allowed concluding that experimental data do not differ, on average, more than 10%.

A DOE approach was used to model and optimize the process performance. The model considered to describe our data was a second order polynomial, and the corresponding coefficients were calculated from the experimental responses by means of least squares regression, using the JMP501 software [11].

3.3 Results and Discussion

3.3.1 Preliminary Experiments

Figure 2.3 shows the dye molecule, which is basically consisted by an azo ($\text{N}=\text{N}$) linkage, a benzene ring and a naphthalene ring, all of them exhibiting different absorbance peaks. Indeed, the chromophore-containing azo linkage has absorption in the visible region, while the benzene ring and the naphthalene ring absorb in the UV. Besides, the naphthalene ring absorption wavelength is higher than that of the benzene one. The exact values can be seen in Fig. 3.1, which shows the UV-Vis spectra recorded before and after oxidation. The spectrum recorded for the original dye solution is the expected one [12,13], with the characteristic absorbance peaks at around 235, 315 and 486 nm. Figure 3.1 also puts into evidence that the treated dye sample was almost colourless and did not show significant absorbance in the visible region, indicating that colour removal was practically complete (for the employed conditions). Indeed, the disappearance of the absorbance signal at 486 nm reflects, unequivocally, an almost complete decolourization and the breakdown in the chromophoric group. However, the spectrum in the UV region shows that the dye was not mineralized completely, though absorption reduced over the UV range. The diminution of the absorbance peak at 235 nm is related to the cleavage of the benzene group present in the original structure of the dye (*cf.* Fig. 2.3).

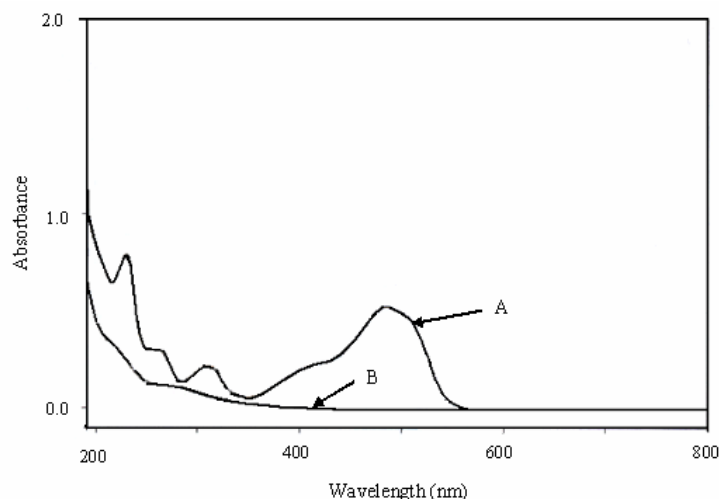


Fig. 3.1 – UV-Vis absorption spectra of Orange II before (A) and after (B) oxidation, in the following conditions: $T = 28.9^{\circ}\text{C}$, $C_{\text{H}_2\text{O}_2} = 1 \times 10^{-2} \text{ M}$ and $\text{Fe}^{2+}/\text{H}_2\text{O}_2$ ratio = 0.125 (w/w). Initial pH = 3.

Blank experiments showed that neither decolourization nor mineralization of Orange II occurs in the presence of Fe^{2+} ions alone (Figs. 3.2A and 3.2B). Colour removal was also negligible in the presence of only H_2O_2 (Fig. 3.2A), but in such conditions a slight TOC reduction was noticed (Fig. 3.2B).

In Fig. 3.2 are also shown, merely as illustrative examples, some other curves, which illustrate that after 2 h of oxidation decolourisations as high as 99.0% can be achieved, but after 10 min of operation a colour removal of 97% was already reached. Simultaneously, it is possible to attain mineralization efficiencies above 70% in 2 h of operation.

For most of the experiments where a significant colour (and/or TOC) removal was reached, it is evident that the process is much faster in the first 5-10 min, and then it proceeds at a slower reaction rate. Recently, a similar behaviour was found during cork cooking wastewater mineralization [14], while Malik and Saha [9] also found that direct dyes are decomposed in a two-stage reaction with Fenton's reagent. In the first stage dyes are decomposed rapidly and somewhat less rapidly in the second stage. The main reason for this well-known behaviour is that ferrous ions react very quickly with hydrogen peroxide (rate constant is $53 \text{ mol}^{-1}\text{dm}^3\text{s}^{-1}$) to produce large amounts of hydroxyl radicals (Eq. (3.1)), which can then react rapidly with the dye (so-called $\text{Fe}^{2+}/\text{H}_2\text{O}_2$ stage) [9].



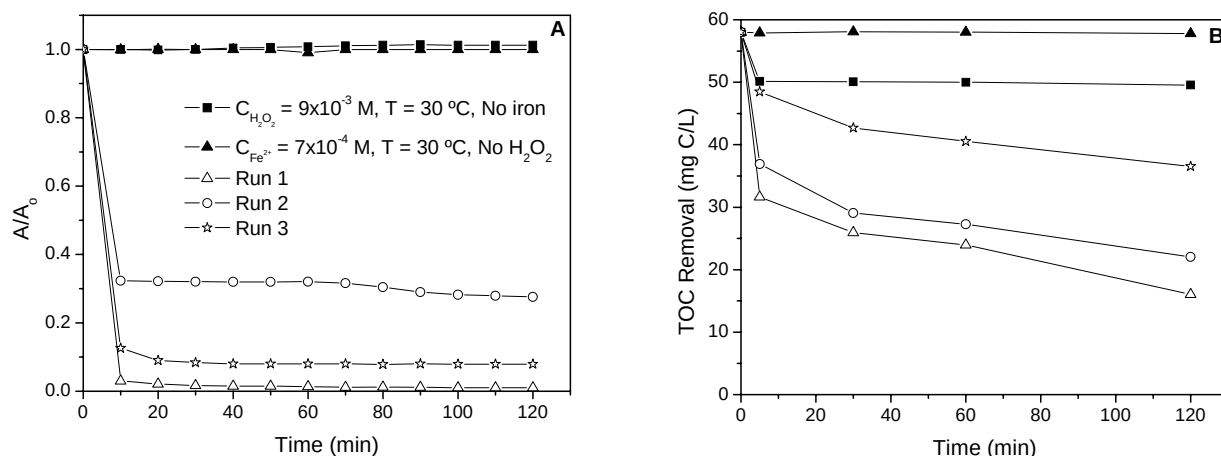


Fig. 3.2 – Discolouration (A) and mineralization (B) of the Orange II solution as a function of time. For the experimental conditions of runs 1 to 3, please refer to Table 3.1.

Ferric ions produced can react with H_2O_2 to produce hydroperoxyl radicals ($HO_2^\bullet$) and restore ferrous ions through the following reaction scheme [15,16]:



However, the reaction rate for iron regeneration is much slower than that in Eq. (3.1) (rate constant is now $2 \times 10^{-2} \text{ mol}^{-1} \text{ dm}^3 \text{ s}^{-1}$) [9]. Consequently, the rate of oxidation in the second stage (Fe^{3+}/H_2O_2 stage) is slower than in the first one due to the slow production of $Fe(II)$ from $Fe(III)$. Concluding, we can say that the reaction rate decrease on the 2nd stage of the Fenton oxidation is basically due to the fact that ferrous ions are consumed quickly, but reproduce slowly. Consequently, the oxidation rate of organic compounds is fast when large amounts of ferrous ions are present because large amount of hydroxyl radicals are produced. However, due to the slow Fe^{2+} production/regeneration, the Fenton's reaction slows down. Moreover, the hydroperoxyl radicals produced in the second stage have a much smaller oxidation potential compared to $HO^\bullet$ [17], thus also justifying the slower oxidation rate in the second step. Finally, there are several competitive reactions that also consume hydroxyl radicals, or reactions with the intermediate products formed from the dye decomposition when the process advances, which hinder the decay of the parent compound. In conclusion, there are several factors that contribute to the decrease of the Orange II decomposition rate at

higher times of reaction, and this is the reason why several authors propose two kinetics for the Fenton's reaction with organic compounds. The experimental results of this work also demonstrate this situation.

3.3.2 Design of Experiments

A central composite design (response surface design) was carried out considering the minimum and maximum levels for temperature (10-50 °C), $C_{H_2O_2}$ (3×10^{-3} - 1.5×10^{-2} M) and Fe^{2+} : H_2O_2 ratio (0.05-0.2 w/w). It is noteworthy that the ranges considered for the three studied variables were chosen based on literature findings [6,8-10,18], as well as in experiments previously performed by the author [7]. Assuming a second order polynomial model, at least 13 experiments must be carried out to solve the matrix (including the cross effects between variables and two centre points), for which software JMP 501 was used. Table 3.1 shows the description of the experiments and the relationship between codified and real values. Low and high levels are denoted by (-1) and (+1), respectively, and the central points as (0). It is noteworthy that the methodology used requires that experiments outside the experimental range previously defined should be performed to allow prediction of the response outside the cubic domain (denoted as +1.682).

As above-mentioned, the objective functions to maximise are both the colour and TOC removal (after 120 min of oxidation). These are the responses which will be called Y_1 and Y_2 , respectively. The 13 experiments indicated in Table 3.1 were then performed in a random order to minimise systematic errors, and the response factors evaluated. Table 3.2 shows the experimental responses.

The coefficients of the quadratic model in the polynomial expression were then calculated by multiple regression analysis, using the above-mentioned DOE software. It must be stressed that such coefficients represent the weight of each variable by itself, the weight of the quadratic effect and the weight of the first order interactions between the coded variables. Equations (3.4) and (3.5) represent the two responses, where Y_1 and Y_2 are in %:

$$Y_1 = 98.42(\pm 4.47) + 4.52(\pm 2.16)A_2 - 2.73(\pm 2.16)A_3 - 5.26(\pm 2.69)A_2^2 - 2.71(\pm 2.69)A_3^2 - 4.00(\pm 2.24)A_1A_2 - 5.75(\pm 2.24)A_1A_3 - 3.75(\pm 2.24)A_2A_3 \quad (3.4)$$

$$Y_2 = 56.92(\pm 5.22) + 8.02(\pm 2.52)A_1 + 19.02(\pm 2.52)A_2 - 2.73(\pm 2.52)A_3 - 5.39(\pm 3.15)A_1^2 - 11.93(\pm 3.15)A_2^2 - 2.75(\pm 2.62)A_1A_3 \quad (3.5)$$

where:

$$A_1 = \frac{X_1 - 30}{20}; \quad A_2 = \frac{X_2 - 9}{6}; \quad A_3 = \frac{X_3 - 0.125}{0.075} \quad (3.6)$$

X_1 , X_2 and X_3 denote the variables temperature, H_2O_2 concentration and $Fe^{2+}:H_2O_2$ ratio, respectively. Since the different factors present different units, they are given in the form of dimensionless coded variables (A_1 to A_3) in order to permit comparison between them. It must be remarked that in the cases where the error in Eqs. (3.4) and (3.5) was equal or higher than the corresponding coefficient, the associated variable, quadratic effect or first-order interaction was ignored and was not expressed in the models, as usual [1].

Table 3.1 – Codified and experimental values of the experimental design.

Codified values				Experimental values		
Run No.	Temperature	$C_{H_2O_2}$	$Fe^{2+}:H_2O_2$	Temperature (°C)	$C_{H_2O_2}$ (mM)	$Fe^{2+}:H_2O_2$ (w/w)
1	+1	+1	-1	50	15	0.05
2	+1	+1	+1	50	15	0.2
3	+1	-1	-1	50	3	0.05
4	0	0	+1.682	30	9	0.25
5	+1	-1	+1	50	3	0.2
6	-1	+1	-1	10	15	0.05
7	-1	-1	-1	10	3	0.05
8	0	+1.682	0	30	19.1	0.125
9	-1	-1	+1	10	3	0.2
10	+1.682	0	0	63.6	9	0.125
11	-1	+1	+1	10	15	0.2
12	0	0	0	30	9	0.125
13	0	0	0	30	9	0.125

As can be seen in Fig. 3.3, the values predicted by the second order models agree reasonably with the experimental data. For instance, in what concerns the colour removal, absolute errors are always below 6.6% (with an average of 2.7%). Even for the

other response, both values are very close, indicating a good correspondence between the model prediction and the experiments (average absolute error of 3.7%). In addition, the analysis of variance yielded significance probabilities (*F*-test) of 95.2% and 95.9% for colour and TOC removal, respectively (95% confidence level), thus evidencing the existence of a regression effect [11].

Table 3.2 – Experimental results of the experimental design for Orange II oxidation.
Responses considered are: Y_1 - colour removal (%) and Y_2 - TOC removal (%).

Run No.	Experimental results	
	Y_1	Y_2
1	99.0	72.3
2	72.1	62.0
3	92.1	37.0
4	91.6	66.5
5	80.2	22.8
6	97.8	56.4
7	74.7	14.1
8	96.2	61.0
9	86.1	19.1
10	97.9	60.3
11	93.9	47.7
12	98.1	58.2
13	98.4	55.7

Considering just the first order effects of each variable in Eqs. (3.4) and (3.5), it is clear that the main factor that affects colour removal is the H_2O_2 concentration, while for TOC reduction temperature also plays a significant role. In both cases, all the cross and quadratic effects are negative, suggesting that optimum values must exist for each parameter, as discussed below.

Figure 3.4 presents the response surface modelling in a three dimensional representation to put into evidence the effects of temperature, H_2O_2 concentration and $Fe^{2+}:H_2O_2$ ratio on the colour removal after 2 hours of reaction.

As a general trend, we can see that depending on the reaction temperature, the H_2O_2 concentration and $Fe^{2+}:H_2O_2$ ratio may have a positive or negative effect on dye decolouration (Fig. 3.4A). Indeed, for low temperatures both parameters seem to affect positively the final performance, while for high temperatures an excessive oxidant load

may have a detrimental effect. At the highest temperature ($T=50^{\circ}\text{C}$) low catalyst doses are required, possibly because reactions are faster.

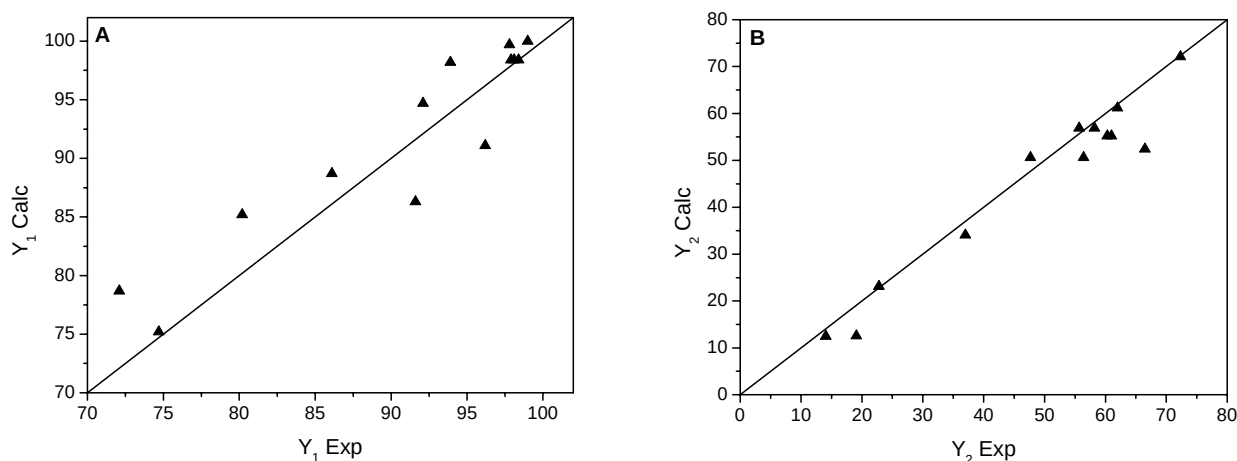


Fig. 3.3 – Experimental and calculated results of the experimental design for Orange II oxidation. Responses considered are: Y_1 - colour removal (%) and Y_2 - TOC removal (%).

A similar behaviour is noticed when changing the temperature and H_2O_2 concentration, at constant $\text{Fe}^{2+}:\text{H}_2\text{O}_2$ ratio (Fig. 3.4B). Thus, we can say that all variables may affect positively or negatively the colour removal, depending on the values of the other experimental conditions (cross effects). This justifies the use of DOE tools for process optimisation. It must however be remarked that in some cases the second-order model yields response values slightly above 100%, which is due to the error in the numerical fit and reflects the problem associated with the interpolation once very high colour removal efficiencies were attained.

The fact that in some conditions very high H_2O_2 concentration values lead to a decrease in the final discolouration is possibly due to the competition between these species for hydroxyl radicals. Indeed, $\text{HO}^{\bullet}$ radicals are quite non-selective, reacting with the organic matter present but also with other species. A maximum value for the discolouration performance is achieved with a peroxide concentration of ca. 10 mM due to the following reaction [10,19,20]:



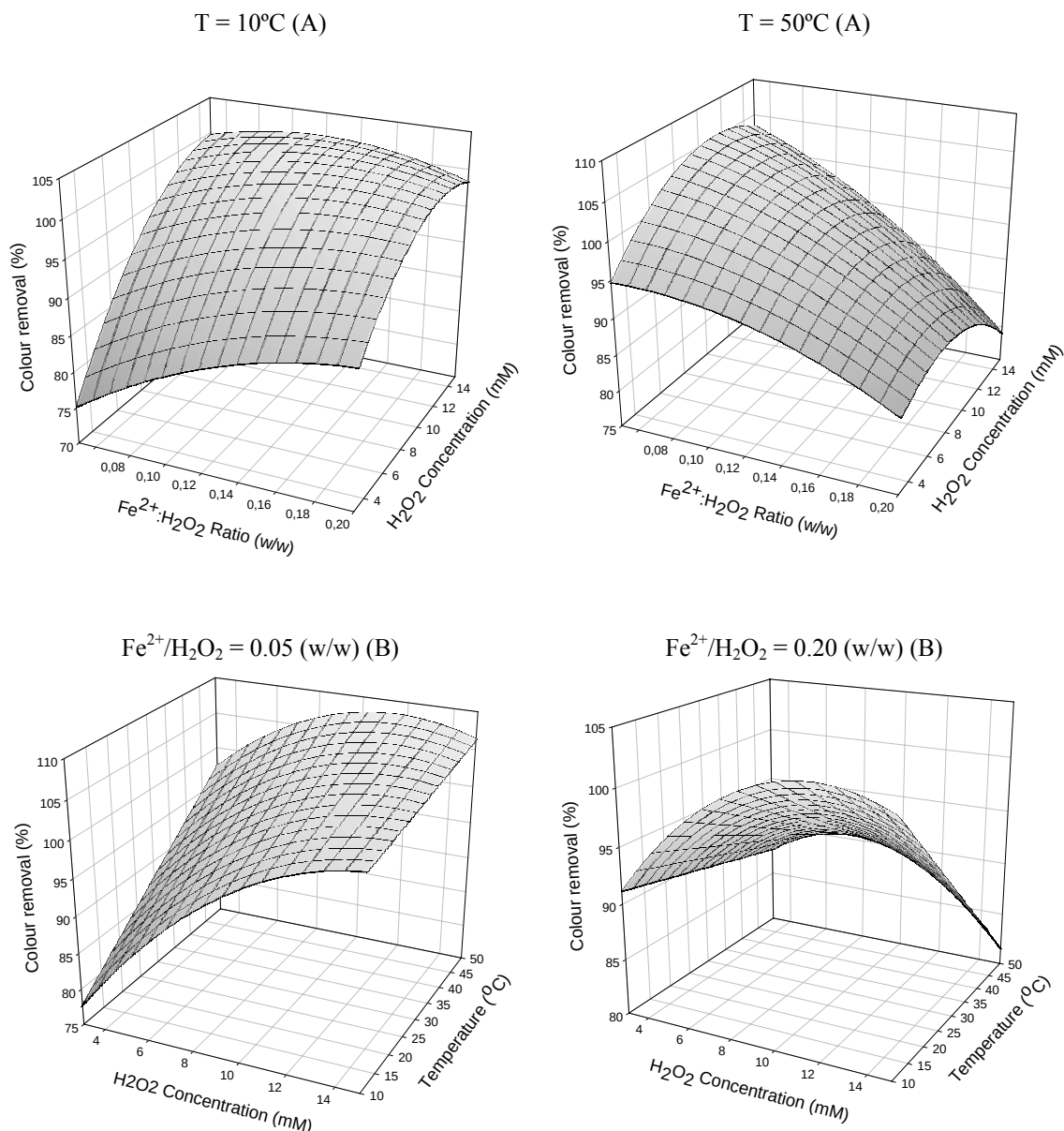


Fig. 3.4 – Response surface showing the colour removal (%) of the Orange II solution as a function of: A) Fe²⁺/H₂O₂ ratio and H₂O₂ concentration (for different temperatures) and B) H₂O₂ concentration and temperature (for different Fe²⁺:H₂O₂ ratios).

Therefore, at high oxidant loads such scavenging effect becomes more significant, which leads to the non-productive decomposition of hydrogen peroxide and limits the yield of hydroxylated (oxidised) organic compounds. Although other radicals ($HO_2^\bullet$) are produced, their oxidation potential is much smaller than that of the $HO^\bullet$ species [17]. It must however be stressed that when increasing the H₂O₂ concentration, keeping the Fe²⁺:H₂O₂ ratio constant, higher catalyst loads are employed, which may also have a scavenging effect, as discussed below (see Eq. (3.8)). Thus, this effect may also contribute to the decline in the overall efficiency recorded at high oxidant loads.

In this work it was found that the discolouration rate (and also the TOC reduction rate) is strongly dependent on the amount of H_2O_2 added. But the effect caused by temperature is also considerable; when the reaction was performed at low temperatures ($\sim 10^\circ C$) both rates decreased, due to the Arrhenius dependence of the kinetic constants. However, data shown in Figs. 3.4A and 3.4B refer to the performance achieved after 2h of oxidation. It is visible that depending on the experimental conditions, the colour removal may be positively affected by the reaction temperature, while in some cases high temperatures lead to a decrease in the overall performance. Thus, an optimum value must exist, what is in agreement with other results found in the literature [14,21]. Some authors [14,18] report that at high temperatures hydrogen peroxide decomposition into oxygen and water becomes very fast, leading to a decline in the overall efficiency. This was confirmed experimentally in this work (*cf.* section A1 of appendix I).

Finally, for the $Fe^{2+}:H_2O_2$ ratio an optimum range was also noticed, and this behaviour was also found by other authors in the Fenton process [e.g., 9]. An increase in the $Fe^{2+}:H_2O_2$ ratio implies higher Fe^{2+} loads, and therefore more $HO^\bullet$ radicals are available for oxidation. Excess catalyst may however lead to a loss of $HO^\bullet$ species by the following scavenging reaction [19]:



The polynomial expression in Eq. (3.5) was used to calculate the response surface illustrated in Figs. 3.5A and 3.5B, showing the TOC removal after 2 hours of reaction (initial TOC = 58.6 mg/L). Conclusions are similar to those described for colour removal, evidencing that process variables may have a positive or negative effect on the final performance, depending on the other experimental parameters. Once again, optimum values for both H_2O_2 concentration and temperature are found, although shifted for higher values as compared to colour removal. This could be expected, once to achieve mineralization more aggressive conditions are required than those employed to simply break the chromophore group.

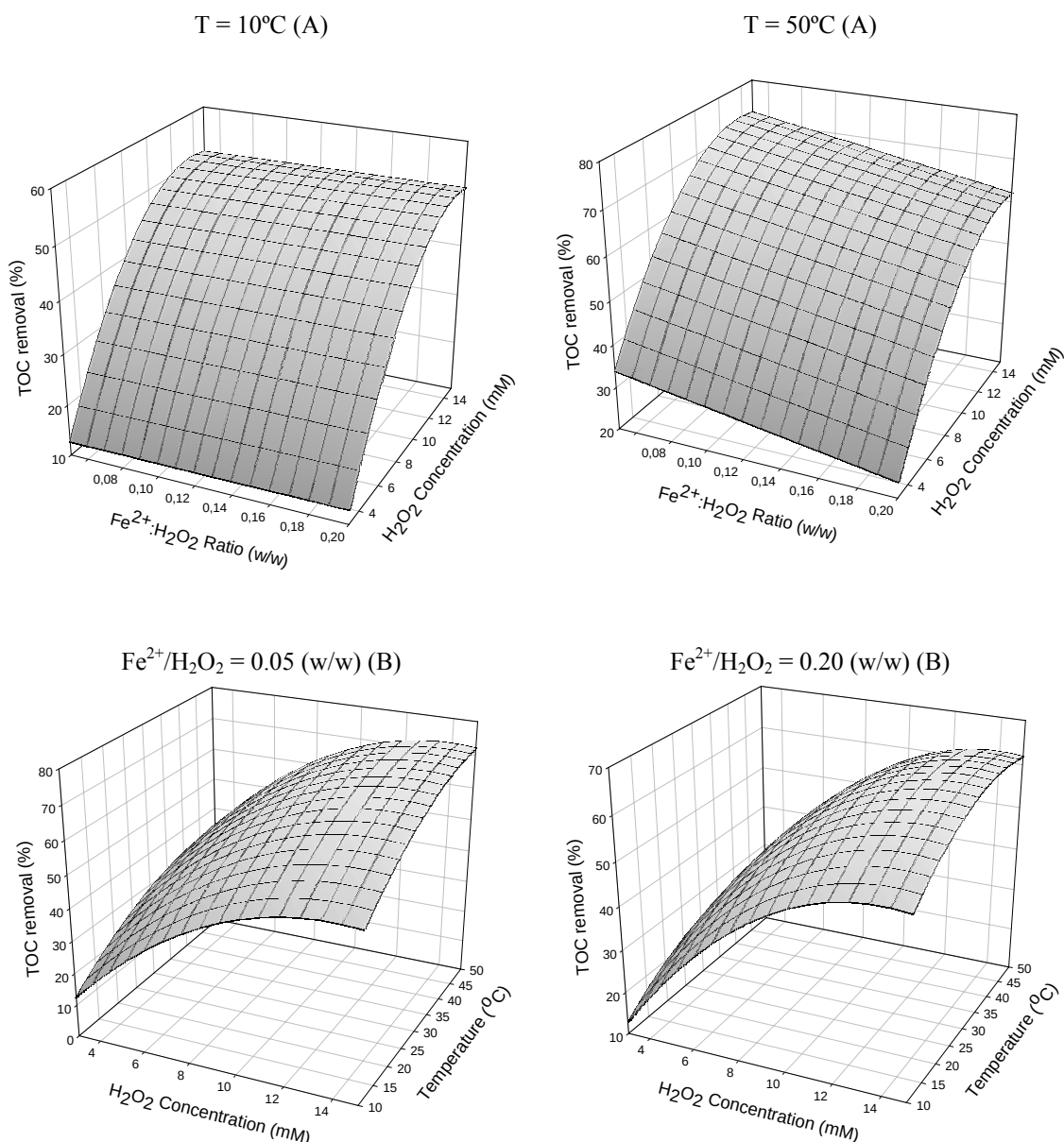


Fig. 3.5 – Response surface showing the TOC removal (%) of the Orange II solution as a function of: A) $\text{Fe}^{2+}/\text{H}_2\text{O}_2$ ratio and H_2O_2 concentration (for different temperatures) and B) H_2O_2 concentration and temperature (for different $\text{Fe}^{2+}/\text{H}_2\text{O}_2$ ratios).

It is known that complete discolouration of the solution does not mean that the dye is completely oxidised, and so the mineralization and colour removal processes were investigated simultaneously. Consequently, the TOC of the reaction mixture was also measured along time in all experiments, some of them shown in Fig. 3.6. For run no. 1 a TOC removal of 72% was reached after 2h, with ~99% of colour removal (Table 3.2). It must however be stressed that good conditions for mineralization do not necessarily imply good results for decolourisation. For instance, in run no. 2 a good TOC reduction was attained (62%), with a very inefficient colour removal (see Table 3.2).

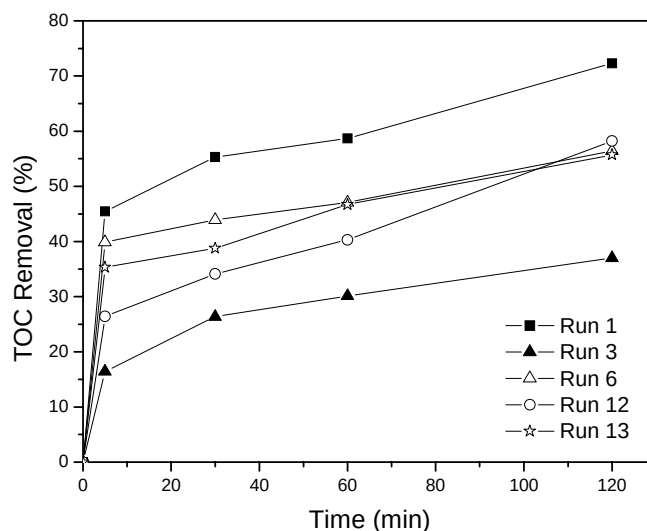


Fig. 3.6 – TOC removal of the Orange II solution along time, for some runs (experimental conditions shown in Table 3.1).

With the goal in mind of process optimization, two more experiments were performed in the optimum conditions found regarding colour and TOC removal. These runs also allowed us to check the validity of the developed models. Once Eq. (3.4) predicts that colour can be completely removed in a wide range of the experimental parameters, we decided to use conditions that do not require excessive consumption of reagents neither too high temperatures. For TOC, the optimum values found through nonlinear optimization (maximum in Eq. (3.5)) were employed. The experimental conditions are described in the caption of Fig. 3.7. It is noteworthy that a high H_2O_2 load and temperature is required for good TOC reduction, while for colour removal reaction conditions do not need to be so severe. For those experiments the model predicts efficiencies of 99.9% and 72.6%, for colour and TOC reduction, respectively. It is remarkable that an experimental decolourisation of 99.7% was reached after 2 h (see detail in Fig. 3.7A). In what concerns the TOC removal, a mineralization degree of 70.7% was achieved (Fig. 3.7B). However, this figure suggests that higher mineralization degrees could be achieved with longer experiments. As shown in Fig. 3.7A, colour removal is very fast, being possible to achieve a performance above 98% in just 5 min. On the other hand, complete oxidation proceeds at a much slower reaction rate.

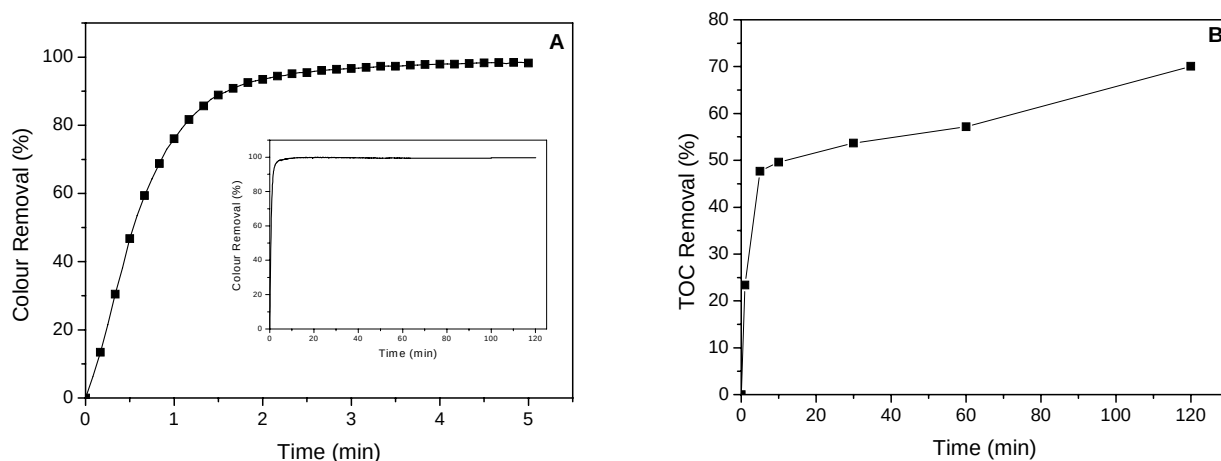
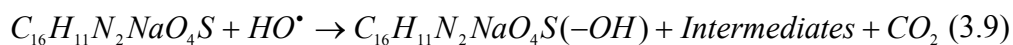


Fig. 3.7 – Colour (A) and TOC (B) removal along time using the optimized conditions: A) Colour removal with $T = 29^{\circ}\text{C}$, $C_{\text{H}_2\text{O}_2} = 1 \times 10^{-2} \text{ M}$ and $\text{Fe}^{+2}:\text{H}_2\text{O}_2$ ratio = 0.08 w/w; B) TOC removal with $T = 50^{\circ}\text{C}$, $C_{\text{H}_2\text{O}_2} = 1.4 \times 10^{-2} \text{ M}$ and $\text{Fe}^{+2}:\text{H}_2\text{O}_2$ ratio = 0.05 w/w.

The DOE methodology used has shown to be a valuable tool to model a complex process such as the Fenton oxidation, and to achieve optimal experimental conditions without a detailed knowledge of the reaction sequences involved, which are most often complex. In fact, the DOE approach allows the modeling of the process through statistically significant but empirical models, of the “black-box” type. However, a deep knowledge of the process is of crucial importance, particularly in what concerns the reaction mechanism and reaction kinetics (although requiring a mathematical description of the phenomena involved in the process). Nevertheless, it is reasonable to assume that mineralization of the dye might yield HSO_4^- and predominantly NH_4^+ (among other compounds) [6], but the formation of intermediate Fe-complexes consisting of Fe-chelates leading to carboxylic acids should be also considered, as found in previous studies. In particular, oxalic, formic, and acetic acid along with smaller concentrations of other short non-branched and branched aliphatic acids ($\text{C}_3\text{--C}_7$) have been reported [22]. In what concerns possible reaction intermediates, it is also important to remark the nice study presented by Nam *et al.* [23] using the $\text{Fe}^{\text{III}}\text{-EDTA-H}_2\text{O}_2$ system. The authors propose a detailed mechanism for the Orange II degradation, with several intermediates involved, particularly 4-hydroxybenzenesulfonic acid and 1,2-naphtoquinone. Finally, the work by Bandara *et al.* [6] should be also stressed, although the results concern the use of sunlight induced reactions. Based on their results, the following mechanism could be suggested for the

decomposition of Orange II, taking also into account the above-mentioned equations, particularly Eqs. (3.1) to (3.3):



where the oxidized intermediates might, through subsequent reactions with the $HO^{\bullet}$ radicals, lead to aromatic and aliphatic intermediates, and finally to carbon dioxide and water (along with NO_3^- , NH_4^+ , $NaHSO_4^-$ and H^+). Among other compounds, the formation of nitrogen and sulfo-containing products is described by the authors, being also noteworthy the evolution of N_2 when the $N=N$ bond is cleaved [6].

3.4 Conclusions

- A central composite design was used to evaluate the effect of temperature, H_2O_2 concentration and $Fe^{+2}:H_2O_2$ ratio in the Fenton's oxidation of the azo dye Orange II, at $pH = 3$. The responses considered were the colour (Y_1) and TOC (Y_2) removal after 2h of oxidation. It was found that the second order models developed for both Y_1 and Y_2 fit quite reasonably the experimental data in the ranges studied.
- The dye seems to be decomposed in a two-stage reaction with the Fenton's reagent, being degraded very quickly in the first 5-10 min (Fe^{2+}/H_2O_2 stage), with a slower reaction rate later on (Fe^{3+}/H_2O_2 stage). The first stage is particularly fast for colour removal, being possible to achieve a decolourisation above 98% in just 5 min of reaction time, although in some cases efficiencies higher than 90% can be reached in only 1 min.
- Data obtained revealed that the Fenton's reagent is promising for degradation of the dye, as decolourisation efficiencies clearly above 99% and mineralization degrees higher than 70% were reached in 2h. However, to achieve these results, operating conditions must be carefully selected. Indeed, the surface response plots of the models showed that for both factors (Y_1 and Y_2) optimum values for the process variables exist, what is a typical behaviour in the Fenton process. Though TOC reduction requires aggressive conditions (high H_2O_2 concentration and temperature) decolourisation does not requires high stringency. The

hydrogen peroxide concentration and the temperature showed to be the variables with higher impact into the final performance. In particular, temperature turns into a key parameter when it is desirable to reduce reagents consumption.

- Although the model predicts that colour can be completely removed for a wide range of experimental conditions, we decided to test its validity with an additional run where excessive use of reagents and high temperature should be avoided. An additional experiment was also carried out in the conditions found by nonlinear optimization regarding TOC reduction (maximum of Y_2). The following performances were achieved:
 - Colour removal = 99.7%, for $T = 29^\circ\text{C}$, $C_{\text{H}_2\text{O}_2} = 1 \times 10^{-2} \text{ M}$ and $\text{Fe}^{+2}:\text{H}_2\text{O}_2$ ratio = 0.08 (w/w);
 - TOC removal = 70.7%, for $T = 50^\circ\text{C}$, $C_{\text{H}_2\text{O}_2} = 1.4 \times 10^{-2} \text{ M}$ and $\text{Fe}^{+2}:\text{H}_2\text{O}_2$ ratio = 0.05 (w/w).

References

1. D.C. Montgomery. Design and analysis of experiments, Fifth Edition, John Wiley & Sons, New York, **2001**.
2. Öberg, T. G.; Deming, S. N. Find optimum operating conditions fast. Chemical Engineering Progress **2000**, 96, 53.
3. Machado, H.; Coelho, V.; Feyer, I.; Braga, F.; Oliveira, F.; Nogueira, J.; Mendes, A. Cost optimisation by using DOE. European Coatings Journal **2003**, 3, 279.
4. Fernandez, J.; Kiwi, J.; Lizama, C.; Freer, J.; Baeza, J.; Mansilla, H. D. Factorial experimental design of Orange II photocatalytic discolouration. Journal of Photochemistry and Photobiology A: Chemistry **2002**, 151, 213.
5. Baçaoui, A.; Dahbi, A.; Yaacoubi, A.; Bennouna, C.; Maldonado-Hódar, F. J.; Rivera-Utrilla, J.; Carrasco-Marín, F.; Moreno-Castilla, C. Experimental design to optimize preparation of activated carbons for use in water treatment. Environmental Science and Technology **2002**, 36, 3844.
6. Bandara, J.; Morrison, C.; Kiwi, J.; Pulgarin, C.; Peringer, P. Degradation/decoloration of concentrated solutions of Orange II. Kinetics and quantum yield for sunlight induced reactions via Fenton type reagents. Journal of Photochemistry and Photobiology A: Chemistry **1996**, 99, 57.

7. Ramirez, J. H.; Costa, C. A.; Madeira, L. M. Descoloração do corante Orange II usando reagente de Fenton. in Proc. XIX Simposio Iberoamericano de Catálisis (México) **2004**, p. 14 (CD: p. 259).
8. Swaminathan, K.; Sandhya, S.; Sophia, A. C.; Pachhade, K.; Subrahmanyam, Y. V. Decolorization and degradation of H-acid and other dyes using ferrous–hydrogen peroxide system. *Chemosphere* **2003**, 50, 619.
9. Malik, P. K.; Saha, S. K. Oxidation of direct dyes with hydrogen peroxide using ferrous ion as catalyst. *Separation and Purification Technology* **2003**, 31, 241.
10. Neyens, E.; Baeyens, J. A review of classic Fenton's peroxidation as an advanced oxidation technique. *Journal of Hazardous Materials* **2003**, 98, 33.
11. SAS, JMP, The statistical discovery software, www.jmp.com/product/jmp_intro.shtml. Last access April 25, **2008**.
12. Mielgo, I.; Moreira, M. T.; Feijoo, G.; Lema, J. M. A packed-bed fungal bioreactor for the continuous decolourisation of azo-dyes (Orange II). *Journal of Biotechnology* **2001**, 89, 99.
13. Mu, Y.; Yu, H. Q.; Zheng, J. C.; Zhang, S. J. TiO₂-mediated photocatalytic degradation of Orange II with the presence of Mn²⁺ in solution. *Journal of Photochemistry and Photobiology A: Chemistry* **2004**, 163, 311.
14. Guedes, A. M. F. M.; Madeira, L. M. P.; Boaventura, R. A. R.; Costa, C. A. V. Fenton oxidation of cork cooking wastewater—overall kinetic analysis. *Water Research* **2003**, 37, 3061.
15. Chen, R.; Pignatello, J. J. Role of quinone intermediates as electron shuttles in Fenton and photoassisted Fenton oxidations of aromatic compounds. *Environmental Science and Technology* **1997**, 31, 2399.
16. Pignatello, J. J. Dark and photoassisted Fe³⁺-catalyzed degradation of chlorophenoxy herbicides by hydrogen peroxide. *Environmental Science and Technology* **1992**, 26, 944.
17. Bigda, R. J. Consider Fenton chemistry for wastewater treatment. *Chemical Engineering Progress* **1995**, 91, 62.
18. Dutta, K.; Mukhopadhyay, S.; Bhattacharjee, S.; Chaudhuri, B. Chemical oxidation of methylene blue using a Fenton-like reaction. *Journal of Hazardous Materials* **2001**, 84, 57.
19. Walling, C. Fenton's reagent revisited. *Accounts of Chemical Research* **1975**, 8, 125.
20. Fernández, J.; Kiwi, J.; Baeza, J.; Freer, J.; Lizama, C.; Mansilla, H. D. Orange II photocatalysis on immobilised TiO₂: Effect of the pH and H₂O₂. *Applied Catalysis B: Environmental* **2004**, 48, 205.
21. Lin, S. H.; Lo, C. C. Fenton process for treatment of desizing wastewater. *Water Research* **1997**, 31, 2050.

22. Nadtochenko, V.; Kiwi, J. Photoinduced adduct formation between Orange II and $[\text{Fe}^{3+}(\text{aq})]$ or $\text{Fe}(\text{ox})_3^{3-}$ - H_2O_2 Photocatalytic degradation and laser spectroscopy Journal of the Chemical Society, Faraday Transactions **1997**, 93, 2373.
23. Nam, S.; Renganathan, V.; Tratnyek, P. G. Substituent effects on azo dye oxidation by the Fe^{III} -EDTA- H_2O_2 system. Chemosphere **2001**, 45, 59.

CHAPTER 4 – MODELLING OF THE SYNTHETIC DYE ORANGE II DEGRADATION USING FENTON'S REAGENT: FROM BATCH TO CONTINUOUS REACTOR OPERATION *

Abstract

In this chapter, a simple kinetic model was used to study the degradation of the azo dye orange II (OII) using Fenton's reagent, in the Fenton-like stage. The effect of pH, temperature, Cl^- concentration and initial concentrations of OII, hydrogen peroxide (H_2O_2) and ferrous ion catalyst (Fe^{2+}) on the degradation rate has been investigated in a batch reactor. The apparent kinetic constants, k_{ap} , for OII degradation were determined in the following range of experimental conditions: $2.0 \leq \text{pH} \leq 4.0$, $283 \leq T \leq 323 \text{ K}$, $0 \leq C_{\text{Cl}^-} \leq 1 \times 10^{-2} \text{ M}$, $3 \times 10^{-5} \leq C_{\text{OII}_o} \leq 1 \times 10^{-4} \text{ M}$, $1 \times 10^{-4} \leq C_{\text{H}_2\text{O}_2_o} \leq 1 \times 10^{-3} \text{ M}$ and $2.5 \times 10^{-6} \leq C_{\text{Fe}^{2+}_o} \leq 2 \times 10^{-5} \text{ M}$. A pseudo-first-order reaction rate with respect to OII concentration was found to be adequate to fit the data in these experiments, in which the apparent kinetic constant depends on the initial conditions following a power-law dependency (at optimum pH of 3 and absence of chloride ions). This equation, without further fitting parameters, was used to validate the experiments performed in a continuous stirred tank reactor, particularly when using a range of experimental conditions within the range used in the batch reactor.

* Adapted from: Ramirez, J. H.; Duarte, F. M.; Martins, F. G.; Costa, C. A.; Madeira, L.A. submitted.

4.1 Introduction

Recent progress in the decontamination of wastewater has led to the development of advanced oxidation processes. Among them, the oxidation using Fenton's reagent has proved to be a promising and attractive treatment method for the effective decolourization and degradation of dyes, as well as for the destruction of a large number of hazardous and organic pollutants [1-4]. Moreover, the process is simple, taking place at low temperatures and atmospheric pressure [5].

Oxidation with Fenton's reagent is based on ferrous ion and hydrogen peroxide and exploits the very high reactivity of the hydroxyl radical produced in acidic solution by the catalytic decomposition of H_2O_2 , *cf.* Eq. (4.1) [6]. The mechanism of Fenton's oxidation involves basically the following steps (Eqs. (4.1) - (4.6)), wherein the kinetic constants are given in $M^{-1}s^{-1}$ (with the exception of k_5) and were taken from the literature [6-12]:



The $HO^\bullet$ species produced through reaction given by Eq. (4.1) will then attack the organic matter present in the reaction medium, because the hydroxyl radical is a powerful inorganic oxidant that reacts non-selectively with numerous compounds (rate constants in the range $10^7-10^{10} M^{-1}s^{-1}$) [6,13]:



Several studies can be found in the literature focusing the kinetic analysis of the Fenton process. However, due to the associated complexity (besides the above-mentioned many other reaction steps have to be taken into account), a

phenomenological study requires a set of at least 20 or 30 differential equations. Even so, the rate constants vary from paper to paper, and for several of them activation energies are not documented. Therefore, it is also a main goal of the present chapter to find a simple empirical equation that describes the kinetic degradation of Orange II in a batch reactor by the Fenton's reagent, information that is required for modeling, design and optimization of chemical reactors for pollutants degradation. Many operational parameters, such as pH, OII concentration, H_2O_2 dosage, Fe^{2+} concentration and temperature, affecting the OII degradation efficiency, were investigated. Also, the effect of Cl^- concentration on the oxidation efficiency was studied, because this species is usually present in the textile effluents and is inhibitory in the Fenton process. Finally, the kinetic law obtained is used to validate the experiments carried out in a continuous reactor. To the best of the author knowledge, there are available only a few studies about Fenton's reagent application in continuous reactors [e.g., 7,14,15], and none was found for the OII dye.

4.2 Materials and Methods

Chemical oxidation of azo dye Orange II aqueous solutions was conducted in two stirred jacketed glass reactors; the first one a batch and the second one a continuous stirred tank reactor (CSTR), with 0.30 L and 0.92 L capacity, respectively. Both set-ups and operation procedures are described with more detail in chapter 2.

In the CSTR operation, all the runs were carried out at pH $\sim$ 3.0. Besides, in experiments carried out in duplicate, conversion varied by less than 10%.

To obtain the residence time distribution in the continuous reactor, i.e., for studying the mixing characteristics in such reactor, a tracer stimulus-response technique was used. The reactor was fed with distilled water and after being filled the tracer (OII in this work) was suddenly added (pulse input with a syringe). Then, its concentration was measured along time in the outlet stream. Runs were performed at different feed flow rates.

4.3 Results and Discussion

4.3.1 Batch Reactor - Kinetic Study

In the Fenton's process, it is generally considered that the reactions between hydrogen peroxide and ferrous iron in acidic aqueous medium involve the steps presented above (Eqs. (4.1)-(4.6)), although some authors propose a much more complex mechanism, with several other reactions and involving many radicals [e.g., 16]. In this process, the formation of hydroxyl radicals was demonstrated by several researchers [17] and has been suggested to be the main oxidant species. In spite of the oxidation kinetics complexity, it is often assumed that, under certain conditions, the mechanism of the process can be significantly simplified, being of particular relevance reaction given by Eq. (4.7) [17]. The corresponding kinetic equation for OII and $HO^\bullet$ reaction, assumed to be elementary, can thus be expressed as follows:

$$(-r_{OII}) = k_7 C_{HO^\bullet} C_{OII} = k_{ap} C_{OII} \quad (4.8)$$

where k_{ap} is an apparent pseudo first-order kinetic constant that involves the radical $HO^\bullet$ concentration (assumed to remain constant along one experiment, due to the hypothesis of a pseudo steady-state concentration of hydroxyl radicals). The value of this rate constant depends therefore on the initial reactants concentrations (H_2O_2 and Fe^{2+}), temperature and also on the concentration of scavenger species present in the reaction mixture (such as intermediates, $HOO^\bullet$, etc.) [17]. On the other hand, these scavenger species concentrations depend on the initial orange II concentration, and for this reason k_{ap} is a function of all these variables [17]: $k_{ap} = f(C_{OIIo}, C_{H_2O_2o}, C_{Fe^{2+}o}, T)$.

The dependence of k_{ap} from the operating conditions can be found by performing independent experiments, changing each factor at a time, after appropriate linearization of the data. This can be achieved from the corresponding mass balance in the batch reactor ($dC_{OII} / dt = -k_{ap} \cdot C_{OII}$, wherein the hypothesis of ideal mixing conditions has been verified by simple tracer experiments), thus yielding:

$$\ln \frac{C_{OII}}{C_{OIIo}} = -k_{ap} t \quad (4.9)$$

If the relationship between $\ln(C_{OII}/C_{OII_0})$ vs. time (t) is linear, then the degradation of OII will follow a pseudo-first-order reaction and the values of k_{ap} , at given experimental conditions, can be obtained from the slopes of these plots. However, the reaction exhibits a change on its kinetics, which is a consequence of the complexity of the mechanism. This has been widely reported in the literature associated with the Fenton process, and for that reason the k_{ap} values were calculated from experimental data covering only the Fenton-like phase of the process, this means where most of the Fe^{2+} has been converted into Fe^{3+} (also called as stage II). Actually, it is known that the Fenton process is divided in two stage-reactions. In the first stage the organic compounds are decomposed rapidly and somewhat less rapidly in the second one, as described in chapter 3. The main reason for this well-known behaviour is that ferrous ions react very quickly with hydrogen peroxide to produce large amounts of hydroxyl radicals (*cf.* Eq. (4.1) and corresponding rate constant), which can then react rapidly with the dye (so-called Fe^{2+}/H_2O_2 stage) [3]. Ferric ions produced can then react with H_2O_2 to produce hydroperoxyl radicals and restore ferrous ions (*cf.* Eq. (4.3)). However, the rate of oxidation in the second stage (Fe^{3+}/H_2O_2 stage) is slower than in the first one due to the slow production of Fe^{2+} from Fe^{3+} [18]. Because the reaction in which Fe^{2+} is converted into Fe^{3+} is very fast, the first stage is short (or very short) and afterwards the process enters into a so-called pseudo steady-state, wherein Fe is mainly in the 3+ oxidation state.

Figure 4.1 shows the transient OII concentration curve in a typical experiment, evidencing clearly the existence of this two-stage process. For that reason the fitting of a single kinetic equation along all the process is not straightforward and so we used data only in the second stage of the process (pseudo steady-state, $t > t_I$). This means that, in general, ca. 90% of the experimental data in a single run are used in the regression, and in all cases it is warranted that the conversion of Fe^{2+} into Fe^{3+} is higher than 95% (*cf.* Eq. (4.10), derived from Eq. (4.1), taking into account that H_2O_2 is present in large excess with respect to Fe^{2+}). In all experiments fitting of Eq. (4.9) to experimental data provided average relative error below 6.5 %, as described in the following section.

$$t_1 > -\frac{\ln 0.05}{k_1 \cdot C_{H_2O_2}} \quad (4.10)$$

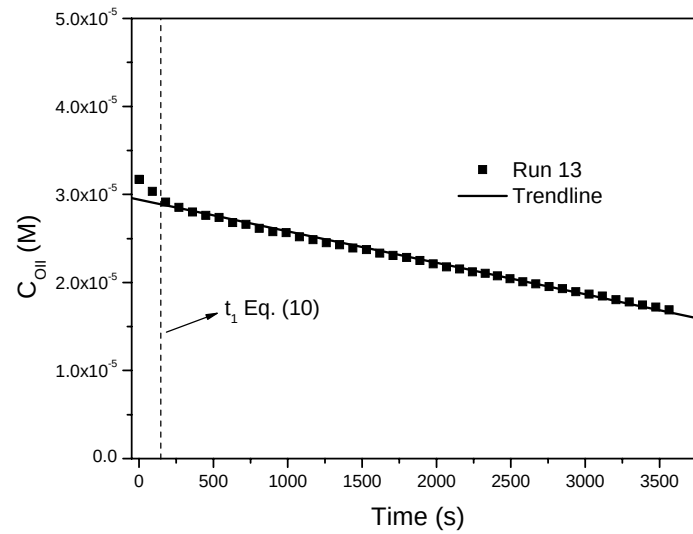


Fig. 4.1 – Typical plot of the OII concentration over time in the batch reactor. Experimental conditions: $C_{OII_o} = 1.1 \times 10^{-4} M$, $C_{H_2O_2} = 2 \times 10^{-4} M$, $C_{Fe^{2+}} = 5 \times 10^{-6} M$, $T = 303 K$ and $pH = 3$.

4.3.2 Batch Reactor – Effect of the Main Operating Conditions

In the closed reactor, several experiments on Orange II degradation by Fenton's reagent were conducted by varying the temperature (283-323 K) and the initial concentrations of OII (3×10^{-5} - $1 \times 10^{-4} M$), H_2O_2 (1×10^{-4} - $1 \times 10^{-3} M$) and Fe^{2+} (2.5×10^{-6} - $2 \times 10^{-5} M$). The effect of the pH and of a scavenger usually present in textile effluents (chloride ion), was also analysed.

4.3.2.1 Effect of the pH

The influence of initial pH in the degradation of OII was first studied. Figure 4.2 shows the fittings to the dye concentration data over time using Eq. (4.9), showing clearly that the OII degradation in the Fenton-like stage (data in the first stage were omitted) fits well the pseudo-first order kinetic model (average relative error < 1.0 %), whatever is the reaction pH (in the range 2-4).

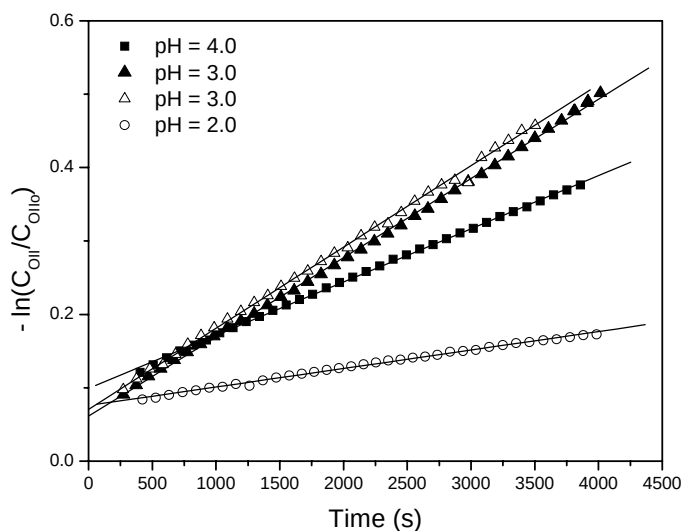


Fig. 4.2 – Plot of the linearized (ln) normalized dye concentration over time in the Fenton-like stage at different pH values. For the experimental conditions please refer to Table 4.1.

Table 4.1 shows the effect of the pH on the apparent kinetic constant (runs 1-4), from which it is evident that when the initial pH increases from 2 to 3 the value of k_{ap} quickly increases, and then suddenly decreases when the pH is raised from 3 to 4. This behaviour was mentioned in the previous chapter and agrees with literature findings, as it is usually accepted that acidic pH levels near 3 are usually optimum for Fenton oxidation [6,7,19]. At $\text{pH} < 3$, the process becomes less effective. Indeed, in such conditions the regeneration of Fe^{2+} (through reaction between Fe^{3+} and H_2O_2) is inhibited, because the formation of the Fe^{3+} -peroxocomplexes (as intermediates) decreases [20]. At a pH above 3.5 the performance significantly decreases, mainly because the dissolved fraction of iron species decreases [21]. Actually, at high pHs Fe(III) precipitates, therefore decreasing the concentration of dissolved Fe(III) . Consequently, the concentration of Fe(II) species also decreases because iron(III) hydroxides are much less reactive than dissolved Fe(III) species towards H_2O_2 . The process performance is then affected because a smaller steady-state concentration of hydroxyl radicals is attained.

It is worth noting that two experiments performed at pH 3.0 provided k_{ap} values that differ just 2.7%.

Table 4.1 – Effect of initial pH, chloride ion, dye, hydrogen peroxide or ferrous ion concentrations and temperature on the apparent pseudo-first-order rate constant (k_{ap}).

Run	pH	$C_{Cl^-} (M)$	$C_{OII_o} (M)$	$C_{H_2O_2_o} (M)$	$C_{Fe^{2+}_o} (M)$	T (K)	$k_{ap} (s^{-1})$
1	2.0						2.5×10^{-5}
2	3.0						1.1×10^{-4}
3	3.0	0	5.0×10^{-5}	2.0×10^{-4}	5.0×10^{-6}	303	1.1×10^{-4}
4	4.0						7.3×10^{-5}
5		0					1.1×10^{-4}
6		1.0×10^{-3}					7.3×10^{-5}
7	3.0	4.0×10^{-3}	5.0×10^{-5}	2.0×10^{-4}	5.0×10^{-6}	303	4.9×10^{-5}
8		1.0×10^{-2}					5.8×10^{-5}
9			1.1×10^{-4}				6.7×10^{-5}
10			5.9×10^{-5}				9.7×10^{-5}
11	3.0	0	5.1×10^{-5}	2.0×10^{-4}	5.0×10^{-6}	303	1.1×10^{-4}
12			4.1×10^{-5}				1.2×10^{-4}
13			3.2×10^{-5}				1.6×10^{-4}
14				1.0×10^{-4}			7.4×10^{-5}
15				2.0×10^{-4}			9.8×10^{-5}
16				4.0×10^{-4}			1.6×10^{-4}
17	3.0	0	5.0×10^{-5}	6.0×10^{-4}	5.0×10^{-6}	303	3.1×10^{-4}
18				8.0×10^{-4}			3.2×10^{-4}
19				1.0×10^{-3}			4.0×10^{-4}
20					2.5×10^{-6}		4.7×10^{-5}
21					5.0×10^{-6}		1.1×10^{-4}
22	3.0	0	5.1×10^{-5}	2.0×10^{-4}	1.0×10^{-5}	303	4.0×10^{-4}
23					1.5×10^{-5}		5.8×10^{-4}
24					2.0×10^{-5}		8.3×10^{-4}
25						283	2.0×10^{-5}
26						293	5.3×10^{-5}
27	3.0	0	5.3×10^{-5}	2.0×10^{-4}	5.0×10^{-6}	303	1.1×10^{-4}
28						313	2.2×10^{-4}
29						323	4.2×10^{-4}

4.3.2.2 Effect of the Chloride Anion Concentration

Inorganic anions (Cl^- , SO_4^{2-} , $\text{H}_2\text{PO}_4^-/\text{HPO}_4^{2-}$, etc.) present in wastewater may have a significant effect on the overall reaction rates in the Fenton process [22]. Moreover, the textile effluents contain a large number of inorganic salts [23] and inorganic anions, such as chloride ions, are very common in most wastewaters [24]. Therefore, it is important to evaluate their effect on the performance of the process.

The effect of the chloride anion (Cl^-) on the degradation of OII by Fenton's reagent was thus investigated and the results are shown in Table 4.1. It can be seen that the oxidation power of the Fenton process was decreased in the presence of Cl^- , as revealed by its effect on the kinetic constant associated with the reaction between OII and $\text{HO}^\bullet$ species (k_{ap}). The reason for this might therefore be attributed to a decrease in the amount of hydroxyl radicals available as a consequence of the following parallel scavenging reactions [3]:



This inhibitory effect is in agreement with others reported in the literature for 2,4-dichlorophenol [25], Orange II [26] and other dyes [27] degradation, although some others point for other parallel reactions between Cl anions and other species [22, 26]. Finally, it is worth mentioning that Malik and Saha [3] reported that the presence of Cl^- on direct dyes oxidation decreases the extent of degradation, when Cl^- concentration ranges similar to those used in this chapter were employed.

The effect of the remaining operating variables will now be addressed, in order to establish the reaction rate equation, in absence of chloride ions and at the optimum pH of 3.

4.3.2.3 Effect of the Initial Orange II Concentration

The effect of the initial dye concentration was tested at constant initial H_2O_2 and Fe^{2+} concentrations, 2×10^{-4} and 5×10^{-6} M, respectively, with $T = 303$ K and initial pH = 3. Results are shown in Fig. 4.3A, with the corresponding fitting lines (in the Fenton-

like stage), and the obtained apparent kinetic constants are reported in Table 4.1 (runs 9-13). Results show that the degradation rate decreases for increasing C_{OII_o} , in the chosen range. The apparent rate order for Orange II was then determined to be -0.67 from a $\ln k_{ap}$ vs. $\ln C_{OII_o}$ plot (Fig. 4.3B). The negative effect of the parent organic compound on the apparent kinetic constant was also reported by other authors [e.g., 17,28]. Because the amount of hydrogen peroxide molecules available is the same, this indicates that the higher the dye concentration in the reactor, the smaller is the hydroxyl radicals concentration at the pseudo steady-state.

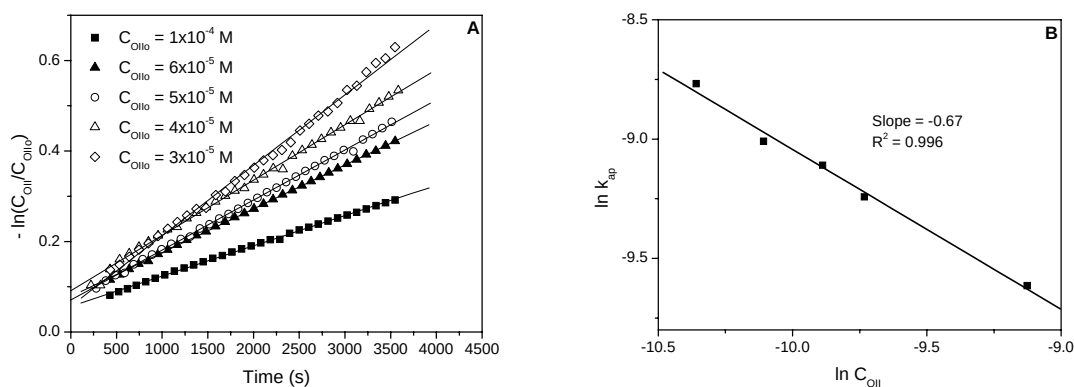


Fig. 4.3 – (A) Plot of the linearized (ln) normalized dye concentration over time in the Fenton-like stage at different initial OII concentrations. (B) Effect of the initial OII concentration on the apparent rate constant of OII degradation. For the experimental conditions please refer to Table 4.1.

4.3.2.4 Effect of the Initial Hydrogen Peroxide Concentration

Figure 4.4A shows the normalized OII concentration histories for different oxidant doses and the corresponding fittings, from which the apparent kinetic constants were computed.

The effect of the initial hydrogen peroxide concentration ($C_{H_2O_{2o}}$) on k_{ap} can be observed in runs 14-19 (Table 4.1), and the results show that the degradation rate increases for increasing hydrogen peroxide loads, in the range studied. This trend was expectable. However, in the previous chapter it was found that when the value of $C_{H_2O_{2o}}$ is very high, the degradation efficiency keeps constant or even decreases. The fact that in some conditions very high H_2O_2 concentration values lead to a decrease in the final discolouration and rate of degradation is possibly due to the competition between these species for hydroxyl radicals (scavenging effect, Eq. (4.4)). Indeed, HO radicals are

quite non-selective, reacting with the organic matter present but also with other species. Laat and Gallard [8] have also stated that when the molar ratio $C_{H_2O_2} / C_{Fe^{2+}}$ is very high (> 500), a detrimental effect might be observed. This was not observed in this work and much lower ratios have been employed (< 200).

The apparent rate order for initial H_2O_2 concentration was determined to be 0.77 from a $\ln k_{ap}$ vs. $\ln C_{H_2O_2}$ plot (see Fig. 4.4B).

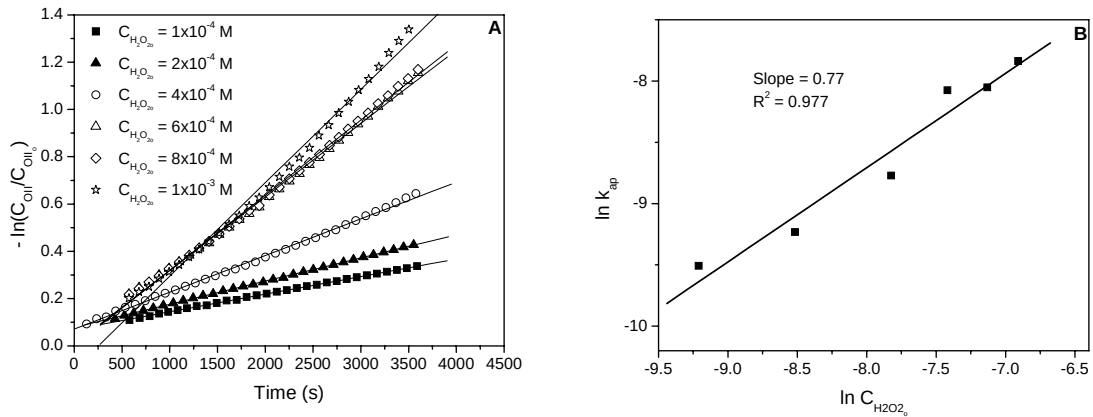


Fig. 4.4 – (A) Plot of the linearized (ln) normalized dye concentration over time in the Fenton-like stage at different initial H_2O_2 concentrations. (B) Effect of the initial H_2O_2 concentration on the apparent rate constant of OII degradation. For the experimental conditions please refer to Table 4.1.

4.3.2.5 Effect of the Initial Ferrous Ion Concentration

The procedure described above was also applied to analyze the effect of $C_{Fe^{2+}}$ (Fig. 4.5A and Table 4.1). The linear fit is once again quite reasonable (average relative error $< 6.5\%$), even for the higher iron concentrations for which dye conversion is above $\sim 90\%$ at the end of the run (and therefore its concentration is in the range of 10^{-6} M).

Data obtained put into evidence that the degradation rate is very sensitive to the iron concentration, because it acts as catalyst in the Fenton or Fenton-like process. In the range used, i.e., $2.5 \times 10^{-6} < C_{Fe^{2+}} < 2.0 \times 10^{-5}$ M and $10 < C_{H_2O_2} / C_{Fe^{2+}} < 80$ (mol.), the degradation rate increases with the ferrous iron content. Other authors found that, if the ratio $C_{H_2O_2} / C_{Fe^{2+}}$ is between 50-500, k_{ap} increases linearly with $C_{Fe^{2+}}$ [8]. The rate order for initial Fe^{2+} dose was determined to be 1.43 from a $\ln k_{ap}$ vs. $\ln C_{Fe^{2+}}$ plot (Fig. 4.5B) with a very good linear fit.

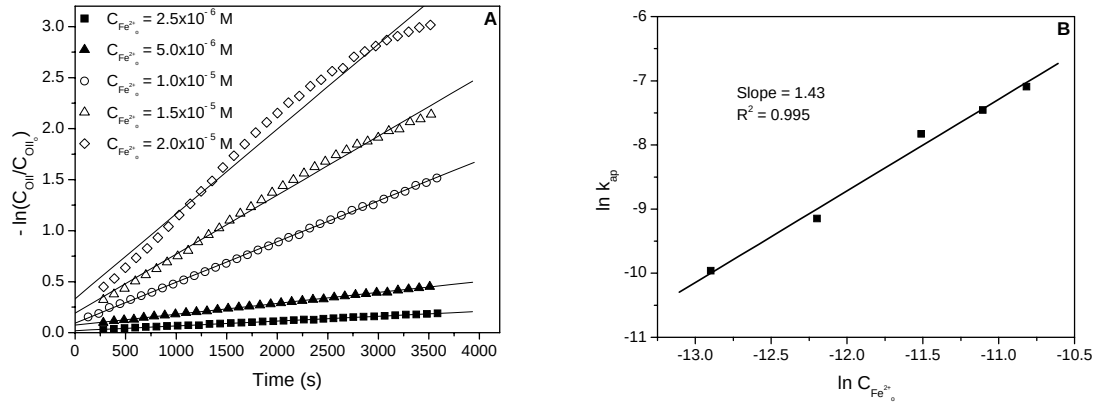


Fig. 4.5 – (A) Plot of the linearized (ln) normalized dye concentration over time in the Fenton-like stage at different initial Fe^{2+} concentrations. (B) Effect of the initial Fe^{2+} concentration on the apparent rate constant of OII degradation. For the experimental conditions please refer to Table 4.1.

4.3.2.6 Effect of the Temperature

The temperature effect on k_{ap} , deduced again from the fittings shown in Fig. 4.6A, can be observed in runs 25-29, with constant $C_{OII,0}$, $C_{H_2O_{2,0}}$, pH and $C_{Fe^{2+},0}$ (Table 4.1). It is observed that the temperature has a strong effect on the OII degradation rate, which is increased at high temperatures due to an increment in the pseudo-first-order rate constant. The data exhibit Arrhenius-type behaviour, with an apparent activation energy of 58.1 kJ mol^{-1} , calculated from the usual $\ln k_{ap}$ vs. $1/T$ plot (Fig. 4.6B). The value obtained is very similar to that reported in chapter 6 for a Fe-impregnated activated carbon (56.1 kJ mol^{-1}). It is interesting to note that such activation energies are somewhat higher than the values measured for: i) photo-assisted catalytic decomposition of Orange II through a Fe/C structured solid - $43.55 \text{ kJ mol}^{-1}$ [29] and ii) photo-Fenton reactions on structured C-Nafion/Fe-ion surfaces - $41.03 \text{ kJ mol}^{-1}$ [30].

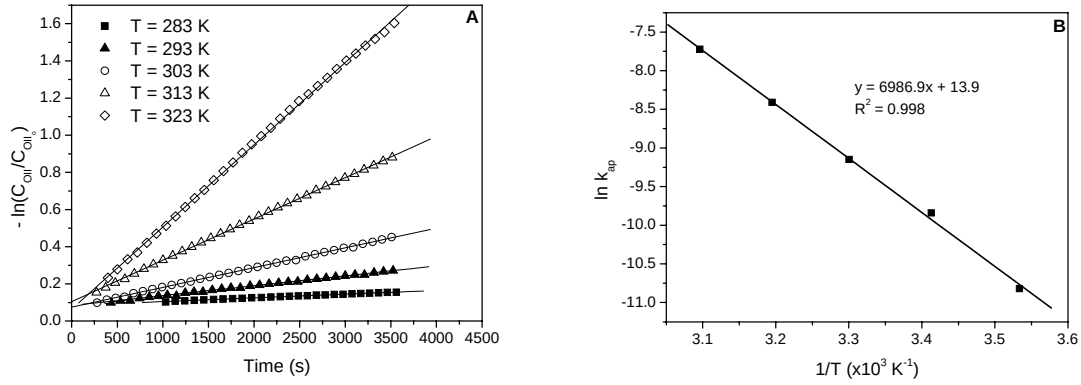


Fig. 4.6 – (A) Plot of the linearized (ln) normalized dye concentration over time in the Fenton-like stage at different temperatures. (B) Arrhenius plot of the apparent rate constant of OII degradation. For the experimental conditions please refer to Table 4.1.

4.3.2.7 Rate Equation for the Degradation of OII in a Batch Reactor

The rate equation can be expressed in a simple way (pseudo first-order), as shown in Eq. (4.8), wherein k_{ap} depends on the initial conditions as follows:

$$k_{ap} = AC_{OII_0}^a C_{H_2O_2_0}^b C_{Fe^{2+}_0}^c \exp(-Ea / RT) \quad (4.13)$$

where Ea is the apparent activation energy for OII degradation and the exponents a , b and c represent the apparent reaction orders for OII, H_2O_2 and Fe^{2+} , respectively. The pre-exponential coefficient A was then calculated by regression minimising the sum of the square residues between the k_{ap} data obtained from Eqs. (4.9) and (4.13), for each experiment. The value obtained with this procedure was $A = 4.06 \times 10^{13} \text{ s}^{-1}$ and the resulting parity plot is shown in Fig. 4.7, evidencing a good agreement between the data. Concluding, the power-law equation for the apparent rate constant of OII oxidation via Fenton's reagent, in the Fenton-like stage, is given by:

$$k_{ap} = 4.06 \times 10^{13} C_{OII_0}^{-0.67} C_{H_2O_2_0}^{0.77} C_{Fe^{2+}_0}^{1.43} \exp(-58092 / RT) \quad (4.14)$$

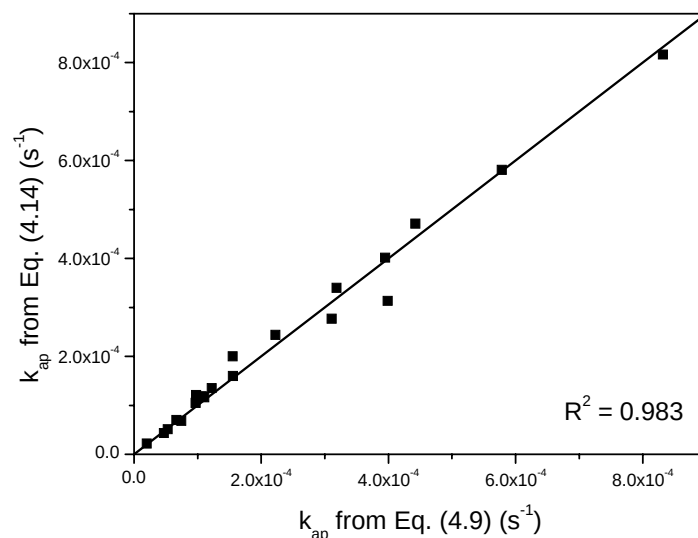


Fig. 4.7 – Plot of k_{ap} obtained from Eq. (4.9) and predicted from Eq. (4.14).

Up to now it was established a first-order rate law for OII degradation, which can be useful for predicting the pseudo steady-state (i.e., when Fe is essentially at the 3+ oxidation state) in a chemical reactor. Obviously, in a batch system this can fail (and really does, as shown below), depending on the initial conditions and extension of the initial (Fenton) phase, which is most experiments performed is short. However, it can be valuable to predict the behaviour of open reactors, operating at steady-state conditions, if the residence time is enough so that Fe^{2+} is almost completely converted into Fe^{3+} .

To predict the dye concentration history in the batch reactor, the mass balance yields the typical exponential curve (Eq. (4.9)), where k_{ap} is computed from Eq. (4.14). Figures 4.8A to 4.8D show the transient curves in which experimental and model results are compared, for the main parameters studied in this work. In most runs there is an underprediction of the model, which has also some problems in predicting the initial data, as expected (Fenton stage). It is worth noting that the model has a better accuracy when a fast transition from stage I to stage II is ensured. This means high concentration of hydrogen peroxide (average absolute error of 4.9 % vs. 6.5 % for the lowest concentration, Fig. 4.8B) or high temperature (average absolute error of 1.2 % vs. 7.0 % for the lowest temperature, Fig. 4.8D), which is in good agreement with Eq. (4.10). In Fig. 4.8A the concentration of orange II was varied, but again for simplicity only two experiments of those used in the kinetic study are shown in the graphic, corresponding to the highest and lowest dye concentrations used. An additional run was still carried

out at a higher temperature, putting into evidence the better adherence of the model under such conditions.

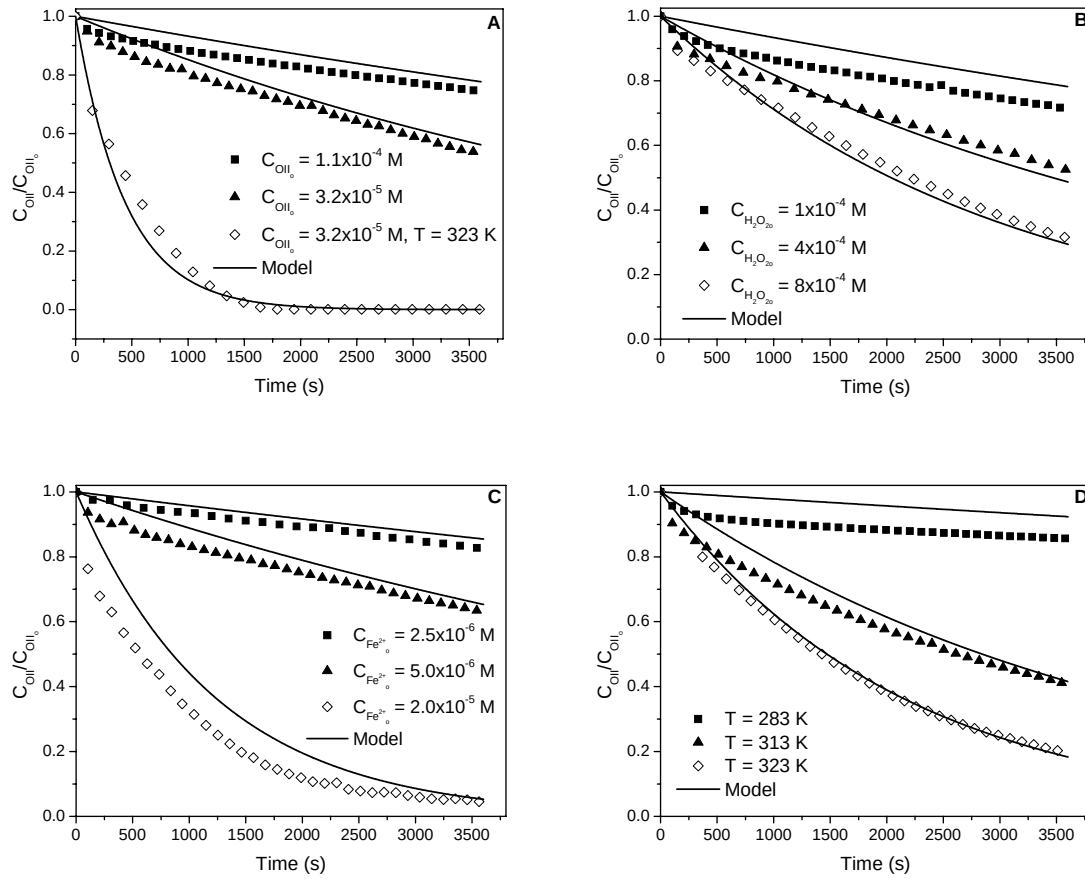


Fig. 4.8 – Orange II concentration histories in the batch reactor when changing: (A) the initial OII concentration; (B) the initial H_2O_2 concentration; (C) the initial Fe^{2+} concentration; and (D) the temperature. For the experimental conditions please refer to Table 4.1.

4.3.3 Continuous Stirred Tank Reactor (CSTR) Experiments

In an ideal CSTR (or perfectly mixed reactor), the contents are well-stirred and uniform throughout; therefore the exit stream has the same composition as the fluid within the vessel. Tracer experiments have confirmed that the reactor used in this chapter closely matches these ideal mixing conditions, as evidenced in Fig. 4.9, where the theoretical curve is given by the typical Danckwerts' C curve, i.e., the normalized response to a pulse input [31, 32]:

$$C(t) = \frac{C_{out}(t)}{C^o} = \exp\left(-\frac{t}{\tau}\right) \quad (4.15)$$

For a CSTR, the space-time in Eq. (4.15) is equal to the mean residence time. In this case, the difference between the residence time obtained from the experimental tracer data fit and the formula value ($\tau = V/Q$) varies between 2.4 and 5.0 %, for different flow rates in the range of the experiments.

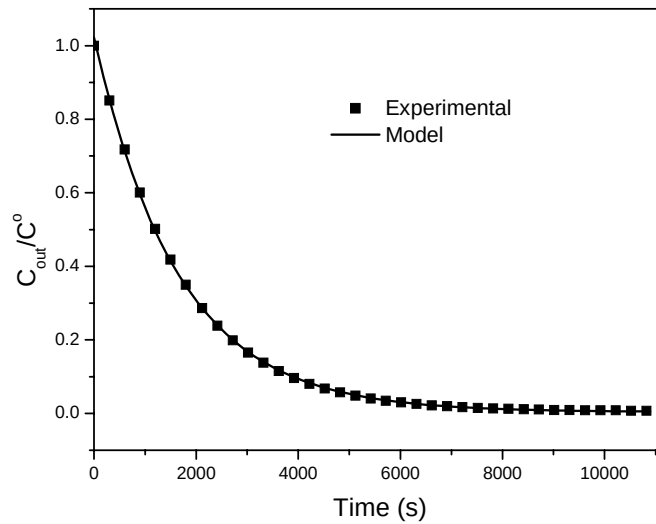


Fig. 4.9 – Typical experimental data (Danckwerts' C curve) for a tracer experiment and corresponding model fit. Flow rate = 0.58 ml s⁻¹.

Table 4.2 shows the experiments carried out in the continuous reactor at different experimental conditions. In this case, the inlet OII, H₂O₂ and Fe²⁺ concentrations, temperature and residence time were changed, within the range used in the batch reactor. However, experiments out of such range were also performed, shown in Table 4.3, in which higher catalyst dosages have been used in order to shift the steady-state conversions to values close to 100%. Both tables include also the experimental conversion and the model prediction (described later on), calculated as follows:

$$X = \frac{C_{OII_{in}} - C_{OII_{out}}}{C_{OII_{in}}} \times 100 \quad (4.16)$$

where $C_{OII_{in}}$ is the inlet OII concentration and $C_{OII_{out}}$ the outlet one.

Table 4.2 – Experimental and model prediction of OII conversion in the continuous stirred tank reactor, under conditions within the batch study range.

Run	$C_{OII_{in}} (M)$	$C_{H_2O_{2in}} (M)$	$C_{Fe^{2+}_{in}} (M)$	$\tau (s)$	T (K)	$X_{exp}(\%)$	$X_{mod} (\%)$
1	4.0×10^{-5}			1136.7		18.0	21.0
2	7.0×10^{-5}	4.0×10^{-4}	5.0×10^{-6}	1142.2	303	16.0	15.5
3	1.0×10^{-4}			1147.2		12.9	12.7
4		4.0×10^{-4}		1221.6		69.2	64.0
5		3.0×10^{-4}		1222.7		63.8	58.7
6	5.0×10^{-5}	2.0×10^{-4}	2.0×10^{-5}	1199.7	303	58.3	50.6
7		1.0×10^{-4}		1195.8		50.8	37.4
8		5.0×10^{-5}		1238.1		34.6	26.7
9		2.5×10^{-5}		1284.31		2.1	3.0
10		5.0×10^{-5}		1284.31		5.5	5.0
11	5.0×10^{-5}	2.0×10^{-4}	5.0×10^{-6}	1268.26	303	13.2	13.0
12		4.0×10^{-4}		1268.26		20.3	20.3
13		9.0×10^{-4}		1278.29		27.4	32.4
14			5.0×10^{-6}	1302.3		23.1	20.7
15	5.0×10^{-5}	4.0×10^{-4}	1.0×10^{-5}	1265.4	303	46.0	40.6
16			2.0×10^{-5}	1221.6		70.0	64.0
17				1284.31	288	9.2	7.2
18	5.0×10^{-5}	4.0×10^{-4}	5.0×10^{-6}	1284.31	318	46.3	43.4
19				1268.26	333	71.5	67.0
20				1136.7		18.0	21.0
21	5.0×10^{-5}	4.0×10^{-4}	5.0×10^{-6}	1485.5	303	25.3	25.7
22				2341.3		36.8	35.3

Table 4.3 – Experimental and model prediction of OII conversion in the continuous stirred tank reactor, under conditions above the batch study range.

Run	$C_{OII_{in}} (M)$	$C_{H_2O_{2in}} (M)$	$C_{Fe^{2+}_{in}} (M)$	$\tau (s)$	T (K)	$X_{exp}(\%)$	$X_{mod} (\%)$
23	3.0×10^{-5}			1247.1		95.3	92.4
24	4.0×10^{-5}			1302.3		89.3	91.5
25	5.0×10^{-5}	4.0×10^{-4}	6.0×10^{-5}	1302.3	303	87.2	90.1
26	7.0×10^{-5}			1247.1		72.9	87.4
27	1.0×10^{-4}			1247.1		64.5	84.8
28			3.0×10^{-5}	1265.0		77.8	76.6
29			4.0×10^{-5}	1265.4		81.4	83.2
30	5.0×10^{-5}	4.0×10^{-4}	6.0×10^{-5}	1302.3	303	87.2	90.1
31			1.0×10^{-4}	1228.7		87.8	94.7
32			2.0×10^{-4}	1302.3		90.0	98.1
33				1238.1	283	75.0	62.9
34				1247.1	296	80.8	83.4
35				1302.3	303	87.2	90.1
36				1247.1	315	89.4	95.5
37				1238.1	323	93.5	97.4
38	5.0×10^{-5}	4.0×10^{-4}	6.0×10^{-5}	1238.1	336	94.6	98.8
39				2054.5	283	77.8	74.6
40				2060.7	299	94.2	91.8
41				2504.3	300	90.2	93.6
42				2476.2	323	96.3	98.7
43				2407.9	334	97.3	99.3
44				1302.3		87.2	90.1
45	5.0×10^{-5}	4.0×10^{-4}	6.0×10^{-5}	1760.6	303	88.9	92.5
46				2504.3		90.2	94.6

In the next plots (Figs. 4.10 to 4.14) the effect of the reagents concentrations (at the reactor inlet), temperature and residence time on the steady-state conversion is shown. In all of them closed symbols refer to conditions within the batch range, whereas open symbols to values above it, in terms of iron concentration. It can be concluded that the effect of each parameter on the OII conversion is similar to that observed in the batch reactor.

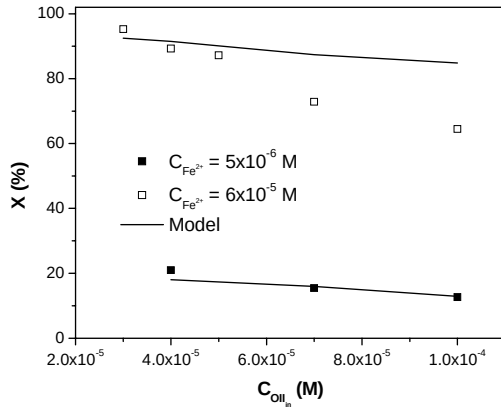


Fig. 4.10 – Effect of the inlet dye concentration on the steady-state OII conversion in the continuous reactor. For the experimental conditions please refer to Tables 4.2 and 4.3.

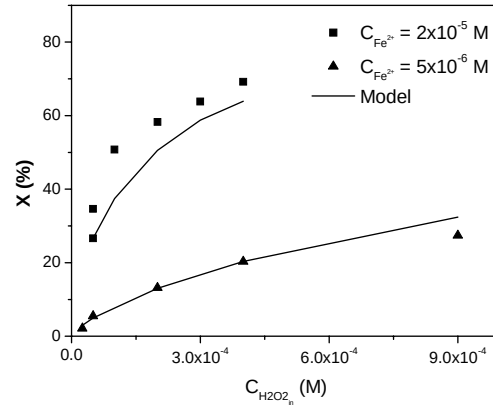


Fig. 4.11 – Effect of the inlet H_2O_2 concentration on the steady-state OII conversion in the continuous reactor. For the experimental conditions please refer to Table 4.2.

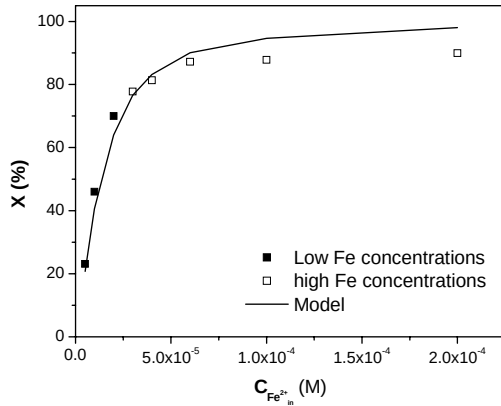


Fig. 4.12 – Effect of the inlet Fe^{2+} concentration on the steady-state OII conversion in the continuous reactor. For the experimental conditions please refer to Tables 4.2 and 4.3.

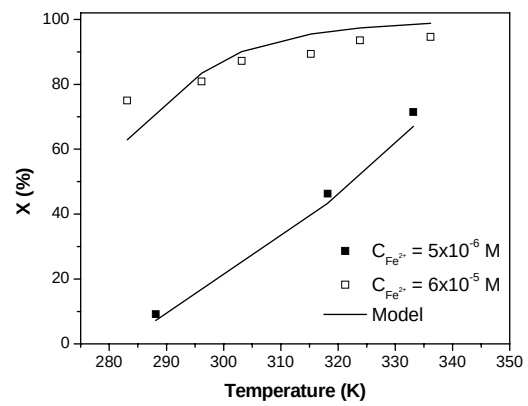


Fig. 4.13 – Effect of the temperature on the steady-state OII conversion in the continuous reactor. For the experimental conditions please refer to Tables 4.2 and 4.3.

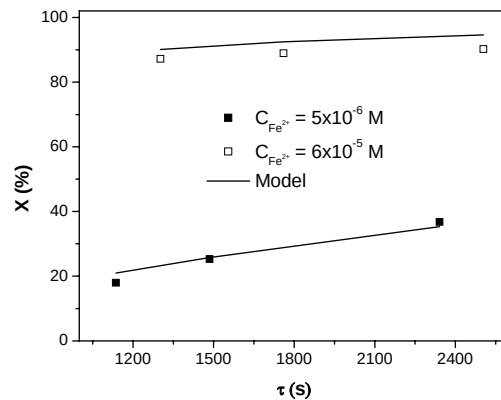


Fig. 4.14 – Effect of the space time on the steady-state OII conversion in the continuous reactor. For the experimental conditions please refer to Tables 4.2 and 4.3.

First, the OII conversion decreases when the dye concentration in the reactor feed increases (see Fig. 4.10). In terms of hydrogen peroxide concentration (Fig. 4.11), it is evident that when the H_2O_2 concentration is increased in the feed, an increment in the OII conversion is noticed, because more hydroxyl radicals are available for oxidation, in the range studied. The same behavior is observed when the ferrous iron is changed, as showed in the previous figures and also in Fig. 4.12. In the latter, an increase in the Fe^{2+} load fed to the reactor from 5×10^{-6} to 6×10^{-5} M lead to an increase in the steady-state OII conversion from 23% to 87%, however runs carried out at higher Fe^{2+} doses ($1-2 \times 10^{-4}$ M) resulted in no appreciable differences in terms of OII removal (up to 90%). Temperature effect was investigated in the range 283 to 336 K, showing to be an important parameter in the Fenton process (Fig. 4.13), particularly when low catalyst doses are employed. Finally, when the residence time was incremented, better results were obtained in terms of OII conversion at steady-state, as expected (see Fig. 4.14).

4.3.4 Validation of the Model in the Continuous Reactor

From a simple mass balance to the CSTR, at steady-state:

$$F_{OII_{in}} = F_{OII_{out}} + (-r_{OII})_{out} V \quad (4.17)$$

where $F_{OII_{in}}$ and $F_{OII_{out}}$ denote the dye molar flow rate at the reactor inlet and outlet, respectively. Since the reaction is of a pseudo first-order type (Eq. (4.8)), the outlet concentration of OII can be give by:

$$C_{OII_{out}} = \frac{C_{OII_{in}}}{1 + k_{ap} \tau} \quad (4.18)$$

where $\tau = V/Q$ is the space-time, V is the reactor volume (0.92 L), Q is the total flow rate and k_{ap} is obtained by Eq. (4.14), based on the concentration of each species at the reactor inlet, because these are the conditions that determine the steady-state radicals concentration. This issue can also be rationalized from the well known total segregation model [31,32], which assumes that all fluid elements having the same age (residence time) “travel together” in the reactor and do not mix with elements of different ages,

until they exit the reactor. Because there is no interchange of matter between fluid elements, each one acts as a batch reactor and so the mean steady-state conversion in the reactor is given by:

$$X = \int_0^{\infty} X_{batch}(t) \cdot E(t) dt \quad (4.19)$$

where $X_{batch}(t)$ refers to the transient conversion equation in a batch reactor ($X_{batch} = 1 - e^{(-k_{ap} t)}$, because the reaction is pseudo first-order - cf. Eq. (4.9)), and $E(t)$ is the residence-time distribution function ($E(t) = C(t)/\tau = 1/\tau \exp(-t/\tau)$, cf. Eq. (4.15)). What is important to remark is that in this model, the computation of conversion in a continuous reactor by Eq. (4.19) makes use of an expression for a “micro” batch reactor that is based on the reactor feed conditions.

The model conversion (X_{mod}) was then obtained using Eqs. (4.16) and (4.18) (the total segregation model yields the same value, because the reaction is pseudo first order – linear system). The previous figures (4.10 to 4.14) show the model predictions for all the experiments performed.

In what concerns the effect of the inlet OII concentration (Fig. 4.10), it is remarkable the adherence of the model to experimental data in which iron concentrations within the range used in the batch runs have been employed (maximum absolute error of 3%). However, even when catalyst doses one order of magnitude higher are employed, the model is able to predict the negative effect of increasing dye concentrations, although with higher deviations. This negative effect is related with a decrease in the number of oxidant molecules (or radicals) available per dye molecule (lower H_2O_2/OII ratios).

The model fits also reasonably the data obtained in experiments where increasing oxidant dosages are employed (Fig. 4.11), particularly for low iron loads. The model adherence is however worst when the catalyst concentration approaches the upper limit employed in the kinetic study. The difficulty in predicting conversions under experimental conditions in the limits of the range employed in the kinetic study is also evident in terms of hydrogen peroxide concentrations. This can be seen in the first data series, for lower Fe^{2+} loads (5×10^{-6} M), because the radicals scavenging effect that

occurs at high oxidant loads (*cf.* Eq. (4.4)) is not taken into account in the power law type rate equation.

Figure 4.12 reinforces what was said in the previous paragraph, i.e. the good adherence of the model to experimental data when using conditions (now iron concentrations) within those employed when establishing the rate equation. However it has some difficulties to predict the scavenging effect, i.e., the parallel and undesirable reaction that occurs between the catalyst and the hydroxyl radicals (Eq. (4.2)) at high Fe loads.

The results obtained when the temperature and residence time were changed (Figs. 4.13 and 4.14, respectively) show that the model also predicts well the positive effect of both parameters; this applies particularly for low iron loads, and even reasonably when iron concentrations above those employed in the kinetic study were used.

Finally, in Fig. 4.15 is shown the comparison between the experimental conversion data and the model prediction, for all experiments of Tables 4.2 and 4.3. In the parity plot it is observed that there is a reasonably good adherence of the model, in spite no fitting parameters exist. The more significant deviations concern experiments performed off the kinetic study range (e.g. runs 26 and 27, absolute errors of 15 and 20%, respectively), although on average predictions differ less than 5%. The model revealed, therefore, to be effective for predicting either experiments carried out within the range used in the batch reactor or out of it (high catalyst concentrations), the later being performed also with the goal of extending the OII conversion range, approaching values close to 100%.

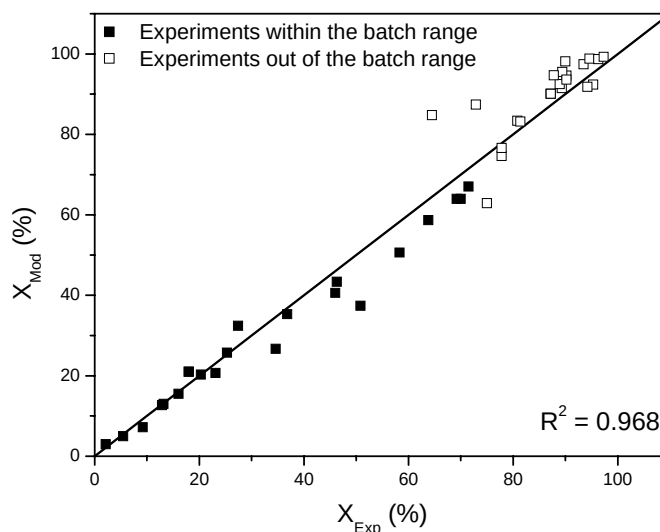


Fig. 4.15 – Parity plot comparing OII conversion obtained experimentally versus OII conversion predicted by the CSTR model.

4.4 Conclusions

- Performances reached during Orange II degradation by means of Fenton's reagent highly depend on operating conditions, i.e. reagents dosage, temperature, pH and time of reaction (batch reactor) or residence time (continuous reactor).
- In this study, and particularly in the batch reactor experiments, low initial concentrations of hydrogen peroxide and ferrous ion were applied to eliminate the useless use of excessive reagent doses, usually found at high Fe^{2+} and/or H_2O_2 doses. Depending on the initial conditions, about 14-95 % of Orange II was removed in 1 h.
- Experiments carried out in the batch reactor evidenced that the optimum pH is around 3 and the negative effect of Cl^- concentrations. It was also observed the positive effect of increasing the reaction temperature, H_2O_2 or Fe^{2+} concentrations, and the negative effect of increasing dye concentrations, trends that were corroborated with experiments in the CSTR.
- The dye history concentration showed a change in the kinetics, typical of this process, being initially very rapid (Fenton stage) and afterwards the slower Fenton-like stage proceeds, where iron is mostly in the 3+ oxidation state. For the longer and last stage a pseudo steady-state approach was employed to

deduce the reaction rate, which was found to be of the first-order type with respect to OII concentration. The dependence of the apparent kinetic constant on the initial operating conditions was then deduced, leading to a power-law rate equation with Arrhenius dependency (apparent activation energy of 58.1 kJ mol⁻¹). In experiments carried out in duplicate, k_{ap} varied by less than 10%.

- This rate equation revealed to be somewhat useful to predict dye concentration histories in the batch reactor (based on the known initial conditions) and the steady-state dye conversion in the CSTR (based on inlet conditions), wherein Fe is essentially at the 3+ oxidation state. However, under certain conditions some underprediction was observed.
- A large set of experiments was performed in the continuous reactor, in order to analyze the effect of all the variables involved. In all cases it was observed a reasonably good agreement between experimental and model results, even for experiments performed with iron concentrations out of the range used in the batch kinetic study. It is important to remark the ability of the model to predict data in a wide range of dye conversions values, from 2 to 97 %.

References

1. Dutta, K.; Mukhopadhyay, S.; Bhattacharjee, S.; Chaudhuri, B. Chemical oxidation of methylene blue using a Fenton-like reaction. *Journal of Hazardous Materials* **2001**, 84, 57.
2. Swaminathan, K.; Sandhya, S.; Sophia, A. C.; Pachhade, K.; Subrahmanyam, Y. V. Decolorization and degradation of H-acid and other dyes using ferrous-hydrogen peroxide system. *Chemosphere* **2003**, 50, 619.
3. Malik, P. K.; Saha, S. K. Oxidation of direct dyes with hydrogen peroxide using ferrous ion as catalyst. *Separation and Purification Technology* **2003**, 31, 241.
4. Lin, S. H.; Lo, C. C. Fenton process for treatment of desizing wastewater. *Water Research* **1997**, 31, 2050.
5. Bigda, R. J. Consider Fenton chemistry for wastewater treatment. *Chemical Engineering and Processing* **1995**, 91, 62.
6. Walling, C. Fenton's reagent revisited. *Accounts of Chemical Research* **1975**, 8, 125.
7. Rivas, F. J.; Navarrete, V.; Beltran, F. J.; Garcia-Araya, J. F. Simazine Fenton's oxidation in a continuous reactor. *Applied Catalysis B: Environmental* **2004**, 48, 249.

8. De Laat, J.; Gallard, H. Catalytic decomposition of hydrogen peroxide by Fe(III) in homogeneous aqueous solution: mechanism and kinetic modeling. *Environmental Science and Technology* **1999**, 33, 2726.
9. Dionysiou, D. D.; Suidan, M. T.; Baudin, I.; Lafine, J. M. Effect of hydrogen peroxide on the destruction of organic contaminants-synergism and inhibition in a continuous-mode photocatalytic reactor. *Applied Catalysis B: Environmental* **2004**, 50, 259.
10. Henle, E. S.; Luo, Y.; Linn, S. Fe^{2+} , Fe^{3+} , and oxygen react with DNA-derived radicals formed during iron-mediated Fenton reactions. *Biochemistry* **1996**, 35, 12, 212.
11. Rivas, F. J.; Beltran, F. J.; Frades, J.; Buxeda, P. Oxidation of p-hydroxybenzoic acid by Fenton's reagent. *Water Research* **1997**, 35, 387.
12. Chen, R.; Pignatello, J. J. Role of quinone intermediates as electron shuttles in Fenton and photoassisted Fenton oxidations of aromatic compounds. *Environmental Science and Technology* **1997**, 31, 2399.
13. Haag, W. R.; Yao, C. C. D. Rate constants for reaction of hydroxyl radicals with several drinking water contaminants. *Environmental Science and Technology* **1992**, 26, 1005.
14. Zhang, H.; Choi, H. J.; Huang, C. P. Treatment of landfill leachate by Fenton's reagent in a continuous stirred tank reactor. *Journal of Hazardous Materials* **2006**, 136, 618.
15. Oh, S. Y.; Chiu, P. C.; Kim, B. J.; Cha, D. K. Enhancing Fenton oxidation of TNT and RDX through pretreatment with zero-valent iron. *Water Research* **2003**, 37, 4275.
16. Gallard, H.; De Laat, J. Kinetic modelling of Fe(III)/ H_2O_2 oxidation reactions in dilute aqueous solution using atrazine as a model organic compound. *Water Research* **2000**, 34, 3107.
17. Sun, J. H.; Sun, S. P.; Fan, M. H.; Guo, H. Q.; Qiao, L. P.; Sun, R. X. A kinetic study on the degradation of p-nitroaniline by Fenton oxidation process. *Journal of Hazardous Materials* **2007**, 148, 172.
18. Benitez, F. J.; Real, F. J.; Acero, J. L.; Garcia C.; Llanos E. M. Kinetics of phenylurea herbicides oxidation by Fenton and photo-Fenton processes. *Journal of Chemical Technology and Biotechnology* **2007**, 82, 65.
19. Neyens, E.; Baeyens, J. A review of classic Fenton's peroxidation as an advanced oxidation technique. *Journal of Hazardous Materials* **2003**, 98, 33.
20. Pignatello, J. J. Dark and photoassisted iron(3+)-catalyzed degradation of chlorophenoxy herbicides by hydrogen peroxide. *Environmental Science and Technology* **1992**, 26, 944.
21. Pera-Titus, M.; Garcia-Molina, V.; Baños, M. A.; Gimenez, J.; Esplugas, S. Degradation of chlorophenols by means of advanced oxidation processes: A general review. *Applied Catalysis B: Environmental* **2003**, 47, 219.

22. De Laat, J.; Giang T. L.; Legube, B. A comparative study of the effects of chloride, sulfate and nitrate ions on the rates of decomposition of H_2O_2 and organic compounds by $\text{Fe(II)/H}_2\text{O}_2$ and $\text{Fe(III)/H}_2\text{O}_2$. *Chemosphere* **2004**, 55, 715.
23. Chen, G.; Chai, X.; Yue, P.; Mi, Y. Treatment of textile desizing wastewater by pilot scale nanofiltration membrane separation. *Journal of Membrane Science* **1997**, 127, 93.
24. Lu, M. C.; Chen, J. N.; Chang, C. P. Effect of inorganic ions on the oxidation of dichlorvos insecticide with Fenton's reagent. *Chemosphere* **1997**, 35, 2285.
25. Tang, W. Z.; Huang, C. P. 2,4-Dichlorophenol oxidation kinetics by Fenton's reagent. *Environmental Technologies* **1996**, 17, 1371.
26. Kiwi, J.; Lopez, A.; Nadochenko, V. Mechanism and kinetics of the OH-radical intervention during Fenton oxidation in the presence of a significant amount of radical scavenger (Cl^-). *Environmental Science and Technology* **2000**, 34, 2162.
27. Guillard, C.; Lachheb, H.; Housa, A.; Ksibi, M.; Elaloui, E.; Herrmann, J. M. Influence of chemical structure of dyes, of pH and of inorganic salts on their photocatalytic degradation by TiO_2 comparison of the efficiency of powder and supported TiO_2 . *Journal of Photochemistry and Photobiology A: Chemistry* **2003**, 158, 27.
28. Rodriguez, M. L.; Timokhin, V. I.; Contreras, S.; Chamarro, E.; Esplugas, S. Rate equation for the degradation of nitrobenzene by 'Fenton-like' reagent. *Advances in Environmental Research* **2003**, 7, 583.
29. Yuranova, T.; Enea, O.; Mielczarski, E.; Mielczarski, J.; Albers, P.; Kiwi, J. Fenton immobilized photo-assisted catalysis through a Fe/C structured fabric. *Applied Catalysis B: Environmental* **2004**, 49, 39.
30. Parra, S.; Guasaquillo, I.; Enea, O.; Mielczarski, E.; Mielczarki, J.; Albers, P.; Kiwi-Minsker, L.; Kiwi, J. Abatement of an azo dye on structured C-Nafion/Fe-ion surfaces by photo-Fenton reactions leading to carboxylate intermediates with a remarkable biodegradability increase of the treated solution. *Journal of Physical Chemistry B* **2003**, 107, 7026.
31. Fogler, H. S. Elements of chemical reaction engineering. Prentice-Hall, 3rd ed., N.J. **1999**.
32. Rodrigues, A. E. Theory of residence time distributions, *in* Multiphase Chemical Reactors, A.E. Rodrigues, J.M. Calo and N.H. Sweed (Eds.), NATO ASI Series, Sijthoff Noordhoff, **1981**, 51, Vol. I, 225.

PART IV

HETEROGENEOUS SYSTEM

CHAPTER 5 – FENTON-LIKE OXIDATION OF ORANGE II SOLUTIONS USING HETEROGENEOUS CATALYSTS BASED ON SAPONITE CLAY^{*}

Abstract

In this chapter, the degradation and mineralization of Orange II solutions (1×10^{-4} M) using catalysts based on pillared saponite impregnated with different iron salts is reported. Oxidation is carried out in a batch reactor, in presence of various hydrogen peroxide concentrations, and in a wide range of temperature and pH values. Twelve samples were prepared, with three different iron loads (7.5, 13.0 and 17.0 wt. %), and using four iron salts as precursors, namely Fe(II) acetate, Fe(II) oxalate, Fe(II) acetylacetonate and Fe(III) acetylacetonate. The samples were characterized using X-ray diffraction, thermal analysis, infrared spectroscopy, energy dispersive spectroscopy and adsorption of nitrogen at 77 K. The catalytic results show that these solids present good catalytic properties for the degradation and mineralization of Orange II solutions, allowing to reach, in the best conditions and after 4 h of oxidation, 99% of dye degradation with 91% of TOC (Total Organic Carbon) reduction (at 70 °C), using only ca. 90 mg of clay catalyst per liter of solution. Nevertheless, 96% of dye removal with 82% of mineralization were also reached at 30 °C. Besides, the amount of iron released into the final solution is lower than 1 ppm, in the worst of the cases, and 0.09 ppm in the best case.

^{*} Adapted from: Ramirez, J. H.; Costa, C. A.; Madeira, L. M.; Mata, G.; Vicente, M. A.; Rojas-Cervantes, M. L.; Lopez-Peinado, A. J.; Martin-Aranda R. M. *Applied Catalysis B: Environmental* **2007**, 71, 44.

5.1 Introduction

The oxidation using Fenton's reagent (a powerful source of oxidative $HO^\bullet$ radicals generated from H_2O_2 in the presence of added Fe^{2+} ions [1]) has proved to be a promising and attractive treatment method for the effective destruction of a large number of hazardous and organic pollutants [2-6]. The generated $HO^\bullet$ radicals are highly oxidative, non-selective, and able to decompose many organic compounds, including dyes [7]. However, it should be pointed out that the homogeneous Fenton process has a significant disadvantage. Homogeneously catalysed reactions need up to 50-80 ppm of Fe ions in solution, which is well above the European Union directives that allow only 2 ppm of Fe ions in treated water to dump directly into the environment [8]. In addition, the removal/treatment of the sludge-containing Fe ions at the end of the wastewater treatment is expensive and needs large amount of chemicals and manpower.

To overcome the disadvantages of the homogeneous Fenton process, and also considering the possibility of recovering the catalyst, some attempts have been made to develop heterogeneous catalysts, prepared by incorporating Fe ions or Fe oxides into porous supports [9-14]. Even so, some works can be found in the literature with other transition metals and different types of supports, as mentioned in chapter 1.

Among the above-mentioned catalyst supports, pillared clays (PILCs in short) is one of the families of microporous solids developed by Molecular Engineering that have been more studied in recent years, because of their particular properties and structures (with tunable pore size), as well as the abundance and low cost of natural clay minerals. Besides, they lead to active and stable solids in aqueous media, usually being very stable against leaching [15]. The PILCs synthesis procedure can be divided into three main steps: i) preparation of polyoxocations by careful hydrolysis of certain multivalent cations, which under appropriate conditions give rise to cationic polymeric species, ii) ionic exchange of the original charge-compensating cations of swellable smectite clays by the polyoxocations before synthesized, this exchange giving rise to the so called "intercalated clays", and iii) stabilisation of the intercalated clays by calcination at relatively high temperatures, which transform the metastable polyoxocations into "pillars", stable metallic clusters, close to oxi-hydroxidic phases, which maintain the layers of the clays separated to a long distance [16], thus able to accommodate large molecules susceptible to undergo chemical transformations. These solids are called "pillared clays", showing a bidimensional microporous network of

molecular dimensions, with the pillars occupying the interlayer space defined by the clay layers. The number and size of the pillars in the interlayer region are responsible for the pore parameters of the pillared clay structure [17].

Recently, Feng and co-workers [18,19] synthesized clay-based Fe nanocomposites by the so-called pillaring technique and used them as heterogeneous catalysts for the photo-Fenton discoloration and mineralization of azo-dyes. Their results clearly indicate that the solids are promising photo catalysts, but the use of light increases the costs of the overall process as compared to dark Fenton oxidation. However, in their conditions the oxidation is faster, which is also important to be taken into account in economical analysis.

In this chapter, several heterogeneous catalysts based on Al-pillared saponite impregnated with iron salts were prepared, which advantages were previously remarked (*cf.* 1st chapter, section 1.6.2). A saponite has been intercalated with Al polycations, and the pillared solid obtained after calcination at 500 °C has been used as support for the impregnation with iron. Four iron salts have been used as precursors with three different loads of iron. The obtained heterogeneous catalysts were tested in the Fenton-like oxidation of the non-biodegradable azo-dye Orange II (OII) in water solution, using a slurry batch reactor. The effectiveness of these catalysts in the oxidation of the dye, as well as the influence of the synthesis variables and of the reaction conditions on the catalytic activity are discussed.

5.2 Materials and Methods

5.2.1 Preparation and Characterization of the Catalysts

The procedure used to synthesize the clay-based catalysts is described in detail elsewhere (*cf.* chapter 2), as well as the techniques employed to characterize the solids. As mentioned above, four iron salts (namely, Fe(II) acetate, Fe(II) oxalate, Fe(II) acetylacetonate and Fe(III) acetylacetonate) have been used as precursors and three different loads of iron have been used (7.5, 13.0 and 17.0 wt. %). These catalysts are designated herein by a precursor-amount notation, for example Fe(II) acetate 7.5 designates the solid prepared using Fe(II) acetate as precursor and containing 7.5 wt. % of Fe in the final catalyst.

5.2.2 Catalytic Activity

Chemical oxidation of Orange II was carried out using 1 L of a 1×10^{-4} M solution in a batch reactor, under continuous stirring and with a permanent control of the temperature (*cf.* chapter 2), which is in the range of azo dyes' concentrations usually found in industrial waste streams [20]. It is worth of mentioning that due to the low mass of catalyst used (91.5 mg, with an average volumetric diameter of $3.342 \mu\text{m}$ – determined in a Coulter Counter particle size analyser, ref.: LS230), no interference in the absorbance data was noticed. In the runs where a significant concentration of clay was used (1 g/L), samples taken along time were filtered before measurement of absorbance. All the experiments were repeated at least twice (the average relative error along the runs was of 11%, while at the end of the oxidation, $t = 4\text{h}$, conversion values differed only, on average, 2%).

5.3 Results and Discussion

5.3.1 Characterization of the Catalysts

Intercalation/pillaring experiment, as described in chapter 2, was carried out under standard conditions, and proceeded successfully. The solid intercalated with Al_{13} polycations and then calcined at 500°C , used as support for further experiments, shows the typical features of Al-PILCs. It has a layered structure with a basal spacing of $18.2 \text{ \AA}$ (Fig. 5.1), and a BET specific surface area of $240 \text{ m}^2/\text{g}$. Its thermal analysis curves and FT-IR spectrum (*vide infra*) also show the typical behaviour of Al-PILCs.

The impregnated solids also maintain the layered structure, but with a remarkable loss of ordering if compared to the support. These catalysts, once calcined at 500°C , show a weak diffraction peak, between 16.8 and $17.3 \text{ \AA}$ ($2\theta = 5\text{-}7^\circ$), due to 001 reflection (Fig. 5.1). However, as can be observed in these diffractograms, although the long-range ordering in the c -axis is low, it is not negligible, and all solids show a certain degree of layered-structure ordering. At the same time, the impregnation-drying process, mainly in the solids treated with acetylacetonate solutions, for which various impregnation cycles are needed, and the further calcination at 500°C , produce a certain collapse and delamination of the structure. Reflections independent of c -axis ordering

do not show any variation with respect to the support, indicating that the impregnation does not affect the individual layers, but only their stacking.

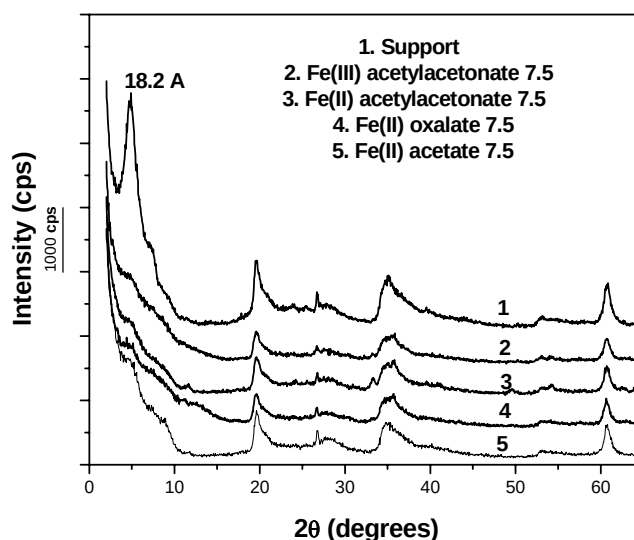


Fig. 5.1 – XRD diffractograms of the support and catalysts with 7.5 wt.% of iron, calcined at 500 °C.

On the other hand, it may be underlined that no peaks due to iron phases are observed in the diffractograms, even for samples with 17.0 wt.% of iron (not shown in the figure). Considering the preparation method used and the results obtained from other techniques, it may be reasonably expected that phases of composition close to Fe_2O_3 be formed after calcination of the impregnated solids at 500 °C, by the removal of the organic moieties of the precursors, and oxidation, if needed, of iron. However, no peaks of oxides or oxi-hydroxides are found in the diffractograms, although the amounts of iron used in the impregnations are relatively high. So, it may be proposed that iron is in form of a very disperse phase on the surface of the support (very small crystallite size, thus not detected by XRD). The presence of such well dispersed phase on the catalyst surface, particularly Fe(III) oxide, was confirmed by XPS.

FT-IR spectra of the support and of various impregnated solids, both dried and calcined, are shown in Fig. 5.2. The FT-IR spectrum of the support shows, as indicated before, the characteristic bands of Al-PILCs. Thus, in the high wave number region, the spectrum is dominated by the stretching vibrations of the hydroxyl groups bonded to metallic cations and to water molecules. Bending of water molecules also produces an important effect close to 1630 cm^{-1} , while the bands characteristic of the tetrahedral layer of the clay dominate the region of low wave numbers, the band at 1007 cm^{-1} , assigned to Si-O-Si bonds, being the most intense of the spectrum, and the bands due to

M-O bonds in the octahedral layer (mainly Mg-O and Fe-O, because of the chemical nature of saponite, see Table 2.1) appearing at lower wave numbers.

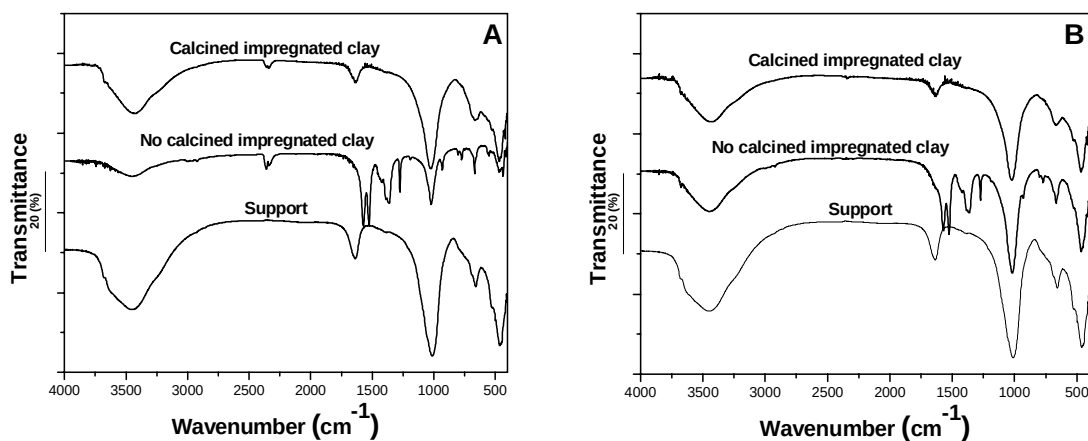


Fig. 5.2 – FT-IR spectra of the support and impregnated solids, before and after calcination: (A) Fe(II) oxalate 17.0 and (B) Fe(II) acetylacetonate 17.0.

Spectra of solids impregnated and dried show, in all cases, the bands due to the support and bands assigned to the precursors. The first bands do not display important variations with respect to those of the support (they only show small differences in the intensity). This is an expectable observation, because of the low influence of the impregnation on the structural bonds of the clay, where only surface hydroxyl groups may be affected, giving rise to interfacial coordination bonds with Fe^{2+} and Fe^{3+} cations of the precursors. On the other hand, the bands due to the precursors are strongly intense, as can be expected because precursors containing organic moieties have been employed. The characteristic bonds of each precursor are observed in each case, with vibrations of C-H bonds, carboxylate or carbonyl groups, etc. All these bands disappear completely when the impregnated solids are calcined at 500 °C, meaning that organic moieties are completely removed at this temperature, by transformation of the precursor molecules into iron oxide-like phases. However, no peak due to Fe-oxides neither oxy-hydroxides are observed in the spectra.

The contents of Fe (determined by elemental analyses) present in the final catalysts are shown in Table 5.1, together with the BET specific surface areas. Slight variations (<8.3%) are noticed between the expected and the determined iron content of the samples, which is due to the high hydration degree of the solids at different stages of the preparation procedure, thus making difficult to obtain the targeted iron contents. The

values of specific surface areas are comprised between 128 and 192 m²/g, which represents a percentage of 53 - 80% of the value of the support. These values are relatively high considering the subsequent steps of the preparation of the catalysts, including impregnation, drying, and calcination at 500 °C. It has been reported that the impregnation of clay supports with precursors containing organic moieties causes a strong decrease in surface area, by blocking of the interlayer porosity by such organic groups, sometimes the impregnated solids only showing the external surface area of the support. However, the further calcination of the impregnated solids produces, if the temperature is high enough to remove all the organic moieties, the recuperation of the access to the internal porosity of the support [16]. Sometimes, these successive processes cause a strong deleterious effect in the surface properties of the solids, although this is not the case for the solids prepared in this work. It may be noticed that part of this surface area may be due to the particles of iron incorporated, considering that they form phases of composition close to iron oxide phase and that they are very dispersed on the support surface.

The thermogravimetric analyses curves of the impregnated samples are displayed in Fig. 5.3. Several weight losses can be observed. The removal of adsorbed water and physisorbed solvent occurs until ca. 150 °C. This is associated with a weight loss of around 7-8 wt. % for samples containing acetate and lower (3 wt. %) for those prepared with oxalate and acetylacetonates. The decomposition of the organic precursors occurs in the 150-325 °C range for Fe(II) acetate and Fe(II) acetylacetonate samples and in a wider range (150-425 °C) for the rest of samples. In addition, when using oxalate and acetylacetonate as precursors, the complexity of the salts, which are decomposed in several successive steps, determines the presence of more steps of weight loss in the corresponding TG curves of these samples than in those of the acetate samples.

Table 5.1 – Characterization data and catalytic behavior of the catalysts.

Sample	Fe content (wt. %) ^a	BET surface area (m ² /g)	TOC removal (%) ^b	Iron leached (wt. %) ^{b,c}
Fe (II) Acetate 7.5	8.12	170	66.7	7.5
Fe (II) Acetate 13.0	13.85	192	68.3	8.0
Fe (II) Acetate 17.0	16.50	141	70.9	4.0
Fe (II) Oxalate 7.5	7.87	160	70.3	2.6
Fe (II) Oxalate 13.0	13.81	151	72.8	4.2
Fe (II) Oxalate 17.0	17.29	141	81.6	1.4
Fe (II) Ac. Acetate 7.5	8.02	155	62.1	2.6
Fe (II) Ac. Acetate 13.0	13.89	162	68.0	0.9
Fe (II) Ac. Acetate 17.0	17.03	137	68.9	0.6
Fe (III) Ac. Acetate 7.5	7.54	154	53.2	2.2
Fe (III) Ac. Acetate 13.0	14.02	136	63.8	1.2
Fe (III) Ac. Acetate 17.0	17.56	128	69.5	2.2

^a The Fe content was determined over the catalysts calcined at 500 °C and kept in closed polyurethane flasks;
^b T = 30 °C, pH = 3, $CH_2O_2 = 6 \times 10^{-3}$ M;
^c Amount (wt. %) of iron lost into the solution after reaction as refereed to the total Fe initially present in the catalyst.

The values of total weight loss of the samples prepared in this work are comprised between 19.5 wt.% for Fe 7.5 acetate and 47 wt.% for Fe 17.0 oxalate, the values depending on the nature of the precursor used and the load of the same. The final weight loss observed in all cases in the 415-825 °C range is due to the dehydroxilation of the clay. For all samples, it is clear that the temperature of calcination guarantees the removal of the organic fragments and the obtaining of iron-like phases.

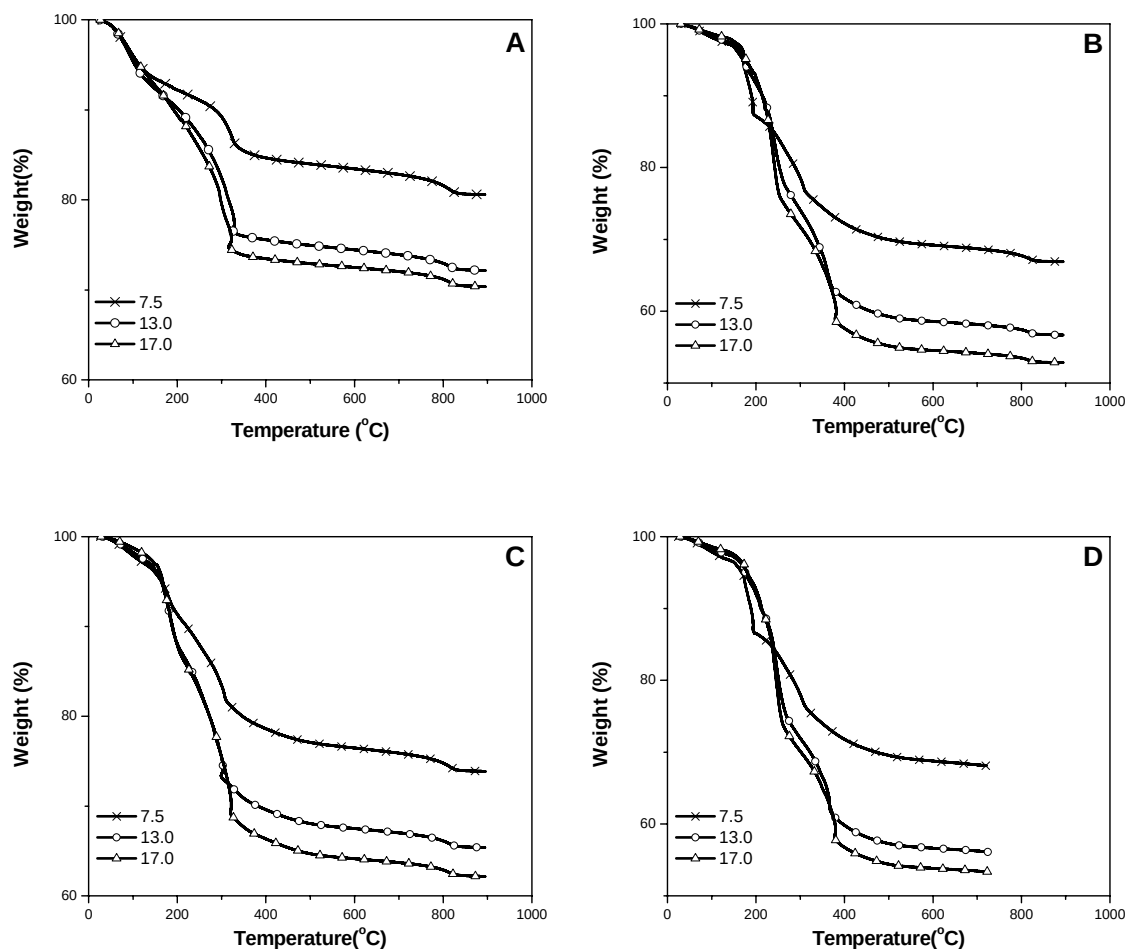


Fig. 5.3 – Thermogravimetric analysis of different dried samples: (A) Fe(II) acetate, (B) Fe(II) oxalate, (C) Fe(II) acetylacetonate and (D) Fe(III) acetylacetonate.

The DSC curves for the samples containing 13 wt.% of Fe are shown in Fig. 5.4. An endothermic peak is observed in the 30-150 °C for the sample containing acetate (Fig. 5.4A), as consequence of the highest weight loss of adsorbed water and solvent detected in the TG curve of this sample, with respect to those prepared with other precursors. The DSC peak corresponding to the decomposition of the most part of the organic material is centred at around 315 °C for acetate, 275 °C for Fe(II)

acetylacetonate and 350 °C for oxalate and Fe(III) acetylacetonate. For these last three samples, other exothermic peaks of lower intensity can be observed in the 150-275 °C interval with associated weight losses in their corresponding TG curves. The removal of the last hydroxyl groups in the clay is observed as a clear weight loss close to 800°C, associated to an endothermal effect, and once this dehydroxilation is completed, it is followed by an exothermal effect corresponding to the phase transformation from saponite to enstatite, not associated with any weight loss in the TG curves. No peaks that could be associated to transformation of iron phases are observed.

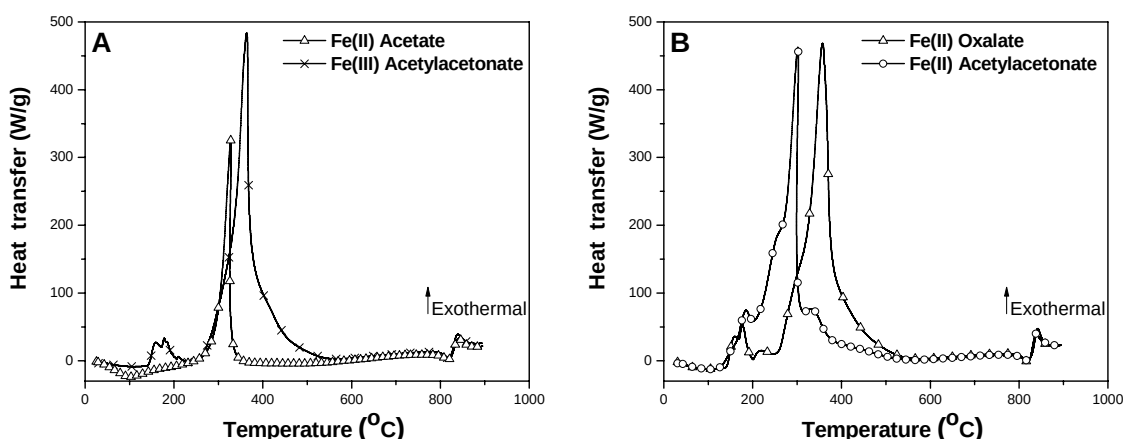


Fig. 5.4 – DSC curves of the samples impregnated with 13.0 wt. % of Fe: (A) Fe(II) acetate and Fe(III) acetylacetonate and (B) Fe(II) oxalate and Fe(II) acetylacetonate.

5.3.2 Catalytic Behaviour

5.3.2.1 Effect of the Precursor Nature and Iron Load on the Degradation of OII Solution

Although the natural clay has already some iron (ca. 1 wt.%, see Table 2.1), no degradation of the OII solution was noticed when using it as catalyst under the typical conditions adopted in this work ($C_{H_2O_2} = 6 \times 10^{-3}$ M, $T = 30^\circ\text{C}$, $\text{pH} = 3$, $w_{\text{clay}} = 91.5$ mg/L, $t = 4\text{h}$), which may be related to the inaccessibility of such iron, located in the octahedral positions of the clay structure. Besides, dye removal by adsorption (blank run in the same conditions but without hydrogen peroxide) was not detectable, what is due to the remarkably low concentrations of clay used in this work. Actually, the use of $w_{\text{clay}} = 1$ g/L, an amount commonly found in the literature, provided about 36% removal by adsorption after 4 h (but no equilibration was yet reached).

Figure 5.5 shows the UV/Vis spectrum obtained for the dye solution (1×10^{-4} M) and also for samples taken along time in a typical experiment. Regarding the dye spectrum, it is characterized by two bands in the ultraviolet region located at ca. 235 and 315 nm and by one band in the visible region, with a maximum located at 486 nm. The absorbance peaks in the UV region are due to the benzene and naphthalene rings of OII, respectively [21], while the band in the visible region is due to the chromophore-containing azo linkage [22] (*vide* Fig. 2.3). If one compares the original spectrum with that achieved after 240 min of oxidation, it is evident that the treated dye sample was almost colourless and did not show significant absorbance in the visible region, indicating that colour removal was practically complete. The disappearance of the absorbance peak at 486 nm reflects, unequivocally, the breakdown in the chromophoric group. However, the spectrum in the UV region shows that the dye was not completely mineralized, even though the absorption intensity was reduced within the UV range. The slower decrease of the intensities of the bands at 235 and 315 nm, with respect to that of the azo bond, can be attributed to the formation of intermediates, resulting from the degradation of the azo dye, which still contain benzoic- and naphthalene-type rings. Another issue of interest is that the spectrum of the 60 min sample is, in the visible region, quite similar to that of the OII solution. Actually, both spectra almost overlap (by multiplying the original one by a factor smaller than 1), and no additional bands appear, indicating that intermediates formed do not absorb in the visible wavelengths, although they do it in the UV. This is also corroborated by other authors. For instance, Bandara and Kiwi [23] mention that in later stages discoloration of the OII leads to long-lived intermediates which absorb the smaller UV component, while Fernández *et al.* [24] refer that no coloured intermediate species were generated in solution.

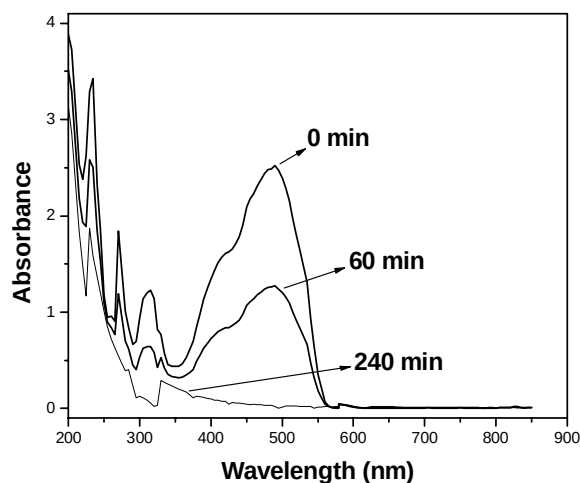


Fig. 5.5 – UV-Vis spectral changes of OII solution along time using as catalyst the Fe (II) oxalate 13.0 sample. Reaction conditions: pH = 3, $C_{H_2O_2} = 6 \times 10^{-3}$ M, T = 30 °C.

Mechanistic studies reported in the literature, either in homogeneous or heterogeneous processes, point for numerous intermediates formed from OII degradation, which include, among others, HSO_4^- , NH_4^+ , and NO_3^- , 4-hydroxybenzenesulfonic acid, nitrogen and sulfo-containing products, benzenesulfonate, carboxylic and dicarboxylic acids and their anions, and also iron complexes [25-30]. However, none of these compounds absorb in the visible region, indicating that the absorbance decrease at 486 nm is only due to the dye degradation.

The results obtained for the oxidation of OII solution with the twelve catalysts prepared are displayed in Fig. 5.6. The effect of the nature of the precursor as well as the amount of active phase used on the catalytic activity can be observed. In each case, the referred concentration of OII is normalized with respect to the initial one (1×10^{-4} M), and plotted as a function of the reaction time. The degradation reached after 4 h was, in most cases, quite significant. For the catalyst with lowest (7.5 wt.%) and highest (17.0 wt.%) iron contents, the best results were always reached when using the oxalate precursor (Figs. 5.6A and 5.6C, respectively), while for the catalysts containing the intermediate concentration (13.0 wt.%), the best sample seems to be that prepared with the acetate precursor (Fig. 5.6B). Using the clay impregnated with 13.0% of Fe(II) acetate and 17.0% of Fe(II) oxalate, degradations of 95.2 and 95.9% were obtained after 4 h, respectively. In contrast, the precursor that gave rise to the less active catalysts was the Fe(II) acetylacetonate with 13.0% of Fe, which produced an efficiency of only 66.4%.

It is noteworthy that for samples with ca. 7.5, 13.0 or 17.0 wt. % of Fe, Figs. 5.6A, 5.6B and 5.6C, respectively, there is no apparent relationship between the reaction rate for each set of catalysts and the effective amount of iron in the samples. This means that the slight differences in the amount of iron between different samples, which range between 7.54-8.12, 13.81-14.02 and 16.50-17.56 wt. % of Fe, respectively, for each one of the iron contents targeted (see Table 5.1), are not responsible for the differences recorded. On the other hand, the sample that exhibits higher reaction rate in Fig. 5.6B (Fe(II) acetate) is the one that loses more iron (Table 5.1), suggesting that the homogeneous process contribution could be of importance. However, for the samples with 7.5 or 17.0% of Fe (Figs. 5.6A and 5.6C, respectively) such relationship is not observed. Therefore, not only the homogeneous, but also the heterogeneous catalytic process, seems to have an important role in the degradation reaction.

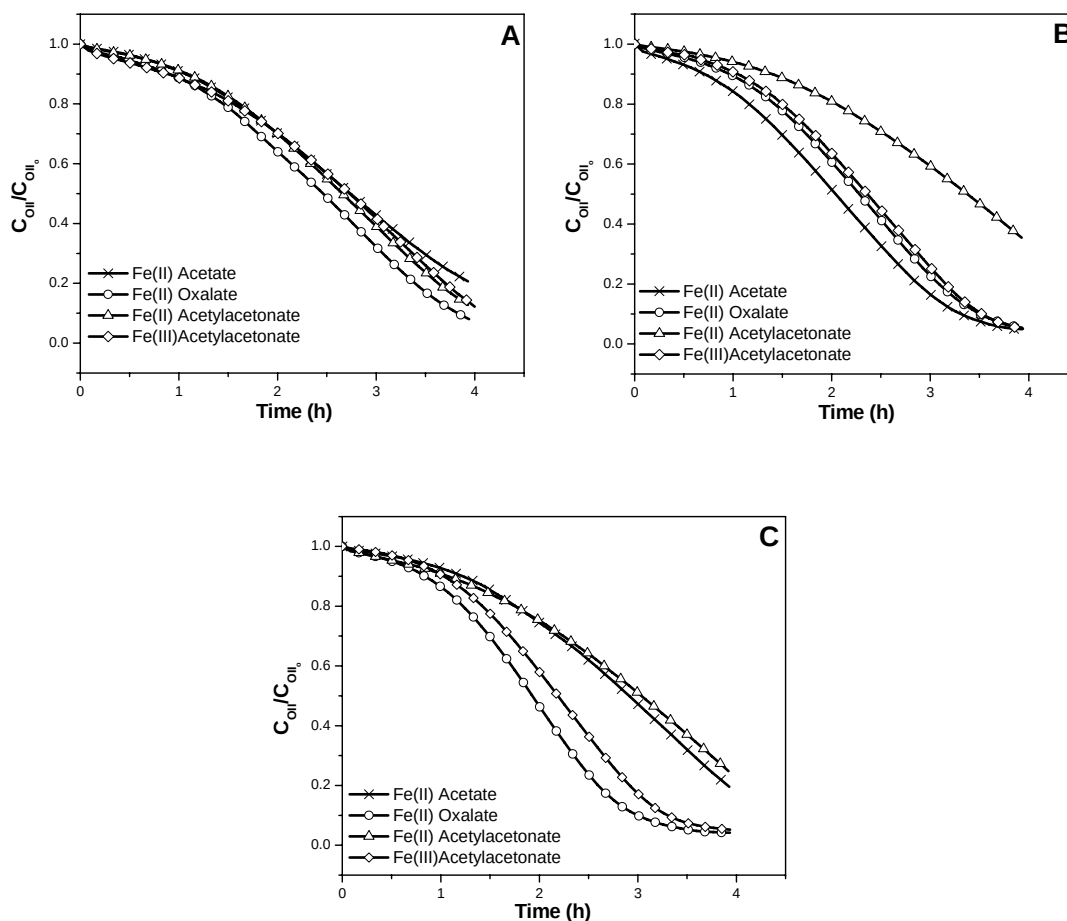
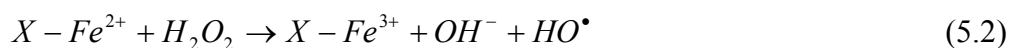
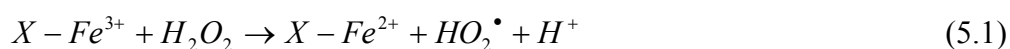


Fig. 5.6 – Effect of the precursor nature on the degradation of the OII solution for different iron loads: (A) 7.5 wt. %; (B) 13.0 wt. % and (C) 17.0 wt. %. pH = 3, $C_{H_2O_2} = 6 \times 10^{-3}$ M, T = 30 °C.

It can also be observed in Fig. 5.6 that the influence of the iron concentration on the degradation of Orange II is not equal for all the precursors, but, in general, the final performances are not too different (with a few exceptions). The reason behind this fact is not yet clear, and a deeper insight regarding the mechanisms occurring in the system is required. Nevertheless, Table 5.1 shows clearly that TOC elimination, at the end of the runs, increases, for each precursor, with the iron load. This increment in the mineralization with the iron concentration occurs because when the amount of catalyst increases, more radicals are produced for the oxidation reaction (Eqs. (5.1)-(5.2), where X represents the surface of the catalyst, *cf.* section 1.6.2):



To use a heterogeneous catalytic system in industrial practice, it is important to evaluate the loss of catalyst from the support. This was done by measuring the iron concentration in the solution along time (samples were taken every hour, although in Table 5.1 only data after 4 h of reaction time are shown). Some important results must be stressed. First, in almost all cases the iron leaching is considerably low (<1 mg/L, thus being below the EU directives (<2 mg/L)). Secondly, catalysts that exhibit higher iron leaching values are those prepared with the acetate precursor, independently of the iron load. Finally, the 17.0 wt.% samples are those that loose a smaller percentage of iron (except Fe (III) acetylacetonate). This is particularly interesting from the practical point of view due to the possibility of using these last catalysts for a longer operation time (slower deactivation). In this concern, it is especially remarkable the Fe(II) oxalate 17.0 catalyst, which shows a very good behavior in terms of mineralization (81.6% of TOC reduction) and discoloration (95.9% of OII removal), and its performance seems to be mainly due to the heterogeneous Fenton-like process.

The importance of the heterogeneously catalyzed reaction is also put in evidence when one compares the performance of the catalysts prepared with precursors of Fe(II) vs. Fe(III). While OII degradation is much more significant for the Fe(III) acetylacetonate 17.0 sample as compared with the Fe(II) one (Fig. 5.6), in agreement with the iron leaching (Table 5.1), thus supporting the importance of the homogeneously catalyzed process, any relationship exists between these parameters for

the 13 wt. % catalysts. In this case, the Fe(III) sample shows again better catalytic performance, without significant difference in iron leaching, which mean an involvement of the solid surface on the catalytic process.

The catalytic differences observed when different precursors are used are not clear, and could be the aim of further work (anion nature and iron oxidation state effect). Nevertheless, several factors might be indicated, which are known to affect the catalytic performance: i) the iron dispersion [31], ii) the Fe_2O_3 crystalline form (hematite or maghemite-Q) [19], iii) the location of the iron species (bonded to the aluminium pillars or engaged in small oxide clusters dispersed in the solid, inside or outside the porosity) [32], or iv) the oxidation states, nature and coordination of the iron species [15].

Based on the results described above, two catalysts were chosen to study into more detail the effect of the temperature, pH and initial H_2O_2 concentration. They were those prepared with oxalate with Fe content of 7.5 and 17.0 wt. %. As shown in Table 5.1, the best performances for mineralization are achieved for the catalysts prepared with oxalate, for all the iron contents. The same applies for the color removal, except for the 13.0 wt. % samples, where Fe(II) acetate 13.0 provides the best results (Fig. 5.6B). However, this sample loses much more iron than the rest (Table 5.1). Among the 13.0 wt. % catalysts, the Fe(II) oxalate sample also shows good decolorisation results, but differences between performances achieved by this catalyst and the Fe(II) oxalate 7.5 are minimal, thus being preferable, from an economical point of view, to use the catalyst with less iron content.

5.3.2.2 Temperature Effect

The results obtained for the OII degradation at four different temperatures (10, 30, 50 and 70 °C), using catalysts prepared with Fe(II) oxalate with 7.5 and 17.0 wt. %, are shown in Fig. 5.7. The results show clearly that the reaction rate increases when increasing the temperature, which was expected due to the exponential dependency of the kinetic constants with the reaction temperature (Arrhenius law). Nevertheless, the final OII concentrations, after 4 hours of oxidation, are very similar at 50 and 70 °C. In fact, the eliminations obtained at these temperatures are already quite similar after two hours of reaction, with values around 98%, whereas at 10°C the elimination is practically negligible (ca. 8% after 4 h of reaction for both samples). Other authors have

also found similar results during catalytic wet peroxide oxidation of phenol over Fe-exchanged clays [33,34].

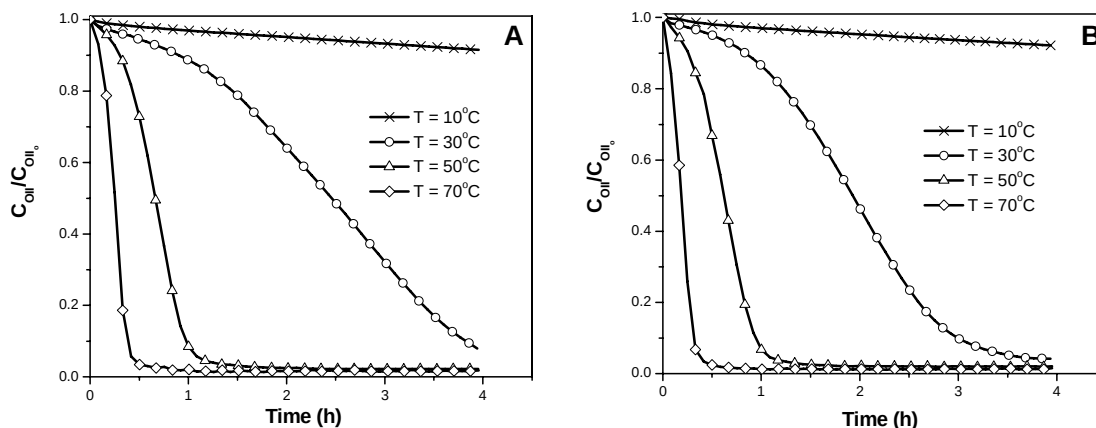


Fig. 5.7 – Temperature effect on the degradation of OII solution using different catalysts: (A) Fe(II) oxalate 7.5 and (B) Fe(II) oxalate 17.0. pH = 3, $C_{H_2O_2} = 6 \times 10^{-3}$ M.

Table 5.2 shows the overall TOC removal for both catalysts at different temperatures (Runs 1 to 4). Once again, and as expected, the mineralization increases with the temperature, the performances reached being better for Fe oxalate 17.0, in agreement with previous results (Table 5.1). For this sample, it is remarkable that the TOC removal is near 91% at $T = 70^\circ\text{C}$ and around 82% at 30°C . The fact that at higher temperatures performances do not increase so markedly as at lower temperatures can be due to the accelerated decomposition of hydrogen peroxide into oxygen and water [33,34].

Although lower than those obtained at higher temperatures, the values of OII and TOC removal achieved at 30°C might be considered satisfactory. Taking into account that a lower temperature might reduce the process costs, 30°C was then chosen to carry out the following runs, where other parameters are changed. In addition, the iron leaching is smaller at 30°C than at 70°C and is not very significant after 4 h (<0.25 mg/L, thus being below the value of the EU directives).

Table 5.2 – TOC removal (%) after 4h of oxidation.

Run No.	Experimental conditions			Catalyst	
	Temperature (°C)	pH	$C_{H_2O_{2o}}$ (M)	Fe(II) oxalate 7.5	Fe(II) oxalate 17.0
1	10	3.0	6×10^{-3}	8.0	8.2
2	30	3.0	6×10^{-3}	70.3	81.6
3	50	3.0	6×10^{-3}	80.5	87.5
4	70	3.0	6×10^{-3}	84.7	90.6
5	30	2.0	6×10^{-3}	61.6	71.8
6	30	3.5	6×10^{-3}	39.8	44.3
7	30	3.0	3×10^{-3}	67.3	75.4
8	30	3.0	1.2×10^{-3}	64.6	78.1
9	30	3.0	2.4×10^{-3}	66.2	74.6

5.3.2.3 pH Effect

The results obtained for the OII degradation using the Fe(II) oxalate catalysts at three different pH values are displayed in Fig. 5.8. The best results of the OII degradation were obtained at pH 3.0, for both iron loads. At the lowest value of pH tested, pH = 2.0, the reaction is very slow and an important increase of decolorisation activity was only noticed after ca. 2.5 hours of reaction. However, at pH 3.5 performances achieved are even worst, with color removals after 4h of only 43 and 51% for 7.5 or 17.0 wt.% of Fe, respectively (Figs. 5.8A and 5.8B). It must be stressed that additional experiments have also been performed at pH 4.0 (not shown) but practically no dye degradation was produced, even for much longer reaction times. Regarding TOC removal, conclusions are similar, with better performances for both samples at pH 3.0 (Table 5.2). Curiously, this was exactly the best pH value found by Feng *et al.* [35] during OII degradation using clay-based Fe nanocomposites with photo-Fenton process, with a reaction rate decrease similar to that reported by us when one deviates from such pH value. Other authors also found, using pillared clays, that the reaction rate was much higher for the pH value corresponding to the optimum pH determined when homogeneous Fe species were used as catalysts [36].

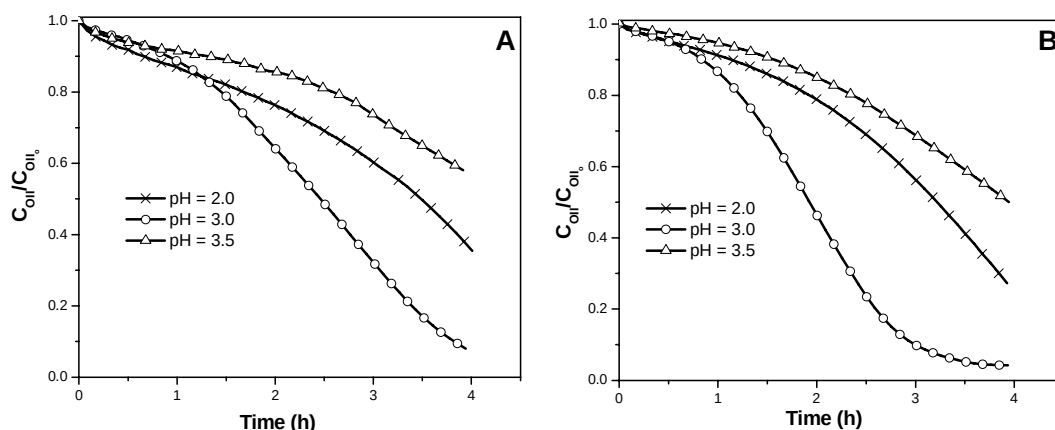


Fig. 5.8 – pH effect on the degradation of OII solution using different catalysts: (A) Fe(II) oxalate 7.5 and (B) Fe(II) oxalate 17.0. $C_{H_2O_2} = 6 \times 10^{-3}$ M, $T = 30$ °C.

A dependence of the reaction performance with the pH similar to that reported in Fig. 5.8 is normally observed in homogenous reaction, and the decreased performance at lower pHs is usually attributed to the inhibition of the reaction between Fe^{3+} and hydrogen peroxide, because the formation of the iron(III) peroxocomplexes (as intermediates) decreases when pH decreases [37]. Besides, the stability of H_2O_2 , which is independent of having a homogenous or heterogeneous process, is affected by the pH, with the lower degree of decomposition observed at pH values between 3 and 4 [34]. Above pH 4 the rapid H_2O_2 decomposition produces molecular oxygen without formation of appreciable amounts of hydroxyl radicals.

Figure 5.9 shows the effect of the reaction pH on the iron leaching. It is clear that iron lost is more significant at pH 2.0, especially for the 7.5 wt.% catalyst. Therefore, for long-term stability it would be preferable to work at higher pH values. Feng *et al.* [35] also found that iron leaching was much more significant at pH around 2. The Fe leaching at this low initial solution pH can be attributed to the dissolution of iron oxide at very acidic conditions.

At pH 2.0 the amount of iron leached into solution is much higher for the Fe oxalate 7.5 than for the Fe oxalate 17.0 (Fig. 5.9A vs. 5.9B), although the catalytic performance of the first catalyst is not better (Fig. 5.8A vs. 5.8B and Table 5.2), thus supporting the importance of the heterogeneous catalytic process. Finally, it is noteworthy that in the pH range studied (2.0-3.5) the sample with more iron (17.0 wt.%) shows almost always lower percentages of iron lost (Figs. 5.9A and 5.9B), and thus can be in practice used for more operation cycles.

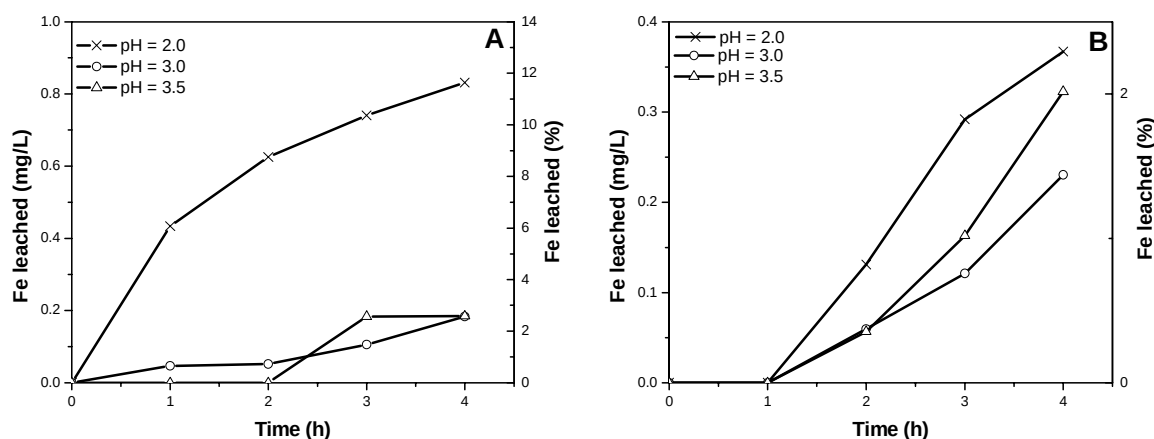


Fig. 5.9 – Iron leaching for experiments at different pH values and using different catalysts: (A) Fe(II) oxalate 7.5 and (B) Fe(II) oxalate 17.0. $C_{H_2O_2} = 6 \times 10^{-3}$ M, $T = 30^\circ\text{C}$.

5.3.2.4 Initial H_2O_2 Concentration Effect

The initial hydrogen peroxide concentration was varied between 3×10^{-3} and 2.4×10^{-2} M, using the same catalysts as in previous sections. The results obtained (Fig. 5.10) show, for both samples, a similar behavior in terms of dye degradation for the intermediate H_2O_2 concentrations (6×10^{-3} and 1.2×10^{-2} M), whereas the reaction goes by more slowly when the concentration is lower (3×10^{-3} M) or higher (2.4×10^{-2} M). The increase of the oxidant concentration from 3×10^{-3} to 1.2×10^{-2} M leads to an increase in the reaction rate, as expected, because more radicals will be formed (Eqs. (5.1)-(5.2)). Nevertheless, for a very high hydrogen peroxide concentration (2.4×10^{-2} M) the performance decreases. The existence of an optimum hydrogen peroxide concentration is typical and well-known in Fenton's oxidation. This optimum value was previously found to be 1×10^{-2} M for OII degradation in homogenous Fenton reaction, using a solution of Fe(II) sulphate as catalyst (*cf.* chapter 3). At higher H_2O_2 concentrations the scavenging of $HO^\bullet$ radicals will occur, which can be expressed by the following reaction:



Although other radicals ($HO_2^\bullet$) are produced, their oxidation potential is much smaller than that of the $HO^\bullet$ species [38].

It is important to remark that all decolorisation curves in Fig. 5.10 show a sigmoidal profile, which is typical for autocatalytic or radical reactions, and that it was also observed in other studies concerning organics degradation with pillared clay catalysts [34]. Basically two regions can be identified, the initial one representing the induction period, and the second one after the inflection point representing the steady-state.

The influence of the H_2O_2 concentration on the mineralization (see Table 5.2) is similar as for decolorisation, with an optimum oxidant concentration of 6×10^{-3} M for both catalysts. In spite of the final performances attained seem to be only slightly affected by the peroxide dose, it is clear that for H_2O_2 concentrations above that value the final TOC removal decreases a little bit, this effect being similar to those reported by other researchers [39,40].

Regarding iron leaching, it is noteworthy that, once again, the concentrations reached are always small (below 0.4 mg/L for both samples), but we haven't found any relationship between the loss of catalyst from the support and the hydrogen peroxide concentration.

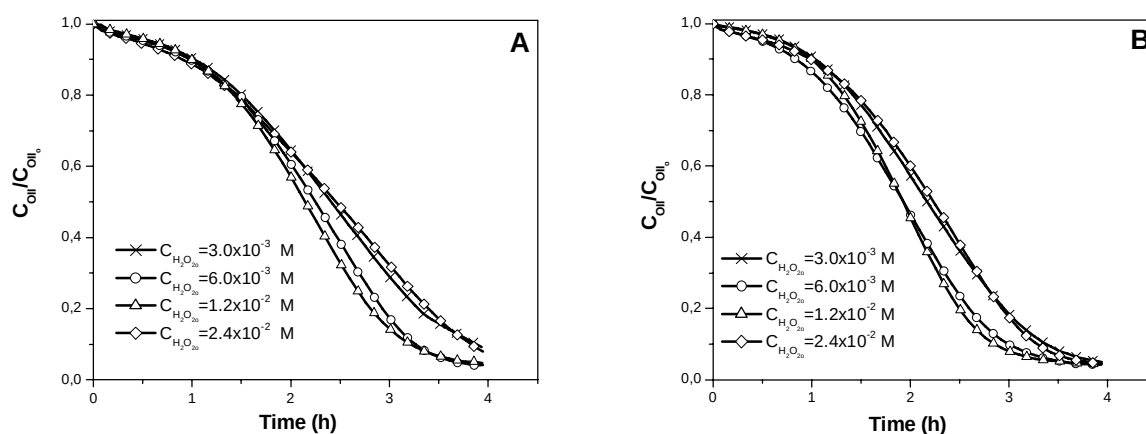


Fig. 5.10 – Effect of the hydrogen peroxide concentration on the degradation of OII solution using different catalysts: (A) Fe(II) oxalate 7.5 and (B) Fe(II) oxalate 17.0. pH = 3, T = 30 °C.

5.3.2.5 Stability and Recycling of the Catalyst

For a practical implementation of a heterogeneous catalytic system, it is crucial to evaluate the stability of the catalysts. For that purpose, a sample that shows a low iron leaching, but presenting simultaneously good catalytic performance, should be selected. The Fe (II) oxalate 17.0 sample meets all these criteria, as shown before (see section 5.3.2.1).

Figure 5.11 shows the performance reached in terms of OII degradation in 4 consecutive runs. To recover the catalyst, the final effluent was filtered. After the first cycle, and in order to check if the leached iron was responsible for the catalytic activity, both OII and H_2O_2 were added to the solution in the same concentrations as at the beginning of the experiment. Figure 5.11 shows that in these conditions OII conversion is only a very small fraction of that recorded in the presence of the pillared clay, thus demonstrating that the Fe leached is not capable to destroy the dye, i.e., the process is essentially heterogeneous. For subsequent cycles, the filtered clay was dried overnight between consecutive runs. Even though a slight activity decay is observed, which might be due to the iron loss (ca. 1.5% per cycle that represents a final concentration smaller than 0.3 mg/L), OII conversion decreases only from 95.8 to 90.3% in 4 cycles, i.e., 16 h of operation. Regarding TOC reduction, in the 4 cycles final values were: 81.6, 81.4, 78.5 and 77.1%. In practice, this small deactivation could be compensated, if required, by adapting the reaction conditions (for instance slightly increasing the temperature along time). Other authors reported similar results, but they attributed the loss of activity to poisoning of the active catalytic sites due to adsorbed organic species [41]. However, this could be avoided by submitting the catalyst to an intermediate calcination step, thus restoring its catalytic activity [41]. Nevertheless, catalyst deactivation may occur due to a diversity of factors, as pointed by Guo and Al-Dahhan [34], including reduction of the catalyst specific surface area, poisoning of the catalytic agents by compounds formed during oxidation, surface deposition and strong adsorption of a polymeric carbon layer or even the dissolution of some metal oxides from catalysts into the hot acidic reaction medium.

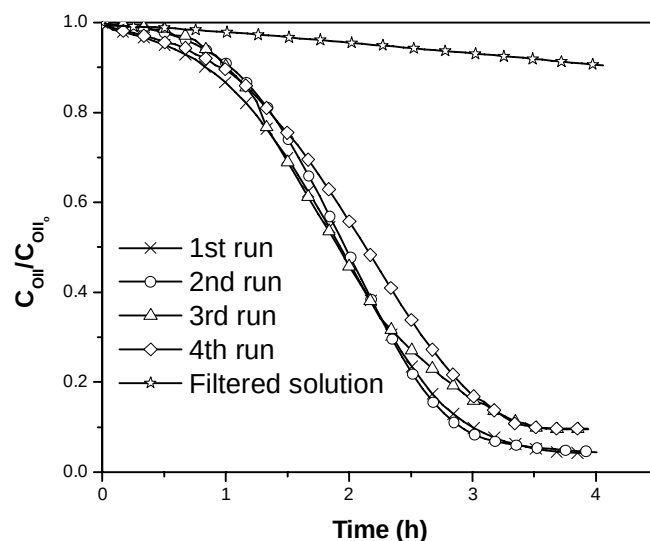


Fig. 5.11 – Effect of consecutive experiments with the Fe(II) oxalate 17.0 catalyst on the degradation of OII solution. pH = 3, T = 30 °C, $C_{H_2O_2} = 6 \times 10^{-3}$ M.

5.4 Conclusions

- Twelve supported Fe-saponite catalysts have been prepared, by means of the incipient wet impregnation method, using a pillared clay support and four salts of Fe precursors at different Fe loads. The characterization of the catalysts shows that the decomposition of the precursors gives rise to solids that present laminar structure, with active phases of Fe highly dispersed on the support, and high specific surfaces (in most of the cases with values comprised between 130 and 170 m²/g), characteristics that make them potentially good catalysts for oxidation in the Fenton-like process.
- All the catalysts revealed to be quite active in the Fenton-like oxidation of Orange II, because clay concentrations used are much below than those usually found in the literature (typically around 1 g/L).
- The effects of the nature of the catalyst's precursor, hydrogen peroxide concentration, temperature and pH of the reaction medium were analysed in the present work. The obtained results show a high degradation of OII and of the intermediary oxidised compounds. At optimal conditions, 99% discoloration and 91% of mineralization were reached (after 4 h of reaction), using the catalyst prepared from Fe(II) oxalate with 17.0 wt.% of Fe and in the following reaction

conditions: $T = 70^{\circ}\text{C}$, $\text{pH} = 3.0$ and $C_{\text{H}_2\text{O}_2} = 6\text{mM}$. However, good performances with high selectivities to CO_2 and H_2O were also reached at significantly lower temperatures (30°C).

- All the catalysts exhibit not only good catalytic activity but also a reasonable small iron leaching (below the EU directives values), indicating that the active phases are strongly fixed to the support (possibly iron strongly bonded to the aluminium pillars or engaged in small oxide clusters dispersed in the solid, inside or outside the porosity). This characteristic makes possible the Fe-saponite catalysts to have long-term stability, without generating iron hydroxide sludges.
- It was shown that the nature of the salt and the content of iron used to prepare the catalyst have a significant effect on the process performance, the Fe(II) oxalate 17.0 being the most promising one. Consecutive reaction cycles carried out with this sample showed a minor deactivation, which is possibly due to some iron leaching, thus evidencing the possibility of being used in continuous processes.

References

1. Walling, C. Fenton's reagent revisited. *Accounts of Chemical Research* **1975**, 8, 125.
2. Kavitha, V.; Palanivelu, K. Destruction of cresols by Fenton oxidation process. *Water Research* **2005**, 39, 3062.
3. Oliveira, R.; Almeida, M. F.; Santos, L.; Madeira, L. M. Experimental design of 2,4-Dichlorophenol oxidation by Fenton's reaction. *Industrial and Engineering Chemistry Research* **2006**, 45, 1266.
4. Pignatello, J. J.; Sun, Y. Organic intermediates in the degradation of 2,4-dichlorophenoxyacetic acid by iron(3+)/hydrogen peroxide and iron(3+)/hydrogen peroxide/UV. *Journal of Agriculture and Food Chemistry* **1993**, 41, 1139.
5. Sedlak, D. L.; Andren, W. A. Oxidation of chlorobenzene with Fenton's reagent. *Environmental Science and Technology* **1991**, 25, 777.
6. Xiang-Rong, X.; Zhen-Ye, Z.; Xiao-Yan, L.; Ji-Dong, G. Chemical oxidative degradation of methyl tert-butyl ether in aqueous solution by Fenton's reagent. *Chemosphere* **2004**, 55, 73.

7. Swaminathan, K.; Sandhya, S.; Sophia, A. C.; Pachhade, K.; Subrahmanyam, Y. V. Decolorization and degradation of H-acid and other dyes using ferrous–hydrogen peroxide system. *Chemosphere* **2003**, 50, 619.
8. Sabhi, S.; Kiwi, J. Degradation of 2,4-Dichlorophenol by immobilized iron catalysts. *Water Research* **2001**, 35, 1994.
9. Gemeay, A. H.; Mansour, I. A.; El-Sharkawy, R. G.; Zaki, A. B. Kinetics and mechanism of the heterogeneous catalyzed oxidative degradation of indigo carmine. *Journal of Molecular Catalysis A: Chemical* **2003**, 193, 109.
10. Ishtchenko, V. V.; Huddersman, K. D.; Vitkovskaya, R. F. Part 1. Production of a modified PAN fibrous catalyst and its optimization towards the decomposition of hydrogen peroxide. *Applied Catalysis A: General* **2003**, 242, 123.
11. Letaief, S.; Casal, B.; Aranda, P.; Martín-Luengo, M. A.; Ruiz-Hitzky, E. Fe-containing pillared clays as catalysts for phenol hydroxylation. *Applied Clay Science* **2003**, 22, 263.
12. Tachiev, G.; Roth, J. A.; Bowers, A. R. Kinetics of hydrogen peroxide decomposition with complexed and free iron catalysts. *International Journal of Chemical Kinetics* **2000**, 32, 24.
13. Neamtu, M.; Zaharia, C.; Catrinescu, C.; Yediler, A.; Macoveanu, M.; Kettrup, A. Fe-exchanged Y zeolite as catalyst for wet peroxide oxidation of reactive azo dye Procion Marine H-EXL. *Applied Catalysis B: Environmental* **2004**, 48, 287.
14. Dantas, T. L. .P.; Mendonça, V. P.; Jose, H. J.; Rodrigues, A. E.; Moreira, R. F. P. M. Treatment of textile wastewater by heterogeneous Fenton process using a new composite Fe₂O₃/carbon. *Chemical Engineering Journal* **2006**, 118, 77.
15. Catrinescu, C.; Neamtu, M.; Miehe-Brendle, J.; Garcia, M. G.; Kettrup, A. Catalytic wet peroxide oxidation of reactive azo dyes over iron-containing pillared beidellite catalyst. In: M.A. Vicente, M. Suarez, V. Rives, M. J. Sanchez (Eds.), *Materiales Arcillosos: de la Geología a las Nuevas Aplicaciones*, Salamanca, **2006**, 87.
16. Belver, C.; Banares-Munoz, M. A.; Vicente, M. A. Fe-saponite pillared and impregnated catalysts: I. Preparation and characterization. *Applied Catalysis B: Environmental* **2004**, 50, 101.
17. Vicente, M. A.; Gil, A.; Gandia, L. M. Recent advances in the synthesis and catalytic applications of pillared clays. *Catalysis Reviews, Science and Engineering* **2000**, 42, 145.
18. Feng, J.; Hu, X.; Yue, P. L.; Zhu, H. Y.; Lu, G. Q. A novel laponite clay-based Fe nanocomposite and its photo-catalytic activity in photo-assisted degradation of Orange II. *Chemical Engineering Science* **2003**, 58, 679.
19. Sum, O. S. N.; Feng, J.; Hu, X.; Yue, P.L. Pillared laponite clay-based Fe nanocomposites as heterogeneous catalysts for photo-Fenton degradation of acid black 1. *Chemical Engineering Science* **2004**, 59, 5269.

20. Ong, S. A.; Toorisaka, A.; Hirata, M.; Hano, T. Decolorization of azo dye (Orange II) in a sequential UASB–SBR system. *Separation and Purification Technology* **2005**, 42, 297.
21. Feng, W.; Nansheng, D.; Helin, H. Degradation mechanism of azo dye C. I. reactive red 2 by iron powder reduction and photooxidation in aqueous solutions. *Chemosphere* **2000**, 41, 1233.
22. Bauer, C.; Jacques, P.; Kalt, A. Photooxidation of an azo dye induced by visible light incident on the surface of TiO₂. *Journal of Photochemistry and Photobiology A: Chemistry* **2001**, 140, 87.
23. Bandara, J.; Kiwi, J. Fast kinetic spectroscopy, decoloration and production of H₂O₂ induced by visible light in oxygenated solutions of the azo dye Orange II *New Journal of Chemistry* **1999**, 23, 717.
24. Fernandez, J.; Kiwi, J.; Lizama, C.; Freer, J.; Baeza, J.; Mansilla, H. D. Factorial experimental design of Orange II photocatalytic discolouration. *Journal of Photochemistry and Photobiology A: Chemistry* **2002**, 151, 213.
25. Bandara, J.; Morrison, C.; Kiwi, J.; Pulgarin, C.; Peringer, P. Degradation/decoloration of concentrated solutions of Orange II. Kinetics and quantum yield for sunlight induced reactions via Fenton type reagents. *Journal of Photochemistry and Photobiology A: Chemistry* **1996**, 99, 57.
26. Nadtochenko, V.; Kiwi, J. Photoinduced adduct formation between Orange II and [Fe³⁺(aq)] or Fe(ox)³⁺—H₂O₂ Photocatalytic degradation and laser spectroscopy *Journal of the Chemical Society, Faraday Transactions* **1997**, 93, 2373.
27. Nam, S.; Renganathan, V.; Tratnyek, P. G. Substituent effects on azo dye oxidation by the Fe^{III}–EDTA–H₂O₂ system. *Chemosphere* **2001**, 45, 59.
28. Liakou, S.; Kornaros, M.; Lyberatos, G. Pretreatment of azo dyes using ozone. *Water Science and Technology* **1997**, 36, 155.
29. Yuranova, T.; Enea, O.; Mielczarski, E.; Mielczarski, J.; Albers, P.; Kiwi, J. Fenton immobilized photo-assisted catalysis through a Fe/C structured fabric. *Applied Catalysis B: Environmental* **2004**, 49, 39.
30. Styliadi, M.; Kondarides, D. I.; Verykios, X. E. Pathways of solar light-induced photocatalytic degradation of azo dyes in aqueous TiO₂ suspensions. *Applied Catalysis B: Environmental* **2003**, 40, 271.
31. Carriazo, J.; Guelou, E.; Barrault, J.; Tatibouet, J. M.; Molina, R.; Moreno, S. Catalytic wet peroxide oxidation of phenol by pillared clays containing Al–Ce–Fe. *Water Research* **2005**, 39, 3891.
32. Barrault, J.; Abdellaoui, M.; Bouchoule, C.; Majesté, A.; Tatibouët, J. M.; Louloudi, A.; Papayannakos, N.; Gangas, N. H. Catalytic wet peroxide oxidation over mixed (Al–Fe) pillared clays. *Applied Catalysis B: Environmental* **2000**, 27, 225.

33. Catrinescu, C.; Teodosiu, C.; Macoveanu, M.; Miehe-Brendle, J.; Dred, R. L. Catalytic wet peroxide oxidation of phenol over Fe-exchanged pillared beidellite. *Water Research* **2003**, 37, 1154.
34. Guo, J.; Al-Dahhan, M. Catalytic wet oxidation of phenol by hydrogen peroxide over pillared clay catalyst. *Industrial and Engineering Chemistry Research* **2003**, 42, 2450.
35. Feng, J.; Hu, X.; Yue, P. L. Effect of initial solution pH on the degradation of Orange II using clay-based Fe nanocomposites as heterogeneous photo-Fenton catalyst. *Water Research* **2006**, 40, 641.
36. Barrault, J.; Tatibouët, J. M.; Papayannakos, N. Catalytic wet peroxide oxidation of phenol over pillared clays containing iron or copper species. *Comptes Rendus de l'Académie des Sciences - Series IIC – Chemistry* **2000**, 3, 777.
37. Pignatello, J. J. Dark and photoassisted Fe^{3+} -catalyzed degradation of chlorophenoxy herbicides by hydrogen peroxide. *Environmental Science and Technology* **1992**, 26, 944.
38. Bigda, R. J. Consider Fenton chemistry for wastewater treatment. *Chemical Engineering and Processing* **1995**, 91, 62.
39. Guedes, A. M. F. M.; Madeira, L. M. P.; Boaventura, R. A. R.; Costa, C. A. V. Fenton oxidation of cork cooking wastewater—overall kinetic analysis. *Water Research* **2003**, 37, 3061.
40. Dutta, K.; Mukhopadhyay, S.; Bhattacharjee, S.; Chaudhuri, B. Chemical oxidation of methylene blue using a Fenton-like reaction. *Journal of Hazardous Materials* **2001**, 84, 57.
41. Centi, G.; Perathoner, S.; Torre, T.; Verduna, M. G. Catalytic wet oxidation with H_2O_2 of carboxylic acids on homogeneous and heterogeneous Fenton-type catalysts. *Catalysis Today* **2000**, 55, 61.

CHAPTER 6 – AZO-DYE ORANGE II DEGRADATION BY HETEROGENEOUS FENTON-LIKE REACTION USING CARBON-Fe CATALYSTS^{*}

Abstract

In this work, the degradation and mineralization of the non-biodegradable azo dye Orange II (OII) was studied, making use of a heterogeneous Fenton-like oxidation process. For that, hydrogen peroxide activation was achieved by means of two different carbon-based catalysts, which have been impregnated with 7 wt.% of iron. The carbon supports employed are quite different, being one of them an activated carbon prepared from agricultural by-products (olive stone), while the other one is a carbon aerogel, prepared by carbonization of an organic resorcinol-formaldehyde polymer. The solids have been characterized using several techniques, namely N₂ and CO₂ adsorption at -196 and 0° C, respectively, mercury porosimetry, SEM, HRTEM, XRD and XPS. Then, the catalyst's performances in the Fenton-like oxidation of OII were compared, and the effects of the most relevant operating conditions (pH, catalyst concentration, H₂O₂ concentration and temperature) analyzed for the most promising one (the carbon aerogel based catalyst). In this catalyst, characterization data point for a very good iron dispersion on the carbon surface. This sample showed very good catalytic performances, with mineralization degrees as high as 90%. However, iron leaching from the support is also considerable leading to a progressive deactivation in consecutive reaction cycles.

^{*} Adapted from: Ramirez, J. H.; Maldonado-Hodar, F. J.; Perez-Cardenas, A. F.; Moreno Castilla, C.; Costa, C. A.; Madeira, L. M. *Applied Catalysis B: Environmental* **2007**, 75, 312.

6.1 Introduction

The homogeneous Fenton process has a significant disadvantage, as mentioned in the previous chapter: homogeneously catalyzed reactions need up to 50–80 ppm of Fe ions in solution, which is well above the European Union directives that allow only 2 ppm of Fe ions in treated water to dump directly into the environment [1]. In addition, the removal/treatment of the sludge-containing Fe ions at the end of the wastewater treatment is expensive and needs large amount of chemicals and manpower.

To overcome the disadvantages of the homogeneous Fenton or Fenton-like processes (the later one referring to the use of ferric rather than ferrous ions), the immobilization of the catalyst on inert support surfaces has been tried in order to avoid the catalyst-recovering step. Indeed, some attempts have been made to develop heterogeneous catalysts, prepared by incorporating Fe ions or Fe oxides into porous supports, subsequently used in a wide range of applications. Among others, it is worth of mentioning the use of clays as supports for dyes degradation [2], of activated carbons for phenol [3], textile wastewaters [4] or 4-chlorophenol [5] oxidation, or of zeolites for phenol [6] or ethanol [7] oxidation.

This chapter deals with the degradation of the non-biodegradable azo dye Orange II by heterogeneous Fenton's reagent (a catalytic wet peroxide oxidation – CWPO – process) using carbon based-catalysts. Two different types of carbon materials were used as Fe supports: i) an activated carbon (herein denoted as carbon H) prepared from agricultural by-products (olive stone) and ii) a carbon aerogel (sample M) prepared by sol-gel technology. Both types of materials can be considered as examples of the classical and new carbon materials form. Both of them present different characteristics that could determine their applications: classical activated carbon are cheap materials prepared from very different raw precursors, but are heterogeneous solids with variable composition, depending on the raw material used. On the contrary, carbon aerogels offer purity, homogeneity and controlled porosity, but are however more expensive because the synthesis method needs very specific equipment, such as the supercritical drying. The performance of both materials was compared and the effect of the most relevant operating conditions in Fenton's oxidation evaluated.

6.2 Materials and Methods

6.2.1 Preparation and Characterisation of the Catalysts

As above-mentioned, two different carbon materials were used as Fe-supports, an activated carbon and a carbon aerogel, which synthesis is described in chapter 2, along with the procedure employed for their impregnation (with 7 wt. % of iron). In that chapter is also provided information regarding the techniques used for the catalyst's characterisation.

6.2.2 Catalytic Activity

Chemical oxidation of Orange II was carried out using 0.2 L of a 1×10^{-4} M solution, in a jacketed glass batch reactor as described in chapter 2. Along the reaction, the solution pH kept almost unchangeable (± 0.1), which is certainly related to the low concentration of the OII solution used. Replicates of some of the experiments allowed to conclude that, for each run, experimental data do not differ, on average, more than 5% (maximum errors recorded in a single data were below 10%).

The Total Organic Carbon (TOC) and the total Fe in the solution were measured using the equipments described in chapter 2.

6.3 Results and Discussion

6.3.1 Catalysts Characterization

The morphology of the catalysts was analyzed by SEM. Their structures, which are defined by those of the corresponding supports, are shown in Fig. 6.1. The carbon aerogel structure (Fig. 6.1A) is composed by nearly spherical particles with smooth surfaces and nanometric size forming a network with “coral type” structure. According to its pore texture the microporosity is located into these primary particles, while the meso and macropore volume is determined by the inter-particle space, and therefore is related with the primary particle size, shape and overlapping degree [8]. The activated carbon morphology shown in Fig. 6.1B however presents a more heterogeneous appearance with large pores and large edges that come from the decomposition of the

lignocellulosic materials. Both kinds of structures were previously observed in materials of similar origin [9,10].

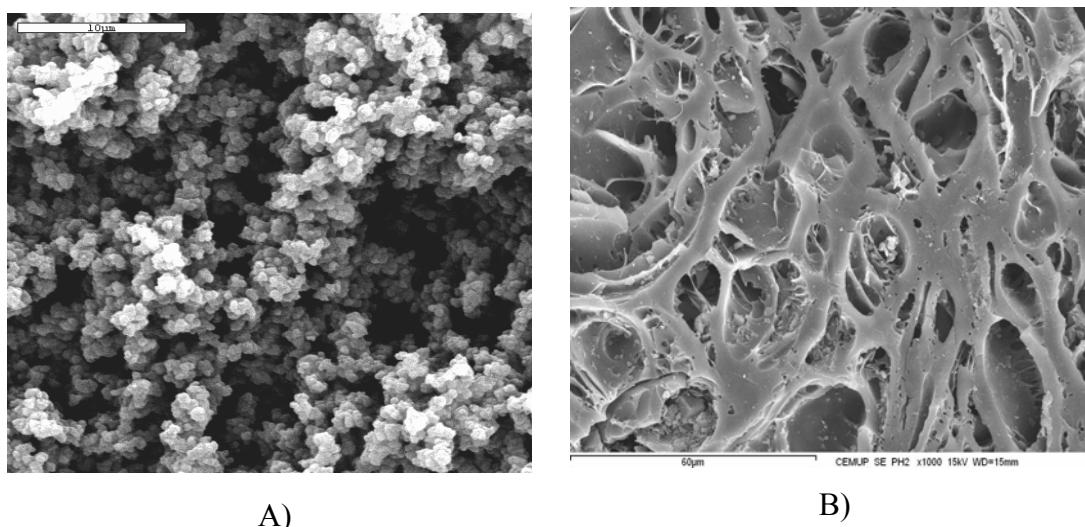


Fig. 6.1 – SEM images of the carbon M-Fe (A) and H-Fe (B) catalysts.

Textural data of both supports are presented in Table 6.1. The BET surface areas of both supports obtained from the N₂ adsorption isotherms are similar. However, the CO₂ adsorption experiments, usually developed to study the narrowest microporosity [11], pointed out that support H has a more developed microporosity (W_0 , L_0) favoured by the CO₂ activation process. On the contrary, the porosity range studied by mercury porosimetry is larger for support M. This support presents high values of meso (V_2) and macropores (V_3) volumes and a high external surface (S_{ext}). Moreover, support H is mainly a macroporous material, and thus the external surface area is lower than for support M. The corresponding pore size distributions (PSD) are shown in Fig. 6.2. It is observed that support H presents a monomodal PSD centred in macropores with 150 nm of radius, while the typical porosity in carbon M are mesopores with 5 nm of radius.

Table 6.1 – Textural data of the supports used.

Sample	V_2 (cm ³ / g)	V_3 (cm ³ / g)	W_0 (cm ³ / g)	L_0 (nm)	S_{ext} (m ² / g)	S_{BET} (m ² / g)
Support M	1.02	0.99	0.19	0.61	337	641
Support H	0.12	0.41	0.29	1.10	55	691

V_2 - volume of pores with a diameter between 3.7 and 50 nm; V_3 - volume of pores with a diameter larger than 50 nm; W_0 – micropore volume; L_0 – mean micropore width; S_{ext} - external surface area of pores with a diameter larger than 3.7 nm and smaller than 50 nm; S_{BET} - BET surface area obtained by N₂ adsorption.

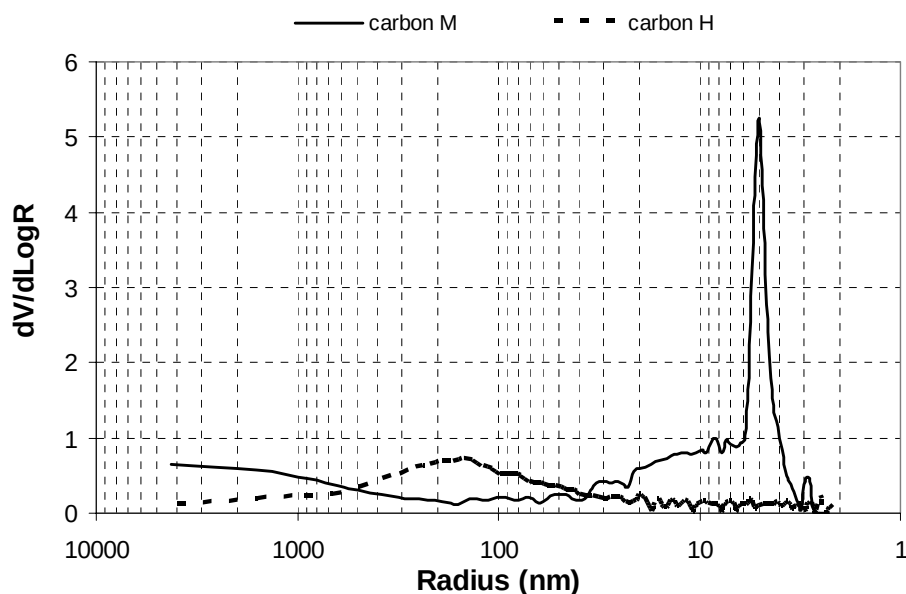


Fig. 6.2 – Pore size distribution in the meso and macropore range of both carbon supports, obtained by mercury porosimetry.

The composition of both supports, determined by elemental analysis, is shown in Table 6.2. The main composition difference between both supports is due to the higher oxygen content of the carbon aerogel. It is well known that the chemical structure of resorcinol-formaldehyde aerogels is defined by the formation of methyl and methyl-ether bridges between aromatic resorcinol structures, that also maintain unreacted -OH groups [8]. The low carbonization temperature of this carbon aerogels favour the high oxygen content observed which brings about a surface with a lower pH_{pzc} than the activated carbon H.

Table 6.2 – Elemental analysis of both supports (data given are in a weight percent basis).						
Support	pH _{pzc}	% C	% H	% N	% O	% Ash
H	9.9	95.7	0.4	0.5	3.0	0.4
M	8.4	87.2	2.6	0.0	10.2	0.0

The iron chemical state and dispersion were studied by XRD, XPS and HRTEM. When carbon H is used as support, the XRD pattern of the corresponding Fe-catalyst (Fig. 6.3) shows small and width diffraction peaks at $2\theta = 35.48, 62.62, 30.12, 57.02$ and 43.12° that were assigned to (311), (440), (220), (511) and (400) planes of Fe_3O_4 (JCPDS 88-0866), together with two broad bands, located at around 22 and 42° , associated to the 002 and 101 diffraction peaks of graphite, respectively. Obviously, only the latter can be found in the XRD analysis of the H support. When carbon M was used as iron

support, the XRD pattern do not present any diffraction peaks (Fig. 6.3). It is worth noting that the iron particles in this catalyst are difficult to detect even using HRTEM, as shown in Fig. 6.4. These results pointed out that in spite Fe is well dispersed in both cases, dispersion is worse when support H is used, probably due to the smaller external surface area (*cf.* Table 6.1).

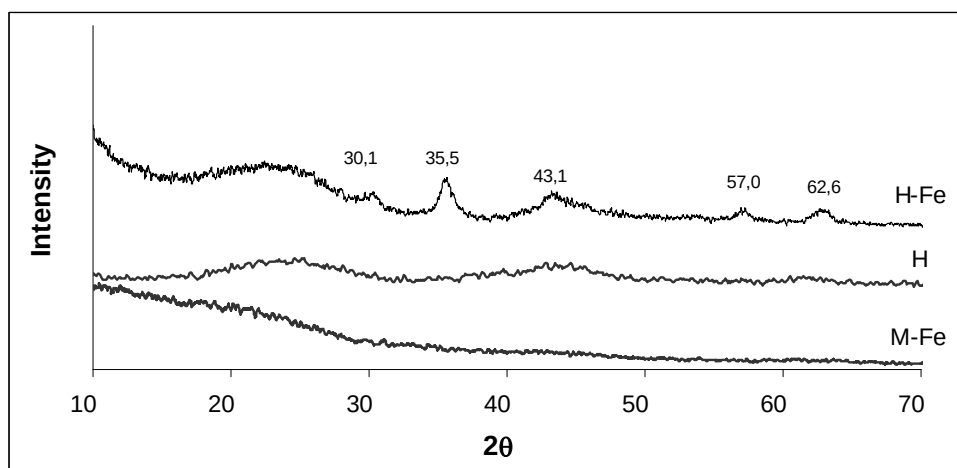


Fig 6.3 – XRD-patterns of the catalysts and of the H support.

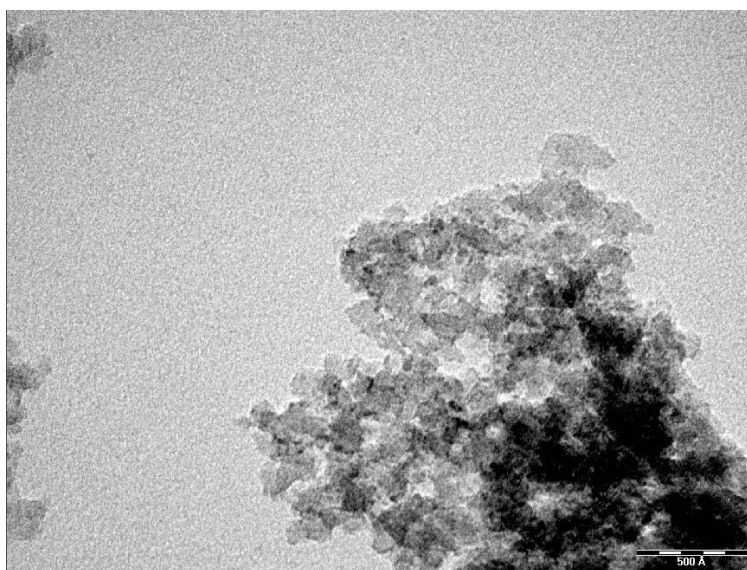


Fig. 6.4 – High-resolution transmission electron microscopy of the M-Fe catalyst.

Looking information about the chemical state of iron on support M, the corresponding catalyst was analyzed by XPS. The surface metal content determined by this technique is 6.2 wt.%, thus, taking into account that the total loading is 7.0%, it is also deduced that iron is uniformly distributed and highly dispersed. The XPS pattern of

the Fe2p region is shown in Fig. 6.5. Two components are observed, located at 711.1 and 713.4 eV respectively. These components are indicative of the presence of iron with different oxidation states and are consistent with the binding energy (BE) values previously published for magnetite (Fe_3O_4) [12] and ferric ions, either as hydrated (goethite, FeOOH) or anhydrous (Fe_2O_3) oxides [13,14], although in our case BE appear at around 0.5 eV higher. This occurs because the neighbour atoms in a disperse system are fewer than in the bulk, and so the electrons are also fewer. The consequence is a less effective core-hole screening and the BE of the orbital shifts to higher energy [15].

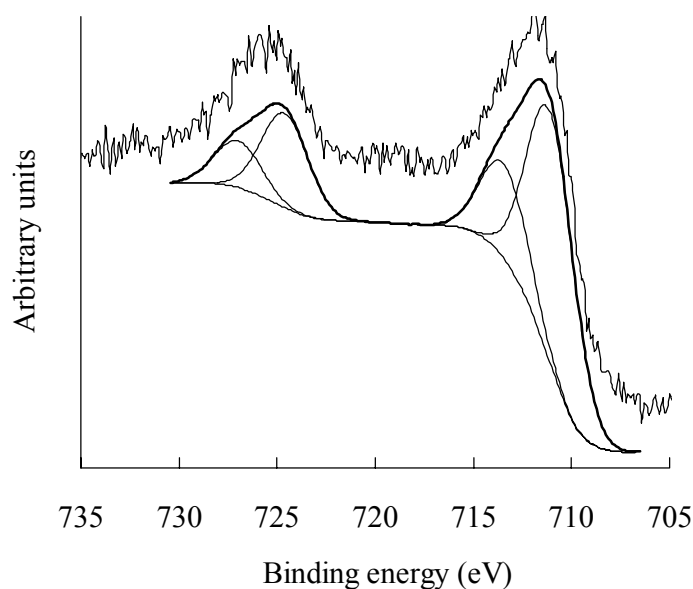


Fig. 6.5 – XPS patterns of the Fe2p region for catalyst M-Fe and deconvolution of the corresponding peaks (BE = 711 and 713 eV confirm the presence of Fe(II) and Fe(III)).

6.3.2 Catalytic Activity

6.3.2.1 Role of the Supports

Before comparing the behavior of both iron-containing catalysts, it is important to evaluate the OII elimination process, i.e., if OII removal occurs through adsorption, through a catalytic reaction or through both processes. For that reason, several runs were then performed.

The first one was a blank, carried out to evaluate the ability of H_2O_2 to eliminate OII in aqueous solutions without the addition of any heterogeneous catalyst. Figure 6.6 shows that OII degradation due to hydrogen peroxide is almost negligible (<1.0% after 4 h and 3.6% after 20 h), which might be attributed to its low oxidation potential as compared to hydroxyl or perhydroxyl radicals [16].

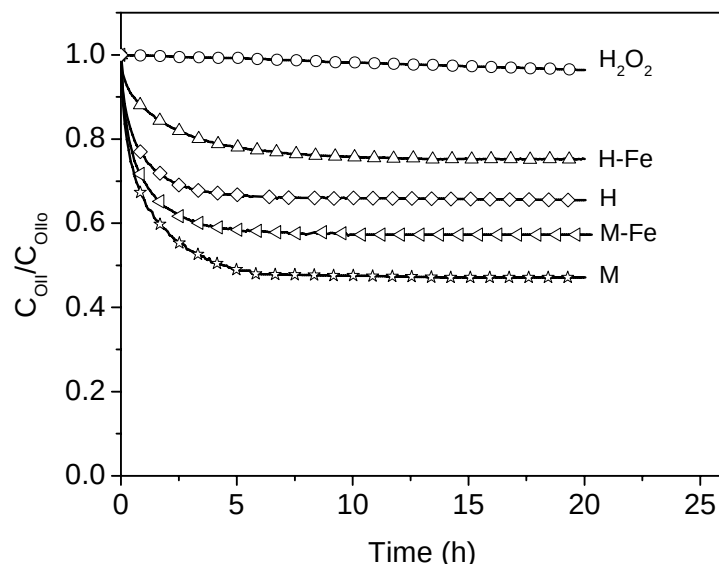


Fig. 6.6 – Un-catalyzed orange II removal by hydrogen peroxide ($C_{\text{H}_2\text{O}_2} = 6 \times 10^{-3}$ M) and adsorption on supports H and M and iron catalysts, H-Fe and M-Fe ($C_{\text{carbon}} = 0.2$ g/L, $T = 30$ °C, $\text{pH} = 3$).

To determine the influence of the adsorption processes experiments without H_2O_2 were carried out. Figure 6.6 shows that both carbon supports have a high adsorption capacity, being more important for carbon M (53.0 vs. 34.5% after 20h). The different adsorption capacities are related with the differences in the pore size distribution, thus the adsorption capacity is greater in support M in spite of the greater micropore volume of sample H, pointing out the importance of mesoporosity in the adsorption of large macromolecules. Figure 6.6 also shows that the adsorption capacity of the catalysts is, in both cases, smaller than those of the corresponding support.

Whether this adsorption is an advantage or not is not yet clear. While most authors consider that this pre-concentration of the substrates to be oxidized in the vicinity of reactive centres is beneficial, Georgi and Kopinke [17] consider to be a disadvantage because they claim that the predominant degradation pathway is the attack of $\text{HO}^\bullet$ species on the organic contaminants fraction that is freely dissolved in the aqueous pore volume of the activated carbon, whereas the adsorbed fraction is nearly unreactive.

Carbon materials are, moreover, good catalyst in different reactions [e.g., 18,19]. For that reason, the catalytic behaviour of both supports was evaluated in the presence of H_2O_2 (Fig. 6.7). The decolourization percentage increases regarding the adsorption conditions showing that both supports are catalytically active. The pollutant is however more deeply degraded in the presence of support H. Different aspects of the samples can contribute to this behaviour. First, the large microporosity of sample H, that is not accessible to the dye, can however favour the H_2O_2 decomposition. On the other hand, it is well known that the interaction of carbon materials with pollutants in aqueous solution strongly depends on their surface chemistry [20]. For instance, Huang *et al.* [21] found that the H_2O_2 decomposition was suppressed by decreasing the pH_{pzc} of granular activated carbons, however, the degradation of 4-chlorophenol by H_2O_2 is enhanced by the same acid groups. On the other hand, Oliveira *et al.* [22] indicate that basic sites generated during H_2 pre-treatment at different temperatures enhanced the formation of $HO^\bullet$ species from H_2O_2 .

The obtained results are therefore in good agreement with these conclusions. The catalytic activity of the supports seems to be more directly related with their different surface chemistry. The greater activity of support H is favoured by its heterogeneous structure, and greater basic character pointed out by the values of pH_{pzc} (Table 6.2).

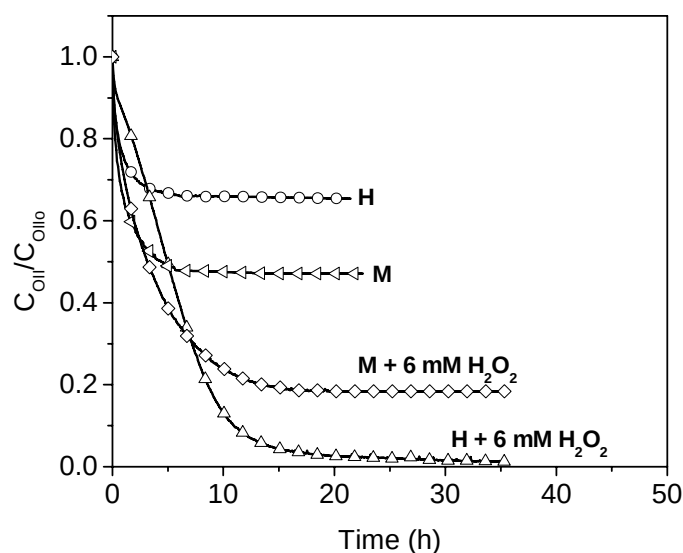


Fig. 6.7 – Orange II removal through adsorption and through oxidation on both carbon supports and catalysts ($T = 30\text{ }^{\circ}\text{C}$, $\text{pH} = 3$, $C_{\text{carbon}} = 0.2\text{ g/L}$, $C_{H_2O_2} = 6 \times 10^{-3}\text{ M}$).

6.3.2.2 Influence of the Experimental Conditions in the Iron-Supported Catalysts Performance

Although the results summarized in Fig. 6.7 puts into evidence the possibility of using directly the carbon supports as catalysts, the catalytic role of iron is clearly evidenced in this section when one compares the performances shown by the supports with those exhibited by their corresponding Fe-catalysts. Actually, while with the best support (support H) one needs 15-20 h to reach high OII degradation levels (>95%), with the Fe-catalysts this can be achieved in only ca. 1.5-3 h in the same experimental conditions. Thus, while the use of carbon materials as catalysts can present several advantages such as lower price or no leaching of metallic pollutants, the use of iron catalyst is necessary when operation time should be shortened. The parameters that control their catalytic performance will be studied bellow.

- Influence of pH

The catalytic performances of Fe-catalysts are obviously better than their corresponding support. It is well known that this metal is able to transform H_2O_2 into $\text{HO}^\bullet$ species [23]. Figure 6.8 shows a comparative performance of both catalysts at different pH values. It is noteworthy that the M-Fe catalyst is more active than the H-Fe one at any pH studied (between 2 and 4) in spite of the greater catalytic activity of support H. This fact should be related with the better dispersion of Fe into the large external surface provided by mesoporosity of sample M, although the hypothesis that the larger adsorption capacity of this sample can favour the degradation of pollutants in neighbour Fe particles can not be ruled out. The importance of the iron dispersion in composite materials for Fenton oxidation was also pointed out by other authors [24].

With both catalysts used, the higher the pH (in the range 2-4), the slower is the reaction rate (Fig. 6.8A). For catalyst M-Fe, dye degradation at pH 2 or 3 proceeds at almost the same rate, being practically complete after 2 h of reaction. This is an important advantage because it allows using less acid to acidify the medium. It must be stressed that another experiment, performed at pH 1 with the M-Fe catalyst, showed a marked decrease in the performance: 72.2% after 4h; the reason for this was previously discussed (*cf.* section 5.3.2.3)

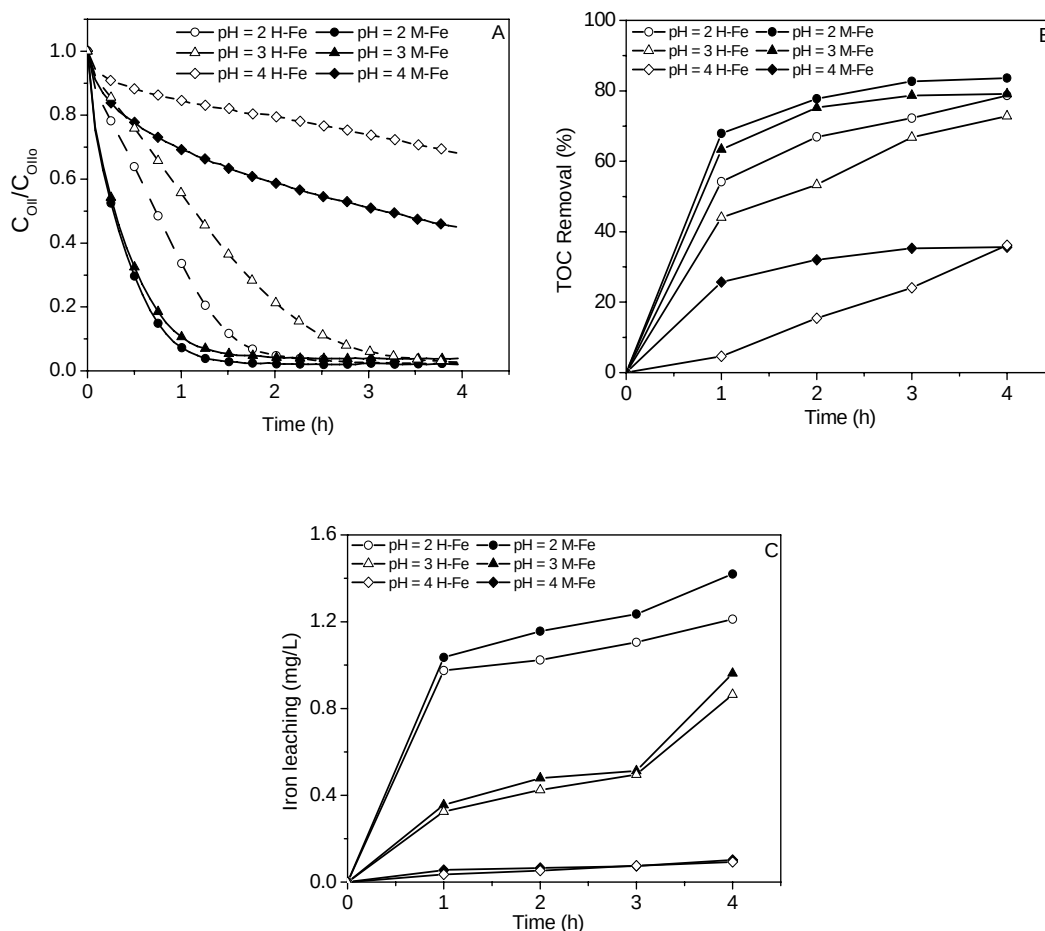


Fig. 6.8 – pH effect on the degradation of OII solution (A), in TOC removal (B) and in iron leaching (C) using M-Fe and H-Fe catalysts ($T = 30\text{ }^{\circ}\text{C}$, $C_{cat.} = 0.2\text{ g/L}$, $C_{H_2O_2} = 6 \times 10^{-3}\text{ M}$).

In terms of TOC removal (Fig. 6.8B), conclusions are similar as for OII degradation: for both carbons a better performance is reached when the pH is lower. In addition, catalyst M-Fe shows always better performances as compared to H-Fe, reaching mineralization degrees after 4 h above 80%. Thus, while almost total elimination of OII pollutant is achieved, its oxidation produces intermediate products which mineralization is not complete at any pH. The worst performance of both samples at high pH values can be ascribed to the stability of H_2O_2 , which starts to rapidly decompose into molecular oxygen without formation of appreciable amounts of hydroxyl radicals [25]. In the mild operating conditions used, it is expected that the formed O_2 is not capable to efficiently oxidize the organics.

Another important parameter to quantify is the iron leaching, which should ideally be null to provide long-term stability. Figure 6.8C shows that leaching increases when the medium is more acid. This result is in agreement with other authors [3,26].

Carbon M shows slightly higher iron lixiviation, especially at pH = 2, what is probably related with the better dispersion and accessibility of Fe-particles. On the other hand, the activity of the leached iron could, in part, explain the better performance of this sample. However, not only the homogeneous but also the heterogeneous process is of importance. This can be concluded from the OII degradation and mineralization degrees at pH 2 or 3, which are similar (Figs. 6.8A and 6.8B), in spite of the higher Fe loss from the support for pH 2 vs. pH 3 (10.1% vs. 6.9% after 4h for carbon M, where the values refer to the amount - wt.% - of Fe lost as referred to the total Fe initially present in the catalyst).

It can therefore be concluded that the better experimental conditions are reached using pH = 3 with sample M, where the OII degradation is similar than at pH = 2, but lower iron leaching is produced. The subsequent runs will consequently be carried out at pH 3 using the best sample: the Fe-M catalyst.

- Effect of the Catalyst Concentration

As expected, when the amount of catalyst employed increases, OII and TOC elimination rates also increase (Figs. 6.9A and 6.9B), due to the increasing amount of active sites for H₂O₂ decomposition and, less important but also of concern, for organic compounds adsorption. Nevertheless, the maximum mineralization reached is around 90% (only attained for a catalyst concentration of 0.30 g/L at $t = 4$ h), although decolourisation is almost complete for any catalyst concentration used. Moreover, while differences in terms of dye removal for catalyst concentrations between 0.2 and 0.3 g/L are not too significant, TOC removal homogeneously increases with the catalyst concentration. It is also noteworthy that, as found by other authors [3], a high reduction of TOC is observed at the reaction beginning, but the rate of mineralization slows down possibly due to the lower oxidation rate of reaction products and the development of parallel reactions between excess ferrous iron and hydroxyl radicals (as occurs in a homogeneous process – *cf.* Eq. (4.2)), or to the scavenging of those or other radicals by present iron species [23,27,28]:





These undesirable reactions may also account for the very similar OII history profiles in Fig. 6.9A when the catalyst concentration is 0.20 or 0.30 g/L. For this reason, subsequent runs will be performed using a catalyst concentration of 0.20 g/L.

Finally, iron concentration in solution increases with the amount of M-Fe catalyst used (Fig. 6.9C), reaching however values always below EU guidelines (< 2 ppm), even when using a catalyst concentration of 0.3 g/L. In terms of percentage of iron lost from the solid, referred to the total Fe initially incorporated, Fig. 6.9D shows that differences are small, i.e., the percentage of iron that has been leached out does not depend on the catalyst concentration employed in the catalytic runs.

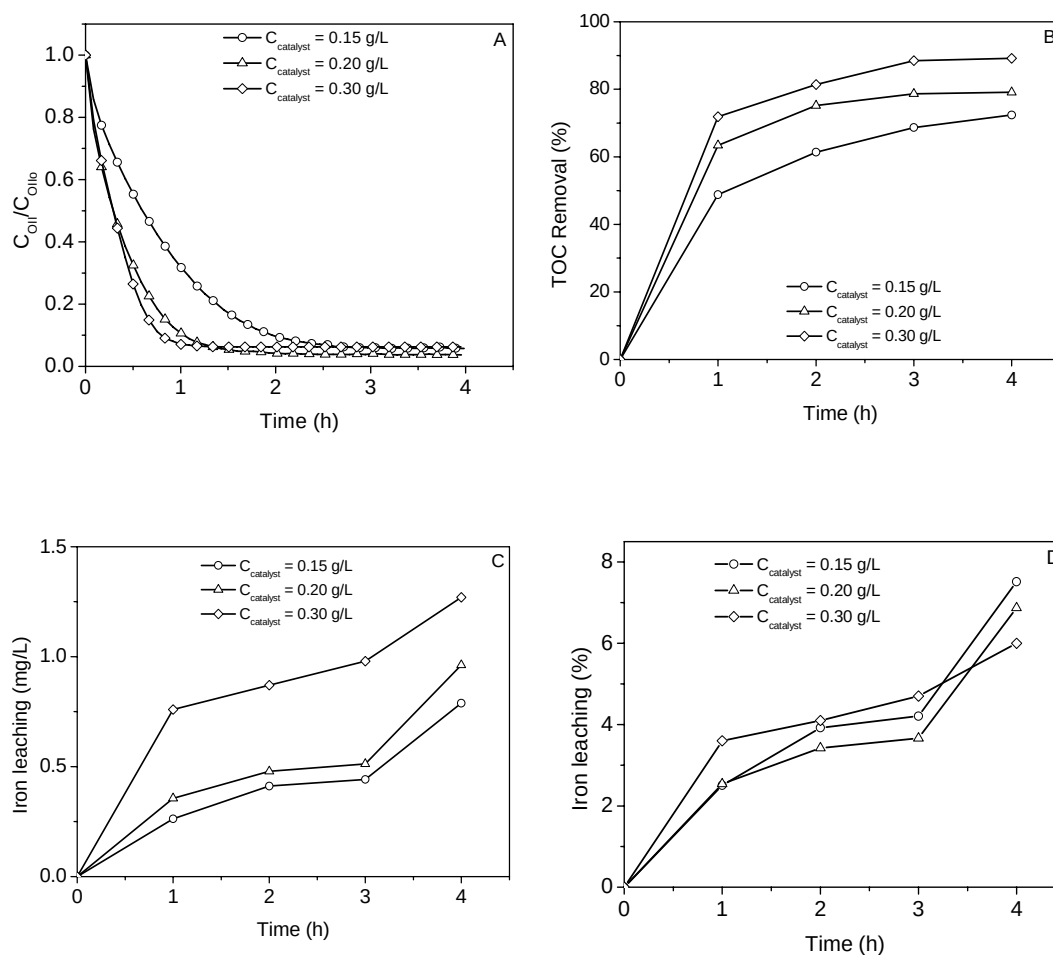


Fig. 6.9 – Effect of catalyst concentration in the degradation of OII solution (A), in TOC removal (B), in iron concentration in solution (C) and in percentage of iron lost by the M-Fe catalysts (D) ($T = 30\text{ }^{\circ}\text{C}$, $\text{pH} = 3$, $C_{H_2O_2} = 6 \times 10^{-3}\text{ M}$).

- Effect of the Hydrogen Peroxide Concentration

The effect of the hydrogen peroxide was analysed by varying its initial concentration between 3×10^{-3} and 4.8×10^{-2} M. According to Feng *et al.* [26], 42 mol of H_2O_2 are theoretically needed to completely degrade 1 mol of the dye ($C_{16}H_{11}N_2NaO_4S + 42H_2O_2 \rightarrow 16CO_2 + 46H_2O + 2HNO_3 + NaHSO_4$). Based on this, the concentrations employed are between 0.71 and 11.4 (molar ratio) of the overall stoichiometry for the complete mineralization of OII.

Increasing H_2O_2 load from 3×10^{-3} to 6×10^{-3} M increases reaction performance (Figs. 6.10A and 6.10B) because more radicals are formed. However, a significant improvement is not seen for a higher concentration ($C_{H_2O_2} = 2.4 \times 10^{-2}$ M). Moreover, performance either in terms of OII degradation or in terms of mineralization drops down for an excessive peroxide load ($C_{H_2O_2} = 4.8 \times 10^{-2}$ M) due to the well-known hydroxyl radicals scavenging effect [23,27]:



Such reaction reduces the probability of attack of organic molecules by hydroxyl radicals, and caused the oxidation rate to drop. Although other radicals ($HO_2^\bullet$) are produced, their oxidation potential is much smaller than that of the $HO^\bullet$ species [16]. Therefore, in the subsequent runs, $C_{H_2O_2} = 6 \times 10^{-3}$ M will be used.

Figure 6.10C evidences that H_2O_2 concentration does not seem to affect iron leaching. This is in agreement with some works found in the literature either with Fe- [29] or Cu-based catalysts [30], showing however that the leaching experiments are nicely reproducible (lines for different runs practically overlap). It is however important to highlight that iron leaching increases from 3 to 4 h of reaction, a behaviour that can also be noticed in other figures, e.g. Fig 6.9. In spite the total amount of iron in the system is the same, a larger fraction is in solution, from which one could expect an increase in the mineralization degree. However, such trend is not accompanied by a significant change in TOC removal, which might indicate that the products formed are refractory, hard to further oxidise. Sotelo *et al.* [30] also pointed for the formation of refractory compounds in the second stage of the degradation kinetics, which showed a

fast removal stage followed by a slower second step where TOC conversion is levelled off.

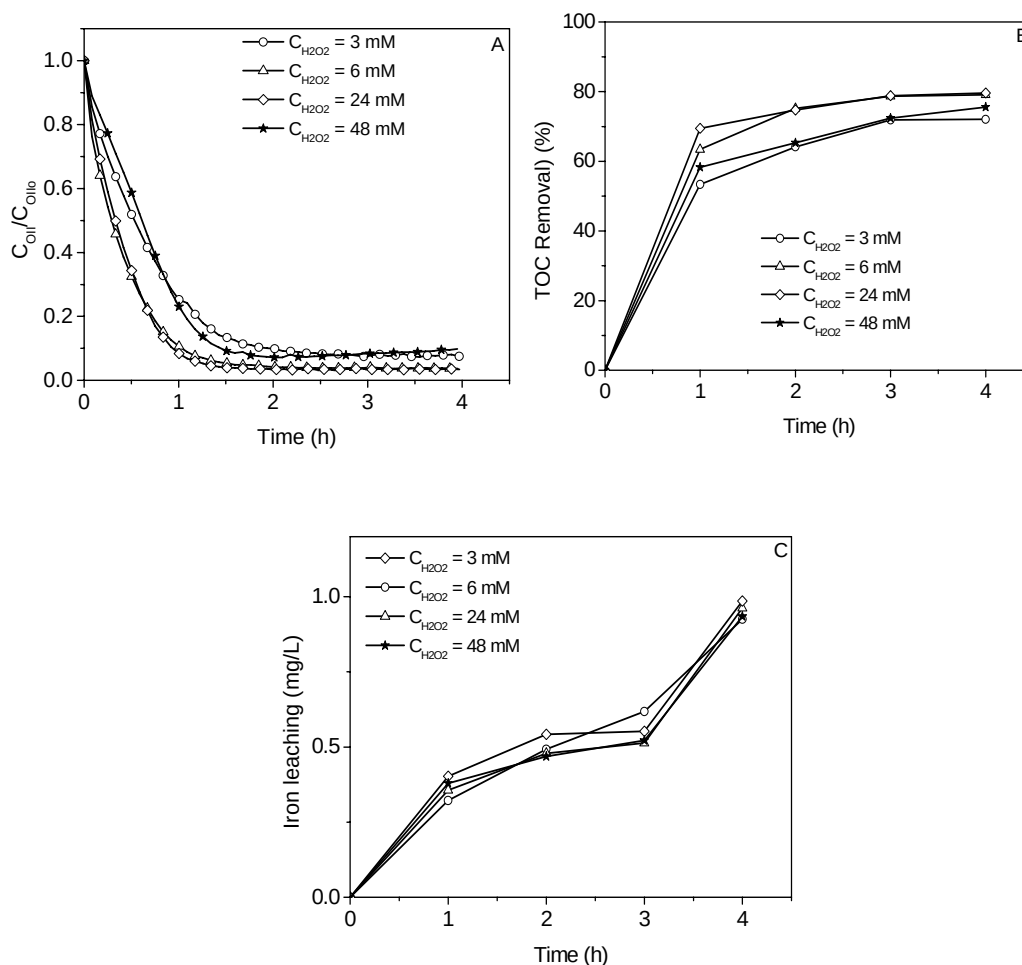


Fig. 6.10 – Hydrogen peroxide concentration effect on the degradation of OII solution (A), in TOC removal (B) and in iron leaching (C) using M-Fe catalysts ($T = 30$ °C, $pH = 3$, $C_{cat.} = 0.2$ g/L).

- Effect of the Reaction Temperature

When the temperature of the reaction medium is increased, oxidation proceeds at a faster rate (Figs. 6.11A and 6.11B) due to the exponential dependence of the kinetic constants on it (Arrhenius law), as shown below. However, after ca. 1.5 h dye degradation is similar for temperatures in the range 30-70 °C (Fig. 6.11A), with almost 100% decolorisation.

The mineralization degree increases with increasing temperature, although total mineralization is not attained even at 70 °C. The most significant difference is noted when reaction temperature increases from 10-30 °C (Fig. 6.11B). In this temperature

range TOC removal increases from ca. 50 to almost 80%, however, each progressive 20°C increase only produces around 3% of TOC increase. This is possibly due to the accelerated thermal decomposition of H_2O_2 into oxygen and water [31-33]. For this reason, final experiments will be carried out at 30 °C. In addition, the higher the reaction temperature, the higher the iron lost from the catalysts (Fig.6.11C), in agreement with other studies reported in the literature [3].

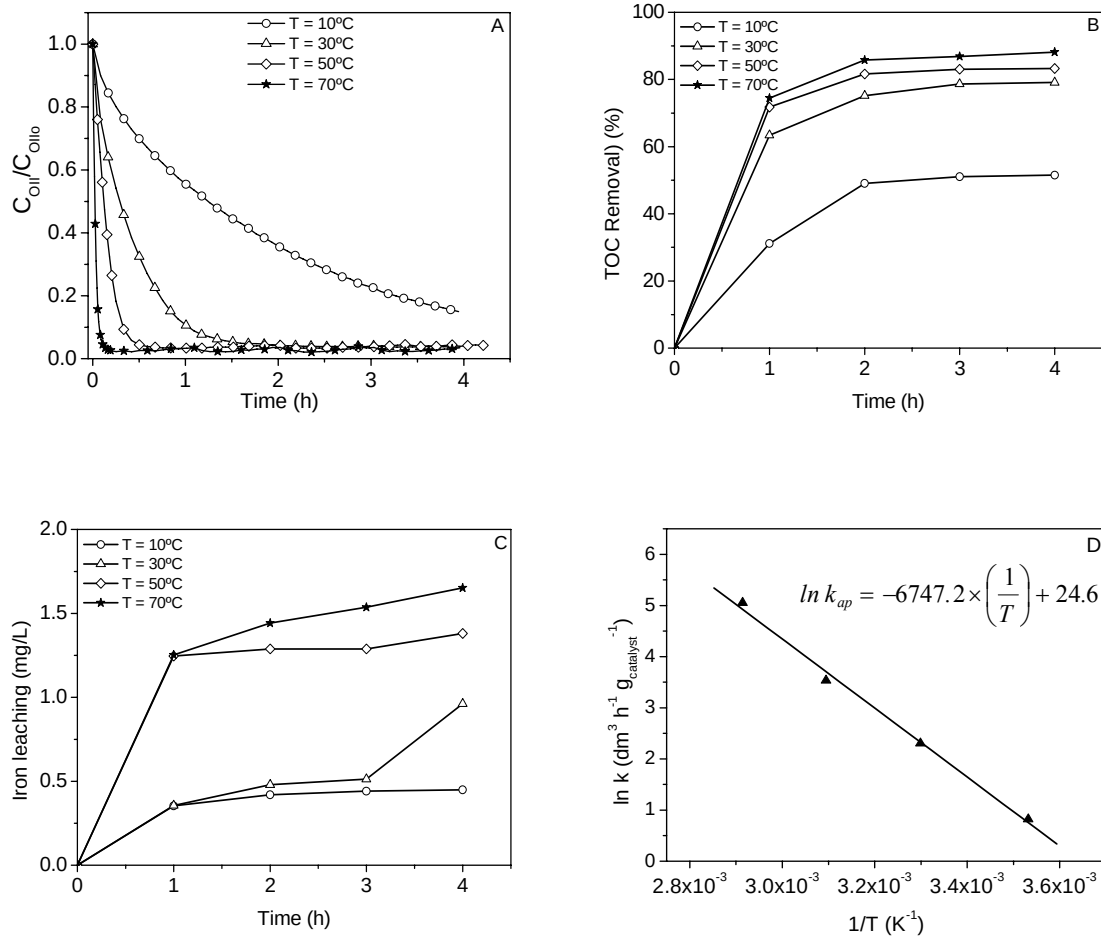


Fig. 6.11 – Temperature effect on the degradation of OII solution (A), in TOC removal (B) and in iron leaching (C) using M-Fe catalysts ($C_{H_2O_2} = 6 \times 10^{-3}$ M, pH = 3, $C_{cat.} = 0.2$ g/L). Plot (D) represents the temperature dependence of the apparent pseudo-first order kinetic constant.

Assuming, as commonly found, a pseudo-first order for the dye degradation, the mass balance in the batch reactor yields:

$$V \frac{dC_{OII}}{dt} = -(-r_{OII})W = -k_{ap} C_{OII} W \quad (6.5)$$

where C_{OII} is the orange II concentration at instant t , k_{ap} is the apparent pseudo-first order kinetic constant, W is the mass of catalyst and V is the reaction volume. Integration of such equation provides the theoretical history profiles:

$$C_{OII} = C_{OII_o} \exp\left(-k_{ap} \frac{W}{V} t\right) \quad (6.6)$$

to which the data shown in Fig. 6.11A were fitted. The fittings ($R^2 > 0.99$) at different temperatures were performed using data up to 95% OII conversion, except for $T = 10$ °C, where all data have been used. The dependence of the kinetic constant on the reaction temperature shown in Fig. 6.11D evidences Arrhenius behaviour, with an activation energy of 56.1 kJ/mol. Others authors [34] have found the same dependence with the temperature in a photo-assisted process through a Fe/C structured catalyst for the degradation of Orange II, and in such case the value of the activation energy for the dye discoloration was 47.4 kJ/mol (in a similar temperature range).

- Stability and Recycling of the Fe-M Catalyst

To use in real practice a heterogeneous catalyst in Fenton-like oxidation, it is crucial to evaluate the stability of the solids. With that goal in mind, consecutive experiments were performed with the same sample, recovered by filtration after each cycle. Figure 6.12 shows that after the first 2 experiments, reaction performance, particularly OII degradation rate, is significantly affected. Mineralization is also affected, with values after 4 h of reaction decreasing in the 3 consecutive cycles from 76.5, to 71.4 and finally to 55.9%. This is in part a consequence of the iron lost from the support, which amounts to 24% of the initial iron after the 3 cycles (ca. 8% per cycle – *cf.* Fig. 6.12C).

The iron leaching is not the only reason for the observed activity decay. Actually, based on the effective amount of iron available at the beginning of each cycle, the initial reaction rates have been computed (using Eq. (6.5) for $t = 0$). The values obtained for the 3 consecutive cycles (5.5×10^{-6} , 4.0×10^{-6} and 1.1×10^{-6} mmol s⁻¹ mg_{Fe}⁻¹, respectively) show that iron deactivation is also produced, although the reasons behind that are not yet clear. Zazo *et al.* [3] attributed the Fe/active carbon catalyst deactivation observed to Fe complexation by oxalic acid (resulting from phenol oxidation) and/or to

active sites blockage due to polymeric deposits, with partial reactivation being reached after washing with 1N NaOH solution.

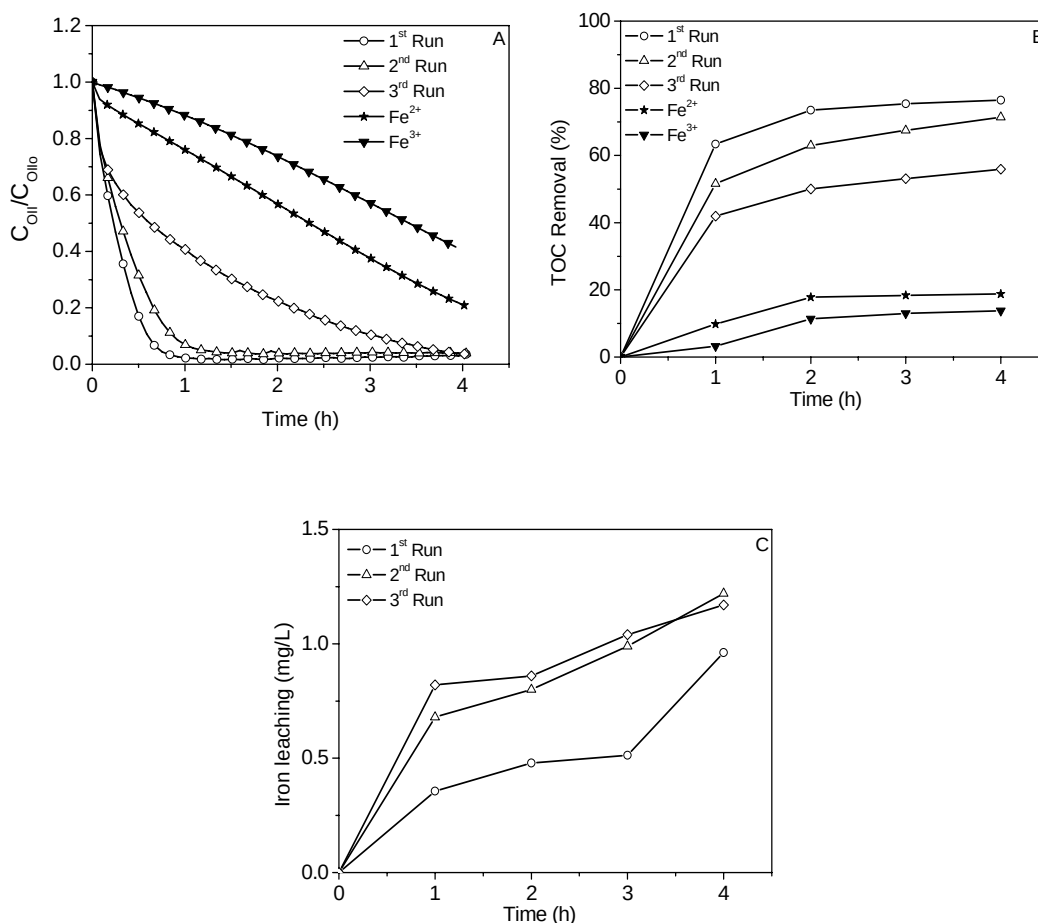


Fig. 6.12 – Effect of consecutive experiments with the M-Fe catalyst on the degradation of OII solution (A), in TOC removal (B) and in iron leaching (C) ($C_{H_2O_2} = 6 \times 10^{-3}$ M, pH = 3, T = 30 °C, $C_{cat.} = 0.2$ g/L). Oxidation performance is also compared with homogeneous catalytic process, using iron (II) or iron (III) salts (1.5 mg/L).

Based on the amount of iron lost from the M-Fe catalyst after the first cycle, two experiments were performed in homogeneous phase using iron salts in similar concentration as that produced by leaching (1.5 mg/L). From Figs. 6.12A and 6.12B one can clearly see that both OII degradation and particularly mineralization with the iron salts proceeds much slower than with the carbon-based catalyst, i.e. the iron (in the 2+ or 3+ oxidation state) present in solution is not capable to catalyze the process so efficiently. Therefore, the process studied in this work using the carbon-based catalysts is essentially heterogeneous, not homogeneous. Finally, the faster reaction rate with $Fe(II)$ vs. $Fe(III)$ salts (Figs. 6.12A and 6.12B) is due to the faster reaction with

hydrogen peroxide in Fenton (reaction with ferrous iron) compared to Fenton-like (reaction with ferric iron) processes [35-37].

Finally, and due to reasonable performances reached by the carbon catalysts, we decided to compare them with catalysts based on pillared saponite impregnated with iron salts, reported in chapter 5. Then, the carbon-based catalysts were tested in identical conditions as clays, which contain the same iron content (ca. 7-8 wt.%). Table 6.3 shows that in terms of OII degradation or TOC removal, the final performance ($t = 4$ h) of the M-Fe catalyst is similar to that found with the best of the clays, i.e., the one using the iron (II) oxalate salt as precursor. However, OII degradation proceeds at a much faster reaction rate with the aerogel catalyst (*cf.* values for $t = 2$ h). Once again, carbon H-Fe presents a worst performance. However, one important disadvantage of the carbon catalysts is the amount of iron lost from the support, which is much higher than that reached with the oxalate clay sample. Nevertheless, if one compares the iron leaching of the carbon catalysts with that of a clay sample in which the iron precursor was the same as in the carbons catalysts, i.e. acetate, it comes that iron lixiviation data become similar, even though catalytic performance of this other clay is worst (Table 6.3). It seems therefore that the precursor used might have an important role in fixing the iron to the support.

Table 6.3 – Comparison of reaction performance in terms of OII degradation, OII mineralization and iron leaching of the carbon catalysts with two clay-based samples.*

Sample	OII degradation, $t = 2$ h (%)	OII degradation, $t = 4$ h (%)	TOC Removal, $t = 4$ h (%)	Iron Leaching, $t = 4$ h (mg/L) ⁺
M-Fe	79.0	94.6	58.8	0.642 (10.0%)
H-Fe	26.2	55.0	23.0	0.498 (7.8%)
Clay Oxalate	35.9	92.9	70.3	0.190 (2.6%)
Clay Acetate	30.5	79.3	66.7	0.558 (7.5%)

* Reaction conditions: $T = 30$ °C, $pH = 3$, $C_{H_2O_2} = 6 \times 10^{-3}$ M, $C_{cat.} = 91.5$ mg/L.

+ Percentage values refer to the amount (wt.%) of Fe lost into the solution after reaction, based on the total iron initially present in the samples.

6.4 Conclusions

- Two carbon samples have been employed as supports for iron particles with the aim of using them in the Fenton-like oxidation of Orange II. The carbon samples used are quite different, a classical activated carbon (sample H) and a carbon

aerogel (sample M). They differ largely in the porosity: while carbon H is a macro and microporous material, carbon M has a large mesopore volume. Chemically, the carbon aerogel has a greater oxygen content, which brings about a lower pH_{pzc} value. The adsorption capacity depends on the textural characteristics, while the catalytic activity in the Orange OII degradation is mostly related with the chemical ones.

- The catalysts have been prepared through wet impregnation using ferrous acetate. The XPS and XRD experiments showed that Fe presents different oxidation state (Fe (II) and Fe (III)) that is more dispersed in the case of support M because of the large mesopore volume and external surface area of this sample.
- The good iron dispersion in carbon M may be one reason for the better catalytic behaviour of this sample in the Fenton-like process. Indeed, the Fe-doped aerogel showed better catalytic performances, mainly higher reaction rates, than those reached with the activated carbon catalyst.
- With both activated carbon-based catalysts, OII elimination is due to two processes – adsorption and catalysis – being however the last the most relevant one. Although a homogeneous catalytic contribution also exists, as a consequence of the iron leaching, the process is essentially heterogeneous. When choosing the reaction conditions, one has to find a compromise between high reaction performances, with low iron leaching. For that reason, it is advisable to operate at pH around 3.0, $T = 30^{\circ}\text{C}$, and a hydrogen peroxide concentration of $6 \times 10^{-3} \text{ M}$ (for a dye concentration of $1 \times 10^{-4} \text{ M}$).
- The catalysts studied have however an important limitation for their use in industrial practice – the high iron loss from the supports. To overcome this, it is advisable the preparation of carbon aerogels in which iron is within the aerogel structure. Nevertheless, even in the worst conditions tested the iron concentration in solution is always below the EU guidelines ($< 2 \text{ ppm}$) and the catalytic performances reached are quite good, with mineralization degrees as high as 90%, for catalysts concentration not higher than 0.20 to 0.30 g/L. Decolourisation might however be almost complete. This means that the dye is being transformed into intermediate products that evolve towards CO_2 and H_2O as the reaction proceeds, remaining however some refractory compounds.

- Finally, consecutive experiments performed with the M-Fe sample showed some activity decay, which is due to both iron leaching and catalyst deactivation.

References

1. Sabhi, S.; Kiwi, J. Degradation of 2,4-Dichlorophenol by immobilized iron catalysts. *Water Research* **2001**, 35, 1994.
2. Sum, O. S. N.; Feng, J.; Hu, X.; Yue, P.L. Pillared laponite clay-based Fe nanocomposites as heterogeneous catalysts for photo-Fenton degradation of acid black 1. *Chemical Engineering Science* **2004**, 59, 5269.
3. Zazo, J. A.; Casas, J. A.; Mohedano, A. F.; Rodriguez, J. J. Catalytic wet peroxide oxidation of phenol with a Fe/Active carbon catalyst. *Applied Catalysis B: Environmental* **2006**, 65, 261.
4. Dantas, T. L. .P.; Mendonça, V. P.; Jose, H. J.; Rodrigues, A. E.; Moreira. R. F. P. M. Treatment of textile wastewater by heterogeneous Fenton process using a new composite Fe₂O₃/carbon. *Chemical Engineering Journal* **2006**, 118, 77.
5. Lücking, F.; Köser, H.; Jank, M.; Ritter, A. Iron powder, graphite and activated carbon as catalysts for the oxidation of 4-chlorophenol with hydrogen peroxide in aqueous solution. *Water Research* **1998**, 32, 2607.
6. Calleja, G.; Melero, J. A.; Martínez, F.; Molina, R. Activity and resistance of iron-containing amorphous, zeolitic and mesostructured materials for wet peroxide oxidation of phenol. *Water Research* **2005**, 39, 1741.
7. Kuznetsova, E. V.; Savinov, E. N.; Vostrikova, L. A.; Parmon, V. N. Heterogeneous catalysis in the Fenton-type system FeZSM-5/H₂O₂. *Applied Catalysis B: Environmental* **2004**, 51, 165.
8. Al-Muhtaseb, S. A.; Ritter, J. A. Preparation and Properties of Resorcinol-Formaldehyde Organic and Carbon Gels. *Advanced Materials* **2003**, 15, 101.
9. Maldonado-Hódar, F. J.; Moreno-Castilla, C.; Pérez-Cadenas, A. F. Surface morphology, metal dispersion, and pore texture of transition metal-doped monolithic carbon aerogels and steam-activated derivatives. *Microporous and Mesoporous Materials* **2004**, 69, 119.
10. Ubago-Pérez, R.; Carrasco-Marín, F.; Fairén-Jiménez, D.; Moreno-Castilla, C. Granular and monolithic activated carbons from KOH-activation of olive stones. *Microporous and Mesoporous Materials* **2006**, 92, 64.
11. Cazorla-Amorós, D.; Alcañiz-Monge, J.; De la Casa-Lillo, M. A.; Linares-Solano, A. CO₂ as an adsorptive to characterize carbon molecular sieves and activated carbons. *Langmuir* **1998**, 14, 4589.

12. Mukh-Qasem, R. A.; Gedanken, A. Sonochemical synthesis of stable hydrosol of Fe₃O₄ nanoparticles. *Journal of Colloid and Interface Science* **2005**, 284, 489.
13. Liu, C.; Tseng, D.; Wang, C. Effects of ferrous ions on the reductive dechlorination of trichloroethylene by zero-valent iron. *Journal of Hazardous Materials* **2006**, 136, 706.
14. Wagner, C. D.; Riggs, W. M.; Davis, L. E.; Moulder, J. F.; Muilenberg, G. E. *Handbook of X-Ray Photoelectron Spectroscopy*, Perkin-Elmer, Physical Electronics Division: Eden Prairie, M.I., **1978**.
15. Kónya, Z.; Kiss, J.; Oszkó, A.; Siska, A.; Kiricsi, I. XPS characterisation of catalysts during production of multiwalled carbon nanotubes. *Physical Chemistry Chemical Physics* **2001**, 3, 155.
16. Bigda, R. J. Consider Fenton chemistry for wastewater treatment. *Chemical Engineering and Processing* **1995**, 91, 62.
17. Georgi, A.; Kopinke, F. D. Interaction of adsorption and catalytic reactions in water decontamination processes: Part I. Oxidation of organic contaminants with hydrogen peroxide catalyzed by activated carbon. *Applied Catalysis B: Environmental* **2005**, 58, 9.
18. Maldonado-Hódar, F. J.; Madeira, L. M.; Portela, M. F. The use of coals as catalysts for the oxidative dehydrogenation of n-butane. *Applied Catalysis A: General* **1999**, 178, 49.
19. Carrasco-Marín, F.; Mueden, A.; Moreno-Castilla, C. Surface-treated activated carbons as catalysts for the dehydration and dehydrogenation reactions of ethanol. *Journal of Physical Chemistry B* **1998**, 102, 9239.
20. Radovic, L. R.; Moreno-Castilla, C.; Rivera-Utrilla, J. *Chemistry and physics of carbon*, V. 27, Marcel Dekker, New York **2000**.
21. Huang, H.; Lu, M.; Chen, J.; Lee, C. Catalytic decomposition of hydrogen peroxide and 4-chlorophenol in the presence of modified activated carbons. *Chemosphere* **2003**, 51, 935.
22. Oliveira, L. C. A.; Silva, C. N.; Yoshida, M. I.; Lago, R. M. The effect of H₂ treatment on the activity of activated carbon for the oxidation of organic contaminants in water and the H₂O₂ decomposition. *Carbon* **2004**, 42, 2279.
23. Walling, C. Fenton's reagent revisited. *Accounts of Chemical Research* **1975**, 8, 125.
24. Oliveira, L. C. A.; Gonçalves, M.; Guerreiro, M. C.; Ramalho, T. C.; Fabris, J. D.; Pereira, M. C.; Sapag, K. A new catalyst material based on niobia/iron oxide composite on the oxidation of organic contaminants in water via heterogeneous Fenton mechanisms. *Applied Catalysis A: General* **2007**, 316, 117.
25. Guo, J.; Al-Dahhan, M. Catalytic wet oxidation of phenol by hydrogen peroxide over pillared clay catalyst. *Industrial and Engineering Chemistry Research* **2003**, 42, 2450.

26. Feng, J.; Hu, X.; Yue, P. L. Effect of initial solution pH on the degradation of Orange II using clay-based Fe nanocomposites as heterogeneous photo-Fenton catalyst. *Water Research* **2006**, 40, 641.
27. De Laat, J. ; Le, T. G. Effects of chloride ions on the iron(III)-catalyzed decomposition of hydrogen peroxide and on the efficiency of the Fenton-like oxidation process. *Applied Catalysis B: Environmental* **2006**, 66, 137.
28. Carriazo, J.; Guélou, E.; Barrault, J.; Tatibouët, J. M.; Molina, R.; Moreno, S. Synthesis of pillared clays containing Al, Al-Fe or Al-Ce-Fe from a bentonite: Characterization and catalytic activity. *Catalysis Today* **2005**, 107-108, 126.
29. Melero, J. A.; Calleja, G.; Martínez, F.; Molina, R.; Pariente, M. I. Nanocomposite Fe₂O₃/SBA-15: An efficient and stable catalyst for the catalytic wet peroxidation of phenolic aqueous solutions. *Chemical Engineering Journal* **2007**, 131, 245.
30. Sotelo, J. L.; Ovejero, G.; Martínez, F.; Melero, J. A.; Milieni, A. Catalytic wet peroxide oxidation of phenolic solutions over a LaTi_{1-x}Cu_xO₃ perovskite catalyst. *Applied Catalysis B: Environmental* **2004**, 47 281.
31. Dutta, K.; Mukhopadhyay, S.; Bhattacharjee, S.; Chaudhuri, B. Chemical oxidation of methylene blue using a Fenton-like reaction. *J. Hazard. Mater.* **2001**, 84, 57.
32. Guedes, A. M. F. M.; Madeira, L. M. P.; Boaventura, R. A. R.; Costa, C. A. V. Fenton oxidation of cork cooking wastewater—overall kinetic analysis. *Water Research* **2003**, 37, 3061.
33. Catrinescu, C.; Teodosiu, C.; Macoveanu, M.; Mieke-Brendle, J.; Dred, R. L. Catalytic wet peroxide oxidation of phenol over Fe-exchanged pillared beidellite. *Water Research* **2003**, 37, 1154.
34. Yuranova, T.; Enea, O.; Mielczarski, E.; Mielczarski, J.; Albers, P.; Kiwi. J. Fenton immobilized photo-assisted catalysis through a Fe/C structured fabric. *Applied Catalysis B: Environmental* **2004**, 49, 39.
35. Chen, R.; Pignatello, J. J. Role of quinone intermediates as electron shuttles in Fenton and photoassisted Fenton oxidations of aromatic compounds. *Environmental Science and Technology* **1997**, 31, 2399.
36. Gallard, H.; De Laat, J. Kinetic modelling of Fe(III)/H₂O₂ oxidation reactions in dilute aqueous solution using atrazine as a model organic compound. *Water Research* **2000**, 34, 3107.
37. De Laat, J.; Gallard, H.; Ancelin, S.; Legube, B. Comparative study of the oxidation of atrazine and acetone by H₂O₂/UV, Fe(III)/UV, Fe(III)/H₂O₂/UV and Fe(II) or Fe(III)/H₂O₂. *Chemosphere* **1999**, 39, 2693.

CHAPTER 7 – EXPERIMENTAL DESIGN TO OPTIMIZE THE OXIDATION OF ORANGE II DYE SOLUTION USING A CLAY-BASED FENTON-LIKE CATALYST^{*}

Abstract

In this work an experimental design methodology was applied to optimize the degradation of an Orange II (OII) solution, while minimizing also the leaching of iron from the catalyst support in a heterogeneous Fenton-like process. The independent variables considered were the temperature, H₂O₂ concentration and catalyst (iron-impregnated pillared saponite clay) load. The multivariate experimental design allowed developing empiric quadratic models for dye degradation, TOC removal and iron leaching after 1, 2, 3 and 4 h of reaction, which were adequate to predict responses in all the range of experimental conditions used. Data obtained revealed that the heterogeneous Fenton-like process is promising for degradation of the studied azo dye. Actually, after 4 hours oxidation color removals near 100% and TOC reductions of at least 65% were experimentally achieved, when the temperature was 40 °C or higher. Iron leaching was also quite small after 4 hours oxidation (in the range 0.7-5.0 %), pointing for a good stability of the catalyst. Besides, the optimal conditions depend on the response factor considered, being advisable to use less-aggressive conditions if responses are taken at longer reaction times. Particularly temperature, but also catalyst concentration, were found out to be the main parameters affecting all the responses (dye degradation, TOC removal and iron leaching), whereas the effect of initial H₂O₂ concentration was found out to be negligible. Finally, the process was optimized considering the three responses simultaneously, allowing defining optimal regions for the significant process variables (temperature and catalyst dose in the slurry batch reactor).

^{*} Adapted from: Ramirez, J. H.; Lampinen, M.; Vicente, M. A.; Costa, C. A.; Madeira, L. M. *Industrial & Engineering Chemistry Research* **2008**, 47, 284.

7.1 Introduction

The oxidation with Fenton's reagent, in either homogeneous or heterogeneous processes, and the advantages of using the latter have been described in the previous chapters, being noteworthy the use of pillared clays because of their particular properties and structures as well as their abundance and low cost.

In the Fenton-like processes, several process variables are involved that affect process efficiency (e.g. pH, temperature, oxidant and catalyst concentrations, etc.). Therefore, process optimization is not straightforward. Although many researchers have usually only focused on the single-factor-at-a-time approach, studying the effect of each experimental parameter on the process performance while keeping all other conditions constant, this approach does not take into account cross-effects from the factors considered, is time consuming and leads to a poor optimization result. When a multifactor system is present, it is more appropriate to employ statistically-based optimization strategies to achieve such goal, with the minimum number of experiments [1-2]. Indeed, an alternative to the above-mentioned strategy is the experimental design approach, which implies the use of statistical tools that allow the simultaneous change of several variables (multivariate analysis) [3].

This study concerns the degradation of the non-biodegradable azo dye orange II (OII) by heterogeneous Fenton's reagent, using as catalyst a pillared clay impregnated with iron (III) acetylacetonate (one of the best samples tested in chapter 5). It is also a main goal of the present work to find the optimum conditions to maximize both color and total organic carbon (TOC) removal, while minimizing the iron loss from the support, and so a design of experiments (DOE) tool will be used.

7.2 Materials and Methods

7.2.1 Catalyst Preparation and Characterization

The catalyst used was a pillared clay (support) impregnated with Fe(III) acetylacetonate, which synthesis has been reported in detail in chapter 2. Iron content of the catalyst prepared was experimentally found to be 26.2 wt. %, the elemental analyses being performed with the microanalysis system coupled to a SEM apparatus (*cf.* section 2.5.1).

7.2.2 Oxidation Runs

All the experiments were conducted in a jacketed glass batch reactor, with a capacity of 1.2 L. More detail about the equipment and reagents used are shown in chapter 2. A reaction volume of 1L with a dye concentration of 1×10^{-4} M (corresponding to a total organic carbon, TOC, content of 19.2 mg/L) was used in every experiment, which is in the range of azo dyes' concentrations usually found in industrial waste streams (between 10 and 50 mg/L) [4].

All of the runs were carried out at pH 3, which was chosen based on the results shown in chapter 5. Along the reaction, the solution pH kept almost unchangeable (± 0.1), which is certainly related to the low concentration of the OII solution used. All experiments were run at least up to 4 h.

For TOC and Fe analysis, samples were withdrawn from the reactor every hour. Used sample volume was 15 mL, and reaction was stopped as described in chapter 2.

The H_2O_2 concentration was determined by a spectrophotometric analysis using the potassium titanium (IV) oxalate method [5].

7.3 Results and Discussion

As above-mentioned, several variables affect the heterogeneous dye oxidation and mineralization efficiency, namely the pH, temperature, hydrogen peroxide concentration and catalyst load, for a given dye concentration. Therefore, the use of a four factor experimental design becomes too heavy when considering the number of runs to be performed [3]. For that reason, and on the basis of the results obtained in chapter 5, the pH was kept constant. Therein, an optimal pH of 3 was found, which is in agreement with most papers reviewed [6-8] that mention the most favourable pH being between 3.0 and 3.5. The analysis of the effect of temperature, catalyst and hydrogen peroxide concentration on the catalytic performance is based on the experiments proposed by the design of experiments, as mentioned below. Nevertheless, two blank experiments were first performed to observe the H_2O_2 and the catalyst effect independently. When an experiment was carried out with a 6×10^{-3} M H_2O_2 concentration and without a catalyst, the color removal was less than 5% after 4 h of reaction. Compared with the results shown below, this performance is almost negligible, proving that although H_2O_2 has some oxidation ability (oxidation potential

of 1.78 V) [9], much more powerful oxidising species have to be formed to initiate the process, breaking down the dye molecules – mainly the hydroxyl radical ($HO^\bullet$ - 2.80 V), with smaller contribution of others (e.g. $HO_2^\bullet$ - 1.70 V) [9]. Likewise, with 91.5 mg/L of catalyst and absence of H_2O_2 the color removal was $< 1\%$ after 4 h, meaning that dye adsorption is negligible. Both experiments were performed at 30 °C and pH 3.

Before proceeding, it is worth noting that it was previously found that the process is essentially heterogeneous, not homogeneous (*cf.* chapter 5). Actually, although the homogeneous contribution due to leached iron from the support cannot be neglected, its contribution to the overall performance is in most conditions minor.

In the following section the effect of the main parameters is briefly discussed, aiming mainly to provide a better insight of the transient evolution of process performance (histories of the three responses), using some of the experiments performed in the DOE, which is analysed in detail afterwards.

7.3.1 *Effect of Operating Conditions on Catalytic Activity*

7.3.1.1 Temperature Effect

From Fig. 7.1A it can be seen that the reaction temperature has an important effect on the dye degradation transient curves. Total color removal can be reached in less than 30 minutes when working at a temperature of 73.6 °C (Run 10, described below), but at lower temperatures the process slows down significantly. This kind of effect was expected, since it is known that kinetic constants (either for radicals productions or for iron regeneration) have exponential dependency with reaction temperature (Arrhenius law), and has also been reported by other authors [10]. For TOC removal (Fig. 7.1B) the same kind of effect can be seen as for dye degradation. Temperature increase leads to better TOC removal but the difference between temperatures of 40 °C and 73.6 °C is not as significant as it was observed for color removal. This is probably due to the fact that H_2O_2 decomposes into oxygen and water at high temperatures (*cf.* Figure A1 of appendix I) affecting mineralization of all of the organics, which proceed more slowly than OII degradation. In addition, when the temperature increases the iron loss also increases (*cf.* Fig. 7.1C), a similar behaviour to that found previously in chapter 6 and by other authors [11].

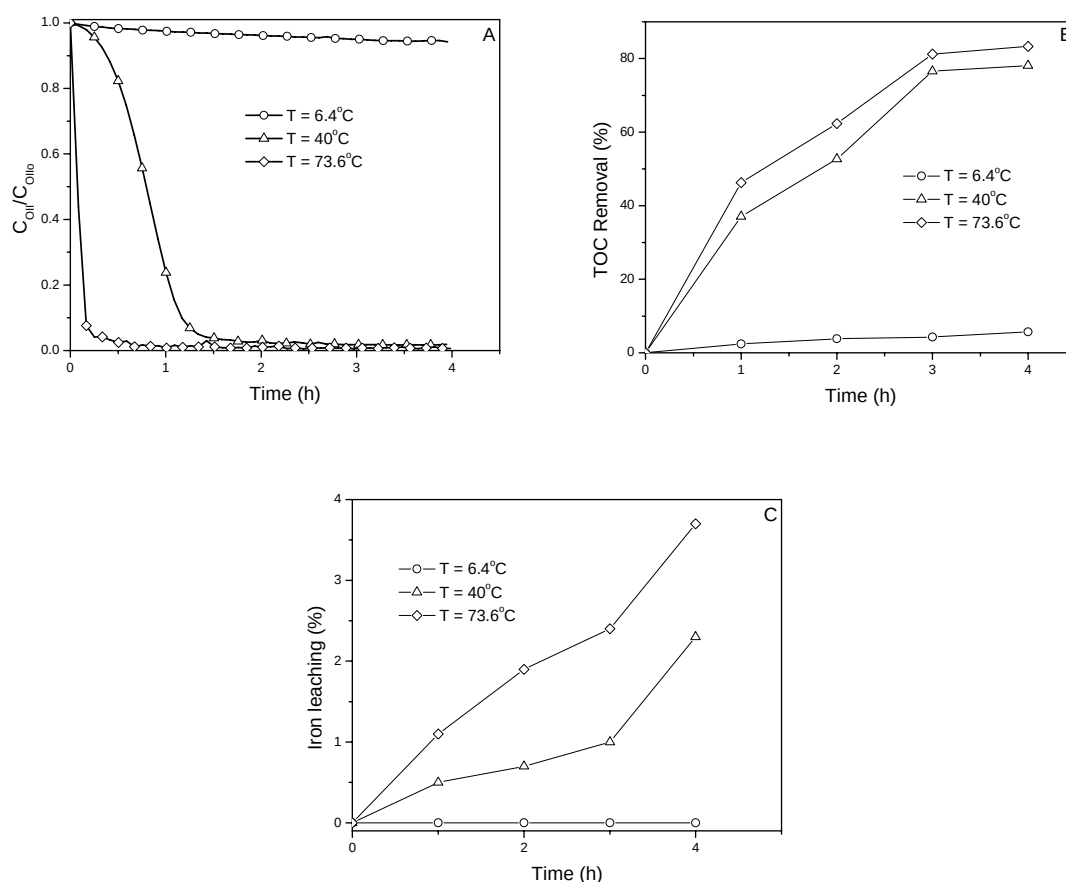


Fig. 7.1 – Temperature effect on: (A) dye degradation (B) mineralization and (C) iron loss.

$$C_{\text{catalyst}} = 70 \text{ mg/L}, C_{H_2O_2} = 1.3 \times 10^{-2} \text{ M}.$$

7.3.1.2 Catalyst Concentration Effect

The effect of the catalyst concentration on the dye degradation histories is shown in Fig. 7.2. It can be seen that the catalyst load affects positively the dye degradation rate, as expected, because more radicals are produced, thus leading to a faster color removal. It is also noteworthy that after three hours the concentration of dye is the same, and practically null, for all catalyst loads (in the conditions tested). In terms of TOC removal, 70 mg/L of catalyst leads to better results as compared to catalyst loads of 19.5 and 120.5 mg/L, which provide similar TOC removals after 3 or 4 hours of oxidation. This indicates that after a certain point the catalyst load has a detrimental effect in the mineralization degree, what can be explained by the formation of iron complexes (iron + organics) when excess amounts of catalyst are present, and other authors have also found this kind of behaviour with heterogeneous systems [12,13]. The scavenging of hydroxyl radicals (reaction (7.1)) might also explain this

kind of effect [14], although other undesirable reactions between iron and other radicals could also be mentioned [14-16]:



Finally, in terms of percentage of iron lost from the solid, referred to the total Fe initially incorporated, Fig. 7.2C shows that differences are small, i.e., the percentage of iron that has been leached out depends only slightly on the catalyst concentration employed in the catalytic runs. It seems however that higher percentages of Fe are lost from the clay support when smaller catalyst doses are used.

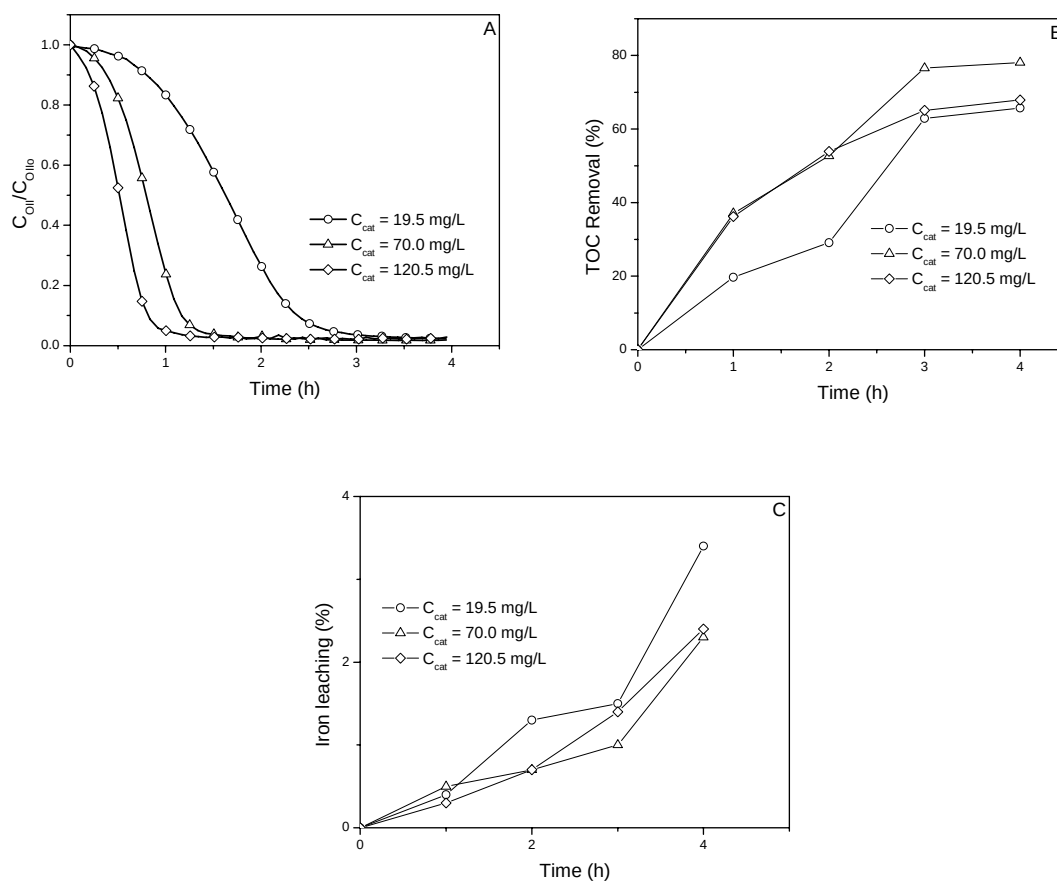


Fig. 7.2 – Catalyst concentration effect on: (A) dye degradation (B) mineralization and (C) iron loss. $T = 40^\circ C$, $C_{H_2O_2} = 1.3 \times 10^{-2} M$, $pH = 3$.

7.3.1.3 Hydrogen Peroxide Effect

The effect of the hydrogen peroxide was analysed by varying its initial concentration in a wide range, between 1.2×10^{-3} and 2.5×10^{-3} M. According to Feng *et al.* [17], 42 mol of H_2O_2 are theoretically needed to completely degrade 1 mol of the dye ($C_{16}H_{11}N_2NaO_4S + 42H_2O_2 \rightarrow 16CO_2 + 46H_2O + 2HNO_3 + NaHSO_4$). Based on this, one can easily conclude that the concentrations employed are between 0.29 and 5.9 (molar ratio) of the overall stoichiometry for the complete mineralization of the OII solution used. The H_2O_2 concentration effect is shown in Fig. 7.3, where it can be seen that the amount of H_2O_2 has a negligible influence on the dye degradation and also quite small in TOC removal and iron lost. The reason why color removal does not increase when increasing H_2O_2 concentration is possible due to the fact that at higher oxidant concentrations the scavenging of $HO^\bullet$ radicals will occur, as expressed by reaction (7.5). This way, there is a competition of H_2O_2 and OII for the $HO^\bullet$ radicals through parallel undesired reactions. Although other radicals ($HO_2^\bullet$) are produced, their oxidation potential is much smaller than that of the $HO^\bullet$ species [9]. It is noteworthy that some authors suggest that the influence of hydrogen peroxide depends on the nature of the organic compounds present in the reaction medium, the oxidation of some being hydrogen peroxide independent [13].



Another explanation for the observed effect is that H_2O_2 is not the only source of oxidant species. This can be inferred from the fact that for a concentration of 1.2×10^{-3} M, which represents 29% of the stoichiometric dose for the mineralization of the dye, one can observe a 75% removal of TOC (Fig. 7.3B). To evaluate the possible effect of dissolved oxygen, its concentration was markedly decreased (by bubbling N_2 through the reaction mixture). Although catalytic activity was affected, pointing for a role of dissolved oxygen as oxidant, the decrease was not too significant (TOC elimination was only ca. 10% smaller). This suggests that iron redox reactions might also have a role in the oxidation process, as suggested by other authors [14].

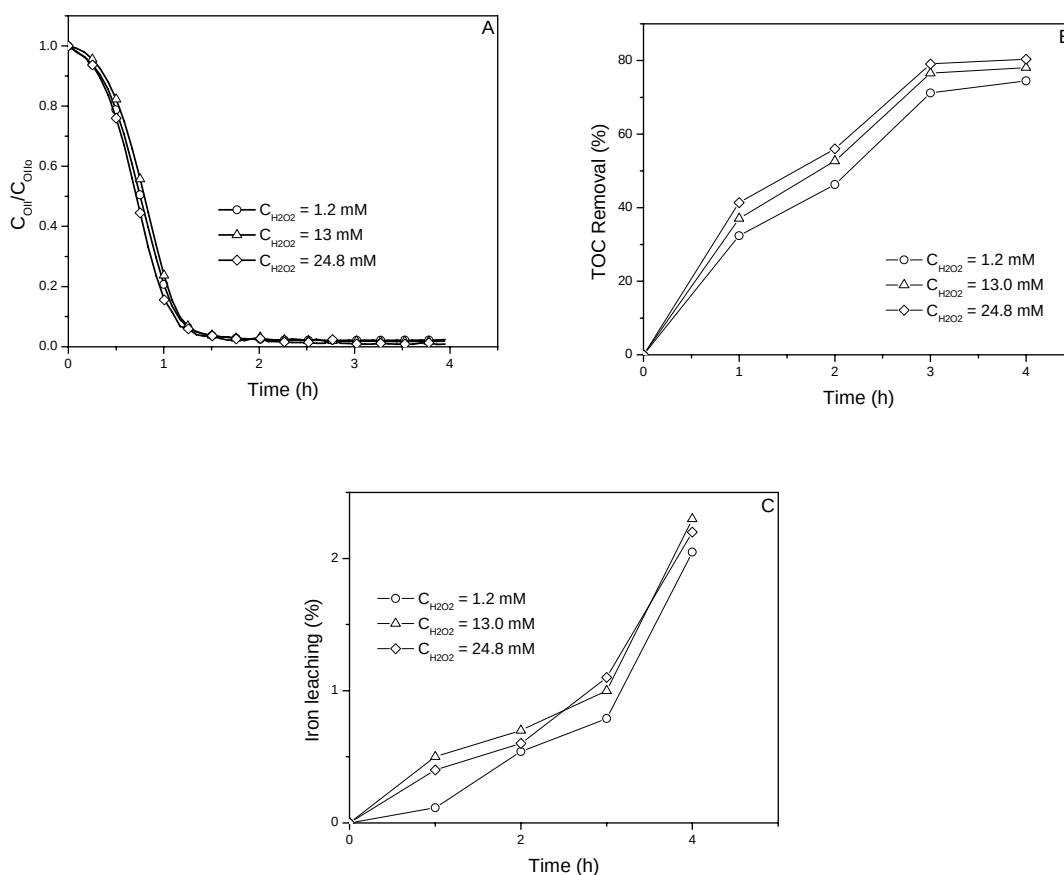


Fig. 7.3 – Hydrogen peroxide concentration effect on: (A) dye degradation (B) mineralization and (C) iron loss. $T = 40$ °C, $C_{catalyst} = 70$ mg/L, $pH = 3$.

The effect of H_2O_2 concentration on iron leaching is almost negligible. In the previous chapters of this dissertation, part IV, it was also found that there is no relationship between iron leaching and the hydrogen peroxide concentration, either when using a clay (chapter 5) or carbon (chapter 6) as Fe support. Similar conclusions were observed by Melero *et al.* [11] using nanocomposite $Fe_2O_3/SBA-15$ as catalyst.

7.3.2 Design of Experiments

The central composite design or CCD is the most popular class of response surface design methodologies used for fitting second-order models in design of experiments (DOE) [3]. The CCD was used in this work, considering the minimum and maximum levels for temperature (20–60 °C), H_2O_2 concentration (6×10^{-3} – 2×10^{-2} M) and catalyst concentration (40–100 mg/L) (*cf.* Table 7.1). It is noteworthy that the ranges considered for the three studied independent variables were chosen based on the

previous experiments reported in chapter 5. Table 7.1 shows the description of the experimental ranges and the relationship between codified and real values. Low and high levels are denoted by (-1) and (+1), respectively, and the central points as (0). The methodology (CCD) used requires that experiments outside the experimental range previously defined should be performed to allow prediction of the response functions outside the cubic domain (denoted as ± 1.682). Because the different factors (natural variables) present different units, they are given in the form of the dimensionless coded variables to permit comparison between them. The transformation is made on the basis of the following equation [3]:

$$X_{ij} = \frac{U_{ij} - U_j^o}{\Delta U_j} \quad (7.6)$$

where X_{ij} is the value of the independent coded variable j in experiment i ; U_{ij} is the value of the natural variable j in experiment i ; U_j^o is the value of the natural variable j in the centre of the domain of interest, which corresponds to $X_j = 0$; and ΔU_j is the variation of the natural variable j corresponding to a variation of the coded variable j equal to +1.

Table 7.1 – Levels of the independent variables used in the experimental design.

Variable	Level				
	-1.682	-1	0	+1	+1.682
T (°C)	6.4	20	40	60	73.6
$C_{H_2O_2}$ (M)	1.2×10^{-3}	6.0×10^{-3}	1.3×10^{-2}	2.0×10^{-2}	2.5×10^{-2}
$C_{catalyst}$ (mg/L)	19.5	40	70	100	120.5

Assuming a second-order polynomial model, at least 17 experiments must be carried out to solve the matrix, for which statistical software JMP 501 was used. Those 17 experiments required are described in Table 7.2. The run corresponding to the central point was repeated three times (runs 11, 13 and 17 in Table 7.2) to check the reproducibility and evaluate the experimental error of the results obtained in the DOE.

Table 7.2 – Codified and experimental values of the runs performed in the experimental design.

Run n°	Codified values			Experimental values		
	Temperature (X ₁)	C _{H₂O₂} (X ₂)	C _{catalyst} (X ₃)	Temperature (°C)	C _{H₂O₂} (M)	C _{catalyst} (mg/L)
1	0	-1.682	0	40	1.2×10 ⁻³	70
2	+1	-1	+1	60	6.0×10 ⁻³	100
3	-1.682	0	0	6.4	1.3×10 ⁻²	70
4	0	0	-1.682	40	1.3×10 ⁻²	19.5
5	+1	-1	-1	60	6.0×10 ⁻³	40
6	-1	-1	+1	20	6.0×10 ⁻³	100
7	0	1.682	0	40	2.5×10 ⁻²	70
8	-1	+1	+1	20	2.0×10 ⁻²	100
9	0	0	1.682	40	1.3×10 ⁻²	120.5
10	1.682	0	0	73.6	1.3×10 ⁻²	70
11	0	0	0	40	1.3×10 ⁻²	70
12	+1	+1	-1	60	2.0×10 ⁻²	40
13	0	0	0	40	1.3×10 ⁻²	70
14	+1	+1	+1	60	2.0×10 ⁻²	100
15	-1	-1	-1	20	6.0×10 ⁻³	40
16	-1	+1	-1	20	2.0×10 ⁻²	40
17	0	0	0	40	1.3×10 ⁻²	70

Each response can be described by an empirical second-order model, adequate for predicting them in the space domain analyzed,

$$Y = a_o + \sum_{j=1}^n a_j X_j + \sum_{j=1}^n a_{jj} X_j^2 + \sum_{i>j}^n \sum_{j=1}^n a_{ji} X_j X_i \quad (7.7)$$

where Y is the response factor or objective function (dependent variable); X_j is the coded independent variable related to parameter j (which, in the present case, varies between 1 and 3); a_o is the intercept term, a constant that corresponds to the response when X_j is zero for each factor; a_1 determines the influence of temperature in the response factor; a_2 is the influence of peroxide concentration; and a_3 is the catalyst concentration effect. Finally, a_{12} , a_{13} , and a_{23} are the interaction effects, while a_{11} , a_{22} ,

and a_{33} can be regarded as curve “shape” parameters. The method of least squares is used to estimate the parameters in the interpolating polynomials.

As above-mentioned, the objective functions to maximise are both the color and TOC removal (to evaluate the catalyst activity), and the objective function to minimize is the iron loss (to evaluate the catalyst stability). These are the response factors which we will call Y_1 , Y_2 and Y_3 , respectively. The 17 experiments indicated in Table 7.2 were then performed in a random order to minimise systematic errors, with experimental data collected every hour (*cf.* Tables A1 and A2 in appendix I), and the response factors evaluated.

The probability values (P value) from the analysis of variance for models Y_1 , Y_2 and Y_3 were then determined (*cf.* appendix I, Tables A3 to A14). The calculation procedure is made by the statistical software JMP to get the values of each column in such tables, the definition of each can be found in most statistics books or relevant literature [3]. Briefly, the analysis of variance allows to conclude that the quadratic models developed are statistically consistent (for a 95% confidence level) and therefore appropriate for predicting all the responses considered, i.e., Y_1 , Y_2 and Y_3 for 1, 2, 3 and 4 h of reaction ($p < 0.05$). Moreover, the determination coefficients (R^2), which will be also included in the inspection of the agreement between the experimental data and the mathematical model, are always above 0.89, indicating that the model can explain at least 89% of the objective function variations. Finally, in the analysis of variance the F values are in all cases higher than the value from Fisher tables ($F_{9,7} = 3.80$, for a 95% confidence level), meaning that the variations in the responses are associated to the model, not to random variations.

The coefficients of the quadratic model in the polynomial expression (*cf.* Eq. (7.7)) were calculated by multiple nonlinear regression analysis, using the above-mentioned DOE software. In the cases where the influence of one factor on the objective function is significant, the corresponding probability (P) value is small (test t of Student). If the P value is larger than 0.05, the confidence level of this factor is below 95%. Therefore, when the P value was equal or higher than 0.05 (see appendix I - Tables A15 to A26), the associated variable, quadratic effect or first-order interaction was ignored and was not expressed in the reduced model, as usual [2,3], resulting in the regression equations shown below (Eqs. (7.8)-(7.19)). In such equations, obtained values are in percentage, and the terms between parentheses describe the error associated to each coefficient of the equation.

1h:

$$Y_1 = 74.23(\pm 12.13) + 39.25(\pm 5.70)X_1 \quad (7.8)$$

$$Y_2 = 41.03(\pm 4.86) + 18.47(\pm 2.28)X_1 - 6.45(\pm 2.51)X_1^2 \quad (7.9)$$

$$Y_3 = 0.40(\pm 0.06) + 0.33(\pm 0.03)X_1 - 0.08(\pm 0.03)X_3 \quad (7.10)$$

2h:

$$Y_1 = 99.64(\pm 10.41) + 37.10(\pm 4.89)X_1 - 21.27(\pm 5.38)X_1^2 \quad (7.11)$$

$$Y_2 = 55.60(\pm 4.67) + 22.55(\pm 2.19)X_1 + 6.49(\pm 2.19)X_3 - 8.83(\pm 2.41)X_1^2 - 5.85(\pm 2.41)X_3^2 \quad (7.12)$$

$$Y_3 = 0.64(\pm 0.14) + 0.48(\pm 0.07)X_1 - 0.16(\pm 0.07)X_3 \quad (7.13)$$

3h:

$$Y_1 = 99.71(\pm 8.01) + 32.08(\pm 3.76)X_1 - 20.34(\pm 4.13)X_1^2 \quad (7.14)$$

$$Y_2 = 76.28(\pm 4.82) + 24.04(\pm 2.26)X_1 + 6.11(\pm 2.26)X_3 - 13.34(\pm 2.49)X_1^2 \quad (7.15)$$

$$Y_3 = 1.07(\pm 0.28) + 0.95(\pm 0.13)X_1 \quad (7.16)$$

4h:

$$Y_1 = 99.37(\pm 6.08) + 25.65(\pm 2.85)X_1 + 8.00(\pm 2.85)X_3 - 13.64(\pm 3.73)X_1X_3 - 18.06(\pm 3.14)X_1^2 \quad (7.17)$$

$$Y_2 = 78.20(\pm 5.60) + 19.79(\pm 2.63)X_1 + 7.88(\pm 2.63)X_3 - 11.31(\pm 3.44)X_1X_3 - 11.60(\pm 2.90)X_1^2 \quad (7.18)$$

$$Y_3 = 2.24(\pm 0.25) + 1.47(\pm 0.12)X_1 - 0.37(\pm 0.12)X_3 - 0.37(\pm 0.16)X_1X_3 \quad (7.19)$$

The results show that the P values for X_1 (temperature) are always smaller than 0.05, meaning that this factor is extremely important in affecting the three responses (Y_1 , Y_2 and Y_3) at any reaction time. In addition, the X_3 factor (catalyst concentration) presents a lower impact than the temperature, in agreement with the results shown above (Figs. 7.1 and 7.2), and in some cases it has no effect at all. Finally, it is worth nothing that the H_2O_2 concentration (X_2) does not affect any response factor, in any

case, corroborating the results shown in Fig. 7.3. The interactive influence of X_1X_3 is observed only after 4 hours of reaction, while the other interactions are not significant. Particularly remarkable are the first-order temperature coefficients, showing its critical influence mainly in the dye degradation and TOC removal, similarly to what was recently found by Melero *et al.* [11] during catalytic wet peroxide mineralization of phenol.

Figure 7.4 shows the predictions of these equations as compared to the experimental data, for 2 and 4 hours of reaction. For other reaction times, the reader can consult the appendix I (Fig. A2). From these figures it can be seen that the values predicted by the second-order models agree reasonably with the experimental data, even though the simplified equations (7.8) to (7.19) have been used. Obviously, the data will fit better when the complete equation, obtained from JMP software, is used. The figures also show that the TOC removal data are smaller than the OII elimination, showing clearly that OII oxidation takes place in multiple steps and results in several by-products rather than CO_2 only. The graphics also put into evidence some problems with the polynomial fit in wide ranges, resulting in some cases in values above 100% or below 0%. As recently pointed by Pérez-Moya *et al.* [18], the failure of this methodological approach is often noticed, due to the wide range of results that the model must cover. In their and in this work, two different tendencies are clearly appearing: from one side, a group of experiments for which the degradation is almost complete, and another set for which the system conditions do not allow further degradation. Multivariate analysis leads to interesting qualitative results (regarding the weight of the different variables in the system response, the trend of this response, and the interaction among the variables). However, the assumption of a polynomial model is questionable from the quantitative point of view [18]. Even so, the models presented herein showed statistical consistency.

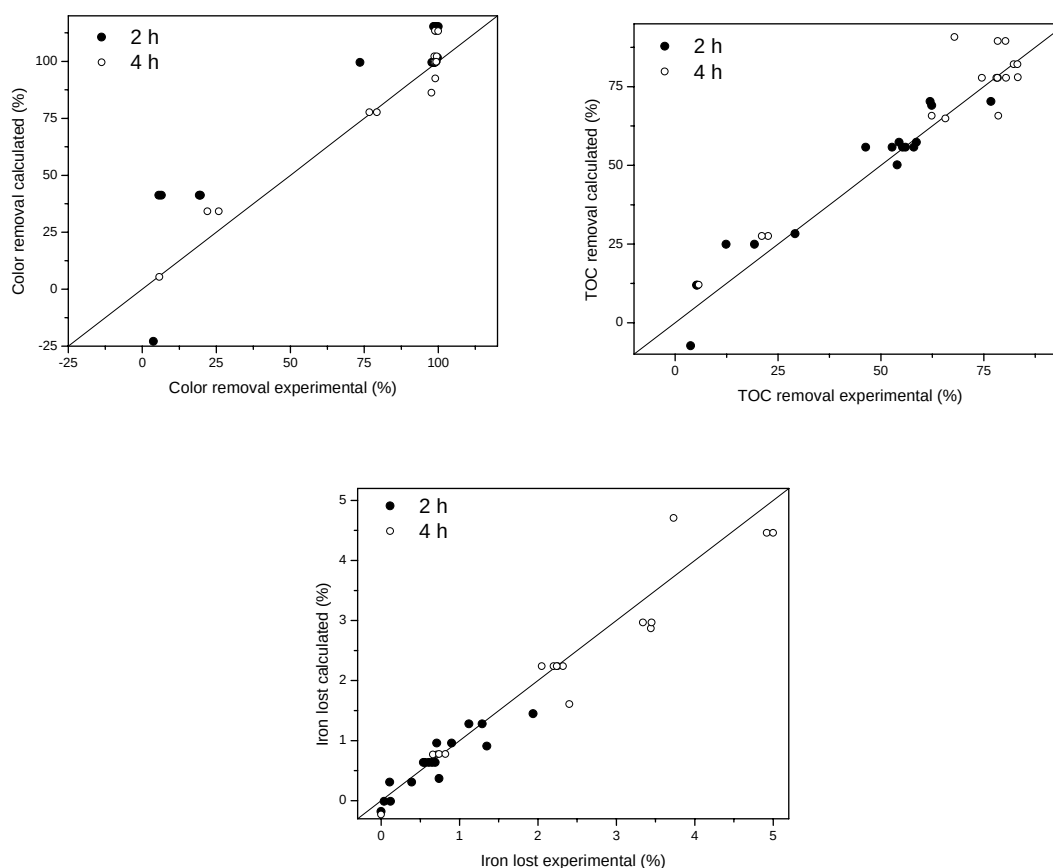


Fig. 7.4 – Experimental and calculated results of the experimental design for OII oxidation after 2 h and 4 h.

Table 7.3 shows the average errors between the experimental data and the model predictions. The values are reasonably acceptable, being evident that the maximum errors occur usually for short reaction times, but for longer times the errors decrease considerably, especially in what concerns prediction of color removal (Y_1).

Table 7.3 – Average absolute differences for the responses (in %).

Time (h)	Y_1	Y_2	Y_3
1	19.7	8.5	0.1
2	14.1	5.2	0.2
3	9.0	7.7	0.4
4	5.5	5.4	0.3

Following the models established for each response, one can represent graphically the corresponding surfaces, at different reaction times. In most cases, all the

cross- and quadratic effects are negative, suggesting that optimum values must exist for each parameter, as shown below.

7.3.2.1 Color Removal

Figure 7.5 shows the response surfaces generated by equations (7.8), (7.11), (7.14) and (7.17). As it can be seen, there is an important influence of the temperature, allowing a relevant increase in the color removal, regardless of the amount of catalyst and hydrogen peroxide concentration employed. This enhancement is more pronounced for initial reaction times, being color removal just temperature dependent for the first 3 h of reaction. In Fig 7.5A, after 1 h of reaction, the trend of the color removal with the temperature is linear, and at ca. 50 °C one can obtain almost 100% dye degradation, using the minimum catalyst load (19.5 mg/L) and hydrogen peroxide concentration (1.2×10^{-3} M). Figures 7.5B and 7.5C show a similar trend (a quadratic behaviour), and in these cases using a temperature of approximately 56 °C the color removal is 100%. Finally, after 4 hours of reaction, several local optimum points exist for the oxidation of Orange II; this means that there is a large region on Fig. 7.5D where the color removal is nearly 100%. Because of the energy cost, this optimum point can be chosen in a medium temperature range (e.g. 46 °C), which requires a medium consumption of catalyst (70 mg/L) and minimum H_2O_2 concentration (1.2×10^{-3} M). On the other hand, if one selects a lower C_{catalyst} , the rate of reaction is slower and in this case we need a higher temperature to obtain complete dye degradation (see Fig. 7.5D). Finally, if initial C_{catalyst} is higher the rate of reaction is higher as well and then operation can be done at a lower temperature. Concluding, as it can be seen from Fig. 7.5, the color removal depends almost exclusively on the temperature, which means that minimal amounts of H_2O_2 and catalyst concentrations could be used. Besides, the optimal temperature decreases along time (*cf.* Table 7.4), implying that for longer reaction times one do not need so critical conditions because thermal decomposition of H_2O_2 (into water and oxygen) might be more important [11], as mentioned above (see also Figure A1 in appendix I).

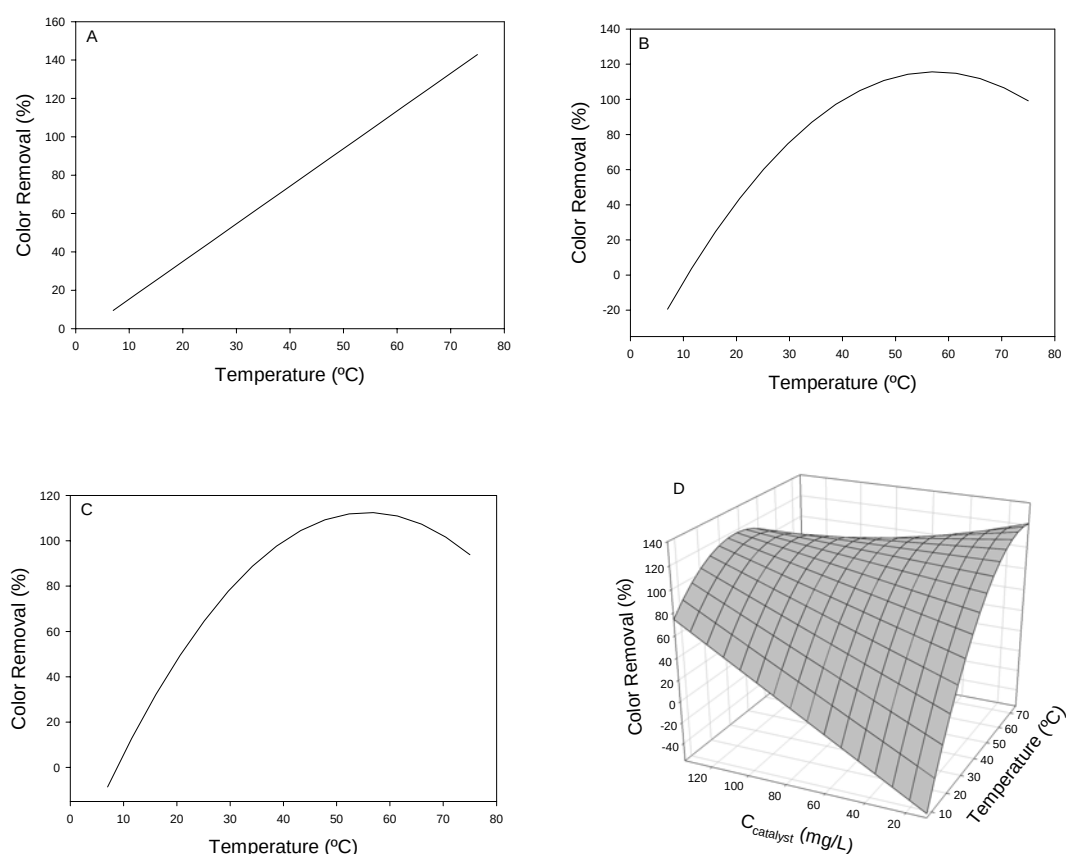


Fig. 7.5 – Effect of process variables in the color removal at different reaction times: (A) 1 h, (B) 2 h, (C) 3 h, (D) 4 h.

Table 7.4 – Optimum values for the maximum color removal.

Time (h)	Color Removal (%) **	T (°C)	C_{catalyst} (mg/L) *	$C_{\text{H}_2\text{O}_2}$ (M) *
1	100	73.6	-	-
2	100	57.4	-	-
3	100	55.8	-	-
4	100	46.0 ***	70.0	-

* In some cases, several parameters do not affect the response (denoted as “-”).

** Model predicts values that are meaningless, i.e. not physically possible.

*** Other temperatures exist which provide also complete OII removal.

7.3.2.2 Total Organic Carbon Removal

Equations (7.9), (7.12), (7.15) and (7.18) are graphically represented in Fig. 7.6, where one can see a significant influence of the temperature, and in some cases of the catalyst concentration, in the TOC removal. The catalyst effect increases when the time increases; this means that for short times the principal variable that affects the TOC

removal is the temperature, while for long times the catalyst concentration becomes also important. Thus, in such circumstances the presence of catalyst to improve reaction performance, that is, to obtain a good mineralization degree, is required. Although the highest TOC conversions are achieved at relatively high temperatures, there is an optimal point for TOC removal (*cf.* Table 7.5), which is due to the predominant non-efficient peroxide decomposition. In some cases one can also see an optimum in terms of catalyst concentration, what can be due to a loss of radicals by the above-mentioned scavenging reactions in the presence of excess of iron (Eqs. (7.1)-(7.4)) and the formation of iron complexes with organics.

Table 7.5 – Optimum values for the maximum TOC removal.

Time (h)	TOC Removal (%)	T (°C)	C _{catalyst} (mg/L)	C _{H₂O₂} (M) *
1	54.3	68.7	-	-
2	72.2	65.8	86.6	-
3	97.5	58.0	120.5	-
4	90.9	40.2**	120.5**	-

* In some cases, several parameters do not affect the response (denoted as “-”).

** Other conditions exist which provide higher TOC reductions.

For 4 h of reaction time, Fig. 7.6D, it is clear that there is a wide range of conditions at which high mineralization degrees can be reached (>90%), similarly to what was previously found in terms of color removal (Fig. 7.5D). Therefore, and for the same reasons above-mentioned, one could select a temperature not too high that provides good TOC reduction performances, even though the optimum (97.4% mineralization degree) is reached at the maximum temperature. Such conditions were included in the last row of Table 7.5, which also shows the optimal values of temperature and catalyst concentration for the maximal TOC removal at smaller times. It is worth noting that, once again, when the time increases the optimal temperature decreases. Mineralization of the organic matter requires more drastic conditions than simple color removal, and therefore the catalyst concentration plays an important role in TOC reduction.

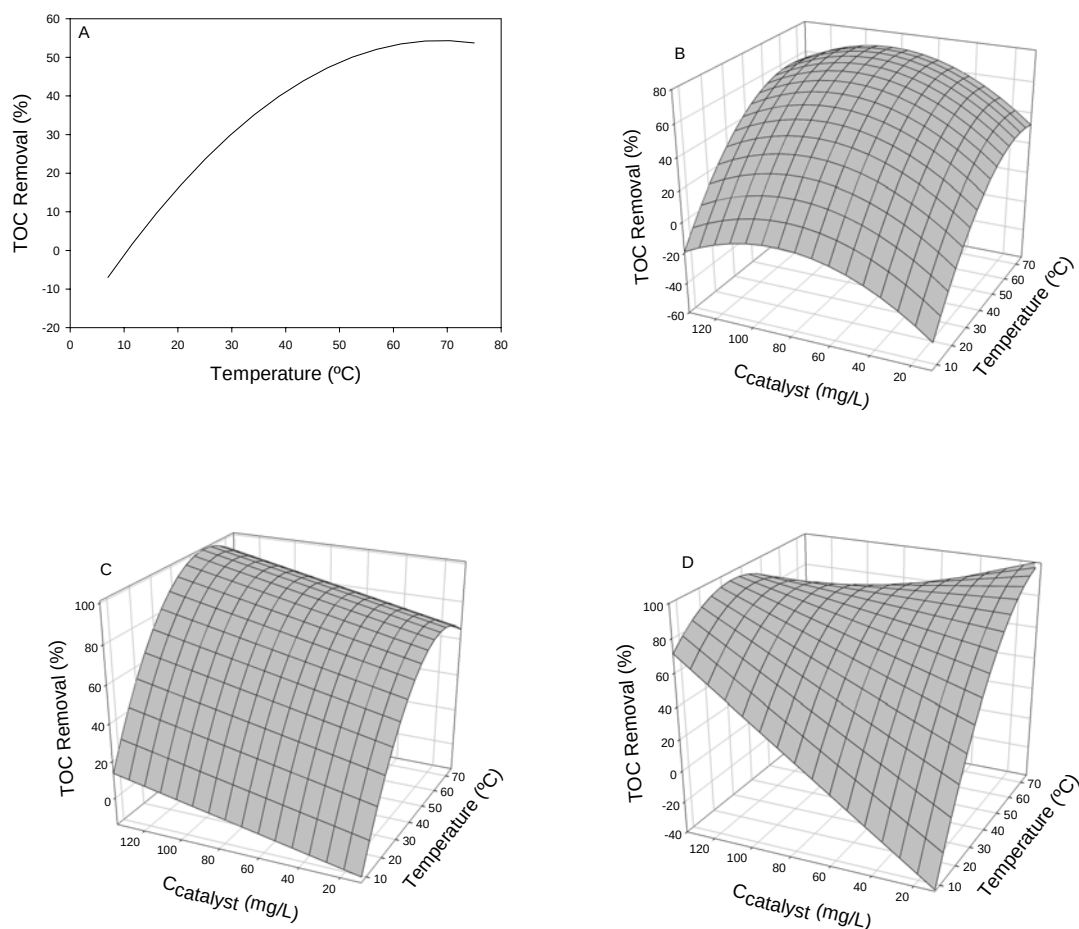


Fig. 7.6 – Effect of the process variables in the TOC removal at different reaction times: (A) 1 h, (B) 2 h, (C) 3 h, (D) 4 h.

7.3.2.3 Iron Leaching

Another important parameter to quantify is the iron leaching, which should ideally be null to provide long-term stability. This is particularly interesting from the practical point of view due to the possibility of using these catalysts for a longer operation time. Figure 7.7 shows the iron loss from the support after 1, 2, 3 and 4 hours of reaction. In all cases it is remarkable the importance of the temperature, although in some the catalyst concentration is also relevant.

It is obvious that the concentration of iron in solution increases with the amount of catalyst within the reactor (data not shown), but in relative terms the percentage of iron leached out from the support behaves differently. That's why a negative effect is observed (*cf.* Fig. 7.7 and corresponding equations).

Figure 7.7 also shows that in terms of iron loss, the process is again practically independent of the H_2O_2 concentration, and in all cases is clear that when working at lower temperatures the iron loss is negligible, thus providing long-term stability for the catalyst.

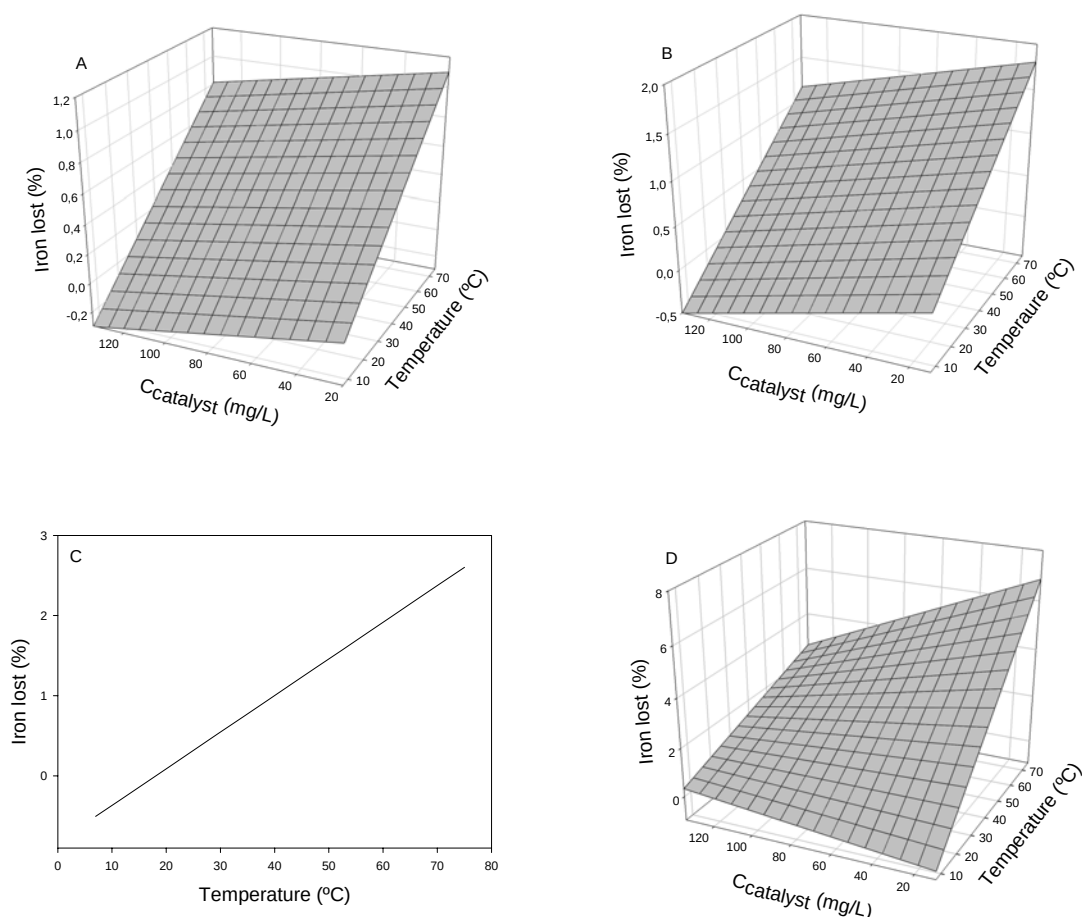


Fig. 7.7 – Effect of the process variables in the iron loss at different reaction times: (A) 1 h, (B) 2 h, (C) 3 h, (D) 4 h.

7.3.3 Optimum Conditions

Figure 7.8 shows the optimal ranges for the variables affecting the process performance (temperature and catalyst concentration) that verify constraints imposed to optimize, at the same time, the three responses at different reaction times. Obviously, the constraints imposed (e.g. $Y_1 > 99\%$, $Y_2 > 60\%$ and $Y_3 < 1.0\%$ for 1h) are more drastic for longer reaction times. In addition, the ranges defined in the graph would become much

wider if less demanding conditions would be imposed. However, this would not affect the conclusions draw.

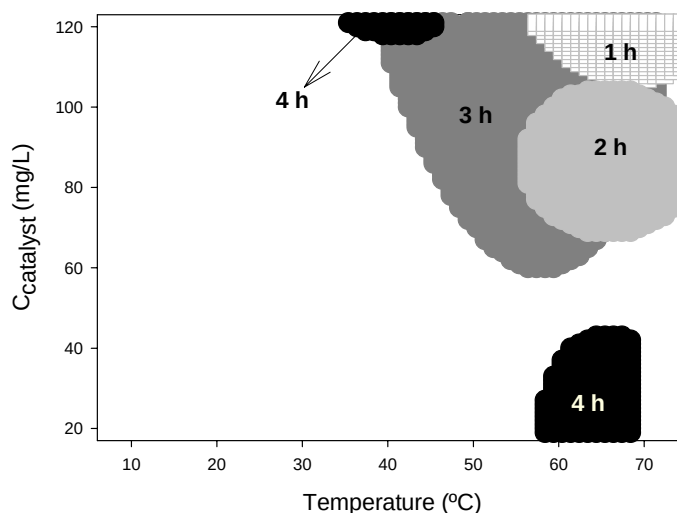


Fig. 7.8 – Optimal ranges of temperature and catalyst concentration that simultaneously satisfy the three responses (Y_1 , Y_2 and Y_3). For 1 h: $Y_1 > 99\%$, $Y_2 > 60\%$, $Y_3 < 1\%$; for 2 h: $Y_1 > 99\%$, $Y_2 > 70\%$, $Y_3 < 2\%$, for 3 h: $Y_1 > 99\%$, $Y_2 > 85\%$, $Y_3 < 3\%$ and for 4 h: $Y_1 > 99\%$, $Y_2 > 90\%$, $Y_3 < 4\%$.

From Fig. 7.8 it is evident that as the time of reaction increases, the range of optimal conditions shifts towards less drastic values (smaller catalyst concentrations and temperatures). For instance, after 1 h of reaction, temperatures above 57 °C and catalyst concentrations higher than 110 mg/L have to be employed (for color removal above 99%, TOC > 60% and iron loss < 1.0%). After 3 h, high color and TOC removals (> 99% and > 85%, respectively) with minimum iron loss (< 3.0%) are possible to obtain in a wide range of conditions (40 °C < T < 71 °C and 60 mg/L < C_{catalyst} < 120.5 mg/L), which are not so demanding as for 1 h because oxidation does not need to proceed so fast. The graph obtained is quite interesting and allows one to select the conditions to adopt, depending on the performances aimed. Obviously, when a wide range is possible for certain objectives, it is more reasonable to use mild temperatures and catalyst concentrations because of the associated costs.

Finally, it is worth noting that after 4 h of reaction it is possible to use either high temperatures with low catalyst concentrations or high catalyst concentrations with lower temperatures to reach very good performances. This is a particular behaviour, but was up to a certain point expected. If highly demanding conditions are employed, reaction rate is fast and good performances are reached at short reaction times. However, the thermal decomposition of hydrogen peroxide and/or the above-mentioned

parallel and undesired reactions associated with high catalyst doses become evident at longer reaction times. So, high values of both variables should not be simultaneously employed, unless one aims to optimize the process having in mind to operate the batch reactor during short times.

7.4 Conclusions

- A central composite design was used to evaluate the effect of temperature, catalyst load and H_2O_2 concentration in the heterogeneous Fenton-like oxidation of the dye Orange II, at pH 3. As catalyst, a Fe-impregnated pillared clay (saponite) was used. Color removal (Y_1) and TOC removal (Y_2) were the responses to maximize after 1, 2, 3 and 4 hours oxidation. Response factor considered to minimize was the iron leaching (Y_3), at the same times of oxidation. It was found out that the second-order models developed for these responses are statistically consistent and fit quite reasonably the experimental data in the ranges studied. The temperature and catalyst load were found out to be the main parameters affecting color and TOC removal and iron leaching, but the effect of temperature was in most cases the predominant one. The effect of initial H_2O_2 concentration was null in all the responses.
- In the dye oxidation process, the relevant independent variables (temperature and catalyst dose) usually have a positive effect, but up to a certain point. In some circumstances, excessive temperatures revealed to be detrimental, attributed to the thermal decomposition of hydrogen peroxide. For the catalyst concentration, a similar effect was recorded, which might be due to undesirable parallel reactions (scavenging of radicals by the catalyst and formation of Fe complexes with organics). These tradeoffs lead to a more complex process optimization.
- The optimal values of temperature and catalyst concentration that should be employed to optimize the process (taking into account simultaneously all the responses) depend on the time of reaction; this means that for short reaction times more drastic conditions are necessary than for longer operation times, at which one cannot use simultaneously high temperatures and high catalyst doses. For instance, and according to the reduced model predictions, high color (>99%) and TOC (>90%) removals with small iron loss from the support (<4%)

can be reached in 4 hours when using either high temperatures ($57\text{ }^{\circ}\text{C} < T < 68\text{ }^{\circ}\text{C}$) with low catalyst concentrations ($C_{\text{catalyst}} < 43\text{ mg/L}$) or low temperatures $35\text{ }^{\circ}\text{C} < T < 45\text{ }^{\circ}\text{C}$ with high catalyst load ($C_{\text{catalyst}} > 118\text{ mg/L}$).

- The Fe-doped pillared clay catalyst employed showed to be very promising as it simultaneously exhibits high activity (high dye oxidation and mineralization rates) with very good stability (low iron leaching, yielding Fe concentrations always below 2 ppm).

References

1. Oliveira, R.; Almeida, M. F.; Santos, L.; Madeira, L. M. Experimental design of 2,4-Dichlorophenol oxidation by Fenton's reaction. *Industrial and Engineering Chemistry Research* **2006**, 45, 1266.
2. Wang, H. C.; Wu, C. Y.; Chung, C. C.; Lai, M. H.; Chung, T. W. Analysis of parameters and interaction between parameters in preparation of uniform silicon dioxide nanoparticles using response surface methodology. *Industrial and Engineering Chemistry Research* **2006**, 45, 8043.
3. Montgomery, C. Design and analysis of experiments, 5th ed.; John Wiley & Sons: New York, **2001**.
4. Ong, S. A.; Toorisaka, E.; Hirata, M.; Hano, T. Decolorization of Azo Dye (Orange II) in a Sequential UASB–SBR System. *Separation and Purification Technology* **2005**, 42, 297.
5. Sellers, R.M. Spectrophotometric Determination of hydrogen peroxide using potassium titanium (IV) oxalate. *Analysts* **1980**, 150, 950.
6. Pera-Titus, M.; García-Molina, V.; Baños, M. A.; Giménez, J.; Esplugas, S. Degradation of chlorophenols by means of advanced oxidation processes: A general review. *Applied Catalysis B: Environmental* **2003**, 47, 219.
7. Guo, J.; Al-Dahhan, M. Catalytic wet oxidation of phenol by hydrogen peroxide over pillared clay catalyst. *Industrial and Engineering Chemistry Research* **2003**, 42, 2450.
8. Feng, J.; Hua, X.; Yue, P. L.; Zhu, H. Y.; Lu, G. Q. A Novel laponite clay-based Fe nanocomposite and its photo-catalytic activity in photo-assisted degradation of Orange II. *Chemical Engineering Science* **2003**, 58, 679.
9. Bigda, R. J. Consider Fenton chemistry for wastewater treatment. *Chemical Engineering and Processing* **1995**, 91, 62.
10. Yuranova, T.; Enea, O.; Mielczarski, E.; Mielczarski, J.; Albers, P.; Kiwi, J. Fenton immobilized photo-assisted catalysis through a Fe/C structured fabric. *Applied Catalysis B: Environmental* **2004**, 49, 39.

11. Melero, J. A.; Calleja, G.; Martínez, F.; Molina, R.; Pariente, M. I. Nanocomposite $\text{Fe}_2\text{O}_3/\text{SBA-15}$: An efficient and stable catalyst for the catalytic wet peroxidation of phenolic aqueous solutions. *Chemical Engineering Journal* **2007**, 131, 245.
12. Zazo, J.A.; Casas, J.A.; Mohedano, A.F.; Rodriguez, J.J. Catalytic Wet peroxide oxidation of phenol with a Fe/Active carbon catalyst. *Applied Catalysis B: Environmental* **2006**, 65, 261.
13. Molina, R.; Martínez, F.; Melero, J. A.; Bremner, D. H.; Chakinala, A. G. Mineralization of phenol by a heterogeneous ultrasound/ $\text{Fe-SBA-15}/\text{H}_2\text{O}_2$ process: Multivariate study by factorial design of experiments. *Applied Catalysis B: Environmental* **2006**, 66, 198.
14. Walling, C. Fenton's reagent revisited. *Accounts of Chemical Research* **1975**, 8, 125.
15. De Laat, J.; Le, T. G. Effects of chloride ions on the iron(III)-catalyzed decomposition of hydrogen peroxide and on the efficiency of the Fenton-like oxidation process. *Applied Catalysis B: Environmental* **2006**, 66, 137.
16. Carriazo, J.; Guélou, E.; Barrault, J.; Tatibouet, J. M.; Molina, R.; Moreno, S. Synthesis of pillared clays containing Al, Al-Fe or Al-Ce-Fe from a bentonite: Characterization and catalytic activity. *Catalysis Today* **2005**, 107–108, 126.
17. Feng, J.; Hu, X.; Yue, P. L. Effect of initial solution pH on the degradation of Orange II using clay-based Fe nanocomposites as heterogeneous photo-Fenton catalyst. *Water Research* **2006**, 40, 641.
18. Pérez-Moya, M.; Graells, M.; Del Valle, L. J.; Centelles, E.; Mansilla, H. D. Fenton and photo-Fenton degradation of 2-Chlorophenol: Multivariate analysis and toxicity monitoring. *Catalysis Today* **2007**, 124, 163.

PART V

CONCLUSIONS AND SUGGESTIONS FOR FUTURE WORK

CHAPTER 8 – CONCLUSIONS AND SUGGESTIONS FOR FUTURE WORK

8.1 Conclusions

The main conclusions of this thesis are divided in two sections; in the first one are mentioned those concerning the homogeneous system, where statistical tools were used and kinetics studies performed to have a better insight of the Fenton's process. In the second section are reported the main conclusions concerning a deep study about the preparation, characterization and use of different kind of heterogeneous catalysts, prepared using two types of supports (clay and activated carbons).

8.1.1 Homogeneous System

In the first stage of this thesis a statistical tool (Design of Experiments - DOE) was used to find optimal conditions regarding Orange II (OII) decolourisation (Y_1) and mineralization (Y_2) in a batch reactor, after 2 hours of reaction. For that a central composite design was used and the effect of temperature, H_2O_2 concentration and $\text{Fe}^{+2}:\text{H}_2\text{O}_2$ ratio was evaluated, at $\text{pH} = 3$. It was found that the second order models developed for both Y_1 and Y_2 fit quite reasonably the experimental data in the ranges studied, the models being subsequently used for the process optimization.

Such study allowed also better understanding the process kinetics. Actually, the dye is decomposed in a two-stage reaction, being degraded very quickly in the first 5-10 min ($\text{Fe}^{2+}/\text{H}_2\text{O}_2$ or Fenton stage), with a slower reaction rate later on ($\text{Fe}^{3+}/\text{H}_2\text{O}_2$ or Fenton-like stage). Data obtained revealed that the Fenton's reagent is promising for degradation of the dye, as decolourisation efficiencies clearly above 99% and mineralization degrees higher than 70% were reached in 2 h. However, to achieve these results operating conditions must be carefully selected, for what the DOE tool revealed to be quite effective. Indeed, the surface response plots of the models showed that for both responses (color and TOC removal) optimum values for the process variables exist. Besides, though TOC reduction requires aggressive conditions, decolourisation does not require high stringency. The hydrogen peroxide concentration and the temperature showed to be the variables with higher impact into the final performance.

In particular, temperature turns into a key parameter when it is desirable to reduce reagents consumption.

The kinetic studies then performed showed that the Orange II degradation by means of Fenton's reagent highly depends on the operating conditions, i.e. reagents dosage, temperature, pH and time of reaction (batch reactor) or residence time (continuous reactor). Besides, the experiments carried out in the batch reactor evidenced that the optimum pH is around 3 and the negative effect of Cl^- , a species usually found in textile dyeing wastewaters that acts as scavenger of the hydroxyl radicals. It was also observed the positive effect of increasing the reaction temperature, H_2O_2 or Fe^{2+} concentrations, and the negative effect of increasing dye concentrations, trends that were corroborated with experiments in a continuous stirred tank reactor (CSTR).

A phenomenological approach that makes use of an empirical power-law equation was adopted to deduce the OII degradation rate law. Accordingly, for the longer and last stage (the Fenton-like one) a pseudo steady-state approach (regarding hydroxyl radicals concentration) was employed to deduce the reaction rate, which was found to be of the first-order type with respect to OII concentration. The dependence of the apparent kinetic constant on the initial operating conditions was then deduced, leading to a power-law rate equation with Arrhenius dependency (apparent activation energy of 58.1 kJ mol^{-1}). This rate equation revealed to be somewhat useful to predict dye concentration histories in the batch reactor and the steady-state dye conversion in the CSTR, both type of experiments being performed in a wide range of experimental conditions. Actually, the range of the CSTR runs was extended using higher iron concentrations in the feed, and even in such conditions it is remarkable the ability of the model to predict data in a range of conversion values from 2 to 97 %, without further fitting parameters.

8.1.2 *Heterogeneous System*

In this section, the main conclusions concerning the studies in which the heterogeneous catalysts have been employed are reported. Firstly, twelve supported Fe-saponite catalysts have been prepared, by means of the incipient wet impregnation method, using a pillared clay support and four salts of Fe precursors at different Fe loads. The characterization of the catalysts showed that the decomposition of the precursors gave rise to solids that present laminar structure, with active phases of Fe

highly dispersed on the support, and reasonably high specific surfaces (in most of the cases with values comprised between 130 and 170 m²/g), characteristics that make them potentially good catalysts for oxidation in the Fenton-like process. This was confirmed experimentally; all the catalysts revealed to be quite active in the Orange II oxidation, requiring clay concentrations much below those usually found in the literature (typically around 1 g/L).

The effects of the nature of the catalyst's precursor, hydrogen peroxide concentration, temperature and pH of the reaction medium were then analyzed, putting into evidence a high degradation of OII and of the intermediary oxidised compounds. Actually, 99% discoloration and 91% of mineralization were reached (after 4 h of reaction), using the catalyst prepared from Fe(II) oxalate with 17.0 wt.% of Fe and in the following reaction conditions: T = 70°C, pH = 3 and $C_{H_2O_2} = 6 \times 10^{-3}$ M. However, good performances with high selectivity to CO₂ and H₂O were also reached at significantly lower temperatures (30 °C).

All the catalysts tested exhibited not only good catalytic activity but also a reasonable small iron leaching (below the EU directives values), indicating that the active phases are strongly fixed to the support. This characteristic makes possible the Fe-saponite catalysts to have long-term stability, without generating iron hydroxide sludges. Actually, a reasonable stable catalytic performance was noticed in consecutive reaction cycles, although a small minor deactivation was recorded, possibly due to some iron leaching. Nevertheless, it was confirmed that the process is predominantly heterogeneous.

In a second stage of this part, two different carbon samples have been employed as supports for the iron particles: i) a classical activated carbon (sample H) and ii) a carbon aerogel (sample M). Both materials can be considered as examples of the classical and new carbon materials form. Moreover, they present different characteristics that could determine their applications, differing largely in the porosity: while carbon H is a macro and microporous material, carbon M has a large mesopore volume.

The catalysts have been prepared through wet impregnation using ferrous acetate and their physical-chemical characterisation showed that Fe is more dispersed in the case of support M because of the large mesopore volume and external surface area of this sample. This may be one reason for the better catalytic behaviour of this sample in

the Fenton-like process. Indeed, the Fe-doped aerogel showed better catalytic performances, mainly higher reaction rates, than those reached with the activated carbon catalyst.

Differently to what happened in experiments performed using the clay-based catalyst, wherein the dye adsorption is almost negligible (in the conditions of the catalytic runs), with both activated carbon-based samples OII elimination is due to two processes – adsorption and catalysis – being however the last the most relevant one. Once again, although a homogeneous catalytic contribution exists, as a consequence of the iron leaching, the process is essentially heterogeneous.

The carbon-based catalysts studied have however an important limitation for their use in industrial practice – the high iron loss from the supports. To overcome this, it is advisable the preparation of carbon aerogels in which iron is within the aerogel structure, as described below. Nevertheless, even in the worst conditions tested the iron concentration in solution is always below the European Union guidelines (< 2 ppm) and the catalytic performances reached are quite good, with mineralization degrees as high as 90%, for catalysts concentration not higher than 0.20 to 0.30 g/L. Decolourisation might however be almost complete. As a consequence of the leaching phenomenon but also due to catalyst deactivation, activity decay in the M-Fe sample was noticed in consecutive cycles. The performance of the carbon-based catalysts was then compared with the clay ones, which revealed to be more promising (from the catalytic point of view), and were therefore used in the following chapter.

In the last chapter of part IV, a central composite design methodology was once again used to evaluate the effect of the experimental variables (at constant pH and dye concentration) in the heterogeneous Fenton-like process. As catalyst, a Fe-impregnated pillared clay (saponite) was used. The responses considered were the color removal (Y_1), the TOC removal (Y_2) and the iron leaching (Y_3), after 1, 2, 3 and 4 hours of oxidation. It was found out that the second-order models developed for these responses are statistically consistent and fit quite reasonably the experimental data in the ranges studied.

In the dye oxidation process, the relevant independent variables (temperature and catalyst dose) usually have a positive effect, but up to a certain point. In some circumstances, excessive temperatures revealed to be detrimental, attributed to the experimentally observed thermal decomposition of hydrogen peroxide. For the catalyst concentration a similar effect was recorded, which might be due to undesirable parallel

reactions (scavenging of radicals by the catalyst and formation of Fe complexes with organics). These tradeoffs lead to a more complex process optimization, a task that becomes facilitated when using the “black-box” type tools employed. Actually, it is in these somewhat complex systems that the usefulness of DOE methodologies becomes more evident, allowing also to reduce the efforts put in terms of experimentation.

The optimal values of temperature and catalyst concentration that should be employed to optimize the process (taking into account simultaneously all the responses) depend on the time of reaction; this means that for short reaction times more drastic conditions are necessary than for longer operation times, at which one cannot use simultaneously high temperatures and high catalyst doses, due to the undesirable effects above-mentioned. Finally, it is worth of noting that the Fe-doped pillared clay catalyst employed showed to be very promising as it simultaneously exhibits high activity (high dye oxidation and mineralization rates) with very good chemical stability (low iron leaching, yielding Fe concentrations always below 2 ppm).

8.2 Future Work

8.2.1 Homogeneous System

Many topics related to the Fenton and Fenton-like systems remain to be explored. For instance, the mechanism and quantification of the elementary rate constants (and associated activation energies) that describe the Fenton's process are still incomplete, possibly due to the complexity of the reaction scheme. For this reason, a deep study of the Fenton's reagent mechanism could be very useful, and for that it is suggested to perform a preliminary analysis in the absence of organic compounds (i.e., with only iron salts and hydrogen peroxide). Then, the system complexity could be increased, with addition of target organic compounds (e.g. Orange II) and identification (and quantification) of reaction intermediates, iron complexes and other species. For example, reactive species such as superoxide (O_2^-) or perhydroxyl radical ($HO_2^\bullet$) are also produced in the Fenton's system, and they can be involved in reactions that transform the parent pollutants or reaction intermediates. A better understanding of this pathway could increase the applicability of the Fenton's system for wastewater treatment and remediation, and could help in process (particularly reactors) design and optimization.

Another topic that needs to be further examined is to evaluate the feasibility of implementing the homogeneous system in practice. In this topic, several issues should be addressed, namely the identification of the oxidation by-products and evaluation of their potential toxicity. Besides, and even though the process can be implemented as a final treatment for simple color removal of treated effluents, it is well known that the Fenton's reagent can increase organics biodegradability, and so its integration with a biological degradation unit is also of importance. In particular, it is suggested the Fenton's process integration with a sequencing batch reactor (SBR) for real wastewaters treatment, for instance containing Orange II or other dyes. That integrated process could then be optimized with the type of DOE tools used in this dissertation.

8.2.2 *Heterogeneous System*

In terms of the heterogeneous systems tested, and particularly in the case of the carbon-based samples, it was observed an important disadvantage from the viewpoint of practical implementation: the deactivation of the catalyst. In this sense it is important to try to reduce the lost of iron from the support, what could be done by synthesizing carbon aerogels with the metal catalyst being incorporated within their structure (i.e., by doping and not impregnation of the support). This would certainly decrease the leaching phenomenon, but would possibly turn the solid into a much less active material (once the metal would be less accessible towards the H_2O_2 molecules). To overcome that, one could use a photo-Fenton process, because radiation would accelerate the radicals generation.

Still in what concerns the carbon aerogel catalysts, it is important to better comprehend the reasons for their deactivation, which are not only due to loss of metal from the support (as remarked in chapter 6). Obviously, it would be also of utmost importance to comprehend how to restore the catalyst activity, for what a deep characterization of the used materials is mandatory.

Future work should also be addressed in trying to establish a phenomenological model for the heterogeneous system(s). Nevertheless, due to the process complexity a lumped model is certainly easier to deal with, and equally important for process/reactor design. This model should be tested for batch experiments and, if possible, validated in a continuous slurry reactor (e.g., CSTR), as performed in chapter 4 for the homogeneous system. For practical applications the continuous reactor could be instead

of the fixed-bed type, and consequently the model should be extended, in particular taking into account flow hydrodynamics and internal/external mass transfer resistances. In such case, the catalysts (carbon aerogels or clays) should be prepared as pellets or monoliths.

APPENDIX I

SUPPORTING INFORMATION

APPENDIX I – SUPPORTING INFORMATION FOR CHAPTER 7*

In this appendix it is presented the history of the hydrogen peroxide decomposition at different temperatures and the main results concerning chapter 7. In this concern, it is included the experimental results of the responses (color removal, TOC reduction and iron leaching) considered in the design of experiments at different times, as well as the analysis of variance for the model and for the responses, and finally the comparison between calculated and experimental results for 1 and 3 hours.

* *Adapted from:* Ramirez, J. H., Lampinen, M.; Vicente, M. A.; Costa, C. A.; Madeira, L. M: *Industrial & Engineering Chemistry Research* **2008**, 47, 284 (Supporting Information).

A.1 Thermal Decomposition of Hydrogen Peroxide

Figure A1 shows the transient evolution of the H_2O_2 concentration in a run carried out without catalyst. As expected, its decomposition is accelerated at higher temperatures, reaching values of 48% at 60 °C after 4h.

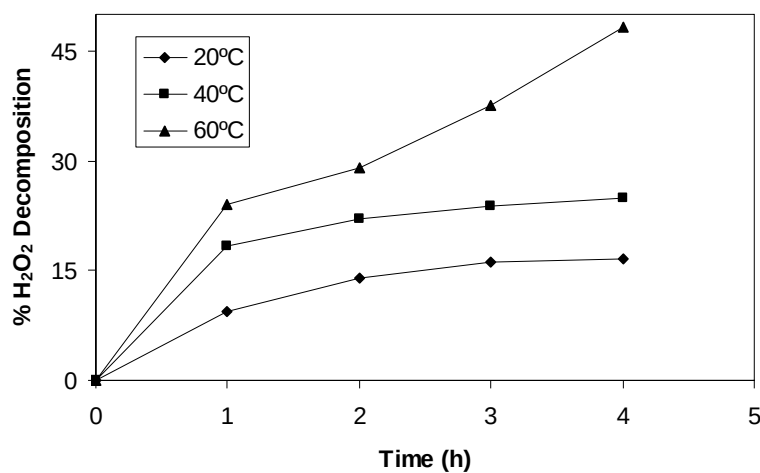


Figure A1 – Hydrogen peroxide decomposition along time for different temperatures.

$$C_{\text{H}_2\text{O}_2} = 1.3 \times 10^{-2} \text{ M, pH} = 3.0.$$

A.2 Design of Experiments – DOE

Tables A1 and A2 show the experimental results obtained in the DOE: OII discoloration (Y_1), TOC removal (Y_2) and iron loss (Y_3) for different times of reaction (1, 2, 3 and 4 h).

Table A1 – Experimental results of the DOE for OII oxidation, TOC removal and iron leaching for 1 and 2h of reaction time.

	1h			2h		
Run no.	Y ₁	Y ₂	Y ₃	Y ₁	Y ₂	Y ₃
1	65.3	32.5	0.11	98.7	46.3	0.54
2	98.0	65.7	0.47	98.7	76.7	0.71
3	2.5	2.4	0.00	3.8	3.8	0.00
4	16.6	19.7	0.35	73.6	29.1	1.35
5	98.5	40.6	0.90	99.3	54.4	1.12
6	6.9	4.2	0.00	19.3	12.4	0.12
7	84.3	41.4	0.40	98.9	56.0	0.65
8	6.8	6.8	0.00	19.7	19.3	0.04
9	94.4	36.2	0.28	98.6	53.9	0.74
10	97.8	46.3	1.13	99.7	62.3	1.94
11	75.9	37.1	0.51	97.9	52.7	0.69
12	99.4	41.7	0.85	100.0	58.6	1.29
13	69.1	40.0	0.32	98.3	55.3	0.56
14	98.5	46.5	0.59	98.4	62.0	0.90
15	2.1	3.4	0.00	5.6	5.3	0.11
16	2.9	1.6	0.22	6.5	5.2	0.39
17	76.2	45.5	0.37	98.5	58.0	0.61

The ANOVA (Analysis of Variance) for the model is presented in Tables A3 to A14. There, several parameters are shown: the degrees of freedom (DF), which total in our case is 16, the sum of squares, the mean of the squares, the *F* ratio that is the ratio between the mean square of the model and the mean square of the error, and finally the value of the probability for a confidence level of 95%.

Table A2 – Experimental results of the DOE for OII oxidation, TOC removal and iron leaching for 3 and 4h of reaction time.

Run no.	3h			4h		
	Y ₁	Y ₂	Y ₃	Y ₁	Y ₂	Y ₃
1	99.2	71.2	0.79	99.4	74.5	2.05
2	98.1	80.6	1.70	98.7	82.3	3.34
3	5.0	4.3	0.00	5.8	5.7	0.00
4	96.4	62.9	1.46	97.7	65.7	3.44
5	99.1	72.2	3.10	99.1	78.4	4.92
6	45.0	39.9	0.38	76.7	62.3	0.71
7	99.0	79.1	1.07	99.4	80.4	2.25
8	46.2	46.2	0.21	79.3	78.5	0.66
9	97.8	65.1	1.38	98.9	67.9	2.40
10	99.4	81.2	2.39	99.0	83.3	3.73
11	98.2	76.6	1.04	98.5	78.1	2.32
12	100.0	73.7	3.90	100.0	80.3	5.00
13	98.7	75.9	0.96	98.9	78.5	2.20
14	98.7	82.4	1.81	99.5	83.2	3.45
15	11.8	12.4	0.43	22.0	22.6	0.74
16	13.6	11.2	0.55	25.8	21.0	0.82
17	98.8	74.9	1.28	99.3	78.3	2.24

Table A3 – Analysis of model for Y₁ after 1 h of reaction.

Source	DF	sum of squares	mean square	F ratio	prob. > F
Model	9	24103.38	2678.15	6.04	0.014
Error	7	3102.62	443.23		
Total	16	27206.00			
R ² =	0.89				

Table A4 – Analysis of model for Y₂ after 1 h of reaction.

Source	DF	sum of squares	mean square	F ratio	prob. > F
Model	9	5709.22	634.36	8.91	0.004
Error	7	498.11	71.16		
Total	16	6207.33			
R ² =	0.92				

Table A5 – Analysis of model for Y₃ after 1 h of reaction.

Source	DF	Sum of squares	mean square	F ratio	prob. > <i>F</i>
Model	9	1.74	0.19	17.83	<0.001
Error	7	0.08	0.01		
Total	16	1.81			
R ² =	0.96				

Table A6 – Analysis of model for Y₁ after 2 h of reaction.

Source	DF	Sum of squares	mean square	F ratio	prob. > <i>F</i>
Model	9	24495.50	2721.72	8.33	0.005
Error	7	2285.98	326.57		
Total	16	26781.48			
R ² =	0.91				

Table A7 – Analysis of model for Y₂ after 2 h of reaction.

source	DF	sum of squares	mean square	F ratio	prob. > <i>F</i>
Model	9	8610.14	956.68	14.59	0.001
Error	7	459.12	65.59		
Total	16	9069.26			
R ² =	0.95				

Table A8 – Analysis of model for Y₃ after 2 h of reaction.

Source	DF	sum of squares	mean square	F ratio	prob. > <i>F</i>
Model	9	3.88	0.43	7.46	0.001
Error	7	0.40	0.06		
Total	16	4.29			
R ² =	0.91				

Table A9 – Analysis of model for Y₁ after 3 h of reaction.

Source	DF	sum of squares	mean square	F ratio	prob. > <i>F</i>
Model	9	19690.88	2187.88	11.33	0.002
Error	7	1352.10	193.16		
Total	16	21042.98			
R ² =	0.94				

Table A10 – Analysis of model for Y₂ after 3 h of reaction.

source	DF	sum of squares	mean square	F ratio	prob. > F
Model	9	10833.87	1203.76	17.23	0.001
Error	7	489.09	69.87		
Total	16	11322.96			
R ² =	0.96				

Table A11 – Analysis of model for Y₃ after 3 h of reaction.

source	DF	sum of squares	mean square	F ratio	prob. > F
Model	9	15.51	1.72	7.25	0.008
Error	7	1.66	0.24		
Total	16	17.17			
R ² =	0.96				

Table A12 – Analysis of model for Y₁ after 4 h of reaction.

source	DF	sum of squares	mean square	F ratio	prob. > F
Model	9	15305.61	1700.62	15.28	0.001
Error	7	779.03	111.29		
Total	16	16084.64			
R ² =	0.95				

Table A13 – Analysis of model for Y₂ after 4 h of reaction.

source	DF	sum of squares	mean square	F ratio	prob. > F
Model	9	9007.82	1000.87	10.59	0.003
Error	7	661.66	94.52		
Total	16	9669.48			
R ² =	0.93				

Table A14 – Analysis of model for Y₃ after 4 h of reaction.

source	DF	sum of squares	mean square	F ratio	prob. > F
Model	9	33.68	3.74	19.25	<0.001
Error	7	1.36	0.19		
Total	16	35.04			
R ² =	0.96				

In Tables A15 to A26 are shown the ANOVA data for each parameter in the equations (responses) at different times of reaction, which were once again obtained by the used DOE software (JMP 501). The parameters indicated in such tables are the coefficients (estimate) and the associated standard error, the t ratio (ratio between the estimate value and the standard error), and the probability value for a confidence level of 95%.

Table A15 – Analysis of variance for the response color removal (Y_1) after 1 h of reaction.

Term	Estimate	Std Error	t ratio	Prob
Intercept	74.23	12.13	6.12	<0.01
X_1	39.25	5.70	6.89	<0.01
X_2	2.49	5.70	0.44	0.67
X_3	10.12	5.70	1.78	0.12
$X_1 * X_2$	0.09	7.44	0.01	0.99
$X_1 * X_3$	-1.26	7.44	-0.17	0.87
$X_2 * X_3$	-0.16	7.44	-0.02	0.98
X_1^2	-10.05	6.27	-1.60	0.15
X_2^2	-1.33	6.27	-0.21	0.84
X_3^2	-8.15	6.27	-1.30	0.23

Table A16 – Analysis of variance for the response TOC removal (Y_2) after 1 h of reaction.

Term	Estimate	Std Error	t ratio	Prob
Intercept	41.03	4.86	8.44	<0.01
X_1	18.47	2.28	8.09	<0.01
X_2	-0.17	2.28	-0.07	0.94
X_3	4.66	2.28	2.04	0.08
$X_1 * X_2$	-2.38	2.98	-0.80	0.45
$X_1 * X_3$	2.99	2.98	1.00	0.35
$X_2 * X_3$	-1.98	2.98	-0.66	0.53
X_1^2	-6.45	2.51	-2.57	0.04
X_2^2	-2.01	2.51	-0.80	0.45
X_3^2	-5.17	2.51	-2.06	0.08

Table A17 – Analysis of variance for the response iron loss (Y_3) after 1 h of reaction.

Term	Estimate	Std Error	t ratio	Prob
Intercept	0.40	0.06	6.67	<0.01
X_1	0.33	0.03	11.68	<0.01
X_2	0.06	0.03	2.02	0.08
X_3	-0.08	0.03	-2.67	0.03
$X_1 * X_2$	-0.02	0.04	-0.51	0.63
$X_1 * X_3$	-0.06	0.04	-1.60	0.15
$X_2 * X_3$	-0.01	0.04	-0.17	0.87
X_1^2	0.06	0.03	1.89	0.10
X_2^2	-0.05	0.03	-1.64	0.14
X_3^2	-0.03	0.03	-0.96	0.37

Table A18 – Analysis of variance for the response color removal (Y_1) after 2 h of reaction.

Term	Estimate	Std Error	t ratio	Prob
Intercept	99.64	10.41	9.57	<0.01
X_1	37.10	4.89	7.59	<0.01
X_2	0.13	4.89	0.03	0.98
X_3	4.88	4.89	1.00	0.35
$X_1 * X_2$	-0.10	6.39	-0.02	0.99
$X_1 * X_3$	-3.63	6.39	-0.57	0.59
$X_2 * X_3$	-0.20	6.39	-0.03	0.98
X_1^2	-21.27	5.38	-3.95	0.01
X_2^2	-4.65	5.38	-0.86	0.42
X_3^2	-9.12	5.38	-1.69	0.13

Table A19 – Analysis of variance for the response TOC removal (Y_2) after 2 h of reaction.

Term	Estimate	Std Error	t ratio	Prob
Intercept	55.60	4.67	11.92	<0.01
X_1	22.55	2.19	10.29	<0.01
X_2	0.93	2.19	0.42	0.69
X_3	6.49	2.19	2.96	0.02
$X_1 * X_2$	-2.16	2.86	-0.75	0.48
$X_1 * X_3$	0.56	2.86	0.19	0.85
$X_2 * X_3$	-1.49	2.86	-0.52	0.62
X_1^2	-8.83	2.41	-3.66	0.01
X_2^2	-2.44	2.41	-1.01	0.34
X_3^2	-5.85	2.41	-2.42	0.04

Table A20 – Analysis of variance for the response iron loss (Y_3) after 2 h of reaction.

Term	Estimate	Std Error	t ratio	Prob
Intercept	0.64	0.14	4.61	<0.01
X_1	0.48	0.07	7.45	<0.01
X_2	0.05	0.07	0.84	0.43
X_3	-0.16	0.07	-2.44	0.04
$X_1 * X_2$	0.02	0.09	0.24	0.82
$X_1 * X_3$	-0.06	0.09	-0.68	0.52
$X_2 * X_3$	-0.04	0.09	-0.50	0.63
X_1^2	0.06	0.07	0.80	0.45
X_2^2	-0.08	0.07	-1.05	0.33
X_3^2	0.08	0.07	1.17	0.28

Table A21 – Analysis of variance for the response color removal (Y_1) after 3 h of reaction.

Term	Estimate	Std Error	t ratio	Prob
Intercept	99.71	8.01	12.45	<0.01
X_1	32.08	3.76	8.53	<0.01
X_2	0.30	3.76	0.08	0.94
X_3	4.82	3.76	1.28	0.24
$X_1 * X_2$	-0.19	4.91	-0.04	0.97
$X_1 * X_3$	-8.51	4.91	-1.73	0.13
$X_2 * X_3$	-0.11	4.91	-0.02	0.98
X_1^2	-20.34	4.13	-4.91	<0.01
X_2^2	-3.75	4.13	-0.91	0.39
X_3^2	-4.47	4.13	-1.08	0.32

Table A22 – Analysis of variance for the response TOC removal (Y_2) after 3 h of reaction.

Term	Estimate	Std Error	t ratio	Prob
Intercept	76.28	4.82	15.84	<0.01
X_1	24.04	2.26	10.63	<0.01
X_2	1.60	2.26	0.71	0.50
X_3	6.11	2.26	2.701	0.03
$X_1 * X_2$	-0.22	2.96	-0.071	0.94
$X_1 * X_3$	-5.67	2.96	-1.92	0.10
$X_2 * X_3$	0.96	2.96	0.32	0.76
X_1^2	-13.34	2.49	-5.36	<0.01
X_2^2	-1.87	2.49	-0.75	0.48
X_3^2	-5.81	2.49	-2.33	0.05

Table A23 – Analysis of variance for the response iron loss (Y_3) after 3 h of reaction

Term	Estimate	Std Error	t ratio	Prob
Intercept	1.07	0.28	3.82	0.01
X_1	0.95	0.13	7.19	<0.01
X_2	0.10	0.13	0.74	0.48
X_3	-0.29	0.13	-2.23	0.06
$X_1 * X_2$	0.12	0.17	0.70	0.51
$X_1 * X_3$	-0.39	0.17	-2.25	0.06
$X_2 * X_3$	-0.12	0.17	-0.71	0.50
X_1^2	0.11	0.15	0.74	0.48
X_2^2	0.01	0.15	0.10	0.93
X_3^2	0.19	0.15	1.29	0.24

Table A24 – Analysis of variance for the response color removal (Y_1) after 4 h of reaction

Term	Estimate	Std Error	t ratio	Prob
Intercept	99.37	6.08	16.35	<0.01
X_1	25.65	2.85	8.98	<0.01
X_2	0.59	2.85	0.21	0.84
X_3	8.00	2.85	2.80	0.03
$X_1 * X_2$	-0.59	3.73	-0.16	0.88
$X_1 * X_3$	-13.64	3.73	-3.66	0.01
$X_2 * X_3$	-0.16	3.73	-0.04	0.97
X_1^2	-18.06	3.14	-5.75	<0.01
X_2^2	-1.44	3.14	-0.46	0.66
X_3^2	-1.83	3.14	-0.58	0.58

Table A25 – Analysis of variance for the response TOC removal (Y_2) after 4 h of reaction

Term	Estimate	Std Error	t ratio	Prob
Intercept	78.20	5.60	13.96	<0.01
X_1	19.79	2.63	7.52	<0.01
X_2	2.00	2.63	0.76	0.47
X_3	7.88	2.63	3.00	0.02
$X_1 * X_2$	-1.48	3.44	-0.43	0.68
$X_1 * X_3$	-11.31	3.44	-3.29	0.01
$X_2 * X_3$	2.10	3.44	0.61	0.56
X_1^2	-11.60	2.90	-4.01	0.01
X_2^2	0.05	2.90	0.02	0.99
X_3^2	-3.71	2.90	-1.28	0.24

Table A26 – Analysis of variance for the response iron loss (Y_3) after 4 h of reaction

Term	Estimate	Std Error	t ratio	Prob
Intercept	2.24	0.25	8.83	<0.01
X_1	1.47	0.12	12.31	<0.01
X_2	0.04	0.12	0.34	0.74
X_3	-0.37	0.12	-3.11	0.02
$X_1 * X_2$	0.02	0.16	0.13	0.90
$X_1 * X_3$	-0.37	0.16	-2.36	0.05
$X_2 * X_3$	-0.01	0.16	-0.08	0.94
X_1^2	-0.11	0.13	-0.81	0.45
X_2^2	-0.01	0.13	-0.04	0.97
X_3^2	0.27	0.13	2.03	0.08

The comparison between experimental and calculated results, for 1 and 3 h hours of reaction, is plot in Figure A2.

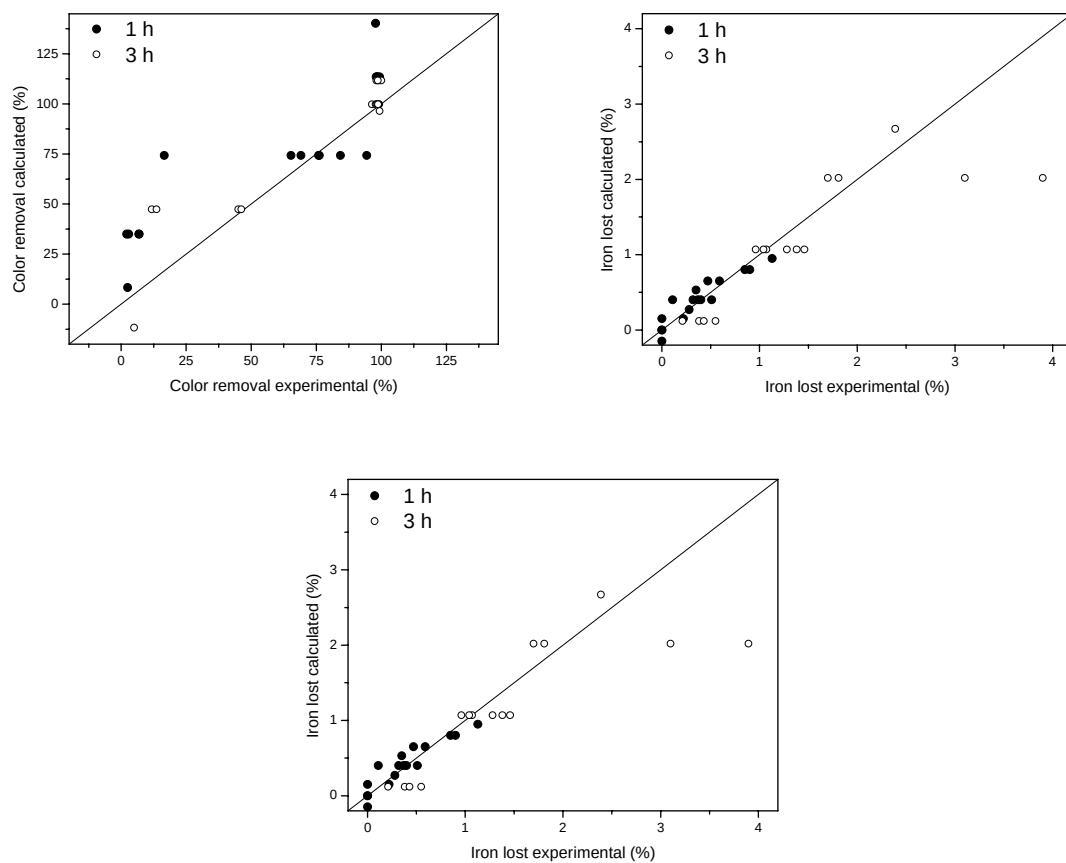


Fig. A2 – Experimental and calculated results of the experimental design for OII oxidation after 1 h and 3 h.

