



## DEGRADATION OF REACTIVE RED 120 AZO DYE IN AQUEOUS SOLUTIONS USING HOMOGENEOUS/HETEROGENEOUS IRON SYSTEMS

## DEGRADACIÓN DEL COLORANTE AZO ROJO REACTIVO 120 EN SOLUCIONES ACUOSAS USANDO SISTEMAS HOMOGÉNEOS/HETEROGÉNEOS DE HIERRO

J. Vergara-Sánchez<sup>1,2\*</sup>, J.P. Pérez-Orozco<sup>1,3</sup>, R. Suárez-Parra<sup>1</sup> and I. Hernández-Pérez<sup>4</sup>

<sup>1</sup>Departamento de Materiales Solares, Centro de Investigación en Energía de la UNAM, Priv. Xochicalco s/n, CP 62580, Temixco Morelos, México.

<sup>2</sup>Facultad de Ciencias Químicas e Ingeniería. Universidad Autónoma del Estado de Morelos. Av. Universidad 1001, Col Chamilpa, Cuernavaca, Mor. CP 62209. México.

<sup>3</sup>Instituto Tecnológico de Zacatepec, Departamento de Ingeniería Química y Bioquímica, Calzada Tecnológico No. 27, Col. Centro, CP 62780 Zacatepec, Morelos, México.

<sup>4</sup>Universidad Autónoma Metropolitana-A, Dpto. de Ciencias Básicas, Av. Sn. Pablo No. 180, CP 02200 México DF, México.

Received 2 of August 2011; Accepted 10 of December 2011

### Abstract

Advanced oxidation processes (AOPs) are the most attractive methods to degrade different organic pollutants. The AOPs have grown extensively because water quality control and regulations have become very strict in many countries. In this study, the dye reactive red 120 (RR-120) was considered for degradation using homogenous (Fenton and Photo Fenton) and heterogeneous (suspension of nanoparticles -NPs- of iron oxyhydroxides and NPs of iron oxyhydroxides supported on a mesoporous material SBA-15) process. The discoloration kinetic study of reactive red 120 solutions with a 100 mg/L concentration and pH ~3 was carried out, with hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>) as oxidant agent and different iron salts types (FeCl<sub>2</sub>, FeCl<sub>3</sub>, FeSO<sub>4</sub> and Fe<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>). The determined discoloration rate constants were higher for the homogeneous than those for heterogeneous catalytic processes. The RR-120 oxidation degree was measured by chemical oxygen demand (COD) with 90 percentages by the photo-Fenton process.

*Keywords:* nanoparticles, azo-dye, discoloration kinetic, oxyhydroxides, COD.

### Resumen

Los procesos avanzados de oxidación (PAOs) son los métodos más utilizados en la degradación de diferentes contaminantes orgánicos. Los PAOs han sido extensamente utilizados porque el control de la calidad del agua y los reglamentos han comenzado a ser muy estrictos en muchos países. En este estudio, se consideró el colorante reactivo rojo 120 (RR-120) para su degradación usando procesos homogéneos (Fenton y Foto-Fenton) y procesos heterogéneos (nanopartículas suspendidas- NPs- de oxihidróxidos de hierro y NPs de oxihidróxidos de hierro suspendidas sobre un material mesoporoso SBA-15). En el estudio de la cinética de decoloración del rojo reactivo 120 se utilizó una concentración de 100 mg/L, a pH ~ 3 utilizando como agente oxidante peróxido de hidrógeno (H<sub>2</sub>O<sub>2</sub>) y diferentes sales de hierro (FeCl<sub>2</sub>, FeCl<sub>3</sub>, FeSO<sub>4</sub> y Fe<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>). La constante de velocidad de decoloración fue mayor para los procesos homogéneos que para los procesos catalíticos heterogéneos. El grado de oxidación del RR-120 fue medido por demanda química de oxígeno (DQO) con un 90% para el proceso Foto-Fenton.

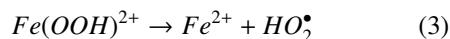
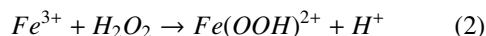
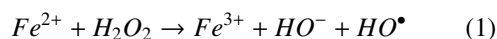
*Palabras clave:* nanopartículas, colorantes azo, cinética de decoloración, DQO.

\*Corresponding author. E-mail: vergara@uaem.mx

## 1 Introduction

Industrial growth produce a great variety of organic products and frequently these substances are complex to degrade. Textile industry generate large amount of wastewater derived to different processes of color impregnation in textile fibers, which has a great amount of detergents, dyes, microfiber (cellulose, wool and synthetic fibers) and inorganic salts. This residual water, with great load pollutants, generates the contaminations of natural waters bodies (Weber and Adams, 1995). Nowadays, more than 50% of dyes used in the textile industry are monoazo, diazo and triazo dyes, considering their chemical stability (recalcitrant) and negative influence on the ecological systems, the regulations of the removal color in the factory effluent is a current issue of discussion all over the world (Carneiro *et al.*, 2004).

In the last years, the problematic of wastewater, with high toxic level, has been tried by Advanced Oxidation Processes (AOPs), including photocatalytic and non photocatalytic processes. The AOPs generate hydroxyl free radical ( $\text{HO}^\bullet$ ), with 2.8 V electrochemical oxidation potential; this radical is a strong oxidant to destroy organic matter that cannot be oxidize by common conventional methods (Al-Kdasi *et al.*, 2004). The Fenton system is one the most used to degrade different azo-dyes by hydroxyl radical generated from the hydrogen peroxide molecules reduction with iron(II) ions at acid pH:



The presence of light radiation in the photo Fenton process improves the azo-dye degradation efficiency due to quick photoreduction of ferric ion to ferrous ion (Saafarzadeh-Amiri *et al.*, 1996).

In the heterogeneous photocatalytic oxidation processes, the reaction takes place on the semiconductor surface under appropriate irradiation ( $h$ ) to form electron/hole pairs ( $e^-/h^+$ ). The semiconductor has the characteristics of non-toxicity, low cost and insolubility under most environmental conditions. In a semiconductor like  $\text{TiO}_2$ , the hole in the valence band may react with water absorbed at the surface to form hydroxyl radicals, and the  $e^-$  in the conduction band can reduce absorbed oxygen to form peroxide radicals anions ( $\text{O}_2^{\bullet-}$ ) that can further react with hydronium ion and hydrogen peroxide to form

hydroxyl radicals (Pera-Titus *et al.*, 2004; Fujishima *et al.*, 2000). Trujillo-Camacho *et al.* (2010) have reported that the use of  $\text{TiO}_2/\text{clinoptilolite}$  composites, synthesized by the sol-gel technique, improved the quality of the materials deposit on glass substrates and also increased the efficiency of the degradation of MV 2B dye.

Some authors have been reported the use of iron oxide NPs as catalyst supported in a mesoporous material (SBA-15) to eliminate phenolic compound in aqueous solutions. The degradation efficiency was favored by hydroxyl species generation on the iron oxide surface in presence of visible radiation (Montiel-Palacios *et al.*, 2009).

The n-type semiconductor  $\alpha\text{-Fe}_2\text{O}_3$  ( $E_g = 2.2$  eV) has been extensively investigated in catalysis owing to the low processing cost and its high resistance to corrosion (Karunakaran and Dhanalakshmi, 2008; Sol and Tilley, 2001; Bandara *et al.*, 2007). A lot of investigators have been developed and explored new strategies in order to tailor the morphology of  $\alpha\text{-Fe}_2\text{O}_3$ . There are an abundant variety of  $\alpha\text{-Fe}_2\text{O}_3$  structures, such as 0D (particles, cubes) (Deng *et al.*, 2010; Reese and Asher, 2002; Qin *et al.*, 2010), 1D (rods, wires, tubes, and belts) (Zhou *et al.*, 2008), 2D (disks, films) (Zhang *et al.*, 2010), 3D (dendrites, flowers, and spheres), (Liu *et al.*, 2008) and hybrids, have already been synthesized by different methods (Hu *et al.*, 2007).

The investigation of Pirillo *et al.* (2009) suggests that iron oxides are promissory adsorbents in the recovery of waste aqueous effluents, this oxides can absorb and degrade reactive dyes over a wide pH range through physical or chemical interactions. The magnetic properties of magnetite particles allowed the fast separation of metal ions from industrial effluents.

The aim of this work is to evaluate the degradation rates of azo dye reactive red 120 by two well-defined catalytic systems: Fenton and photo-Fenton; and compare their degradation kinetics with heterogeneous photocatalysis by iron oxides nanoparticles formed with different iron sources.

## 2 Materials and methods

### 2.1 Chemicals and reagents

Reactive red 120 (RR120) was purchased from RINTEX S.A. The solutions were prepared with distilled water using hydrochloric acid, sulfuric acid, potassium hydroxide, ferrous chloride hydrate ( $\text{FeCl}_2 \bullet$

4H<sub>2</sub>O), ferric chloride hexahydrate (FeCl<sub>3</sub>•6H<sub>2</sub>O), ferrous sulfate heptahydrate (FeSO<sub>4</sub>•7H<sub>2</sub>O), ferric sulfate (Fe<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>•nH<sub>2</sub>O), and hydrogen peroxide (30%), which were purchased from Fermont with analytical grade.

## 2.2 Photoreactor and photodegradation procedure

The degradation of reactive red 120 (RR-120) was carried out by homogeneous (Fenton and Photo-Fenton) and Heterogeneous (oxyhydroxides suspension and oxyhydroxides supported in mesoporous silica SBA-15) processes, using a batch reactor (total volume of 500 mL) under constant agitation with a magnetic stir bar. The source of light in the photocatalytic reaction was a 15W visible light domestic lamp (Phillips) with total radiative output of 2.87W, and very low UV (3%) emission (Orozco *et al.*, 2008). All experiments were performed in acid condition (pH 3), initial azo-dye RR-120 concentration of 100mg/L, and total iron concentration of  $1 \times 10^{-4}$  M obtained from different sources (FeCl<sub>2</sub>•4H<sub>2</sub>O, FeCl<sub>3</sub>•7H<sub>2</sub>O, FeSO<sub>4</sub>•7H<sub>2</sub>O, or Fe<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>•nH<sub>2</sub>O).

In the Fenton process, the aqueous solutions were prepared in acid medium (pH ~ 3), the RR-120 was incorporated, followed by addition of hydrogen peroxide (30%) to reach a concentration of 0.02M in the system. The reaction mixture was stirred in dark condition for 180 min. In the Photo-Fenton process, the procedure was similar, but the lamp was used during the degradations of azo-dye RR-120.

The Oxyhydroxide solutions were prepared by adding iron salt (FeCl<sub>2</sub>•4H<sub>2</sub>O, FeCl<sub>3</sub>•7H<sub>2</sub>O, FeSO<sub>4</sub>•7H<sub>2</sub>O, or Fe<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>•nH<sub>2</sub>O) in distilled water to reach  $1 \times 10^{-3}$ M of iron concentration at pH 4, and they were stored two weeks before to be used in the heterogeneous photocatalytic reactions. In the azo-dye RR-120 degradation with oxyhydroxides supported in mesoporous silica SBA-15, labeled Fe<sub>2</sub>O<sub>3</sub>/SBA-15, 50 mL of oxyhydroxide solution, 0.05g of silica SBA15, and 2 mL of hydrogen peroxide were mixed with 423 mL of distilled water during 30 min in order to form the iron oxide (oxyhydroxides) nanoparticles. After this time, pH was adjusted at ~ 3, finally, the lamp was turned on and the azo-dye RR-120 was added to start the degradation reaction. The process with oxyhydroxides suspension followed the same procedure, except that the silica was not added.

## 2.3 Analytical methods

The color removal of the azo-dye RR-120 solutions was followed quantitatively by measuring the decrease in absorbance at  $\lambda_{max} = 510$  nm using Hach DR5000 spectrophotometer. The chemical oxygen demand (COD) was determined by the methodology described in the Standard Methods of EPA method 410.4 (EPA, 1993).

The decrease of H<sub>2</sub>O<sub>2</sub> concentration during the degradation of RR-120 was followed by titration method using the potassium permanganate (Flaschka *et al.*, 1980; Skoog *et al.*, 2004).

## 2.4 Statistical analyses

The experimental data was statistical analyzed with ANOVA (one-way analysis of variance), this analysis was performed for amount of removal of dye as function of the iron salt in each process, using the Tukey method (comparison of mean and confidence level 95%) with 5 replies.

## 3 Results and discussion

The chemical structure of dye Reactive red 120 (RR-120) contains two groups azo in its structure and chlorine-substituted triazines. The latter groups react through a chlorine atom with hydroxyl groups present in cellulose fibres by a nucleophilic substitution, the other triazine groups contain chromophores, as its shown in Fig. 1, the RR-120 formula is C<sub>44</sub>H<sub>30</sub>Cl<sub>2</sub>N<sub>14</sub>O<sub>2</sub>OS<sub>6</sub> with 4 or 6 Na<sup>+</sup> (Gou *et al.*, 2009; Zhang *et al.*, 2007; Feng *et al.*, 2003; Buki *et al.*, 1987; Yu *et al.*, 2005; Çelekli *et al.*, 2009).

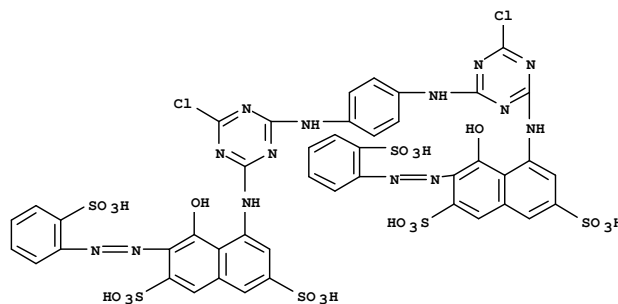


Fig. 1. Chemical structure of C.I. Reactive Red 120.

### 3.1 Discoloration RR-120

The RR-120 discoloration kinetics in aqueous solutions with different iron salts (FeCl<sub>2</sub>, FeCl<sub>3</sub>,

FeSO<sub>4</sub> and Fe<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub> in a homogeneous and a heterogeneous catalytic reaction is shown in Fig. 2. As can be seen in this figure, in both systems the RR120 color is eliminated from the aqueous solutions after 180 min of reaction, and the major color removal efficiency was obtained when using homogeneous systems. The experimental data from the RR-120 color removal were adjusted to pseudo first-order reaction:

$$C = C_0 \exp^{-kt} \quad (4)$$

where  $C_0$  is the initial concentration and  $k$  is the discoloration rate constant. The values of calculated kinetics parameters such  $k$  and the color half-life times ( $t_{1/2}$ , time required to eliminate the number of chromophores groups at the middle) are given in Table 1.

The analysis of variance conducted on discoloration rate constants in the Fenton process indicated a statistically significant differences ( $p < 0.05$ ) between iron salts. The major  $k$  value (0.458) was performed by the system with FeSO<sub>4</sub>,

and the color removal occurred very quick as indicated by the color half-life time in the table 1. The reactivity order of iron salts to eliminate the azo-dye RR-120, in the Fenton system, was FeSO<sub>4</sub> > Fe<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub> > FeCl<sub>3</sub> > FeCl<sub>2</sub>. The use of visible radiation (photo-Fenton process) during the color removal RR-120 from a domestic white lamp, similar to the sun emission spectrum, showed a slight acceleration in the discoloration rates (Fig. 2B) and differences in the  $k$  values between iron sulfate and iron chloride salts (Table 1).

The obtained results in the discoloration of the azo-dye RR-120 are consistent with those reported by Joseph De Laat and Hervea Gallard (1999) when examining the catalytic decomposition of hydrogen peroxide by Fe(III), who determined that for [H<sub>2</sub>O<sub>2</sub>]<sub>0</sub>/[Fe(III)]<sub>0</sub> values lower than 50, an increase of the initial concentration of H<sub>2</sub>O<sub>2</sub> enhances the initial rate of formation of Fe(II) and leads to an increase of the concentration of Fe(II) in the solution that may be oxidized by •OH to yield Fe(III) or may further promote the decomposition of H<sub>2</sub>O<sub>2</sub> (De Laat and Gallard, 1999).

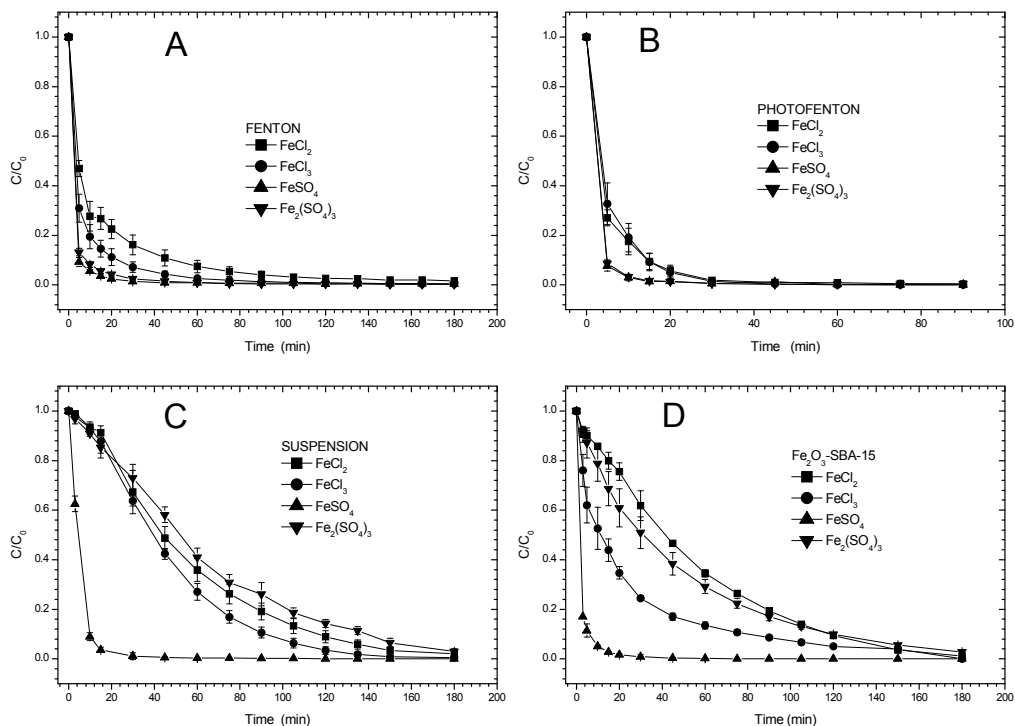


Fig. 2. Comparison of iron salts in the four different methods applied to the discoloration of RR-120. A) Fenton, B) Photo-Fenton, C) Suspension, and D) Fe<sub>2</sub>O<sub>3</sub>/SBA-15.

Table 1. Comparison of the homogeneous and heterogeneous processes of discoloration RR-120

Processes	Salt	$K \times 10^4$ (min <sup>-1</sup> )	$t_{1/2}$ (min)
Fenton	FeCl <sub>2</sub>	957.6±16.18 <sup>a</sup>	7.24
	FeCl <sub>3</sub>	2126.7±13.76 <sup>b</sup>	3.26
	FeSO <sub>4</sub>	4589.3±47.08 <sup>c</sup>	1.51
	Fe <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub>	3748.8±27.14 <sup>d</sup>	1.85
Photo-Fenton	FeCl <sub>2</sub>	2193.5±364.80 <sup>a</sup>	3.16
	FeCl <sub>3</sub>	2121.9±446.00 <sup>a</sup>	3.27
	FeSO <sub>4</sub>	5352.3±200.00 <sup>b</sup>	1.30
	Fe <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub>	4827.5±316.50 <sup>b</sup>	1.44
Fe <sub>2</sub> O <sub>3</sub> /SBA-15	FeCl <sub>2</sub>	175.5±3.90 <sup>a</sup>	39.49
	FeCl <sub>3</sub>	463.2±55.20 <sup>a</sup>	14.96
	FeSO <sub>4</sub>	4682.3±66.80 <sup>b</sup>	1.48
	Fe <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub>	216.5±30.10 <sup>a</sup>	32.02
Suspension	FeCl <sub>2</sub>	171.4±18.40 <sup>a</sup>	40.44
	FeCl <sub>3</sub>	207.2±18.30 <sup>a</sup>	33.45
	FeSO <sub>4</sub>	4737.7±228.20 <sup>b</sup>	3.40
	Fe <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub>	181.9±17.00 <sup>a</sup>	38.11

Different letters on the value denote significant different at  $p < 0.05$ .

In the present work, the proposed condition of  $[H_2O_2]_0/[Fe(II)]_0$  or  $[H_2O_2]_0/[Fe(III)]_0$  equal to 200 promotes the major formation of hydroxyl radical in Fenton reaction resulting in a faster oxidation rate of the azo-dye and its byproducts. The influence of visible light radiation in photo-Fenton process enhance the elimination of the chromophores groups (N=N bonds) of the RR-120 azo-dye due to a faster reduction of Fe<sup>+3</sup> ions by an organic radical. The major color removal efficiency observed for iron sulfate compared to iron chloride salts in the Photo-Fenton reaction, color half-life time ratio of 1:2, could be attributed to reaction between •OH and Cl<sup>-</sup> anions under acidic pH conditions where the Cl<sup>-</sup> acting as strong free radical scavenger (Arslan-Alaton *et al.*, 2009).

The course of RR-120 azo-dye discoloration in heterogeneous catalytic processes (Fig. 2 C-D) revealed that the degradation rate of chromophore groups was diminished. Two causes could be affected the discoloration kinetics. The first cause is related to the degradation process to involve: 1) chemisorption process on the catalytic surface; 2) electron injection from dye to semiconductor valence band; and 3) simultaneous redox reactions (Tanaka *et al.*, 1999). The chemisorption process during discoloration of azo-dye RR-120 is a control stage, due the competitive adsorption of functional groups

in dye molecules structure for active sites in the catalytic surface of iron oxide nanoparticles; for what a stereo chemical and diffusion resistance is generated that retard the discoloration rates of RR-120. The second cause is the presence of SO<sub>4</sub><sup>2-</sup> and Cl<sup>-</sup> anions, Mahmoodi and Arami determined that these anions have a negative effect on photocatalytic discoloration of acid red 14 by photocatalysis using titanium (IV) oxide nanoparticles, due to their reactive with the positive holes and hydroxyl radicals resulting prolonged color removal (Mahmoodi and Arami, 2006). The color half-life times in the heterogeneous photocatalytic oxidation of RR-120 in aqueous media, summarized in table 1, followed the order: FeSO<sub>4</sub> < FeCl<sub>3</sub> < Fe<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub> < FeCl<sub>2</sub>.

The comparative mean analysis of the discoloration rate constants of RR-120 when FeSO<sub>4</sub> was used in the homogeneous and heterogeneous processes showed that there was not a statistically significant differences ( $p < 0.05$ ) among them. The FeSO<sub>4</sub> performed major values of RR-120 discoloration rate due to the high reactivity of sulfato-iron(II) complex (H<sub>2</sub>O<sub>2</sub>-FeSO<sub>4</sub>) that is formed in the homogeneous reaction (De Laat *et al.*, 2004), and a major active sites obtained during the nanoparticles formation in the heterogeneous photocatalytic reactions. These hypotheses we will discuss later during the chemical oxygen demand analysis.

### 3.2 COD removal of RR-120

Although homogeneous or heterogeneous catalytic processes removed the color of azo-dye solutions, the RR-120 azo dye has not been mineralized, completely. For this reason it is necessary consider complementary information about the degradation of the organic pollutants. Chemical Oxygen demand (COD) gives an average measure of the oxidation state of the organic byproducts generated during the degradation of dye RR-120. Fig. 3 shows the COD decay versus degradation time for the homogeneous and heterogeneous catalytic processes. The COD behavior during the azo-dye degradation process follows a first-order kinetic, Eq. (4), and the calculated parameters of degradation rate constants ( $k$ ) and dye half-life times ( $t_{1/2}$ ) are listed in Table 2.

The COD removal percentages of 40% and 85% were obtained for Fenton and Photo-Fenton processes, respectively, and their COD removal kinetics show a similar behavior, however there are significant difference between rate constant values of FeCl<sub>2</sub>

and  $\text{Fe}_2(\text{SO}_4)_3$  salts. Additionally, in the photo-Fenton process, the color half-life time ( $t_{1/2}$ ) is minor than the one observed in Fenton process, generally by a factor of 1:10 (Table 2), as consequence of additional generation of  $\bullet\text{OH}$  radicals from  $\text{H}_2\text{O}_2$  by direct photolysis and its quick decomposition during reduction of Fe(III) to Fe(II). The iron chloride salts showed the lowest COD removal in both processes. This result is explained by two causes: in the first case, the  $\text{Cl}^-$  ions act as trapping of  $\bullet\text{OH}$  radicals and form  $\text{ClOH}^{\bullet-}$  under acidic pH conditions by slowing the oxidation effect in the reaction (Arslan-Alaton *et al.*, 2009); in the second case, the formation of the radicals  $\text{Cl}\bullet/\text{Cl}_2^{\bullet-}$  that react consuming  $\text{H}_2\text{O}_2$  to form the radical  $\text{HO}_2^{\bullet}$ , which has less oxidative power (Machulek and Morales, 2007).

In heterogeneous systems, the behavior of COD abatement occurred similarly, Fig. 3C-D. Statistical

analysis of COD removal showed significant difference between  $\text{FeSO}_4$  with the others iron salts, when using this salt  $t_{1/2}$  was minor in the abatement of dye, 73 and 82 minutes for the cases of suspension and  $\text{Fe}_2\text{O}_3/\text{SBA-15}$  processes, respectively. The use of  $\text{FeSO}_4$  as iron source to form iron oxyhydroxides in the heterogeneous reactions shows similar results as those obtained by Photo-Fenton process ( $\sim 80\%$ ) to degrade the RR-120 azo-dye. These results could be attributed to the iron oxide nanoparticle formation; in the synthesis of iron oxides two mechanism govern the iron formation and its obtained phases: 1) direct precipitation from  $\text{Fe}^{II-}$  or  $\text{Fe}^{III-}$  containing solution, and 2) transformation of an Fe oxide precursor, either by a dissolution/precipitation process or via solid state transformation rearrangements within the structure of the solid precursor.

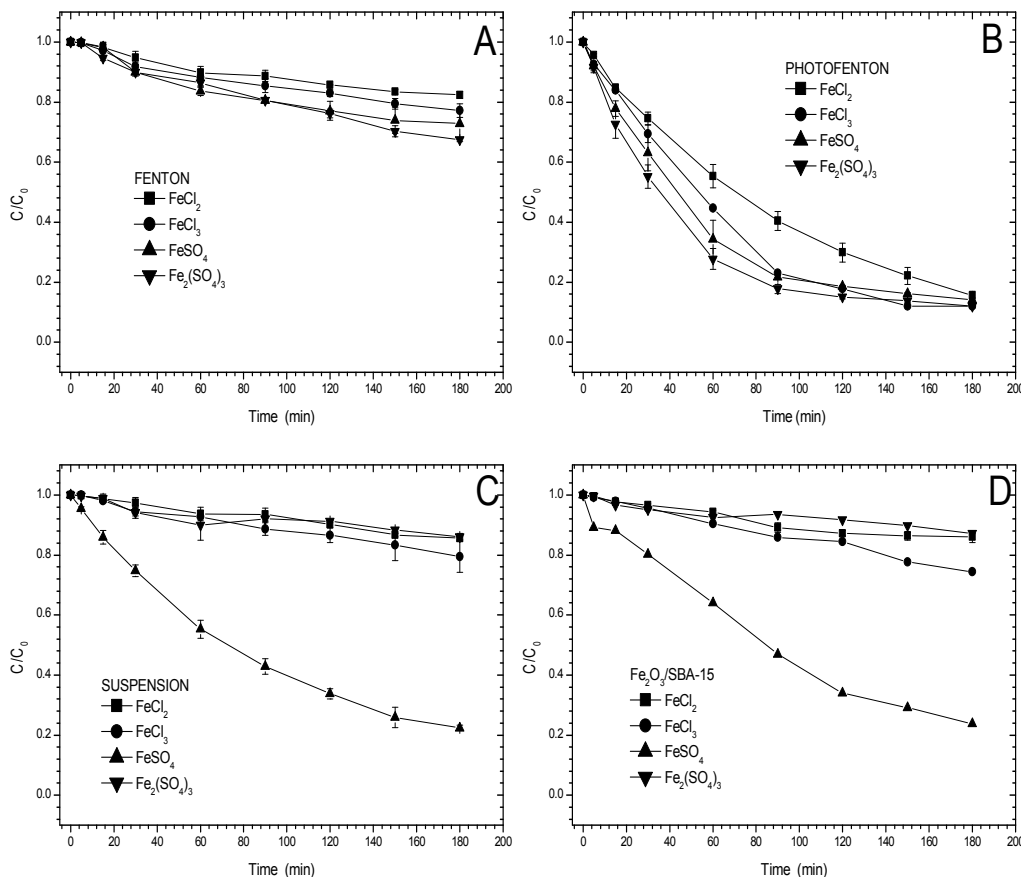


Fig. 3. Comparison of homogeneous and heterogeneous processes in COD removal RR-120, A) Fenton, B) Photo-Fenton, C) Suspension, and D)  $\text{Fe}_2\text{O}_3/\text{SBA-15}$ .

Table 2. Comparison of the homogeneous and heterogeneous processes in the determination of COD by RR-120

Processes	Salt	$K \times 10^4$ (min <sup>-1</sup> )	$t_{1/2}$ (min)
Fenton	FeCl <sub>2</sub>	12.1±0.57 <sup>a</sup>	572.85
	FeCl <sub>3</sub>	15.6±1.30 <sup>a,b</sup>	444.33
	FeSO <sub>4</sub>	20.7±3.32 <sup>b,c</sup>	334.85
	Fe <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub>	23.6±1.77 <sup>c</sup>	293.71
Photo-Fenton	FeCl <sub>2</sub>	100.9±8.76 <sup>a</sup>	68.70
	FeCl <sub>3</sub>	127.9±6.93 <sup>a,b</sup>	54.19
	FeSO <sub>4</sub>	172.6±23.00 <sup>b,c</sup>	40.16
	Fe <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub>	209.3±28.10 <sup>c</sup>	33.12
SBA-15	FeCl <sub>2</sub>	9.77±1.17 <sup>a</sup>	709.10
	FeCl <sub>3</sub>	16.80±1.01 <sup>a</sup>	412.59
	FeSO <sub>4</sub>	84.10±1.12 <sup>b</sup>	82.42
	Fe <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub>	7.82±1.41 <sup>a</sup>	886.38
Suspension	FeCl <sub>2</sub>	8.87±0.63 <sup>a</sup>	781.01
	FeCl <sub>3</sub>	12.80±3.54 <sup>a</sup>	541.52
	FeSO <sub>4</sub>	94.70±4.40 <sup>b</sup>	73.19
	Fe <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub>	8.31±0.64 <sup>a</sup>	834.61

Different letters on the value denote significant different at  $p < 0.05$ .

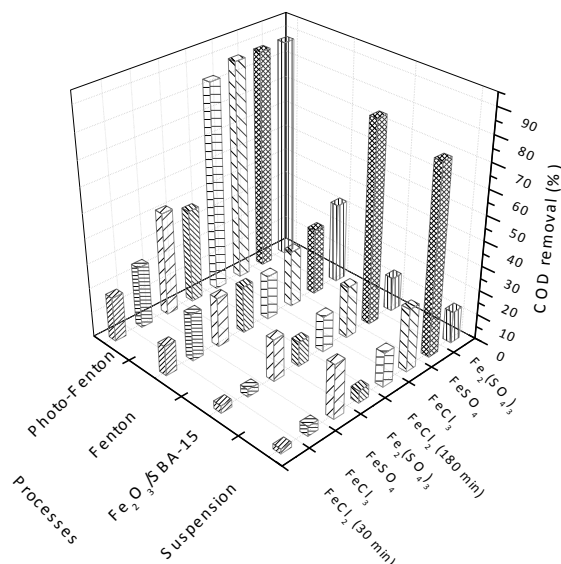


Fig. 4. COD removal at 30 and 180 minutes of degradation process different.

The time required for crystallization, from minutes to years, and also the iron oxide formed by transformation of oxyhydroxides (iron oxides precursors) depend on such factors as temperature, OH/Fe ratio, iron-aqua ions equilibrium  $[\text{Fe}(\text{H}_2\text{O})_n]^{+3}$

or  $[\text{Fe}(\text{H}_2\text{O})_m]^{+2}$  and nature of the anion (Cornelle and Schwertmann, 2003). The solubility conditions of FeSO<sub>4</sub> solutions (pH 4,  $1 \times 10^{-4}$  M) and the addition of hydrogen peroxide after 30 min could lead the formation of iron oxides with more active sites that increased the ability to degrade the RR-120 azo dye. When others iron sources were used (FeCl<sub>2</sub>, FeCl<sub>3</sub> and Fe<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>) the iron oxide nanoparticles should have less catalytic active sites, and their photoreactivity diminished, so the azo-dye molecules were not degraded completely. In all heterogeneous photocatalytic systems, the degradation process occurs by interaction between the iron oxide NPs and visible irradiation to generate the  $e^-/h^+$ ; holes in the valance band lead to partial oxidation of organic compounds, while the electrons in the conduction band reduce the hydrogen peroxide molecules to form the hydroxyl radicals that perform the total oxidation of organic compounds.

Fig. 4 shows a comparison of the removal percentage for the four processes and the different salts used for the degradation of dye RR-120, to the times of at 30 and 180 minutes. The photo-Fenton process had a bigger COD abatement, and the FeSO<sub>4</sub> salt was the best catalyst precursor in any process.

### 3.3 Effect of H<sub>2</sub>O<sub>2</sub> concentration

The hydrogen peroxide concentration was monitored during the RR-120 dye degradation by the homogeneous and heterogeneous reactions for each iron salt, Fig. 5. The linear behavior of experimental data indicated that hydrogen peroxide consume followed zero-order kinetics:

$$C = C_0 - kt \quad (5)$$

where  $k$  is the consume rate constant of H<sub>2</sub>O<sub>2</sub>, and  $C_0$  its initial concentration. Table 3 shows the values of the kinetic parameters obtained by fitting with this model. The means comparative of  $k$  in Fenton processes showed that only FeCl<sub>2</sub> had significant difference compared to the sulfates. In general, a quick discoloration, by Fenton process did not mean a quick and complete RR-120 dye degradation, and these results were reflected in the low and slowly H<sub>2</sub>O<sub>2</sub> consume, less 30% of initial concentration at 180 min (Fig. 5A). Using visible light irradiation in Photo-Fenton process increased \*OH generation due photolysis of H<sub>2</sub>O<sub>2</sub> that consumed around 80% of initial concentration, so more effective discoloration and degradation of RR-120 dye were performed.

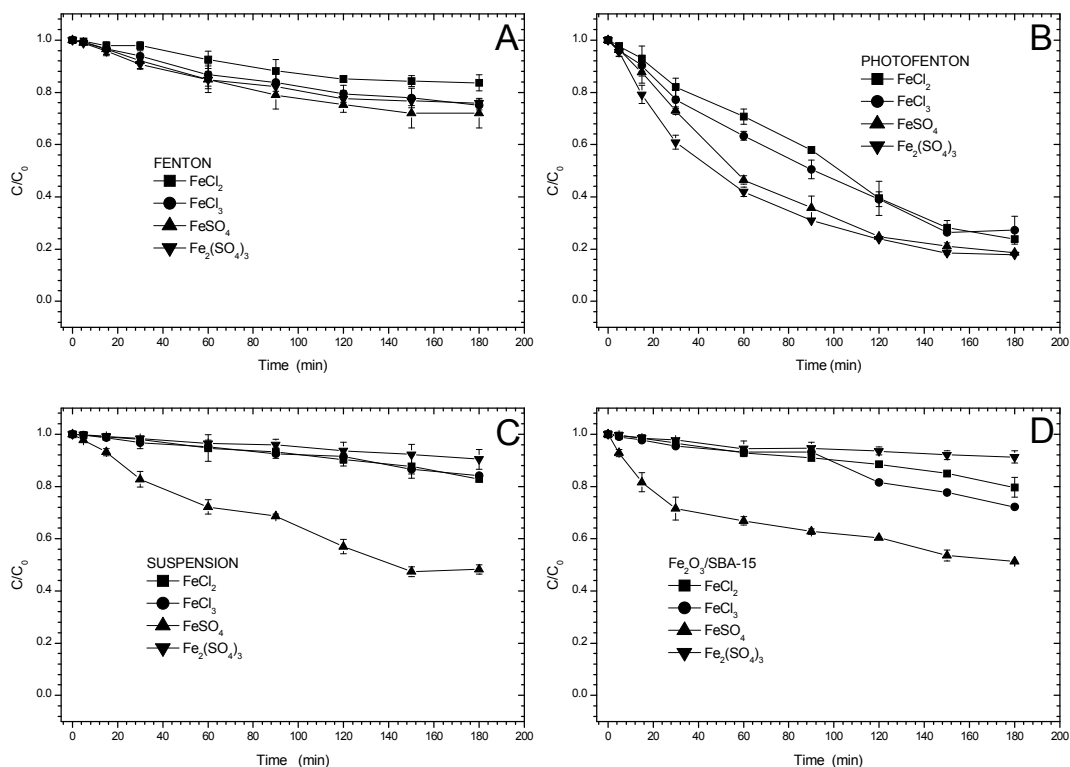


Fig. 5. Comparison of homogeneous and heterogeneous processes in the determination of  $H_2O_2$  during the degradation of RR-120, A) Fenton, B) Photo-Fenton, C) Suspension, and D)  $Fe_2O_3/SBA-15$ .

Table 3. Comparison of the homogeneous and heterogeneous processes in the determination of  $H_2O_2$  during the degradation of RR-120.

Processes	Salt	$K \times 10^5$ (mol/Lmin)
Fenton	$FeCl_2$	$2.29 \pm 0.31^a$
	$FeCl_3$	$3.62 \pm 0.76^{a,b}$
	$FeSO_4$	$4.81 \pm 0.81^b$
	$Fe_2(SO_4)_3$	$4.74 \pm 0.79^b$
Photo-Fenton	$FeCl_2$	$12.31 \pm 2.89^a$
	$FeCl_3$	$17.27 \pm 1.94^b$
	$FeSO_4$	$17.33 \pm 1.11^b$
	$Fe_2(SO_4)_3$	$25.30 \pm 2.06^c$
SBA-15	$FeCl_2$	$4.27 \pm 0.15^a$
	$FeCl_3$	$6.41 \pm 0.00^b$
	$FeSO_4$	$4.03 \pm 0.34^a$
	$Fe_2(SO_4)_3$	$2.37 \pm 0.65^c$
Suspension	$FeCl_2$	$3.95 \pm 0.31^a$
	$FeCl_3$	$3.49 \pm 1.22^a$
	$FeSO_4$	$18.28 \pm 0.85^b$
	$Fe_2(SO_4)_3$	$3.37 \pm 0.52^a$

Different letters on the value denote significant different at  $p < 0.05$ .

The  $H_2O_2$  consume behavior was similar in the heterogeneous processes. Using  $FeSO_4$  to obtain the oxyhydroxides showed the major consume of hydrogen peroxide. This result is consistent with the COD removal of RR-120 dye, and suggests that the iron oxide nanoparticles present more active centers, inducing the performance of the photoreactivity in the system.

## Conclusions

The homogeneous and heterogeneous processes removed the total color in RR-120 azo-dye solutions. The major discoloration rates were performed by Fenton and Photo-Fenton systems, and these were diminished in the heterogeneous processes due to adsorption of dye to active sites of iron oxide nanoparticles.

The azo-dye molecule degradation was influenced by the iron salts sources and the process used. The major COD removal was obtained when using  $FeSO_4$  due to the formation of iron-sulfate complex in the



photo-Fenton, and the iron particle formations with more active sites in the case of the heterogeneous systems.

## Acknowledgments

The authors are thankful to Ivonne Adame Moreno, Gabriela Hernández Domínguez and Rogelio Moran Elvira for the experimental support. J. Vergara-Sánchez acknowledges the financial support received from DGAPA-UNAM. This research was partially supported by PAPIIT IN114609 and CONACYT 82909-Y.

## References

- Al-Kdasi, A., Idris, A., Sead, K. and Guan, C. T. (2004). Treatment of textile wastewater by advanced oxidation processes- a Review. *Global NEST: The International Journal* 6, 221-230.
- Arslan-Alaton, I., Tureli, G. and Olmez-Hanci, T. (2009). Treatment of azo dye production wastewater using Photo-Fenton-like advanced oxidation processes: Optimization by response surface methodology. *Journal of Photochemistry and Photobiology A. Chemistry* 202, 142-153.
- Bandara, J., Klehm, U. and Kiwi, J. (2007). Raschig rings-Fe<sub>2</sub>O<sub>3</sub> composite photocatalyst activate in the degradation of 4-chlorophenol and Orange II under daylight irradiation. *Applied Catalysis B: Environmental* 76, 73-81.
- Buki, K. G., Kirsten, E. and Kun, E. (1987). Isolation of Adenosine Diphosphoribosyltransferase by precipitation with reactive red 120 combined with affinity chromatography. *Analytical Biochemistry* 167, 160- 166.
- Carneiro, P. A., Osugi, M. E., Sene, J. J., Anderson, M. A. and Zanoni, M.V .B. (2004). Evaluation of color removal and degradation of a reactive textile azo dye on nanoporous TiO<sub>2</sub> thin-film electrodes. *Electrochimical Acta* 4, 3807-3820.
- Celekli, A., Yavuzatmaca, M. and Bozkurt, H. (2009). Kinetic and equilibrium studies on the adsorption of reactive red 120 from aqueous solution on *Spirogyra majuscula*. *Chemical Engineering Journal* 152, 139-145.
- Cornelle, R. M. and Schwertmann, U. (2003). *The iron oxides*. Second edition Wiley-VCH GmbH & Co. KGa.A .
- De Laat, J. and Gallard, H. (1999). Catalytic decomposition of hydrogen peroxide by Fe(III) in homogeneous aqueous solution: Mechanism and kinetic modeling. *Environmental Science & Technology* 33, 2726-2732.
- De Laat, J., Le Troung, G. and Legube, B. (2004). A comparative study of the effects of chloride sulfate and nitrate ions on the rates of decomposition of H<sub>2</sub>O<sub>2</sub> and organic compounds by Fe(II)/H<sub>2</sub>O<sub>2</sub> and Fe(III)/H<sub>2</sub>O<sub>2</sub>. *Chemosphere* 55, 715-723.
- Deng, H., Li, X., Peng, Q., Wang, X., Chen, J. and Li, Y. (2010). Monodisperse magnetic single-crystal ferrite microspheres. *Angewandte Chemie International* 44, 2782-2785.
- EPA, Method 410.4. (1993). The determination of chemical oxygen demand by semi-automated colorimetry. Available at: [http://www.caslab.com/EPA-Method-410\\_4/](http://www.caslab.com/EPA-Method-410_4/). Accessed: June, 18, 2011
- Feng, J., Hu, X., Yue, P.L., Zhu, H. Y. and Lu, G.Q. (2003). Discoloration and mineralization of Reactive Red HE-3B by heterogeneous photo-Fenton reaction. *Water Research* 37, 3776-3784.
- Flaschka, H. A., Barnard A. J. and Sturrock, P.E. (1980). *Química Analítica Cuantitativa*. Editorial CECSA Vol. 11, México
- Fujishima, A., Rao, T. N., and Tryk, D. A. (2000). TiO<sub>2</sub> photocatalysts and diamond electrodes. *Electrochemical Acta* 45, 4683-4690.
- Gou, M., Qu, Y., Zhou, J., Ma, F. and Tan, L. (2009). Azo dye decolorization by a new fungal isolate, *Penicillium* sp. QQ and fungal-bacterial cocultures. *Journal of Hazardous Materials* 170, 314-319.
- Hu, X., Yu, J. C. and Gong, J. (2007). Fast production of self-assembled hierarchical r-Fe<sub>2</sub>O<sub>3</sub> nanoarchitectures. *Journal of Physical Chemistry C* 111, 11180-11185.
- Karunakaran, C. and Dhanalakshmi, R. (2008). Semiconductor-catalyzed degradation of phenols with sunlight. *Solar Energy Materials & Solar Cells* 92, 1315-1321.

- Liu, X., Gou, J., Cheng, Y., Li, Y., Xu, G. and Cui, P. (2008). Surfactant-free fabrication of  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> structures with flower-like morphology in aqueous solution. *Journal of Crystal Growth* 311, 147-151.
- Machulek, A. Jr., Morales, J. E. F., Vautier-Giongo, C., Silverio, C. A., Friedrich, L. C., Nascimento, C. A. O., González, M. C. and Quina F.H. (2007). Abatement of the inhibitory effect of chloride anions on the photo-fenton process. *Environmental Science & Technology* 41, 8459-8463.
- Mahmoodi, N. M. and Arami, M. (2006). Bulk phase degradation of Acid Red 14 by nanophotocatalysis using immobilized titanium(IV) oxide nanoparticles. *Journal of Photochemistry and Photobiology A: Chemistry* 182, 60-66.
- Montiel-Palacios, E., Medina-Mendoza, A. K., Sampieri, A., Angeles-Chávez, C., Hernández-Pérez I. and Suárez-Parra, R. (2009). Photocatalysis of phenol derivatives with Fe<sub>2</sub>O<sub>3</sub> nanoparticles dispersed on sba-15. *Journal of Ceramic Processing Research* 10, 548-552.
- Orozco, S. L., Bandala, E. R., Arancibia-Bulnesa, C. A., Serrano, B., Suárez-Parra, R. and Hernández-Pérez, I. (2008). Effect of iron salt on the color removal of water containing the azo-dye reactive blue 69 using photo-assisted Fe(II)/H<sub>2</sub>O<sub>2</sub> and Fe(III)/H<sub>2</sub>O<sub>2</sub> systems. *Journal of Photochemistry and Photobiology A: Chemistry* 198, 144-149.
- Pera-Titus, M., García-Molina, V., Baños, M. A., Jiménez, J. and Espulgas S. (2004). Degradation of chlorophenols by means of advanced oxidation processes: a general review. *Applied Catalysis B: Environmental* 47, 219-156.
- Pirillo, S., Ferreira, M. L. and Rueda, E. H. (2009). The effect of pH in the adsorption of alizarin and eriochrome blue black R onto iron oxides. *Journal of Hazardous Materials* 168, 168-178.
- Qin, W., Yang, C., Yi, R. and Gao, G. (2011). Hydrothermal synthesis and characterization of single-crystalline  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> nanocubes. *Journal of Nanomaterials* 2011, 1-6.
- Reese, C. E. and Asher, S. A. (2002). Emulsifier-free emulsion polymerization produces highly charged, monodisperse particles for near infrared photonic crystals. *Journal of Colloid and Interface Science* 248, 41-46.
- Safarzadeh-Amiri, A., Bolton J.R. and Cater S.R. (1996). Ferrioxalate-mediated photodegradation organic pollutants in contaminated water. *Water Research* 31 (4), 787-798.
- Skoog, D. A., West, D. M., Holler, F. J., and Crouch, S. R. (2004). *Química Analítica*. 7th edition. McGraw-Hill, New York., 474-475.
- Sol, C. and Tilley, R. J. D. (2001). Ultraviolet laser irradiation induced chemical reactions of some metal oxides. *Journal Materials Chemistry* 11, 815-820.
- Tanaka, K., Padermpole, K. and Hisanga, T. (1999). Photocatalytic degradation of commercial azo dyes. *Water Research* 34, 327-333.
- Trujillo-Camacho, M. E., García-Gómez, C., Hinojosa-Palafox, J. F. and Castellón-Barraza, F. F. (2010). Evaluation of TiO<sub>2</sub>/clinoptilolite composites in MV-2B dye photodegradation on CPC solar reactor. *Revista Mexicana de Ingeniería Química* 9, 139-149.
- Weber, E. J. and Adams, R. L. (1995). Chemical- and sediment-mediated reduction of the azo dye disperse blue 79. *Environmental Science & Technology* 29, 1163-1170.
- Yu, Y., Yu, J. C., Chan, C. Y., Che, Y. K., Zhao, J. C., Ding, L., Ge, W. K. and Wong, P. K. (2005). Enhancement of adsorption and photocatalytic activity of TiO<sub>2</sub> by using carbon nanotubes for the treatment of azo dye. *Applied Catalysis B: Environmental* 61, 1-11.
- Zhang, F., Yediler, A. and Liang, X. (2007). Decomposition pathways and reaction intermediate formation of the purified, hydrolyzed azo reactive dye C.I. reactive Red 120 during ozonation. *Chemosphere* 67, 712-717.
- Zhang, Z., Hossain, M. D. F., Miyazaki, T. and Takahashi, T. (2010). Gas phase photocatalytic activity of ultrathin Pt layer coated on  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> films under visible light illumination.

*Environmental Science & Technology* 44, 4741-4746.

Zhou, W., Tang, K., Zeng, S. and Qi, Y. (2008). Room temperature synthesis of

rod-like  $\text{FeC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$  and its transition to maghettite, magnetite and hematite nanorods through controlled thermal decomposition. *Nanotechnology* 19, 1-9.