Rapid decolourization and mineralization of the azo dye C.I. Acid Red 14 by heterogeneous Fenton reaction

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ABSTRACT

The decolourization and mineralization of a solution of an azo dye using a catalyst based on Fe(II) supported on Y Zeolite (Fe(II)-Y Zeolite) and adding hydrogen peroxide (heterogeneous Fenton process) have been studied. The catalyst was prepared by ion exchange, starting from a commercial ultra-stable Y Zeolite. All experiments were performed on a laboratory scale set-up. The effects of different parameters such as initial concentration of the dye, initial pH of the solution of the dye, H_2O_2 concentration, temperature and ratio of amount of catalyst by amount of solution on the decolourization efficiency of the process were investigated. A percentage of colour removal of $99.3 \pm 0.2\%$ and a mineralization degree of $84 \pm 5\%$ of the solution of the dye were achieved in only 6 min of contact time between the catalyst and the solution, under the following conditions: initial concentration of the dye of 50 ppm, pH 5.96, 8.7 mM of H_2O_2, T of $80\,^{\circ}C$ and catalyst concentration of 15 g/L. Moreover, the catalyst Fe(II)-Y Zeolite can be easily filtered from the solution, does not leach any iron into the solution (avoiding any secondary contamination due to the metal) and its effectivity can be reproduced after consecutive experiments.

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1. Introduction

Textile, printing, dyeing, and food industries extensively use synthetic dyes that belong to different families (azo, nitro, indigo, etc.). Among them, textile industries have shown a significant increase in the use of synthetic complex organic dyes as the colouring reagent, generating a coloured wastewater because the dye is not completely absorbed by the fibres and representing an environmental problem [1]. Moreover, in many cases dyes are toxic compounds that can even originate dangerous by-products through oxidation, hydrolysis, or other chemical reactions that can take place in the waste phase, risking the ecosystem they enter in contact with [2]. Furthermore, some of these dyes are able to reach the drinking water representing a human health problem as some of them or their metabolites are carcinogenic in nature [3]. It is, therefore a priority to eliminate these dyes before discharging to the environment, but not only the degradation of the colour but also the mineralization to CO_2 of the dye to ensure the removal of the possible toxic metabolites. But the degradation of the dyes, especially those belonging to the azo family, that contribute to about 70% of all the used dyes, is difficult due to their complex structure and synthetic nature [4]. Azo dyes are characterized by the nitrogen double bond (–N=N–) which is, together with other chromophores, the responsible of the colour [5,6].

Traditionally, the treatment of solutions containing soluble dyes is performed by biochemical and coagulation processes. All these methods are either costly, inefficient or result in the production of secondary toxic waste product. In recent years, an alternative to conventional methods is gaining attention, the called advanced oxidation processes (AOPs) which are based on the generation in the waste solution of very reactive species such as hydroxyl radicals (OH•), which have the ability to oxidize the majority of organic compounds in industrial effluents [7,8]. AOPs have potential for becoming the new technologies for treating compounds in textile wastewaters. The most promising methods within this category, utilizes a reagent which is a mixture of H_2O_2 and Fe(II), typically known as the Fenton's reagent and based on a catalytic reaction [9].

Common homogeneous Fenton processes involve the application of ferrous or ferric salts and hydrogen peroxide in order to produce hydroxyl radical. However, despite the high efficiency, the process is limited by the acidic pH required (pH 2–4) and the high amount of sludge generated in the coagulation step for the elimination of the iron added and which makes the process laborious and not economical [10]. The catalytic degradation of organic contaminants using Fenton system can become more efficient when is carried out in a heterogeneous way, such as zeolites or clays loaded

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Table 1
Characteristics of Acid Red 14.

Chemical structure

Chemical class	Monoazo
Colour	Bluish red
λ_{max} (nm)	516
Formula weight	502.44

with the iron [11–13]. Among them, the use of synthetic zeolites is very promising due to their unique properties [14,15] and their ability to adsorb small organic molecules [16,17]. Moreover, the preparation of Fe-containing zeolite catalyst is rather easy due to zeolite's ion exchange characteristics [18].

The goal of this study was to investigate the performance of a commercial zeolite loaded with iron(II) (Fe(II)-Y Zeolite) in a heterogeneous Fenton-type process for the decolourisation and mineralization of water solutions containing an azo dye under different conditions. The dye Acid Red 14 (AR 14) was used as a model pollutant.

2. Experimental

2.1. Materials and chemicals

AR 14 was obtained from Sigma–Aldrich, Spain, at 50% of purity and was used without further purification. The main characteristics of AR 14 are represented in Table 1. Hydrogen peroxide, perhydrol, 35% w/w, from FLUKA, Spain, sulphuric acid from Scharlau, Spain and sodium hydroxide and $(NH_4)_2$ $Fe(SO_4)_2 \cdot 6H_2O$ both from Panreac, Spain, were all of laboratory reagent grade and used without further purification. All the solutions were prepared with MilliQ, or double deionised, water.

Powdered particles of Y Zeolite (Produced by Zeolyst international, USA) with good thermal stability, homogeneous porosity and strong carboxylic groups interaction, were used as support. The physical properties of zeolite catalyst are shown in Table 2. The pore size of the Y Zeolite was not provided by the manufacturer but it is well known that it is 24.33–24.35 Å [19,20].

2.2. Preparation of the catalyst

Fe(II)-Y Zeolite catalyst was prepared through a cation exchange process. Firstly, Y Zeolite was added slowly as powder into a solution of $(NH_4)_2$ $Fe(SO_4)_2 \cdot 6H_2O$ (0.05 M). Then, the mixture was stirred during 1 h, under N_2 atmosphere and at ambient temperature. Finally, the slurry was filtered, thoroughly washed three times with distilled water and dried in an oven under air at 60 °C overnight [21].

Table 2
Physico-chemical characteristics of the Y Zeolite.

Support	Nature	Surface area (m^2/g)	SiO_2/Al_2O_3 molar ratio	Nominal cation form	Na_2O weight %
CBV 712	Y Zeolite	730	12	Ammonium	0.05

2.3. Catalytic experiments

Chemical oxidation of AR 14 was carried out in a 250 ml thermostatic glass reactor. The conditions of the experiments were set as follows (except when the parameter was optimized): initial concentration of AR 14 of 50 mg/L, pH of the solution of 5.96, concentration of H_2O_2 8.7 mmol/L, temperature was set at 80 °C and concentration of the catalyst of 15 g/L. After stabilisation of temperature and pH, the powder catalyst (Fe(II)-Y Zeolite) was added to 100 ml of the dye. The beginning of the reaction ($t = 0$) was considered when the required amount of H_2O_2 was added. All experiments were carried out under constantly stirring to ensure good dispersion of the catalyst. All experiments were carried out in duplicate and results are expressed as the average ± SD.

2.4. Methodology

Temperature and pH were permanently controlled by thermocouple and pH Meter respectively from Crison Instrument, Spain. At regular time intervals, a sample of the mixture was collected and filtered through Millipore filters (pore size 0.45 μm) and then spectrophotometrically analyzed using a Unicam UV-Vis Spectrophotometer from 300 to 600 nm. A solution of the dye was analyzed, filtered and analyzed again in order to ensure that the dye was not absorbed onto the filter. The efficiency (%) of the colour removal was calculated by measuring the absorbance of the solution before and after the treatment when the different parameters were modified. Decolourisation efficiency was calculated by Eq. (1).

$$\text{Decolorization efficiency (\%)} = \frac{C_i - C_t}{C_i} \times 100 \qquad (1)$$

where C_i and C_t are the concentrations (mg/L) of the dye at time 0 and t, respectively.

The extent of the mineralization of the dye was determined on the basis of total organic carbon measurements using a Shimadzu TOC-5050A analyzer. The mineralization efficiency was calculated by Eq. (2).

$$\text{Mineralization efficiency (\%)} = \frac{\text{TOC}_o - \text{TOC}_t}{\text{TOC}_o} \times 100 \qquad (2)$$

where TOC_t is the value of TOC obtained at time t and TOC_o corresponds to the initial value of TOC.

The total amount of iron loaded onto the zeolite was determined using X-Ray Portable equipment (FP-XRF, Alpha-6500R, Innov-X Systems. 1c, Woburn, MA, USA).

The amount of iron ions leached from the catalyst to the solution was also calculated. To carry out the analysis, different solutions were filtered after the treatment at different conditions and the amount of iron released to the solution was determined by ICP-OES, using an Iris Intrepid II (Thermo Electron, USA).

In order to test the good performance of the catalyst, the Fe(II)-Y Zeolite was recovered by filtration from the solution after one treatment at the optimized parameters, washed with MilliQ water, dried overnight at 60 °C and then used again under the same reaction conditions. The procedure was repeated three times.

3. Results and discussion

3.1. Decolourization and kinetics

In order to elucidate the changes of molecular and structural characteristics of the dye AR 14, a typical time-dependent UV–vis spectrum of the dye solution was obtained. As it can be seen, the spectrum of the initial dye solution (Fig. 1 at 0 min) shows two main peaks, one in the ultraviolet region at 324 and the other in the visible region at 516 nm.
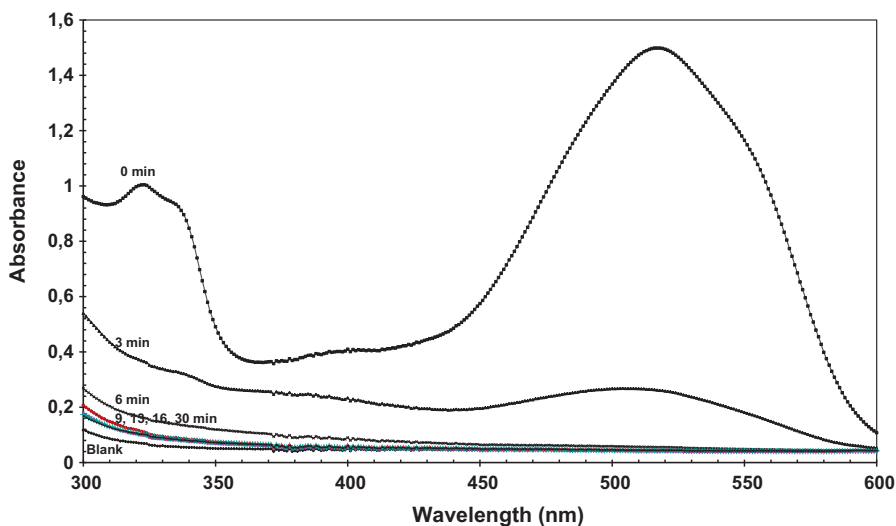
Fig. 1. Spectra of the solution of the dye at different contact time with Fe(II)-Zeolite/H_2O_2 at 80 °C.

The peak at 324 nm corresponds to the absorption of the π–π^* transition related to the naphthalene rings bonded to the –N=N– group in the dye molecule while the band in the visible region has been attributed to the chromophore-containing azo linkage of the dye molecules in the solution [2]. These peaks, decreased as the contact time between the catalyst and the solution increased to finally disappear indicating the degradation of the dye (Table 3). It also indicates that the nitrogen double bond (–N=N–) of the azo dye, is the most active site for oxidative attack.

The effect on the decolourization when H_2O_2 was added, in the absence of any iron, resulted on a $1.9 \pm 0.2\%$ at 6 min. In the same way, the addition of unloaded zeolite or Fe(II)-Y Zeolite in the absence of H_2O_2 shows non changes in the UV–vis spectra of the initial dye solution, even after 24 h of contact. Consequently, it could be concluded that the adsorption of the dye molecules, at the concentration tested, onto zeolite particles does not play a significant role in the decolourization process and that the decolourization is due to the combined action of Fe(II)-Y Zeolite and H_2O_2.

Prior to the absorbance measurements, a calibration curve was obtained in the range 1×10^{-7}–5×10^{-5} mol/L and showed a good linear relationship at 516 nm, characteristic absorption wavelength of AR 14.

The decolourization of the dye by the heterogeneous Fenton's reaction was observed to be a function of time as it was found that the correlation between $-\mathrm{Ln}\,C_t/C_o$ and the contact time (Eq. (3)) was linear, Fig. 2, indicating a typical first order reaction profile.

$$-\mathrm{Ln}\frac{C_t}{C_o} = Kt \tag{3}$$

where C_t is the dye concentration at time t (mol/L); C_o is the dye concentration at initial time ($t = 0$); k is the pseudo-first order rate constant (min^{-1}) and t is the time of reaction in minutes. From the

slope of the regression adjustment, the apparent rate constant is calculated as $k = 0.9051$ min^{-1} with $R^2 = 0.9964$.

3.2. Effect of the initial concentration of the dye

The concentration range chosen for the present study was that usually found in the textile industry wastewaters, between 50 and 250 mg/L.

The influence of the initial dye concentration is shown in Fig. 3. A decrease on the decolourization rate, when increasing the initial dye concentration, is observed before the 6 min of treatment. The colour removal percentages achieved at 6 min were $99.4 \pm 0.8\%$, $98.0 \pm 0.3\%$, $98 \pm 1\%$ and $96 \pm 2\%$ for the initial dye concentrations of 50, 100, 150 and 200 ppm respectively because at higher dye concentration the generation of OH$^\bullet$ radicals on the surface catalyst is reduced since the active sites may be occupied by dye ions and because the number of dye molecules is increased but not the OH$^\bullet$ radical molecules number. After 6 min of contact time, the decolourization efficiency increased to 99–100% for all concentrations.

3.3. Effect of the pH

The solution of the dye showed an initial pH of 5.96. The only addition of H_2O_2 decreased the pH to 4.50. After 2 min it decreased to 4.10 and remained constant at around 4.00 during the rest of the
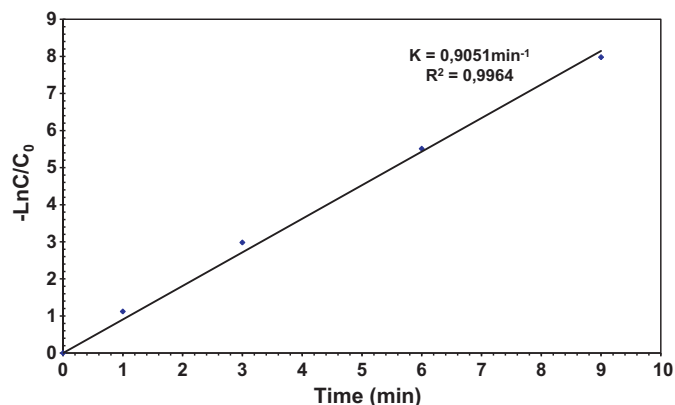
Table 3
Percentage of decolourization of AR 14 with time.

Time	% of decolourization
0	0
3	87.7 ± 5.0
6	99.3 ± 0.2
9	99.7 ± 0.1
13	99.8 ± 0.1
16	99.8 ± 0.4
30	99.9 ± 0.1

Fig. 2. Kinetics of the decolourization of the dye with Fe(II)-Y Zeolite/H_2O_2 at 80 °C.
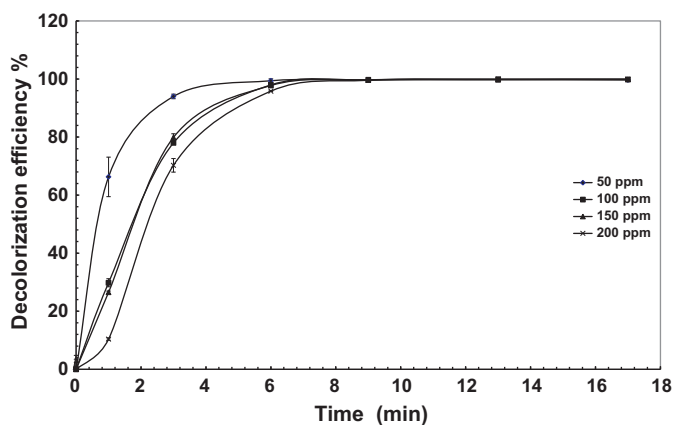
Fig. 3. Effect of the initial dye concentration on the efficiency of the colour removal at 80 °C for 100 ml of solution at pH 5.63, 8.7 mM of hydrogen peroxide and ratio Fe(II)-Y Zeolite/solution volume of 15 g/L.

reaction. In the early part of the reaction, the pH decreased due to the formation of some acidic reaction intermediates.

It is known that the pH plays an important role in the mechanism of the OH• production in the Fenton's reaction [22,23]. To examine this effect, the dye solution was adjusted to the desired pH for each experiment by adding sodium hydroxide or sulphuric acid.

Fig. 4 shows the percentage of the decolourization efficiency for different initial pHs and as a function of the time. The maximum efficiency of colour removal, $99.5 \pm 0.2\%$, was observed, after 6 min of the treatment for all the pH studied. Moreover, the results showed that even up to an initial pH of 9.24, the heterogeneous Fenton process could perform effectively with Fe(II)-Y Zeolite as catalyst. In our studies, it was found that after 6 min of contact between the catalyst and the solution, the decolourization efficiency is nearly independent of the initial pH.

In homogeneous systems (Fe(II)/H₂O₂) it is known that the optimal value of the pH for the azo dye degradation is around 3–4 [10]. As the degradation proceeds, the formation of organic acids leads to a drop of the pH of the solution. At higher initial pH, the iron is precipitated as iron hydroxide but in this case, as Fe(II) is immobilized on the surface of the zeolite, the precipitation is avoided, resulting in a great advantage against the homogeneous Fenton reaction.
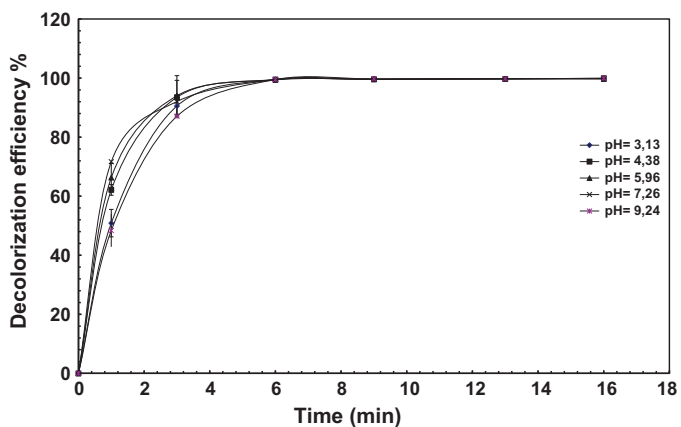

Fig. 4. Effect of the pH on the efficiency of the colour removal for 100 ml of a solution containing 50 ppm of the dye, 8.7 mM of hydrogen peroxide, ratio Fe(II)-Y Zeolite/solution volume of 15 g/L and temperature set at 80 °C.
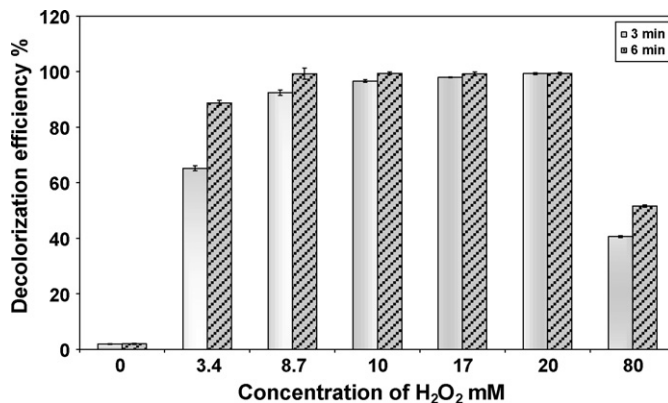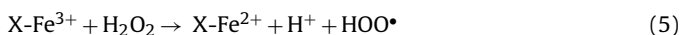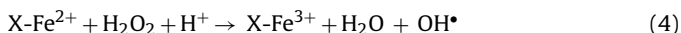

Fig. 5. Effect of the addition of H₂O₂ on the efficiency of the colour removal of 100 ml of a solution containing 50 ppm of the dye, at pH 5.96, with a ratio Fe(II)-Y Zeolite/solution volume of 15 g/L and 80 °C of temperature.

3.4. Effect of the concentration of H_2O_2

The initial concentration of H₂O₂ plays a very important role in the oxidation of organic compounds in the heterogeneous Fenton processes. When hydrogen peroxide concentration increased from 0 to 8.7 mM, as shown in Fig. 5, the colour removal percent increased rapidly from $1.9 \pm 0.2\%$ to $92 \pm 1\%$ in the initial period of the reaction (3 min), and after 6 min of the treatment, the colour removal percent increased from $2.0 \pm 0.2\%$ to $99 \pm 2\%$. The increase of the oxidant concentration leads to an increase in the reaction rate, as expected, because of the increase of radicals' formation (Eqs. (4) and (5)). When hydrogen peroxide concentration was varied from 8.7 to 20 mM, there was no significant variation on the colour removal rate, from $99 \pm 2\%$ for 8.7 mM to $99.3\% \pm 0.5$ for 20 mM of H₂O₂ at 6 min. Nevertheless, for a higher addition of H₂O₂, the colour removal rate decreased due to the scavenging of the OH• radicals, which can be expressed by Eqs. (6) and (7) [24].

$$X\text{-}Fe^{2+} + H_2O_2 + H^+ \rightarrow X\text{-}Fe^{3+} + H_2O + OH^\bullet \tag{4}$$

$$X\text{-}Fe^{3+} + H_2O_2 \rightarrow X\text{-}Fe^{2+} + H^+ + HOO^\bullet \tag{5}$$

$$H_2O_2 + OH^\bullet \rightarrow H_2O + HOO^\bullet \tag{6}$$

$$HOO^\bullet + OH^\bullet \rightarrow H_2O + O_2 \tag{7}$$

So there is a range of H₂O₂ concentration effective for the degradation of the dye and the value was set as the minimum needed (8.7 mM) for the heterogeneous Fenton reaction using Y Zeolite as support of the Fe²⁺.

3.5. Effect of the temperature

The decolourization rate at 25 °C increases as the contact time between the dye solution and the catalyst increases, being of 71% at 7 h and needing 24 h to reach a total decolourization ($99.7 \pm 0.7\%$). But textile effluents have unusually high temperature compared to most of the industrial wastewaters and during the dyeing process, rinse water temperature can increase up to 90 °C [25]. Therefore, a temperature range of 25–100 °C was studied in order to investigate the effect of this parameter on the decolourization of the aqueous dye solutions. The contact time between the solution and the catalyst was chosen as 6 min because previous experiments had shown the complete degradation of the dye at this time for 80 °C. The results are shown in Fig. 6 where it is observed how the decolourization efficiency percentage increases as the temperature increases, reaching decolourization higher than 99% at 60 °C, due to the increase of the reaction rate of the OH• formation. On the other hand, other studies [26,27] mentioned that when the temperature
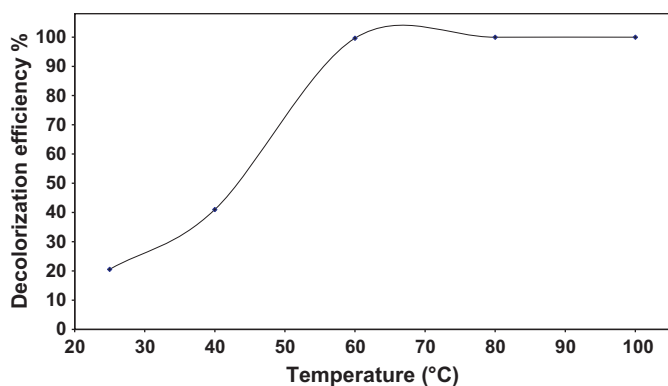
Fig. 6. Effect of temperature on the efficiency of the colour removal for 100 ml of 50 ppm of the dye, at pH 5.63, with 8.7 mM of hydrogen peroxide and ratio Fe(II)-Y Zeolite/solution volume of 15 g/L.

of the solution was higher than 40–50 °C, the removal performance decreased due to the thermal decomposition of hydrogen peroxide into oxygen and water, which seems not to be the most important factor in our study, probably due to the combination of both, the fast reaction rate and the heterogeneous catalyst. Similar results to ours have been reported for Fenton's treatment of a carpet dyeing wastewater [28].

3.6. Effect of the catalyst concentration

The effect of the ratio amount of Fe(II)-Y Zeolite and the solution volume on the decolourization efficiency of AR 14 was studied. Experiments were carried out at 0.83, 1.24 and 1.5 g of Fe(II)-Y Zeolite for 100 ml of the solution of the dye and showed that the efficiency of the heterogeneous Fenton processes increased with the increase of the amount of catalyst (89 ± 3, 97.1 ± 0.3 and 99.1 ± 0.2 respectively). This behavior can be assigned to the fact that the increase in the amount of Fe(II)-Y Zeolite increases the presence of active sites on the catalyst surface as well as the free hydroxyl radical generation. The same observation was reported by Chen and Zhu [29] for heterogeneous UV-Fenton catalytic degradation of dyestuff in water with hydroxyl-Fe pillared bentonite.

3.7. Mineralization, zeolite capacity, leaching test and stability of the catalyst

The TOC of the initial dye solution was measured before and after the Fenton catalyst optimized process (initial dye concentration of 50 ppm, pH 5.96, concentration of H_2O_2 8.7 mM, 80 °C and 15 g of catalyst/L of solution) and mineralization efficiency was calculated by Eq. (2). In less than 30 min, the mineralization degree was found to be $84 \pm 5\%$ what means that a high portion of the dye is mineralized to CO_2, what may decrease not only colour but also toxicity of the solution.

The total amount of iron loaded onto the zeolite was found to be 5.49×10^{-3} g of iron for every 1 g of the prepared Fe(II)-Y Zeolite.

Leaching tests were carried out in order to evaluate the potential loss of iron ions from the zeolite. In all of the experiments performed, the concentration of the iron ions was always below 0.2 ± 0.1 mg/L. So it can be assumed that the iron released from the zeolite to the solution is not significant, and moreover it shows that catalysis performance is mainly due to the heterogeneous effect of the catalyst (Fe(II)-Y Zeolite) and not to the leached iron ions.

The Fe(II)-Y Zeolite was used once at the optimized conditions and the decolourization efficiency was found to be 100.0 ± 0.1. When it was reused for the second time, the result showed no significance difference, 99.8 ± 0.2, and from the third time it was 93 ± 1. So, the Fe(II)-Y Zeolite catalytic performance could be repro-

duced in consecutive experiments without a considerable drop in the process efficiency.

4. Conclusion

The heterogeneous Fenton process using Fe(II)-exchanged synthetic Y Zeolite provides good performance in the decolourization treatment of the C.I. Acid Red 14 in aqueous solution. The best optimized conditions were found to be in the pH range between 3.13 and 7.27, with an amount of catalyst of 15 g/L, concentration of H_2O_2 8.7 mM and at temperature of 80 °C for a dye concentration of 50 ppm. Under these conditions, the complete removal of colour (higher than 99%) and high degree of mineralization (higher than 84%), could be achieved in only 6 min. A recent work [30] shows a decolourization efficiency of 90% for the AR 14, by heterogeneous photo-Fenton process, in 20 min of the treatment, but only a 6.0% of the dye mineralization was achieved during this time. Other studies also present good decolourization but times are longer than 30 min and nothing is said about the mineralization [31]. Other advantages for the heterogeneous system are the no generation of any solid waste (a great disadvantage of the homogeneous Fenton process), the no release of any iron to the solution, the good performance of the catalyst after consecutive experiments, the short contact time needed between the catalyst and the solution and the high effectivity of the catalyst in a wide range of pH and T.

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