Heterogeneous catalysis in the Fenton-type system reactive black 5/H$_2$O$_2$

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Abstract

In this study is demonstrated that hydrogen peroxide (H$_2$O$_2$) can be activated in the presence of a heterogeneous catalyst (Fe^{3+}-containing ashes) to become a powerful oxidant. Fe^{3+} was immobilized by five different methods in fly ash using a thermal procedure. Leaching test carried out in 0.05 M Na$_2$SO$_4$ ($\approx$pH 2.8 adjusted with H$_2$SO$_4$) indicated that more of the 99 wt.% of the iron ion stays in the solid catalysts and the presence of H$_2$O$_2$ does not alter this relation. It is concluded that radical species (HO$_2{}^\bullet$) are formed when H$_2$O$_2$ is activated by the immobilized Fe^{3+}. This approach can be used in effluent treatment and the oxidation efficiency of reactive black 5 (RB5) was investigated in batch tests. RB5 (MW = 991, λ_{max} = 598 nm) is one of the most important azo dyes in the dyeing industry and the oxidation of 0.061 mM RB5 by heterogeneous hydrogen peroxide activation were therefore investigated in mild conditions. In theory, the complete oxidation of RB5 is a 152 electrons oxidation, if sulfur and nitrogen undergoes a complete oxidation, hence, the stoichiometric conversion of 1 mol of RB5 to CO$_2$ requires up to 76 mol of hydrogen peroxide. Main experimental results show that it is possible to oxidize 0.061 mM RB5 (in a media 0.05 M Na$_2$SO$_4$, $\approx$pH 2.8 adjusted with H$_2$SO$_4$) using a stoichiometric amount of H$_2$O$_2$. After 2 h of treatment, reactive solutions were effectively colorless and 80% of the original chemical oxygen demand was removed.
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Keywords: Fenton-type supported catalysts; Azo-dye degradation; Fly ash; Advanced oxidation process; Wastewater treatment

1. Introduction

The elimination of organics from industrial wastewater is an important environmental target. It is estimated that every year more than 1000 new organic compounds are commercialized [1]. The big economic profits resulting from the utilization of new products have usually neglected the environmental risks inherent in their use. In order to minimize or avoid environmental problems, new legislation regarding wastewater has been developed in many countries during the last 25 years [2] and it is rapidly evolving and expanding world-wide [3–5] towards more severe, lower concentration limits of the pollutants. In the future, the objective must surely be zero effluent technology.

Among the most important pollutants found in textile wastewater are synthetic dyes and they represent a large problem because they cannot be destroyed by biological action [6].

At present time, it is estimated that more than 10 000 dyes are consumed in textile processing industries [6,7] and their concentrations in range from 10 to 10 000 mg/L [6], depending on the process. What is worst, is estimated 10–20% of dyes are lost in industrial effluents [8–10]. Color is one of the most hated pollutant, because of several reasons: (i) it is visible and even small quantities of dyes ($\geq$0.005 mg/L) are not allowed [8]; (ii) color can interfere with transmission of sunlight into natural streams; (iii) many of the azo dyes and their intermediate products, such as aromatic amines, are toxic to aquatic life, carcinogenic and mutagenic to humans [10–12]. Consequently, dyes have to be removed from textile wastewater before discharge. For conventional treatment processes, such as landfill, coagulation/flocculation, membrane separation and activated carbon, the main mechanism to eliminate dyes consist of a physical transfer, from one point (wastewater) to another (sludges). Organics in wastewater that cannot easily be destroyed, by biological or conventional routes, have been mainly treated by incineration, catalyzed wet-air oxidation, oxidation under supercritical conditions, use of sodium hydroxide at high temperature and

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pressure, high-temperature reduction with hydrogen and ruthenium tetraoxide oxidation [13,14]. However, the incineration of organic waste can pose emission problems if the combustion conditions are not carefully controlled. Supercritical oxidation and wet-air oxidation are more promising alternatives to incineration. Then again, the high cost of the operating conditions in supercritical oxidation and wet-air oxidation techniques make them less attractive on an industrial scale. But, due to the stability of dyes, their destruction is difficult and forcing conditions are required and the search for new, clean and cheap technologies for the removal of these compounds is justified. Thus the effective removal of dyestuff from wastewater is a current technological challenge.
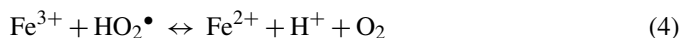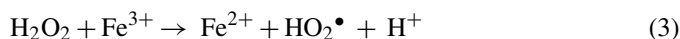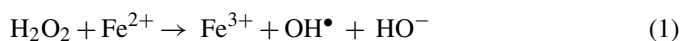
During the last 20 years, applications of clean oxidants such as O_3 and H_2O_2 have been greatly expanded in both scope and scale. Their popularity is due to their environmental acceptability and because reactions in which they are involved can be engineered to be performed under mild conditions. In a good wastewater treatment, any inorganic residuals must be innocuous and the organics in solution must be converted to CO_2 or compounds acceptable to biological treatments. Under these conditions, O_3 and H_2O_2 are ideal candidates, because they lead to no inorganic residue.

Advanced oxidation process (AOP) are based on powerful oxidant such as radical species $OH^\bullet$ and they are formed, basically, when H_2O_2 is reacted in the presence of transition metal ions, UV light, an alkali or acid. More than a century ago, it was reported that dissolved ferrous ion strongly catalyses the oxidation of maleic acid by hydrogen peroxide. But it was not until 40 years later that this homogeneous catalytic reaction received further attention. Since then, a large amount of work has been carried out to understand the mechanism of catalysis [7,15–18] and to apply the hydroxyl radical generated to textile effluent treatment [9,19,20]. Although in all cases, COD was depleted to acceptable limits, the Fenton process is not well understood, because its performance depends on several parameters and all of them are closely related: temperature, pH, catalyst, hydrogen peroxide and pollutant concentration [6].

In order to better understand Fenton process, some authors [9] investigated the degradation of reactive black 5 (RB5) by a Fenton-type process. They suggested that a Fenton process is divided in two stages. The first one is named as Fe^{2+}/H_2O_2 stage and the $OH^\bullet$ formed decomposes azo bonds (N=N) very quickly because they are easier to destroy than aromatic ring structures. The second one is named Fe^{3+}/H_2O_2 stage and its oxidation rate is slower than the first stage due to slow regeneration of Fe^{2+} from Fe^{3+} and this is why a complete mineralization is not achieved. However, some experimental evidences show that the first stage of Fenton process not only occurs very fast, but also it is possible to oxidize azo dye (amaranth), aromatic compounds (phenol, hydroquinone, catechol, *p*-benzoquinone and aniline) and aliphatic acids (oxalic acid) [21]. The second stage of the Fenton process is indeed slow, but it is independent of the couple (Fe^{3+}/H_2O_2 or Fe^{2+}/H_2O_2) and organic compound. Although the Fenton's reaction is not clear it is apparent that, in the first stage, Fe(II) is converted to Fe(III) by reaction either with hydrogen peroxide or other intermediates (e.g. $OH^\bullet$, $HO_2^\bullet$, etc.). In the second stage of the Fenton process, both iron ions (Fe^{2+} and Fe^{3+}) are not detected (electrochemically) in the solution and this causes a loss of catalytic activity for the decomposition of hydrogen peroxide and obviously, Fenton process stops [22]. In order to avoid this problem, homogeneous catalyst (soluble ions Fe^{2+} and Fe^{3+}) should be changed for heterogeneous catalyst (immobilized iron ions Fe^{2+} and Fe^{3+}). This approach has been applied recently with a better catalyst control in the Fenton process [23–25].

Radical species ($HO_2^\bullet$, $OH^\bullet$) are formed when H_2O_2 is reacted in the presence of Fe(II)/Fe(III) under appropriate conditions. A clear description of radical species formation by means of an appropriated set of chemical reactions is a complex task and it varies according to the authors [16,26]. However, main chemical reactions can be summarized as follows [4]:

$$H_2O_2 + Fe^{2+} \rightarrow Fe^{3+} + OH^\bullet + HO^- \tag{1}$$

$$Fe^{2+} + OH^\bullet \rightarrow Fe^{3+} + OH^- \tag{2}$$

$$H_2O_2 + Fe^{3+} \rightarrow Fe^{2+} + HO_2^\bullet + H^+ \tag{3}$$

$$Fe^{3+} + HO_2^\bullet \leftrightarrow Fe^{2+} + H^+ + O_2 \tag{4}$$

Under this approach, $OH^\bullet$ generation is carried out by a very fast reaction (Eq. (1)) but Fe^{2+} can be oxidized (wasted) in the presence of $OH^\bullet$ (Eq. (2)). Although Fe^{+2} can be regenerated by Eqs. (3) and (4), they are so slow that this is the main problem to maintain the redox chain. Nevertheless, the acceptance of the reactive species $OH^\bullet$ as a powerful oxidant in the Fenton process is not universal and some authors doubt about it [27,28]. What is very clear is that a mixture of $H_2O_2/Fe(II)$ or $H_2O_2/Fe(III)$ produces a strong oxidant capable of oxidizing (large and small) organic pollutants in mild conditions and this approach can be applied in wastewater treatment.

Reactive black 5 (RB5) is a large molecule (MW = 991; λ_{max} = 598 nm; dye content = 55%) and its structure is presented in Fig. 1.

The complete oxidation of RB5 is a 152 electrons oxidation if sulfur and nitrogen are transformed in sulfuric and nitric acids respectively:
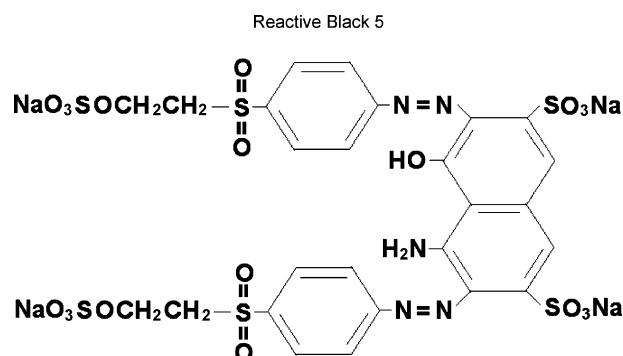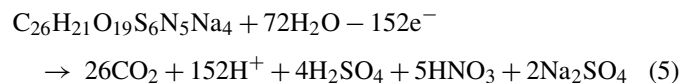
$$C_{26}H_{21}O_{19}S_6N_5Na_4 + 72H_2O - 152e^-$$
$$\rightarrow 26CO_2 + 152H^+ + 4H_2SO_4 + 5HNO_3 + 2Na_2SO_4 \tag{5}$$

Fig. 1. Reactive black 5 (RB5), MW = 991; λ_{max} = 598 nm; dye content = 55%.

Also, H_2O_2 accepts two electrons according to the following equation:

$$H_2O_2 + 2H^+ + 2e^- \rightarrow 2H_2O \qquad (6)$$

Hence, the stoichiometric conversion of 1 mol of RB5 to CO_2 requires up to 76 mol of H_2O_2 if the nitrogen undergoes a complete oxidation:

$$C_{26}H_{21}O_{19}S_6N_5Na_4 + 76H_2O_2$$
$$\rightarrow 26CO_2 + 80H_2O + 4H_2SO_4 + 5HNO_3 + 2Na_2SO_4 \qquad (7)$$
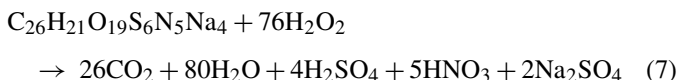
As it was mentioned above, Fenton process stops because iron ions are not under effective control during the oxidation reaction. So, a heterogeneous supported catalyst is proposed in this work to improve the control over iron ions during the oxidation reaction. Fly ash from a coal thermal power plant was used as iron support. The main reason is its high-surface area, which would provide more active sites to the catalyst. Also, Ca, K, Mg, Ti compose the fly ash, among others, and these elements could be exchanged by Fe using proper procedures. The incorporation of Fe to the fly ash would provide more Fenton active sites to the catalytic structure. In addition to that, it is expected that the fly ash from bituminous coal is not so harmful since the content of toxic compounds (i.e. dioxins and furans) could be negligible. In order to produce dioxins or furans, it is necessary the fuel have chloride in its structure; although chloride was not determined, it is expected that its content in the original bituminous coal is minimal, so the possibility they were formed and subsequently adsorbed on the fly ash is remote. Based on that, several studies have been reported where fly ashes coming from bituminous coal are used in water remediation processes to deal with the elimination of many harmful pollutants, including dye colorants and heavy metals, among others [29–54]. In these studies no concerns were raised about dioxins and/or furan water release and contamination after the remediation treatment. Moreover, even in the case these compounds were formed and adsorbed on the surface of the fly ash, they would disappear during the calcination step at 500 °C since it has been reported that they are desorbed from different solids at 300–400 °C [55–60].

Under this theoretical approach, the oxidation of RB5 was investigated in batch test using a beaker containing the working solution (0.05 M Na_2SO_4, pH 2.8 adjusted with H_2SO_4) plus heterogeneous catalyst and H_2O_2.

2. Experimental

2.1. Catalysts preparation

Commercial products were used without further purification. A powder sample (fly ash) was obtained from the Rio Escondido Thermal Power Plant in the north of Mexico. Fe^{3+} was immobilized in the solid by the following five different methods.

Catalyst C1 was prepared supporting the metal by the incipient impregnation method [61]. In this process, 6.0 g of $Fe(NO_3)_3 \cdot 9H_2O$ (Merck) were dissolved in a beaker containing 20 mL of distilled water. Then, 10 g of fly ash were added to this aqueous solution and the agitation mixing of the beaker was kept at 120 rpm and 100 °C until water was evaporated. The sample was dried at 100 °C overnight and then calcined at 500 °C during 4 h.

For catalyst C2 to C5, they were prepared by ion exchange in acid or alkaline media according to the procedure proposed by Centi et al. [62]. Catalyst C2 was prepared by dissolving 40.4 g of $Fe(NO_3)_3 \cdot 9H_2O$ (Merck) in 150 mL of a solution that contained 6.33 g of HNO_3 (Merck). Then, the mixture was mechanically stirred at 120 rpm at room temperature for 1 h. This solution was added to a beaker containing 10 g of a washed fly ash in 150 mL distilled water. This suspension was mechanically agitated at 120 rpm and room temperature for 4 h. Then, the mixture was aged at 60 °C for 7 days. After filtration and washing with double distilled water the sample was dried at 100 °C overnight, and then calcined at 500 °C for 4 h.

Catalyst C3 was prepared in similar way as catalyst C2; the main difference was that ultrasonic energy at 47 kHz (Cole-Parmer, mod 8890R-MTH) was applied instead of mechanical stirring. The objective of applying ultrasonic energy was to reduce the catalyst particle size, and therefore, increase its catalytic activity.

For catalyst C4, an alkaline mixture was prepared by dissolving 40.4 g of $Fe(NO_3)_3 \cdot 9H_2O$ (Merck) and 10.6 g of Na_2CO_3 in 150 mL of distilled water and mechanically stirred (120 rpm) at room temperature for 1 h. Then, this solution was added to a beaker containing 10 g of a washed fly ash in 150 mL distilled water and was mechanically agitated (120 rpm) for 4 h. This mixture was kept at 60 °C for 7 days. After filtration and washing with double distilled water the sample was dried at 100 °C overnight and then calcined at 500 °C for 4 h.

Finally, catalyst C5 was prepared in alkaline media as catalyst C4, but ultrasonic energy was applied in place of mechanical stirring.

2.2. Analytical procedures

The chemical oxygen demand (COD) was analyzed by a Hach procedure using a Spectrophotometer DR/4000 UV–vis. Color spectra were analyzed by means of a Hach Spectrophotometer DR/4000 UV–vis, and a calibration curve, shown in Fig. 2, was built to convert from absorbance at 598 nm (wavelength) to concentration of the RB5 in the solution. Total iron and ferrous iron were analyzed by FerroZine method and 1,10-phenanthroline method, respectively. Both are spectrophotometric Hach methods.

3. Results and discussion

3.1. Catalyst characterization

Atomic absorption: metal contain in the original fly ash was determined by atomic absorption spectroscopy (Spectr AA 220 Varian). Main results are: Mn (0.014 wt.%), K (1.09 wt.%), Na (0.5 wt.%), Mg (0.5 wt.%), Cr (0.02 wt.%), Pb (0 wt.%), Al (14 wt.%), Ti (1 wt.%), Si (26 wt.%), Ca (2 wt.%) and Fe (0.06 wt.%).
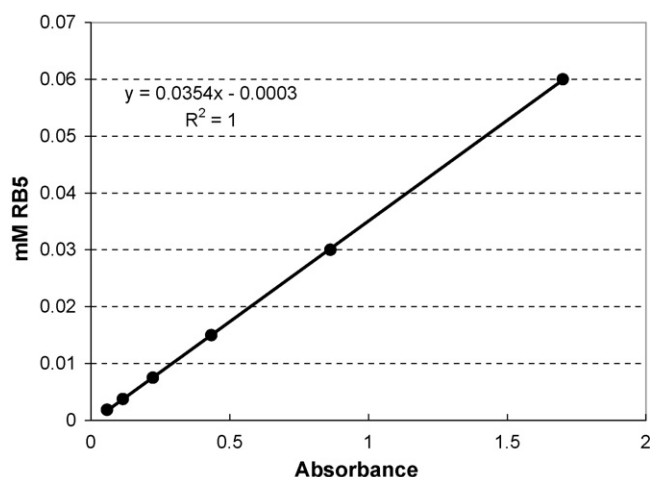
Fig. 2. Calibration curve to relate absorbance at 598 nm (wavelength) to concentration of RB5 in the solution.

Fig. 3. X-ray powder diffraction spectrum of the catalyst C4 after preparation.

X-ray diffraction: X-ray powder diffraction measurements of the catalysts (before and after the preparation) were conducted on a Rigaku (Japan) powder difractometer equipped with Cu Kα radiation in the angle range $2\theta = 4$–$100°$. Fig. 3 shows an X-ray powder diffraction spectrum of the catalyst C4 after preparation. The main mineral found in catalyst C4 are Fe_2O_3 (hematite), graphite, SiO_2 (quartz), $Al_6Si_2O_{13}$ (mullite), $CaAl_4Fe_8O_{19}$ and Al_2SiO_5 (Sillimanite). The rest of catalysts show similar spectrum. Hence, it is deduced that prepared catalysts (Fe^{3+}-containing ashes) mainly consist of Fe_2O_3.

The maximum amount of immobilized Fe^{3+} in the five catalysts was evaluated by dissolving 0.1 g of catalyst following the standardized digestion procedure ASTM-D3682-91. After mix-
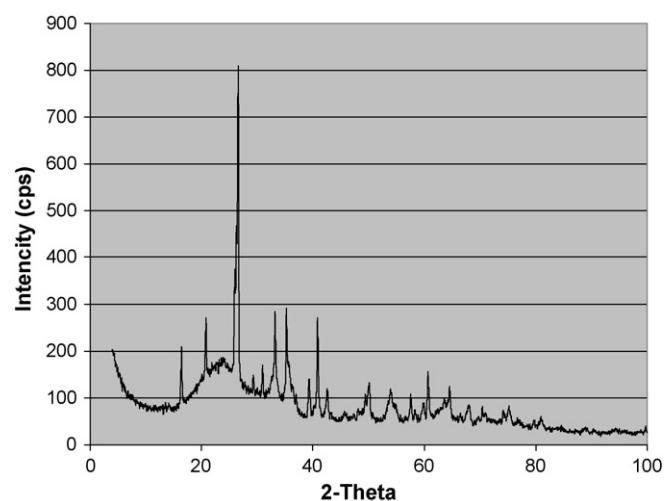
ing and heating until the volume was reduced to 50 mL, this final solution was diluted to 150 mL, and then, total iron and ferrous iron were analyzed. In order to know the amount of initial iron in the original fly ash, it was applied with the same procedure. Table 1 shows main results. As it can be seen, the maximum amount of immobilized Fe^{3+} was achieved by means of the first method.

3.2. Leaching test

The results are reported as well in Table 1. These experiments were carried out in the working solution (0.05 M Na_2SO_4, pH 2.8 adjusted with H_2SO_4) and applying the following proce-

Table 1
Amount of iron found in fly ash as a function of the method applied for immobilizing the iron ion

Catalyst 0.1 g	Amount of immobilized iron		Soluble iron in 0.05 M Na_2SO_4 (pH 2.8 adjusted with H_2SO_4)		Leaching test
	Fe^{3+} mg	Fe^{2+} mg	Fe^{3+} mg	Fe^{2+} mg	
C1	8.2125	0.375	0.0464	0.0036	1
			0.0527	0.0038	2
			0.0496	0.0054	3
			0.1487 (1.8%)	0.0128 (3.4%)	Total iron lost in 6 h
C2	0.600	0.12	0.0028	0.0020	1
			0.0020	0.0025	2
			0.0022	0.0015	3
			0.0070 (1.2%)	0.0060 (5%)	Total iron lost in 6 h
C3	1.4025	0.06	0.0064	0.0025	1
			0.0090	0.0023	2
			0.0061	0.0017	3
			0.022 (1.6%)	0.0065 (11%)	Total iron lost in 6 h
C4	0.7575	ND	0.0035	ND	1
			0.0053	ND	2
			0.0022	ND	3
			0.0108 (1.4%)	ND	Total iron lost in 6 h
C5	0.885	0.495	0.0072	0.0012	1
			0.0033	0.0015	2
			0.0027	0.0020	3
			0.008 (1.5%)	0.0047 (1%)	Total iron lost in 6 h

The initial Fe^{3+} found in 0.100 g of the original fly ash was 0.0459 mg. ND: not determined.

dure at room temperature: 0.1 g of any catalyst was added to a beaker containing 100 mL of the working solution. After stirring (120 rpm) for 2 h, the solution was allowed to settle down, filtrated and then, total iron and ferrous iron were analyzed by Hach methodology; results are labeled as Leaching Test 1. The catalyst was recuperated and added to a second beaker containing a fresh working solution, then, the previous methodology was applied and total iron and ferrous iron were analyzed; results are labeled as Leaching Test 2. Finally, the catalyst was recuperated and added to a third beaker containing a fresh working solution, then the previous methodology was applied and total iron and ferrous iron were analyzed; results are labeled as Leaching Test 3.

In all cases, leaching tests last till 6 h and indicated that ion Fe^{3+} is lost in small amounts from the fly ash at constant rate. Therefore, catalysts are very stable under the experimental studied condition.

3.3. Degradation of RB5

3.3.1. Effect of H_2O_2 concentration

Taking into account the oxidation model represented by Eq. (7), the degradation of an aqueous solution of 0.06 mM RB5 (initial COD was 51 ppm O_2) by means of catalyst C1 was investigated in batch tests following the next procedure: the pH of 100 mL 0.05 M Na_2SO_4 was lowered (with H_2SO_4) to 2.8, then 0.1 g catalyst C1 (this is equivalent to have 1.5 mM Fe^{3+} in solution) and RB5 were added. After a short mixing time a stoichiometric amount of H_2O_2 was added to the batch reactor and the RB5 oxidation started. During the degradation, samples were taken every 10 min and the absorbance of the solution was immediately recorded in order to determine the concentration of RB5 in the reacting solution. Fig. 4 shows RB5 oxidation with 4.56 mM H_2O_2 (stoichiometric amount, curve (a)), 5.0 mM H_2O_2 (10% more than the stoichiometric amount, curve (b)) and 5.5 mM H_2O_2 (20% more than the stoichiometric amount, curve
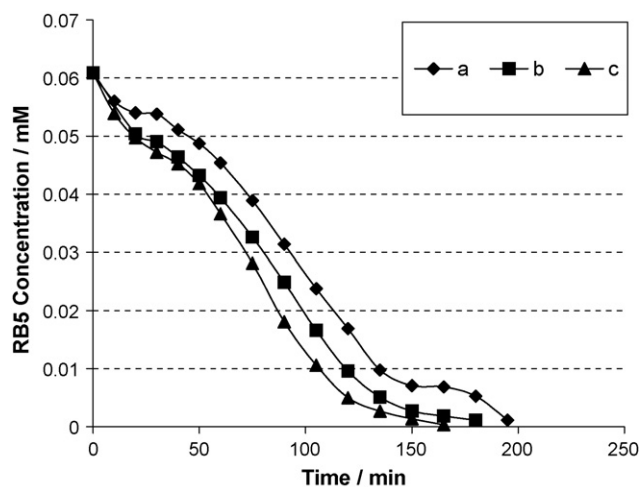

Fig. 4. Degradation of RB5 with activated H_2O_2 by an heterogeneous catalyst (C1). Experimental conditions: 100 mL 0.05 M Na_2SO_4 + RB5 + 0.100 g catalyst C1, pH 2.8 and room temperature. (a) 4.56 mM H_2O_2, (b) 5.0 mM H_2O_2 and (c) 5.5 mM H_2O_2.
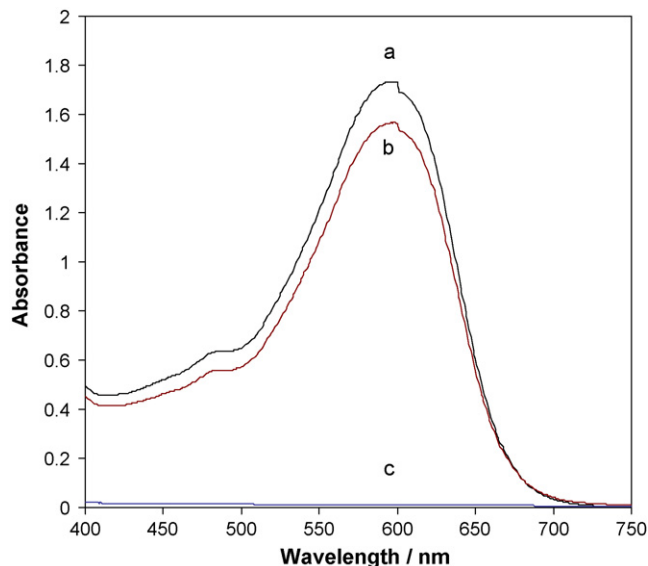

Fig. 5. Absorbance spectra for (a) the initial solution (100 mL 0.05 M Na_2SO_4 + 0.06 mM RB5 + 0.100 g Catalyst 1, pH 2.8), (b) after 195 min of contact time (catalyst C1-RB5) but in the absence of H_2O_2 and (c) after 195 min of Fenton process (100 mL 0.05 M Na_2SO_4 + 0.06 mM RB5 + 0.100 g Catalyst C1, pH 2.8 + 4.56 mM H_2O_2).

(c)). As it was expected, the rate of RB5 degradation increases with H_2O_2 concentration; however, is not advisable to increase further the H_2O_2 concentration, because the Fenton process is not longer profitable. After 165 min of treatment and using 20% excess of H_2O_2 (curve (c) in Fig. 4), the solution was effectively colorless and the final COD was <10 ppm O_2, representing an abatement of more than 80%.

In order to verify if the color and COD abatement from the solution was due to degradation by Fenton process rather than by an adsorption process, some experiments were repeated under the same experimental conditions, but in the absence of H_2O_2 to avoid the Fenton process. Fig. 5 shows the absorbance spectra for: (a) the initial solution, (b) after 180 min of contact time (catalyst C1-RB5), and (c) in the absence of H_2O_2 after 180 min of Fenton process.

As it can be seen from Fig. 5, adsorption process is not playing an important role in color and COD abatement from the solution. Therefore, it is demonstrated that H_2O_2 was activated by the heterogeneous catalyst C1 and Fe^{3+}/H_2O_2 became a powerful oxidant, capable of the RB5 observed degradation, following a Fenton-type path.

3.3.2. Effect of catalyst loading

The effect of catalyst concentration was investigated taking into account that, in general, it is accepted that Fenton process works well in the presence of small (∼1 mM Fe^{2+}) quantities of Fe^{2+} [6,9,22]. Fig. 6 shows color removal as a function of the amount of catalyst C1 under the following experimental conditions: 100 mL 0.05 M Na_2SO_4 + 0.06 mM RB5 + 5.5 mM H_2O_2, pH 2.8 and room temperature. Catalyst concentration—curve (a): 1.2 g original fly ash (0.1 mM Fe^{3+}); curve (b): 0.2 g catalyst C1 (3.0 mM Fe^{3+}); curve (c): 0.1 g catalyst C1 (1.5 mM Fe^{3+}).
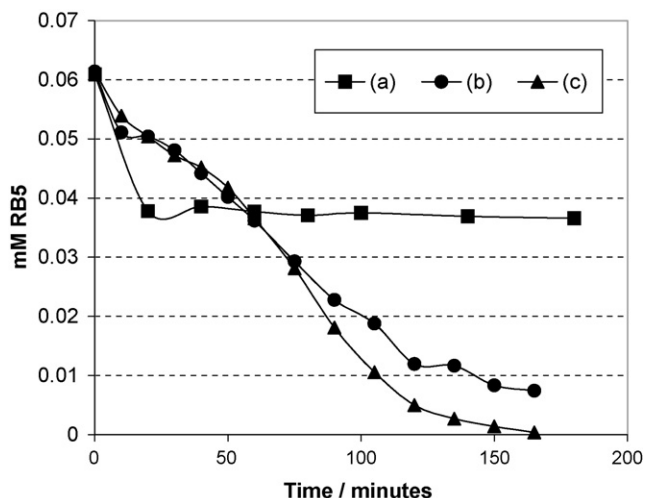
Fig. 6. Degradation of RB5 with activated H_2O_2 by an heterogeneous catalyst (C1). Experimental conditions: 100 mL 0.05 M Na_2SO_4 + RB5 + 5.5 mM H_2O_2, pH 2.8 and room temperature. (a) 1.2 g original fly ash (0.1 mM Fe^{3+}), (b) 0.2 g catalyst C1 (3.0 mM Fe^{3+}) and (c) 0.1 g catalyst C1 (1.5 mM Fe^{3+}).

Although original fly ash comes with a small amount of Fe^{3+}, it is not enough to generate a Fenton process, as it can be seen in curve (a) in Fig. 6. A small amount of catalyst C1 (0.1 g) seems to generate a good Fenton process according to curve (c) in Fig. 6, but higher catalyst concentration does not boost up the RB5 degradation as it is demonstrated in curve (b) in Fig. 6. A similar trend was observed by other authors [6,9].

3.3.3. Performance of heterogeneous catalysts

Applying the same methodology as before, the degradation of an aqueous solution of 0.06 mM RB5 was investigated in batch tests as a function of the prepared catalysts. In order to have always 1.5 mM Fe^{3+} in solution, different amounts of catalysts were used depending on its concentration. Fig. 7 shows color removal as a function of catalysts under the following
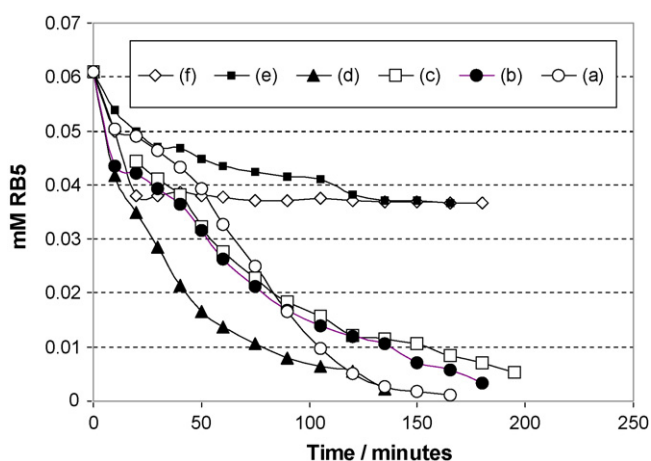

Fig. 7. Degradation of RB5 with activated H_2O_2 by heterogeneous catalysts. Experimental conditions: 100 mL 0.05 M Na_2SO_4 + RB5 + 5.0 mM H_2O_2 + required amount of catalyst, pH 2.8 and room temperature. (a) 0.1 g catalyst C1, (b) 1.2 g catalyst C2, (c) 0.59 g catalyst C3, (d) 1.13 g catalyst C4, (e) 0.90 g catalyst C5 and (f) 1.2 g original fly ash (0.55 mM Fe^{3+}).
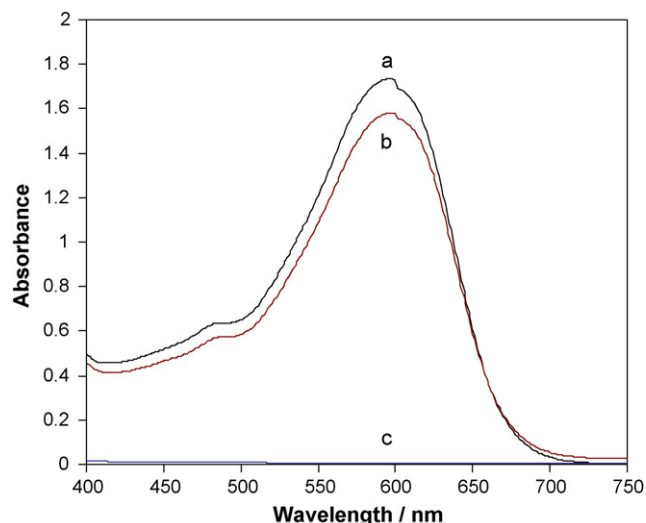

Fig. 8. Absorbance spectra for (a) the initial solution (100 mL 0.05 M Na_2SO_4 + 0.06 mM RB5 + 1.20 g catalyst C2, pH 2.8), (b) after 195 min of contact time (catalyst C2-RB5) but in the absence of H_2O_2 and (c) after 195 min of Fenton process (100 mL 0.05 M Na_2SO_4 + 0.06 mM RB5 + 1.20 g catalyst C2, pH 2.8 + 4.56 mM H_2O_2).

experimental conditions: 100 mL 0.05 M Na_2SO_4 + 0.06 mM RB5 + 4.56 mM H_2O_2 + required amount of catalyst, pH 2.8 and room temperature.

The catalytic performance of catalyst C5 in the degradation of 0.06 mM RB5 was poor and its catalytic activity is similar to that observed in the original fly ash, as can be observed in curves (e) and (f) in Fig. 7. Catalytic performance of catalysts C1, C2 and C3 are similar. These results indicate that H_2O_2 is better activated in the presence of catalyst C4. Also, it is observed that application of ultrasonic energy does not improve the performance of the catalyst; in fact, in acid media (catalysts C2
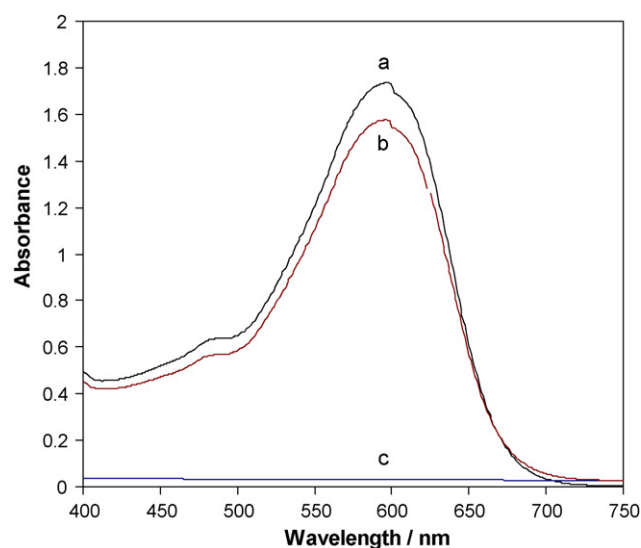

Fig. 9. Absorbance spectra for (a) the initial solution (100 mL 0.05 M Na_2SO_4 + 0.06 mM RB5 + 0.59 g catalyst C3, pH 2.8), (b) after 195 min of contact time (catalyst C3-RB5) but in the absence of H_2O_2 and (c) after 195 min of Fenton process (100 mL 0.05 M Na_2SO_4 + 0.06 mM RB5 + 0.59 g catalyst C3, pH 2.8 + 4.56 mM H_2O_2).
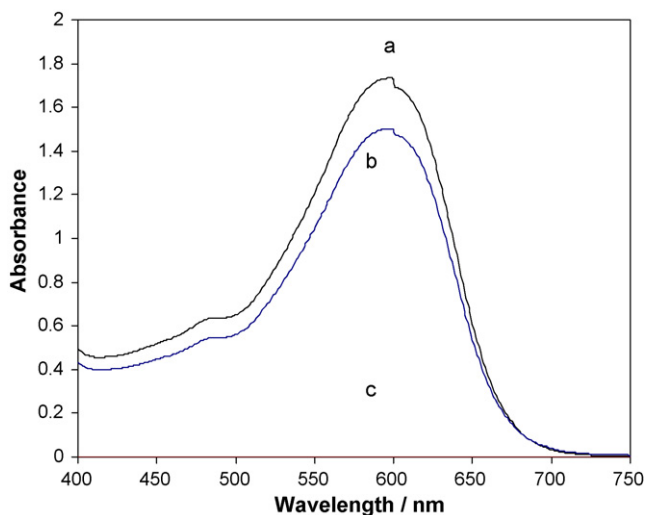
Fig. 10. Absorbance spectra for (a) the initial solution (100 mL 0.05 M Na_2SO_4 + 0.06 mM RB5 + 1.13 g catalyst C4, pH 2.8), (b) after 180 min of contact time (catalyst C4-RB5) but in the absence of H_2O_2 and (c) after 135 min of Fenton process (100 mL 0.05 M Na_2SO_4 + 0.06 mM RB5 + 1.13 g catalyst C4, pH 2.8 + 4.56 mM H_2O_2).

and C3) the activity was almost the same, and in alkaline media (catalysts C4 and C5) the activity of the catalyst prepared with mechanical stirring was much higher than those where ultrasonic energy was applied during the preparation. Except for catalyst C5, the rest of them could abate both the COD (~80%) and the color from the solution.

3.3.4. RB5 adsorption on catalysts

The RB5 adsorption on the catalyst C1 was discussed above and described in Fig. 5. Applying the same methodology as
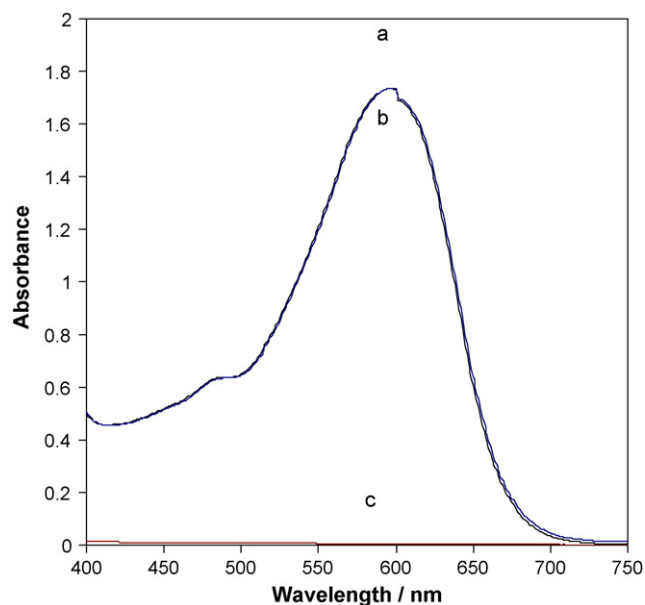

Fig. 11. Absorbance spectra for (a) the initial solution (100 mL 0.05 M Na_2SO_4 + 0.06 mM RB5 + 0.90 g catalyst C5, pH 2.8), (b) after 180 min of contact time (catalyst C5-RB5) but in the absence of H_2O_2 and (c) after 180 min of Fenton process (100 mL 0.05 M Na_2SO_4 + 0.06 mM RB5 + 0.90 g catalyst C5, pH 2.8 + 4.56 mM H_2O_2).
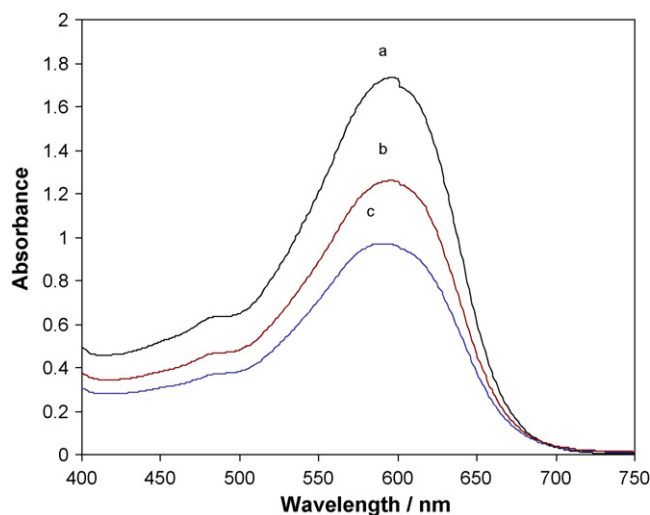

Fig. 12. Absorbance spectra for (a) the initial solution (100 mL 0.05 M Na_2SO_4 + 0.06 mM RB5 + 0.50 g fly ash, pH 2.8), (b) after 180 min of contact time (fly ash-RB5) but in the absence of H_2O_2 and (c) after 180 min of Fenton process (100 mL 0.05 M Na_2SO_4 + 0.06 mM RB5 + 0.50 g fly ash 5, pH 2.8 + 4.56 mM H_2O_2).

before, the magnitude of RB5 adsorption on catalyst 2–5 and the original fly ash are shown in Figs. 8–12, respectively. Except for catalyst C5, the rest of them, including the original fly ash, adsorb a small amount of RB5 that can be negligible.

4. Conclusions

In this study it was demonstrated that the couple Fe^{3+}/H_2O_2 is as efficient as the Fe^{2+}/H_2O_2 during a Fenton-type process. The mixture Fe^{3+}/H_2O_2 produces a strong oxidant ($HO_2^{\bullet}$) capable of oxidizing organic pollutants in mild conditions and this approach might be applied in wastewater treatment in more realistic experiments. Fly ash, from a coal thermal power plant, is an economic material and it was used as iron support because of its high-surface area, which would provide more active sites to the catalyst. Fe^{3+} was effectively immobilized in fly ash using simple thermal procedures. Heterogeneous catalyst (Fe^{3+}-containing ashes) is stable for at least 6 h in aqueous solutions (0.05 M Na_2SO_4, pH 2.8) similar to those found in textile effluents. This implies that, under the heterogeneous catalyst approach, iron ion is better controlled and Fenton process is more efficient than in the homogeneous catalyst approach. The extremely lightweight of fly ash allow a uniform suspension of the heterogeneous catalyst in the solution improving its efficiency in the Fenton process. However, this advantage could be a technological challenge to prevent from clogging an electrochemical flow-cell when this approach is applied in a more realistic experiment.

References

[1] C. Seignez, C. Pulgarin, P. Peringer, Swiss Chem. 1 (1992) 25.
[2] N.L. Weinberg, in: J.D. Genders, N.L. Weinberg (Eds.), Electrochemistry for a Cleaner Environment, Electrosynthesis Co., New York, 1992.

[3] I. Rousar, K. Micka, in: C.A.C. Sequeira (Ed.), Environmental Oriented Electrochemistry, Elsevier Science B.V., Amsterdam, 1994, p. 45.
[4] K. Rajeshwar, J. Ibanes, Environmental Electrochemistry: Fundamentals and Applications in Pollution Abatement, Academic Press Inc., San Diego, 1997.
[5] R. Ganesh, G.D. Boardman, D. Michelsen, Water Res. 28 (1994) 1367–1376.
[6] S. Meriç, D. Kaptan, T. Olmez, Chemosphere 54 (2004) 435–441.
[7] M. Neamtu, I. Siminiceanu, A. Yediler, A. Kettrup, Dyes Pigments 53 (2002) 93–99.
[8] Z. He, S. Song, H. Zhou, H. Ying, J. Chen, Ultrason. Sonochem. 14 (2007) 298–304.
[9] K.T. Chung, S.E.J. Stevens, Environ. Toxicol. Chem. 12 (1993) 2121–2132.
[10] M.S. Lucas, J.A. Peres, Dyes Pigments 71 (2006) 236–244.
[11] N.H. Ince, M.I. Stefan, J.R. Bolton, J. Adv. Oxid. Technol. 2 (1997) 442–448.
[12] K.T. Chung, S.E.J. Stevens, C.E. Cerniglia, Crit. Rev. Microbiol. 18 (1992) 175–197.
[13] J. Skitt, Waste Disposal Management and Practice, Charles Knight & Co. Ltd., London, 1979.
[14] D.E. Daniel, Geotechnical Practice for Waste Disposal, Chapman & Hall, London, 1995.
[15] J.H. Baxendale, J.A. Wilson, Trans. Faraday Soc. 53 (1957) 344–356.
[16] C. Walling, T. Weill, Int. J. Chem. Kinetics 6 (1974) 507–516.
[17] G.V. Buxton, C.L. Greenstock, W.P. Helman, A.B. Ross, J. Phys. Chem. Ref. Data 17 (1988) 513–886.
[18] A.M. El-Dein, J.A. Libra, U. Wiesmann, Chemosphere 52 (2003) 1069–1077.
[19] H.Y. Shu, C.R. Huang, M.C. Chang, Chemosphere 29 (1994) 2597–2607.
[20] B.V. Darinka, M.L. Alenka, Dyes Pigments 59 (2003) 173–179.
[21] A. Alvarez-Gallegos, D. Pletcher, Electrochim. Acta 44 (1999) 2483–2492.
[22] A. Alvarez-Gallegos, D. Pletcher, Electrochim. Acta 44 (1998) 853–861.
[23] J. Fernandez, J. Bandara, J. Kiwi, A. Lopez, P. Albers, Chem. Commun. (1998) 1493–1494.
[24] A. Bozzi, T. Yuranova, J. Mielczarski, A. Lopez, J. Kiwi, Chem. Commun. (2002) 2202–2203.
[25] J. Feng, X. Hu, P.L. Yue, Ind. Eng. Chem. Res. 42 (2003) 2058–2066.
[26] S.S. Lin, M.D. Gurol, Environ. Sci. Technol. 32 (1998) 1417–1423.
[27] S.H. Bossman, E. Oliveros, S. Gob, J. Phys. Chem. A 102 (1998) 5542–5550.
[28] M.L. Kremer, Phys. Chem. Chem. Phys. 1 (1999) 3595–3607.
[29] S.K. Chaudhuri, B. Sur, J. Environ. Eng. 126 (2000) 583–594.
[30] R. Devi, R.P. Dahiya, Water Air Soil Poll. 174 (2006) 33–46.
[31] Y.K. Gong, H.Q. Xiang, F. Liu, J. Liaoning Tech. Univ. 25 (2006) 316–317.
[32] C.F. Cai, J.P. Xu, G.W. Tang, Z. Zheng, J. China Coal Soc. 31 (2006) 227–231.
[33] S. Wang, Y. Boyjoo, A. Choueib, Chemosphere 60 (2005) 1401–1407.
[34] S. Wang, Y. Boyjoo, A. Choueib, Z.H. Zhu, Water Res. 39 (2005) 129–138.
[35] V.K. Gupta, I. Ali, V.K. Saini, T. Van Gerven, B.D. Van Bruggen, C. Vandecasteele, Ind. Eng. Chem. Res. 44 (2005) 3655–3664.
[36] H.Q. Xiang, H. Yang, Z.J. Mo, Modern Chem. Ind. 25 (2005) 53–56.
[37] Y.T. Yu, Powder Technol. 146 (2004) 154–159.
[38] P. Janoš, H. Buchtová, M. Rỳznarová, Water Res. 37 (2003) 4938–4944.
[39] N. Chahbane, S. Souabi, H. Almardhy, K.W. Schramm, D. Lenoir, K. Hustert, A. Kettrup, Fresen. Environ. Bull. 11 (2002) 390–395.
[40] P.C. Kao, J.H. Tzeng, T.L. Huang, J. Hazard. Mater. 76 (2000) 237–249.
[41] A. Papandreou, C.J. Stournaras, D. Panias, J. Hazard. Mater. 148 (2007) 538–547.
[42] M. Ulmanu, T. Matsi, I. Anger, E. Gament, G. Olanescu, C. Predescu, M. Sohaciu, UPB Sci. Bull. Ser. B: Chem. Mater. Sci. 69 (2007) 109–116.
[43] W. Qiu, Y. Zheng, J. Hazard. Mater. 148 (2007) 721–726.
[44] Y.C. Sharma, Y.Ca. Uma, S.N. Singh, Paras, F. Gode, Chem. Eng. J. 132 (2007) 319–323.
[45] I.J. Alinnor, Fuel 86 (2007) 853–857.
[46] L.M. Ottosen, A.J. Pedersen, H.K. Hansen, A.B. Ribeiro, Electrochim. Acta 52 (2007) 3420–3426.
[47] A. Abdul Jameel, J. Sirajudeen, J. Indian Chem. Soc. 83 (2006) 944–945.
[48] S. Wang, H. Wu, J. Hazard. Mater. 136 (2006) 482–501.
[49] H. Cho, D. Oh, K. Kim, J. Hazard. Mater. 127 (2005) 187–195.
[50] K.S. Hui, C.Y.H. Chao, S.C. Kot, J. Hazard. Mater. 127 (2005) 89–101.
[51] S. Bulusu, A.H. Aydilek, P. Petzrick, R. Guynn, J. Geotechnol. Geoenviron. Eng. 131 (2005) 958–969.
[52] J.R. Kastner, K.C. Das, N.D. Melear, J. Hazard. Mater. 95 (2002) 81–90.
[53] K.A. Czurda, R. Haus, Appl. Clay Sci. 21 (2002) 13–20.
[54] N. Moreno, X. Querol, C. Ayora, A. Alastuey, C. Fernández-Pereira, M. Janssen-Jurkovicová, J. Environ. Eng. 127 (2001) 994–1002.
[55] A.M. Cunliffe, P.T. Williams, Chemosphere 66 (2007) 1146–1152.
[56] A.M. Cunliffe, P.T. Williams, Chemosphere 66 (2007) 1929–1938.
[57] R.S. Baker, J. LaChance, G. Heron, Land Contam. Reclam. 14 (2006) 620–624.
[58] M. Kubal, J. Fairweather, P. Crain, M. Kuras, Waste Manage. Environ. II (2004) 13–23.
[59] M.S. Milligan, E.R. Altwicker, Environ. Sci. Technol. 30 (1996) 225–229.
[60] R.T. Yang, R.Q. Long, J. Padin, A. Takahashi, T. Takahashi, Ind. Eng. Chem. Res. 38 (1999) 2726–2731.
[61] J.W. Geus, J.A.R. Von Veen, in: R.A. Von Santer, P.W.N.M. Von Leeumen, J.A. Moulijn, B.A. Averill (Eds.), Catalysis: An Integrated Approach, Elsevier Science B.V., Amsterdam, 1999, p. 459.
[62] G. Centi, S. Perathoner, T. Torre, M.G. Verduna, Catal. Today 55 (2000) 61–69.