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Catalytic wet peroxide oxidation of cosmetic wastewaters with Fe-bearing catalysts

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ABSTRACT

Catalysts based on Fe supported on γ-Al_2O_3 and active carbon (AC) have been prepared and tested for catalytic wet peroxide oxidation (CWPO) of cosmetic wastewaters. The catalysts were characterized by TXRF, XPS, XRD, SEM, elemental chemical analysis, Mössbauer spectroscopy and 77 K N_2 adsorption–desorption. The catalytic performance was monitored in terms of COD, TOC and H_2O_2 conversions. The possible leaching of iron from the catalyst was also checked. The influence of the catalysts preparation conditions (calcination temperature and Fe content) as well as the operating temperature in the oxidation process has been studied with the purpose of optimization. Working at 85 °C with a Fe/γ-Al_2O_3 catalyst calcined at 300 °C and with 4% Fe content, a remarkable COD reduction (around 85%) has been reached. However, lower temperatures are sufficient to fulfill the locally allowable limit of COD for industrial wastewaters discharge into the municipal sewer system. A substantial improvement of biodegradability (BOD_5/COD ratio) was observed. Thus, CWPO could be effectively applied whether as a treatment itself or as a pre-treatment addressed to improve subsequent biodegradability of these wastewaters. The Fe/γ-Al_2O_3 catalyst showed a reasonable stability, a relatively low decrease of activity (15%) being observed after three successive runs.

1. Introduction

The cosmetic industry generates wastewaters which commonly present a relatively high organic load, in terms of chemical oxygen demand (COD) [1], whose effective reduction by conventional biological processes becomes unlikely due to their low biological oxygen demand (BOD_5)/COD ratio. Currently, these wastewaters are mostly treated by coagulation/flocculation processes [2] which usually lead to a significant reduction of COD. Nevertheless, the introduction of more stringent regulations concerning waste disposal makes necessary developing new techniques for a more efficient cleaning of this type of wastewaters. Advanced oxidation can be regarded as a possible solution, whether as a treatment itself or as a pre-treatment addressed to improve the biodegradability by removing or converting recalcitrant pollutants [3,4]. Among the advanced oxidation processes (AOPs), Fenton oxidation has gained a large attention for the latest years. The main advantages are related to its simplicity of design, implementation and operation (near-ambient conditions) and its ability to remove a wide variety of compounds. This oxidation process has been efficiently used to treat and pre-treat different industrial wastewaters [5–7].

Nevertheless, the use of solid catalysts by immobilization of the active iron over a convenient support offers a practical solution to the main drawback of homogeneous Fenton catalytic system where the dissolved iron is lost in the effluent and is precipitated as $Fe(OH)_3$ upon final neutralization. Recent studies have demonstrated that hydrogen peroxide can oxidize organic pollutants in the presence of Fe-bearing solid catalysts in the so-called catalytic wet peroxide oxidation (CWPO). So far, several supports have been used, like zeolites [8–11], pillared clays [12–16], alumina [17,18], silica [19], mesostructured SBA-15 [20,21] and activated carbon [22–25], mostly in the CWPO of model phenolic compounds. However, few studies are found in the literature dealing with the application of this process for the treatment of real wastewaters.

The aim of this study was to evaluate the potential application of own-prepared Fe/γ-Al_2O_3 and Fe/active carbon (Fe/AC) catalysts for the oxidation of cosmetic wastewaters with H_2O_2. The wastewaters used in this work came from a Spanish cosmetic factory and were previously treated in situ by coagulation–flocculation. A representative analysis of the wastewater as received in the lab has been presented elsewhere [26]. The main problem of these wastewaters is that the COD is fairly higher than the regionally allowable limit not only for final disposal but even for discharge into the municipal sewer system (1750 mg/L). Below this value an environmental tax (canon) has to be paid depending on the polluting load. An important amount of that COD

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corresponds to non-biodegradable organic matter. Thus, an effective additional treatment is required. In this work the catalysts preparation conditions (calcination temperature and Fe content) as well as the operating temperature have been tested in order to improve the oxidation process. The stability of the catalysts has been also investigated.

2. Materials and methods

Two samples of wastewater with significantly different values of COD (4730 and 2300 mg/L) and total organic carbon (TOC) (1220 and 686 mg/L) were used in the experiments. In a previous work it was proved that these differences do not affect significantly to the performance of the Fenton process in terms of relative COD or TOC reduction [26]. Aerobic biodegradability of the wastewaters was assessed by the BOD_5/COD ratio as it is a well widespread biodegradability index for industrial wastewaters [4]. The BOD_5/COD ratio was 0.085 and 0.220, respectively, indicative in both cases of a low biodegradability. The samples were stored at low temperature (4 °C) and in dark immediately after reception.

2.1. Catalyst preparation and characterization

The Fe/γ-Al_2O_3 and Fe/AC catalysts were prepared by incipient wetness impregnation of both supports with an aqueous solution of $Fe(NO_3)_3 \cdot 9H_2O$. The Fe load was adjusted to 4 and 8% (w/w, nominal). After impregnation, the catalysts were left at room temperature for 2 h, dried at 60 °C for 12 h and calcined at 200 °C (Fe/AC) and 300 or 450 °C (Fe//γ-Al_2O_3) for 4 h. The catalysts were identified by C (AC-supported) or Al (γ-Al_2O_3-supported) followed by the nominal Fe percentage and the calcination temperature in °C.

Different techniques were used for the characterization of the catalysts. The porous structure of both the catalysts and the corresponding supports was studied by N_2 adsorption–desorption at 77 K, using a Quantachrome Autosorb-1 instrument. The samples were outgassed at 523 K for 12 h to a residual pressure of 10^{-3} Torr. The values of the BET and the external (non-microporous) areas are given in Table 1. The Fe/AC catalysts are predominantly microporous although with a significant contribution of mesoporosity. The Fe/alumina catalysts are mesoporous. The introduction of the active phase, iron, reduces the surface area being that much more accused in the Fe/AC catalysts due to partial blockage of the microporosity. A higher Fe load leads to a more accused reduction of the BET surface area. The iron content of the catalysts was determined by total reflection X-ray fluorescence (TXRF), using a TXRF spectrophotometer 8030c FEI. X-ray diffraction (XRD) using a Siemens model D-5000 diffractometer with Cu Kα radiation was used to determine the crystalline phases present in both the catalysts and supports. The iron phase in the fresh and used catalysts was also identified by Mössbauer spectroscopy. Mössbauer spectra at room temperature and 77 K were recorded in triangle mode using a conventional spectrometer with $^{57}Co(Rh)$ source. The spectra were analyzed by a non-linear fit using the NORMOS program [27] and the energy calibration was made using a α-Fe (6 μm) foil. The elemental composition (C, H, N and S) of the fresh and used catalysts was determined using a LECO CHNS-932 analyzer. X-ray photoelectron spectroscopy (XPS) using a Physical Electronics 5700C Multitechnique System was employed for iron analysis on the surface of the catalysts. The morphology of the fresh and used catalysts was observed by scanning electron microscopy (SEM) using a Philips model XL 30 apparatus.

Table 1
BET and external surface area of the supports and the catalysts.

	S_{BET} (m^2/g)	External area (m^2/g)
AC	974	142
C–4%FeT_{200}	881	113
C–8%FeT_{200}	794	87
γ-Al_2O_3	142	140
Al–4%FeT_{300}	131	114
Al–4%FeT_{450}	128	111
Al–8%FeT_{300}	125	123
Al–8%FeT_{450}	122	122

2.2. CWPO experiments

Oxidation experiments were carried out in batch in 100 mL stoppered glass bottles placed in a thermostatised shaker, which maintains a constant temperature with a stirring velocity equivalent to 200 rpm. The catalysts were used in powdered form (dp < 100 μm) and at 5 g/L in all the experiments. The operating conditions were: $pH_o = 3$, $T = 55–85$ °C, $P = 1$ atm and H_2O_2 starting concentration corresponding to the theoretical stoichiometric dose referred to inlet COD. The pH value during the reaction has not been continuously controlled. The formation of organic acids during the oxidation process may lead to a pH drop. However, some pH measurements were carried out periodically and revealed very small changes, most probably because of the buffering capacity of some of the species present in the wastewaters.

The catalytic activity was evaluated by measuring the TOC, COD and H_2O_2 concentration at different reaction times after filtering the samples through glass microfiber filters (Albet FV-C). The iron leached from the catalyst was also monitored along the treatment. TOC was determined using a Shimadzu model VSCH TOC analyzer. COD was measured following the APHA Standard Method [28] with potassium dichromate. Previous to the COD determination it was necessary to remove the residual H_2O_2 from the sample by adding $FeSO_4 \cdot 7H_2O$ solution up to a final Fe^{2+} concentration of 2000 mg/L and 6N NaOH to stop the reaction. H_2O_2 and iron were analyzed by colorimetric titration with a Shimadzu UV/vis spectrophotometer, model UV-1603, at 410 nm as a complex with Ti^{4+} and at 478 nm as a complex with NH_4SCN in acidic medium, respectively. The 5-day biological oxygen demand (BOD_5) measurements of the raw wastewaters and the effluents after treatment were carried out by means of a BOD apparatus (STC90E, VELP Scientifical). A small amount of washed municipal activated sludge was inoculated.

3. Results and discussion

3.1. Selection of the support

Fig. 1 shows the evolution of TOC and H_2O_2 concentration upon reaction time, using the C–4%FeT_{200} catalyst at 50 °C. Data corresponding to the TOC depletion due only to adsorption are also included. As can be seen, no significant mineralization of the organic matter of these wastewaters was achieved since the small TOC reduction observed (around 15–20%) was essentially due to adsorption onto the catalyst. H_2O_2 is rapidly decomposed during the early stages of reaction, mainly into O_2, by the catalytic action of the carbon surface. Oxygen has a very low oxidation capacity at the operating conditions used. Nevertheless, a similar catalyst has been successfully used in our lab for phenol oxidation [23–25]. It must be considered that this catalyst promotes the decomposition of H_2O_2 by two competing ways, giving rise to $HO^\bullet$ and $HOO^\bullet$ radicals by the action of Fe whereas the bare carbon surface promotes the decomposition into O_2 which is not reactive at the mild temperature used in this work. In the case of phenol the first way prevails whereas the opposite occurs with the cosmetic wastewaters since phenol is adsorbed onto the activated carbon in a much higher amount than the organic matter of these waste-

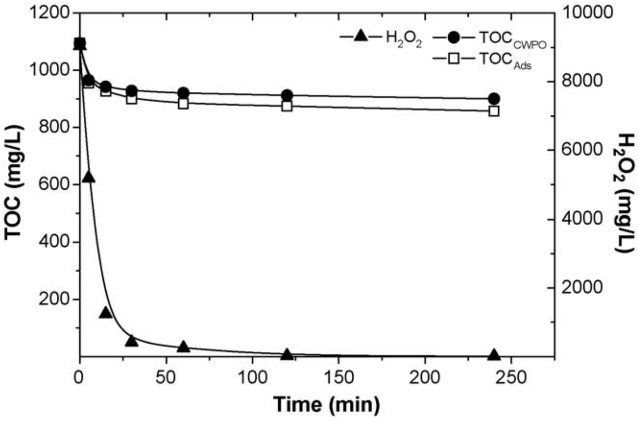

Fig. 1. Time-evolution of TOC and H_2O_2 concentration with the C–4%FeT_{200} catalyst (COD_o = 4260 mg/L; TOC_o = 1100 mg/L; $[H_2O_2]_o$ = 9050 mg/L; T = 50 °C).

waters thus allowing a higher coverage of the carbon surface which inhibits the decomposition of H_2O_2 into O_2.

Fig. 2 shows the time-evolution of TOC and H_2O_2 at 50 °C with the Al–4%FeT_{450} catalyst. As can be seen the removal of TOC by adsorption, also shown, is negligible but the Fe/γ-Al_2O_3 showed to be much more effective than the Fe/AC for the treatment of these cosmetic wastewaters by CWPO. The curve showing the decomposition of H_2O_2 has a fairly different shape since now the support has no action on that respect being active only Fe, which leads to the generation of $HO^\bullet$ radicals. According to these results the alumina-supported catalyst was selected for further experiments.

The XRD patterns of the self-made Fe/γ-Al_2O_3 catalysts showed two crystalline phases, corresponding to γ-Al_2O_3 and hematite (α-Fe_2O_3). XPS spectra confirmed that the main iron species on the surface corresponds to Fe_2O_3, since showed a well defined peak at 710.9–711.1 eV and its doublet separated 13.6 eV. The ratio of the superficial (XPS) to the total (TXRF) iron content of the catalysts increased with the nominal iron content thus indicating a less homogeneous distribution of the active phase onto the alumina particles. This was more accused as the calcination temperature was increased (1.22 and 1.90 at 300 °C versus 0.95 and 2.25 at 450 °C for 4 and 8% nominal Fe, respectively).

The results obtained with the Fe/γ-Al_2O_3 catalyst were compared with those of conventional homogeneous Fenton oxidation. These runs were carried out at 85 °C using the same total amount of Fe in both cases (200 mg/L Fe^{2+} in the Fenton process and 5 g/L of the Al–4%FeT_{300} catalyst in the CWPO). Although the homogeneous process showed a higher oxidation rate, no significant differences were found in the final COD removal, achieving around 80% upon 4 h. Moreover, the leaching of iron from the catalyst was very low (0.5 mg/L in the liquid phase after 4 h, which corresponds to 0.26% of the Fe load). Thus, the use of solid Fenton-type catalysts with γ-Al_2O_3 as support could be a potential alternative to the homogeneous Fenton process for the treatment of those cosmetic wastewaters, avoiding the Fe loss and the need of its removal from the final effluent. Fenton experiments carried out with the negligible amount of Fe leached from the catalyst confirmed that there was no contribution of homogeneous reactions in these conditions.

3.2. Calcination temperature and Fe load of the Al–Fe catalyst

Increasing the calcination temperature of the catalyst decreased both COD and TOC removal, as can be seen in Fig. 3. Mössbauer spectra at 77 K (Fig. 4) showed a higher content of α-Fe_2O_3 nanoparticles in the catalyst calcined at a lower temperature (33% versus 26% at 300 and 450 °C, respectively). This could explain its higher activity in the oxidation process.

Increasing the Fe load of the catalyst beyond 4% did not improve but even decreased COD and TOC removal, as can be seen in Table 2. The less homogeneous Fe distribution indicated before could explain these results. Moreover the SEM micrographs (Fig. 5) show a lower size of the Fe particles in the catalyst with a lower Fe load suggesting a better distribution. An important question regarding the potential application of this catalyst in practice is the possible leaching of iron under the operating conditions. That was always very low, representing <0.3% of the initial load (Table 2). This value is considerably lower than the reported by Al-Hayek et al. [17] in the CWPO of phenol with Fe/Al_2O_3 catalysts. The presence of oxalic acid as a byproduct of CWPO of phenol with activated carbon-supported Fe catalysts has been found as a main cause of Fe leaching [23]. That circumstance does not occur in the case of these cosmetic wastewaters.

3.3. Effect of the reaction temperature

Table 3 reports the COD, TOC and H_2O_2 conversion values obtained after 4 h reaction time with the Al–4%FeT_{300} catalyst at different operating temperatures. The percentages of Fe leached from the catalyst are also included, which were in all cases lower than 0.3% of the initial Fe load. COD and TOC removals as well as H_2O_2 decomposition were significantly increased when increasing the temperature. Below about 70 °C acceptable COD removal could

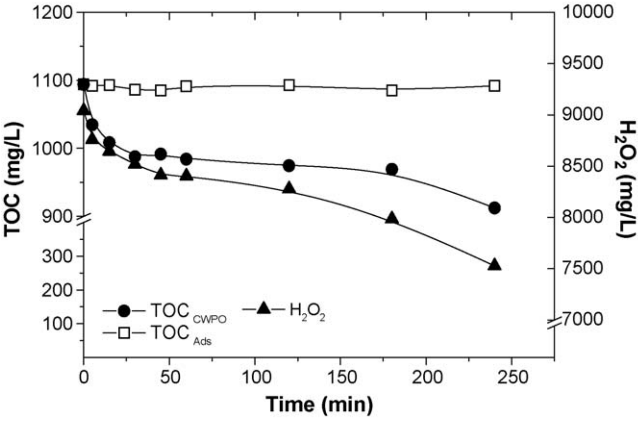

Fig. 2. Time-evolution of TOC and H_2O_2 concentration with the Al–4%FeT_{450} catalyst (COD_o = 4260 mg/L; TOC_o = 1100 mg/L; $[H_2O_2]_o$ = 9050 mg/L; T = 50 °C).

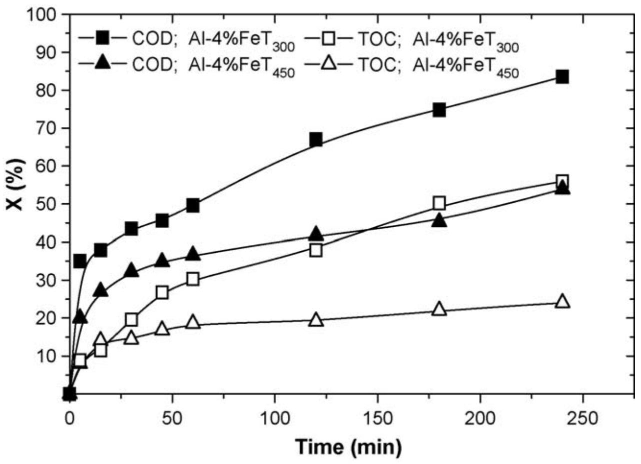

Fig. 3. Effect of the calcination temperature of the catalyst (Al–4%Fe; COD_o = 2070 mg/L; TOC_o = 617 mg/L; $[H_2O_2]_o$ = 4400 mg/L; T = 85 °C).

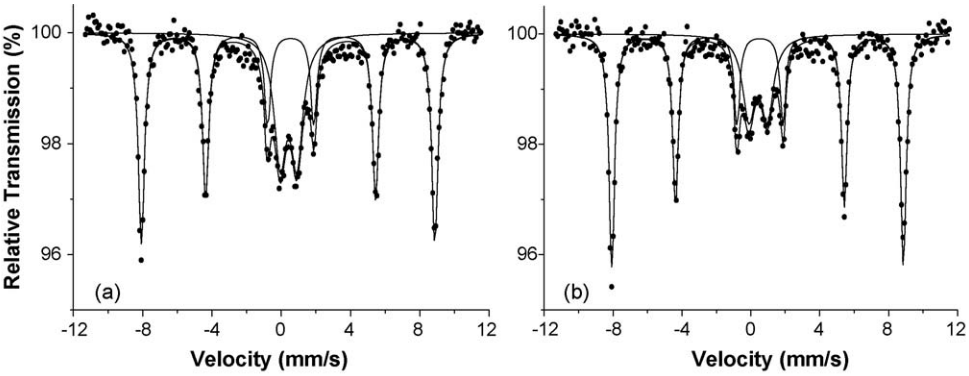

Fig. 4. Mössbauer spectra at 77 K of the Al–4%FeT$_{300}$ (a) and Al–4%FeT$_{450}$ (b) catalysts.

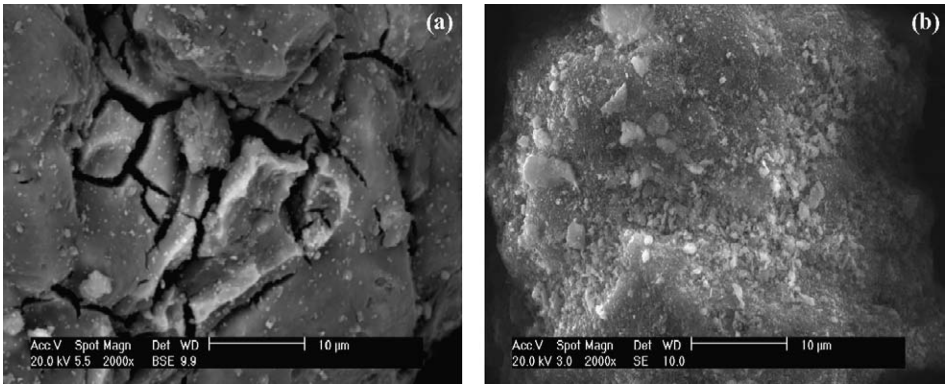

Fig. 5. SEM images of the Al–4%FeT$_{300}$ (a) and Al–8%FeT$_{300}$ (b) catalysts.

not be obtained. An increase of temperature promotes a higher H_2O_2 decomposition into HO$^{\bullet}$ radicals leading to higher COD and TOC reductions. However, high reaction temperatures enhance the thermal degradation of H_2O_2 into O_2. Therefore, the balance between the two competing ways of H_2O_2 decomposition leading to HO$^{\bullet}$ (promoted by Fe) and O_2 (favoured at increasing temperature) is a main factor determining the efficiency of organic matter removal. Liou et al. [29] reached a similar conclusion in CWPO of phenol in aqueous solution using Fe (III) supported on a cation exchange resin. Within the range tested the rate of HO$^{\bullet}$ formation seems to increase more with temperature than that of thermal decomposition thus increasing the efficiency of H_2O_2 consumption. The amount of COD removed per unit H_2O_2 fed varied from 0.21 to 0.39 at 70 and 85 °C, respectively. Working within that temperature range would not represent a drawback in practice, since a major part of the streams integrating these cosmetic wastewaters leave their corresponding operations at temperatures within or close to that range. Furthermore, heat can be recovered by preheating the wastewaters to be treated with the final effluent before discharging this last. Moreover, working within that temperature range an increased biodegradability can be achieved since the BOD$_5$ varies from 455 to 181 mg/L after 4 h reaction time at 85 °C.

Table 2
Effect of the Fe load of the alumina-supported catalysts (COD$_o$ = 2070 mg/L; TOC$_o$ = 617 mg/L; $[H_2O_2]_o$ = 4400 mg/L; T = 85 °C).

Catalyst	X_{COD} (%)	X_{TOC} (%)	$X_{H_2O_2}$ (%)	Fe$_{leached}$ (%)
Al–4%FeT$_{300}$	83.5	55.9	69.5	0.26
Al–8%FeT$_{300}$	75.5	52.0	76.1	0.28

3.4. Stability of the catalyst

The Al–4%FeT$_{300}$ catalyst was used in three successive runs after simply drying at low temperature (60 °C). The results obtained are shown in Fig. 6. The catalyst suffered a decrease of activity of about 15% for COD removal. Nevertheless when operating in continuous in a stirred tank reactor at 85 °C and 9.4 kg$_{cat}$ h/kg$_{COD}$ space-time the decrease of activity was lower than 10% after 100 h of time on stream [30]. The loss of activity cannot be attributed to Fe leaching from the catalyst since it was almost negligible. One important fact may be the presence of residual carbon-containing matter over the surface of the catalyst used, evidenced by elemental analysis. The C content of the catalyst varied from 0.26% after the first run to 1.03% after the third one. The XRD of the fresh and used catalysts showed the same profile except for a new peak appearing in the used catalyst at 2θ around 18°, which may correspond to the aforementioned deposits, since it disappeared when the used catalyst was calcined at 550 °C. This may lead to a partial blockage of active sites. Melero et al. [20] tested a Fe_2O_3/SBA-15 catalyst for the CWPO of phenolic aqueous solutions and they also concluded that the presence of residual organic compounds adsorbed onto the catalyst had a negative effect on its reusability. Nevertheless a BET surface area of

Table 3
Effect of the temperature in the CWPO of cosmetic wastewaters with the Al–4%FeT$_{300}$ catalyst (COD$_o$ = 2070 mg/L; TOC$_o$ = 617 mg/L; $[H_2O_2]_o$ = 4400 mg/L).

Temperature (°C)	X_{COD} (%)	X_{TOC} (%)	$X_{H_2O_2}$ (%)	Fe$_{leached}$ (%)
55	23.6	16.6	12.3	0.05
70	44.1	15.2	37.4	0.16
85	83.5	55.9	69.5	0.26

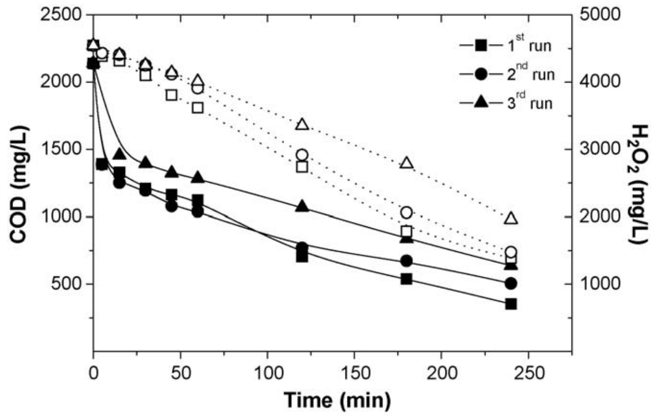

Fig. 6. Stability of the Al–4%FeT$_{300}$ catalyst (COD_o = 2070 mg/L; TOC_o = 617 mg/L; $[H_2O_2]_o$ = 4400 mg/L; T = 85 °C).

128 m^2/g was determined for the three times used catalyst, almost similar to that of the fresh one. The Mössbauer spectra showed some decrease in the percentage of superparamagnetic nanoparticles of α-Fe_2O_3 (27% in the catalyst reused three times versus 33% of the fresh catalyst) suggesting a growth of the hematite particles upon use of the catalyst at 85 °C. This fact could justify the moderate loss of activity observed in the catalyst since larger crystallites would provide a smaller active area. However, further research is needed for a better understanding of the cause of deactivation which could be used as a helpful information for regeneration.

4. Conclusions

An own-prepared Fe on γ-Al_2O_3 catalyst with 4% Fe has shown a potential application for the treatment of cosmetic wastewaters by CWPO. Both COD and TOC removal decreased at increasing the calcination temperature of the catalyst from 300 to 450 °C which could be explained from a decrease on the content of α-Fe_2O_3 nanoparticles evidenced by Mössbauer spectroscopy. The oxidation of the organic matter was not improved by increasing the Fe load of the catalyst beyond 4%. Working at temperatures in the 70–85 °C range the locally allowable COD limit for industrial wastewaters discharge into the municipal sewer system can be reached. Higher temperatures can be used looking for an improved cleaning thus reducing the environmental tax. The biodegradability of these wastewaters was improved from an initial BOD_5/COD ratio of 0.22 to 0.53 after 4 h reaction time at 85 °C. The catalyst showed a moderate decrease of activity upon repeated use in batch. This loss of activity cannot be attributed to Fe leaching which was negligible. Some possible causes of deactivation could be a moderate growth of α-Fe_2O_3 particle size and some partial blockage of active sites by deposition of carbon-containing matter on the catalyst surface.

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