

Comparison of Fenton and Fenton-like oxidation for the treatment of cosmetic wastewater

P. Bautista, J. A. Casas, J. A. Zazo, J. J. Rodriguez and A. F. Mohedano

ABSTRACT

The treatment of cosmetic wastewaters by Fenton ($\text{Fe}^{2+}/\text{H}_2\text{O}_2$) and Fenton-like ($\text{Fe}^{3+}/\text{H}_2\text{O}_2$) oxidation has been studied. From batch and continuous experiments it has been proved that both versions of the Fenton process lead to quite similar results in terms of chemical oxygen demand (COD) and total organic carbon reduction although the COD shows a slightly higher rate in the early stages of reaction. COD reductions of around 55% after 2 h reaction time and 75–80% with 4 h residence time were reached in batch and continuous experiments, respectively, conducted at pH around 3, ambient temperature (20 °C), with 200 mg/L of Fe dose and an initial $\text{H}_2\text{O}_2/\text{COD}$ weight ratio corresponding to the theoretical stoichiometric value. Achieving the locally allowable limit of COD for industrial wastewater discharge into the municipal sewer system takes no more than 30 min reaction time under those conditions by both Fenton systems. However, the Fenton-like process, where iron is fed as Fe^{3+} , would be preferable for industrial applications since the ferric sludge resulting upon final neutralization of the effluent can be recycled to the process. A second-order kinetic equation with respect to COD fitted fairly well the experimental results at different temperatures, thus providing a simple practical tool for design purposes.

Key words | cosmetic wastewater, Fenton, Fenton-like, kinetics, oxidation

P. Bautista
J. A. Casas
J. A. Zazo
J. J. Rodriguez
A. F. Mohedano (corresponding author)
Ingeniería Química, Facultad de Ciencias,
Universidad Autónoma de Madrid,
Campus de Cantoblanco,
28049 Madrid,
Spain
E-mail: angelf.mohedano@uam.es

INTRODUCTION

Industrial wastewaters frequently contain toxic and/or recalcitrant pollutants resistant to conventional biological treatments. The wastewaters from the cosmetic industry present commonly a relatively high organic load, in terms of chemical oxygen demand (COD), with a low biodegradability, as well as high levels of suspended solids and fats and oils (Perdigón-Melón *et al.* 2010; Puyol *et al.* 2011). Research into new and more efficient technologies capable of breaking down that type of compound into simpler easily degradable species is of growing interest. In the last decades, advanced oxidation processes (AOPs), based on the action of hydroxyl radicals, have been applied successfully for the removal or degradation of recalcitrant pollutants. Among these AOPs, Fenton oxidation has demonstrated a high potential whether as a treatment itself or as a pre-treatment to improve the biodegradability by removing or converting recalcitrant pollutants (Chamarro *et al.* 2009; Mantzavinos & Psillakis 2004). This well-established technology is based on the generation of hydroxyl radicals (HO^\bullet) at acidic pH by reaction of hydrogen peroxide with Fe^{2+} acting as homogeneous

catalyst, which is regenerated from the reaction of Fe^{3+} with H_2O_2 or intermediate organic radicals (Pignatello 1992). The hydroxyl radicals, produced upon decomposition of hydrogen peroxide, are strongly oxidant and able to oxidize a wide variety of organic compounds under ambient conditions. Furthermore, this method works with relatively short reaction times (Zazo *et al.* 2005) and uses easy-to-handle reagents (Bigda 1995). Consequently, it has been postulated as one of the most economic alternatives (Esplugas *et al.* 2002; Pérez *et al.* 2002) and has been successfully used with different industrial wastewaters (Papadopoulos *et al.* 2007; Primo *et al.* 2008; Lucas *et al.* 2009; Pliego *et al.* 2012, 2013).

Fe^{3+} can also promote the decomposition of H_2O_2 -promoting oxidative radicals in the so-called Fenton-like process (Tambosi *et al.* 2006; Kiril Mert *et al.* 2010). This oxidation method is based in the catalytic generation of HO^\bullet that results from the chain reaction between ferrous ion (Fe^{2+}) and H_2O_2 , initiated by a ferric ion (Fe^{3+}) catalyst. In most applications, Fe^{2+} or Fe^{3+} can be alternatively used (Ali

& Sreekrishnan 2001), although Pera-Titus *et al.* (2004) suggested that if low doses of Fenton's reagent are used, Fe^{2+} may be preferable.

In this work we study the potential application of both Fenton systems ($\text{Fe}^{2+}/\text{H}_2\text{O}_2$ and $\text{Fe}^{3+}/\text{H}_2\text{O}_2$) for the treatment of real wastewaters from a Spanish cosmetics factory, pre-treated previously *in situ* by coagulation–flocculation, with the aim of reducing the COD below the locally allowable limit so that the resulting effluent can be discharged into the municipal sewer system for further treatment. A representative analysis of the wastewater as received in the laboratory has been presented elsewhere (Bautista *et al.* 2007). The main problem of these wastewaters is that their COD values are well above the regionally allowable limits (10/1993 Act passed by the Community of Madrid (Comunidad Autónoma de Madrid 1993)) not only for final disposal but even for discharge into the municipal sewer system (1,750 mg/L). Thus, the oxidation step is in this case conceived as a pre-treatment rather than a final-discharge solution which would not be a feasible option for these wastewaters having relatively high COD values. The evolution of COD and total organic carbon (TOC) along reaction time has been followed in batch runs. Experiments in a continuous stirred tank reactor (CSTR) have been also carried out. A kinetic analysis based on COD has been performed for the sake of developing a simple tool useful for design purposes.

METHODS

Cosmetic wastewater

A cosmetic wastewater characterized by initial COD and TOC values of 2,376 and 691 mg/L, respectively, was used in the experiments. The 5-day biochemical oxygen demand (BOD_5) to COD ratio was 0.18, indicative of a low biodegradability. The wastewater sample was stored at low temperature (4 °C) and in dark immediately after reception.

Experimental procedure

The operating conditions used in all experiments were: $\text{pH}_0 = 3$, iron concentration = 200 mg/L and a H_2O_2 concentration to COD initial weight ratio corresponding to the theoretical stoichiometric value (Bautista *et al.* 2007).

Batch experiments were carried out in 100 mL stoppered glass bottles placed in a thermostated shaker, with a stirring velocity equivalent to 200 rpm. Each bottle was filled with 45 mL of wastewater. The doses of Fe^{2+} or Fe^{3+} and of H_2O_2 were adjusted by addition of 2.5 mL of

$\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ or $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, respectively, and 2.5 mL of H_2O_2 aqueous solutions of the corresponding concentrations. Each bottle was left to react for a given time and then its content was immediately filtered using glass micro-fiber filters (Albet FV-C) with 1.2 μm nominal pore size. The filtrate was analyzed for TOC, COD, and residual H_2O_2 concentration. Previous to the COD determination it was necessary to remove the residual H_2O_2 from the sample because of its potential interference in the COD determination. This was done by adding $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ solution up to a final Fe^{2+} concentration of 2,000 mg/L and 6 N NaOH. This allows the breaking down of the residual hydrogen peroxide since $\text{Fe}(\text{OH})_3$ catalyzes H_2O_2 decomposition towards O_2 which is not reactive at the temperature used.

Continuous-wise runs were carried out in a 500 mL glass jacketed CSTR at a 125–500 mL/h feeding flow rate. Thus, the residence time was tested within a wide range (1–4 h).

All the experiments were performed, at least, in duplicate and the observed standard deviation was always less than 5% of the reported value.

Analytical methods

TOC was determined using a TOC analyzer (Shimadzu, mod. TOC VSCH). COD was measured following the APHA standard method with potassium dichromate (APHA 1992). H_2O_2 concentration was analyzed by colorimetric titration with a Shimadzu UV/V is spectrophotometer, model UV-1603, at 410 nm as a complex with Ti^{4+} (Eisenberg 1943).

The identification of volatile species in the initial and treated effluents was performed by gas chromatography/ion trap mass spectrometry (GC-MS) (CP-3800/Saturn 2200, Varian, equipped with an automatic injector CP-8200/SPME; solid phase micro-extraction). A 30 m long, 0.25 mm i.d. capillary column (Factor Four VF-5 ms) was used. The carrier gas (helium) flow rate in the GC was 1 mL/min. The SPME was carried out with a fiber cartridge (Carbowax/Divinylbenzene yellow-green), using adsorption and desorption times of 20 and 5 min, respectively. The sample injection was conducted at 220 °C. The temperature programme used during the GC-MS analyses ramped as follows: 40 °C for 15 min and 15 °C/min until 250 °C. The identifications were assessed with the aid of the database library NIST.

RESULTS AND DISCUSSION

Figure 1 shows the TOC and COD conversion values as well as H_2O_2 concentration with reaction time in batch-wise

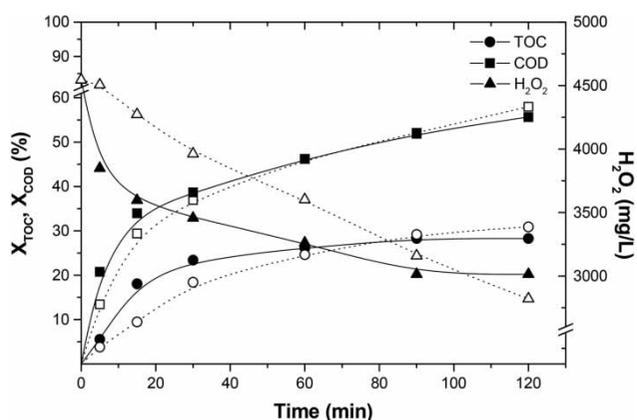
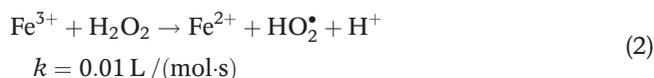
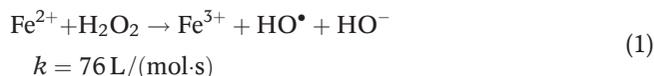


Figure 1 | Time-evolution of TOC and COD conversions (X) and H_2O_2 concentration for Fenton (solid symbols) and Fenton-like (open symbols) processes ($\text{COD}_0 = 2,138 \text{ mg/L}$, $\text{TOC}_0 = 622 \text{ mg/L}$, $[\text{H}_2\text{O}_2]_0 = 4,544 \text{ mg/L}$, $[\text{Fe}^{2+}]_0 = [\text{Fe}^{3+}]_0 = 200 \text{ mg/L}$, $T = 20^\circ\text{C}$).

experiments. Although similar final TOC and COD conversions are achieved with both processes (Fenton and Fenton-like), some differences regarding the oxidation rate can be observed in the early stages of reaction. The initial oxidation rate in the Fenton process is higher than that of Fenton-like, the differences being more pronounced in terms of mineralization (TOC conversion). This is consistent with the higher rate of radical generation upon H_2O_2 decomposition by Fe^{2+} (Equation (1)) than by Fe^{3+} (Equation (2)). The corresponding rate constants significantly differ in value (76 vs $0.01 \text{ L}/(\text{mol}\cdot\text{s})$, respectively). Using Fe^{3+} as catalyst (Fenton-like process) promotes a slow generation of perhydroxyl radicals (HO_2^\bullet), whose oxidation potential is quite lower than that of the hydroxyl radicals (standard values of 1.70 V and 2.80 V, respectively). The HO_2^\bullet radicals react with easily oxidizable organic matter, and the Fe^{2+} generated through Equation (2) promotes the decomposition of H_2O_2 through Equation (1), giving rise to HO^\bullet radicals capable of oxidizing less-reactive species due to their higher oxidation power. Thus, the differences between the Fenton and Fenton-like processes regarding the rate and extent of oxidation disappear after a given reaction time, lower when looking at COD. COD is reduced by a higher percentage than TOC indicating that the Fenton process at the ambient-like temperature tested (20°C) partially oxidizes the organic matter present in these wastewaters but leads mainly to by-products refractory to mineralization. Nevertheless, in our case the locally allowable limits for industrial wastewater discharge into the municipal sewer system concerning organic pollution are so far established in terms of COD. In this sense, the current value ($1,750 \text{ mg/L}$) can be achieved in a relatively short reaction

time of less than 30 min.



The percentages of COD and TOC removal can be significantly improved by increasing the temperature (Table 1). Using temperatures above 50°C with an iron dose of 200 mg/L did not produce any further significant improvement since H_2O_2 decomposition is almost complete (around 97%) at 50°C . A determining factor of the economy of the Fenton and H_2O_2 -based oxidation processes is the consumption of that reagent. The remaining unconverted amount cannot be recovered and moreover has to be removed before discharging the effluent since the ecotoxicity has to be also controlled. Thus, all the H_2O_2 fed to the system has to be accounted as reagent consumption. Table 1 also reports the values of COD removed per unit H_2O_2 fed at different temperatures within the $20\text{--}50^\circ\text{C}$ range using the stoichiometric H_2O_2 dose and 200 mg/L of Fe^{2+} or Fe^{3+} . A somewhat more efficient consumption of the reagent is accomplished when using Fe^{3+} at all temperatures tested, the difference being higher with the increasing temperature. However, the slight increase in COD and TOC reductions attained by Fenton-like oxidation is not significant, allowing the conclusion that Fe^{3+} has comparable catalytic properties to that of the traditional Fe^{2+} Fenton catalyst. A similar conclusion was reported by other authors in the Fenton and Fenton-like treatment of several other types of industrial wastewaters. Thus, Kiril Mert *et al.* (2010) reported that the Fenton-like system can be used as a good pre-treatment solution for olive oil mill effluents prior to discharge into sewage since it showed a

Table 1 | Influence of temperature upon Fenton and Fenton-like oxidation ($[\text{H}_2\text{O}_2]_0 = 4,544 \text{ mg/L}$, $[\text{Fe}^{2+}]_0 = [\text{Fe}^{3+}]_0 = 200 \text{ mg/L}$, Reaction time: 2 h)

Temperature ($^\circ\text{C}$)	X_{COD}		X_{TOC}		$\varepsilon_{\text{Fe}^{2+}}$	$\varepsilon_{\text{Fe}^{3+}}$
	Fe^{2+}	Fe^{3+}	Fe^{2+}	Fe^{3+}		
20	0.56	0.58	0.28	0.31	0.26	0.27
30	0.60	0.67	0.35	0.44	0.28	0.31
40	0.66	0.73	0.49	0.54	0.31	0.34
50	0.76	0.84	0.62	0.63	0.36	0.40

X_{COD} : conversion of COD; X_{TOC} : conversion of TOC; ε : efficiency of H_2O_2 consumption (COD removed/ H_2O_2 fed, w/w).

satisfactory COD, phenol and toxicity removal performance and was a more economic choice than conventional Fenton.

The evolution of the COD/TOC ratio upon Fenton and Fenton-like treatments at 20 °C is shown in Figure 2. Very similar profiles were observed for both processes not only in the conditions of Figure 2 but within the temperature range investigated and with samples of cosmetic wastewaters with different initial organic load. As can be seen, the COD/TOC ratio decreases significantly upon reaction time, being after 2 h around 60% of the starting value. The average oxidation state of carbon atoms (AOSC) of the effluent was calculated by means of Equation (3), which takes into account the TOC and COD values (Mantzavinos et al. 2000)

$$\text{AOSC} = 4 - (1.5\text{COD}/\text{TOC}) \quad (3)$$

AOSC is a useful parameter to estimate the oxidation degree in a complex wastewater. A higher AOSC value indicates a more oxidized state of the organic matter in the wastewater. A negative value of this parameter (-1.1) was obtained for the starting cosmetic wastewater used in this work, which indicates a low oxidation state of the organic pollutants initially present. The AOSC increased upon both the Fenton and Fenton-like treatment up to 0.25 and 0.85 after 1 and 2 h of reaction time, respectively, in the conditions of Figure 2.

The decrease of the COD/TOC ratio seems to be more pronounced during the first stages of reaction (first 10 min of reaction) for Fenton than for Fenton-like due to the aforementioned higher initial generation of HO^{*} radicals, with a higher oxidation potential. From 60 min reaction time the COD/TOC ratio appears relatively similar for Fenton and

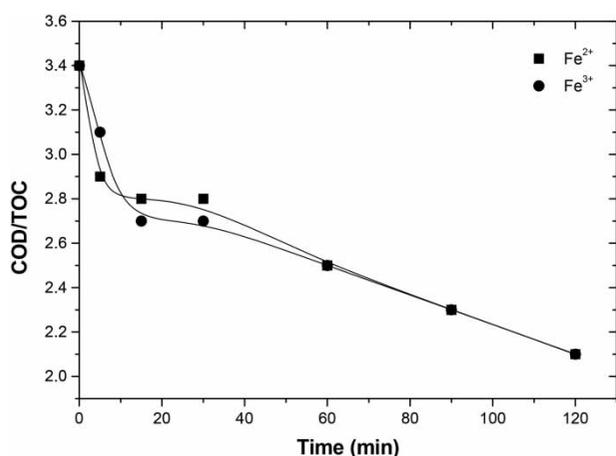


Figure 2 | Evolution of the COD/TOC ratio vs reaction time in Fenton and Fenton-like treatments (COD₀ = 2,138 mg/L, TOC₀ = 622 mg/L, [H₂O₂]₀ = 4,544 mg/L, [Fe²⁺]₀ = [Fe³⁺]₀ = 200 mg/L, T = 20 °C).

Fenton-like experiments. These low COD/TOC values suggest an important relative formation of short-chain organic acids, most probably including dicarboxylic acids. Nevertheless, the complex composition of these industrial effluents and, furthermore, the diversity and complexity of the oxidation by-products, make unpractical a detailed analysis of the species present in the wastewaters and their evolution throughout the process. Short-chain organic acids could not be identified in the starting wastewaters by ionic chromatography, but an attempt has been made to elucidate what kind of carboxylic acids are formed upon Fenton oxidation. The COD/TOC ratio can serve as a first approach. Thus, a representative aromatic acid like benzoic acid yields a theoretical COD/TOC ratio of 2.9, whereas this value varies for short-chain linear acids like formic (1.3), acetic (2.7) or propionic (3.1), or even for dicarboxylic acids like oxalic (0.7), malonic (1.8) or maleic (2.0). A more detailed analysis was accomplished by GC-MS for the sake of identifying representative species and following their evolution upon Fenton and Fenton-like treatments. Figure 3 shows a typical chromatogram of the starting wastewater where the heterogeneous composition and the complexity of the chemical compounds present are evidenced. Both oxidation treatments have shown a tremendous potential for the removal of the organic compounds identified in Figure 3, since a complete depletion was achieved during the first 5 min of reaction at 20 °C. Only benzene, 2,4-diisocyanato-1-methyl (peak 14 of Figure 3) was not completely removed (around 30%).

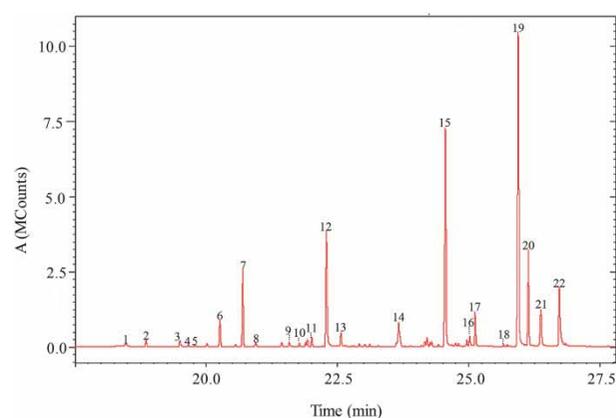


Figure 3 | A representative GC-MS chromatogram of the starting cosmetic wastewater. 1. Benzenesulfonic acid, 4-hydroxy; 2. Ethyl hexanoate; 3. 1-Hexanol, 2-ethyl; 4. Benzyl alcohol; 5. Ethyl 2-hexenoate; 6. 2-Octanol, 2-methyl-6-methylene-; 7. 1,6-Octadien-3-ol, 3,7-dimethyl; 8. Phenylethyl alcohol; 9. Benzyl acetate; 10. 1,6-Nonadien-3-ol, 3,7-dimethyl; 11. 3-Cyclohexene-1-methanol; 12. Ethanol, 2-phenoxy; 13. 2,6-Octadien-1-ol, 3,7-dimethyl; 14. Benzene, 2,4-diisocyanato-1-methyl; 15. Methylparaben; 16. Benzene, (3-methylcyclopentyl); 17. Ethylparaben; 18. Diethyl phthalate; 19. Propylparaben; 20. Methyl 3-oxo-2-pentylcyclopentaneacetate; 21. Isobutylparaben; 22. Butylparaben.

Figure 4 shows the results obtained in continuous experiments (CSTR) at different residence times. As can be seen, the COD conversion significantly increases with residence time within the lower range of this operating variable tested and then a saturation-like effect is observed indicating that around 20–25% of the organic matter measured as COD is refractory to these oxidation processes. Again it was found that ferric ion shows a comparable or even better catalytic effect than that of the traditional ferrous ion in Fenton process. As a practical conclusion, relatively low values of residence time (1 h) are sufficient to achieve a COD reduction which complies with the local limit for industrial wastewater discharge into the municipal sewer system.

As indicated before, one of the disadvantages of the conventional Fenton process is the production of a large volume of iron-containing sludge (mostly ferric hydroxide) which results upon neutralization of the highly acidic effluent exiting the reactor (Benatti *et al.* 2009). The cost of disposal of that waste sludge has prevented a more extended full-scale application of this oxidation process in the industrial wastewaters field. In this sense, an important advantage of using Fe^{3+} instead of Fe^{2+} is that the iron sludge can be recycled into the process after its re-dissolution in acid solution (i.e. aqueous sulphuric acid), which would also serve to bring the pH to the required value for Fenton oxidation. Cao *et al.* (2009) reported that, compared with the cost of disposal of iron sludge, the regeneration and reuses of iron catalyst in the Fenton-like system is a cost-effective solution.

In this work a cost estimation of the application of Fenton oxidation to cosmetic wastewaters has been accomplished

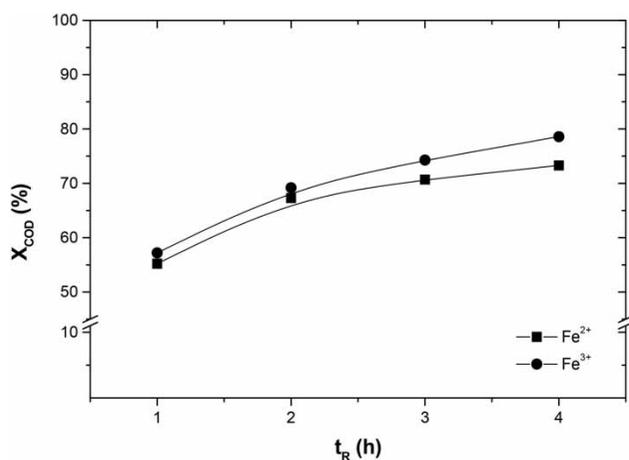


Figure 4 | COD conversion X_{COD} obtained at different residence time (t_r) for Fenton and Fenton-like processes ($\text{COD}_0 = 2,138 \text{ mg/L}$, $\text{TOC}_0 = 622 \text{ mg/L}$, $[\text{H}_2\text{O}_2]_0 = 4,544 \text{ mg/L}$, $[\text{Fe}^{2+}]_0 = [\text{Fe}^{3+}]_0 = 200 \text{ mg/L}$, $T = 20^\circ \text{C}$).

based on a representative scheme of the process shown elsewhere (Bautista *et al.* 2008). The estimated unitary costs are depicted in Table 2. An initial COD value of 3,000 mg/L has been taken, and reduction up to the local limit to allow discharge into the municipal sewer system has been targeted. The operating conditions were fixed at ambient temperature, 200 mg/L Fe^{2+} and an initial $\text{H}_2\text{O}_2/\text{COD}$ weight ratio corresponding to the theoretical stoichiometric value. One of the critical points of the Fenton process is the cost of hydrogen peroxide, which represents more than 80% of the operations and maintenance (O&M) cost. Another important cost of the process is that related to the disposal of the iron sludge formed upon final neutralization of the effluent. Thus, the use of Fe^{3+} instead of the traditional Fe^{2+} could save more than 15% of the O&M cost in a conservative approach since the sludge treatment and disposal cost can be significantly higher than that considered in Table 2 in many circumstances (Cañizares *et al.* 2009).

The complex and variable composition of these wastewaters makes advisable undertaking the kinetic analysis of the oxidation processes investigated from an overall approach based on the evolution of COD, which could serve for practical design purposes. Since COD includes compounds of different susceptibility to oxidation, it has been structured in two blocks: COD_A , which corresponds to easily oxidizable compounds and COD_B , that includes those compounds that are refractory to the treatments investigated. Thus, the following scheme is proposed:



$$\text{COD} = \text{COD}_A + \text{COD}_B \quad (5)$$

Table 2 | Cost estimation of Fenton treatment for cosmetic wastewaters

	Cost (€/m ³)
Investment (I)	1.35
Operation and maintenance (O&M)	
H_2O_2	3.68
Catalyst	0.10
Others	0.20
Electricity (1.9 kW h/m ³)	0.17
Sludge treatment & disposal (90 €/t)	0.90
	5.05
I + O&M	6.40

Table 3 | Values of the rate constants (L/(mg · min)) obtained for Fenton and Fenton-like processes

Temperature (°C)	$k_1 \times 10^5$	$k_2 \times 10^5$	k_2/k_1	r^2
Fe ²⁺ /H ₂ O ₂ system				
20	1.87	2.51	1.34	0.998
30	2.27	3.69	1.63	0.997
40	2.55	4.87	1.91	0.999
50	3.75	8.82	2.35	0.994
Fe ³⁺ /H ₂ O ₂ system				
20	0.81	1.48	1.83	0.999
30	1.03	2.51	2.44	0.998
40	1.12	3.84	3.43	0.999
50	1.40	6.39	4.56	0.993

From this scheme, the following rate equations can be written, where second-order kinetics with respect to COD has been considered:

$$\frac{d\text{COD}_A}{dt} = -(k_1 + k_2) \cdot \text{COD}_A^2 \quad (6)$$

$$\frac{d\text{COD}_B}{dt} = k_1 \cdot \text{COD}_A^2 \quad (7)$$

Table 3 reports the values of the rate constants obtained at different temperatures by fitting these equations with the experimental results using MicroMath® Scientist 3.0 software. Integration was done with the following boundary conditions:

$$t = 0: \text{COD}_A = 2,376 \text{ mg/L}, \quad \text{COD}_B = 0$$

The correlation coefficients are included. The proposed model describes fairly well the evolution of COD for the two oxidation processes investigated at all the temperatures tested (data not shown). The k_2/k_1 ratio can be taken as indicative of the selectivity to mineralization of the organic matter present in these wastewaters. That ratio is higher for the Fenton-like process at all the temperatures tested and for both processes increases with temperature, that effect being more pronounced in the case of Fenton-like.

CONCLUSIONS

Batch and continuous flow experiments with real cosmetic wastewaters have demonstrated that ferric ion (Fenton-like

process) shows comparable or better catalytic effect than the traditionally used ferrous ion (Fenton process). Using an Fe²⁺ or Fe³⁺ dose of 200 mg/L and an initial H₂O₂/COD weight ratio corresponding to the theoretical stoichiometric value, COD reductions higher than 55% can be achieved at 20 °C, allowing compliance with the locally allowable limit of COD for industrial wastewater discharge into the municipal sewer system. For industrial applications the Fenton-like process can be a preferable choice for technical and economic reasons mainly derived from the possibility of recycling the ferric hydroxide resulting upon final neutralization of the effluent. The kinetics of both processes was well described by a simple model based on two second-order kinetic equations with respect to COD useful for practical purposes. The selectivity towards mineralization of the organic matter present in cosmetic wastewaters increases with temperature, being higher in the case of Fenton-like process.

ACKNOWLEDGEMENTS

The authors greatly appreciate financial support from the Spanish Ministerio de Ciencia e Innovación (MICINN) through the project CTQ2008-03988/PPQ. We also express our gratitude to the Comunidad de Madrid (CM) (REMTA-VARES) for financial support to the project (S2009/AMB-1588).

REFERENCES

- Ali, M. & Sreekrishnan, T. R. 2001 *Aquatic toxicity from pulp and paper mill effluents: a review*. *Advances in Environmental Research* **5**, 175–196.
- APHA 1992 *Standard Methods for the Examination of Water and Wastewater*, 18th edn, American Public Health Association, American Water Works Association/Water Environment Federation, Washington, DC, USA.
- Bautista, P., Mohedano, A. F., Gilarranz, M. A., Casas, J. A. & Rodriguez, J. J. 2007 *Application of Fenton oxidation to cosmetic wastewaters treatment*. *Journal of Hazardous Materials* **143**, 128–134.
- Bautista, P., Mohedano, A. F., Casas, J. A., Zazo, J. A. & Rodriguez, J. J. 2008 *An overview of the application of Fenton oxidation to industrial wastewaters treatment*. *Journal of Chemical Technology and Biotechnology* **83**, 1323–1338.
- Benatti, C. T., da Costa, A. C. S. & Tavares, C. R. G. 2009 *Characterization of solids originating from the Fenton's process*. *Journal of Hazardous Materials* **163**, 1246–1253.
- Bigda, R. J. 1995 *Consider Fenton's chemistry for wastewater treatment*. *Chemical Engineering Progress* **91**, 62–66.

- Cañizares, P., Paz, R., Sáez, C. & Rodrigo, M. A. 2009 Costs of the electrochemical oxidation of wastewaters: a comparison with ozonation and Fenton oxidation processes. *Journal of Environmental Management* **90**, 410–420.
- Cao, G., Sheng, M., Niu, W., Fei, Y. & Li, D. 2009 Regeneration and reuse of iron catalyst for Fenton-like reactions. *Journal of Hazardous Materials* **172**, 1446–1449.
- Chamarro, E., Marco, A. & Esplugas, S. 2001 Use of Fenton reagent to improve organic chemical biodegradability. *Water Research* **35**, 1047–1051.
- Comunidad Autónoma de Madrid 2003 Ley 10/1993, de 26 de octubre, sobre vertidos líquidos industriales al Sistema integral de saneamiento (Law 10/1993 of 26 October on the comprehensive industrial liquid waste sanitation system). BOCM no. 269.
- Eisenberg, G. M. 1943 Colorimetric determination of hydrogen peroxide. *Industrial Engineering Chemistry* **15**, 327–328.
- Esplugas, S., Jiménez, J., Contreras, S., Pascual, E. & Rodríguez, M. 2002 Comparison of different advanced oxidation processes for phenol degradation. *Water Research* **36**, 1034–1042.
- Kiril Mert, B., Yonar, T., Kilic, M. Y. & Kestioglu, K. 2010 Pre-treatment studies on olive oil mill effluent using physicochemical, Fenton and Fenton-like oxidations processes. *Journal of Hazardous Materials* **174**, 122–128.
- Lucas, M. S. & Peres, J. A. 2009 Removal of COD from olive mill wastewater by Fenton's reagent: Kinetic study. *Journal of Hazardous Materials* **168**, 1253–1259.
- Mantzavinos, D. & Psillakis, E. 2004 Enhancement of biodegradability of industrial wastewaters by chemical oxidation pre-treatment. *Journal of Chemical Technology and Biotechnology* **79**, 431–454.
- Mantzavinos, D., Lauer, E., Sahibzada, M., Livingston, A. G. & Metcalfe, I. S. 2000 Assessment of partial treatment of polyethylene glycol wastewaters by wet air oxidation. *Water Research* **34**, 1620–1628.
- Papadopoulos, A. E., Fatta, D. & Loizidou, M. 2007 Development and optimization of dark Fenton oxidation for the treatment of textile wastewaters with high organic load. *Journal of Hazardous Materials* **146**, 558–563.
- Pera-Titus, M., García-Molina, V., Baños, M. A., Giménez, J. & Esplugas, S. 2004 Degradation of chlorophenols by means of advanced oxidation processes: a general review. *Applied Catalysis B: Environmental* **47**, 219–256.
- Perdigón-Melón, J. A., Carbajo, J. B., Petre, A. L., Rosal, R. & García-Calvo, E. 2010 Coagulation-Fenton coupled treatment for ecotoxicity reduction in highly polluted industrial wastewater. *Journal of Hazardous Materials* **181**, 127–132.
- Pérez, M., Torrades, F., Domènech, X. & Peral, J. 2002 Removal of organic contaminants in paper pulp effluents by AOPs: an economic study. *Journal of Chemical Technology and Biotechnology* **77**, 525–532.
- Pignatello, J. J. 1992 Dark and photoassisted Fe³⁺-catalyzed degradation of chlorophenoxy herbicides by hydrogen peroxide. *Environmental Science and Technology* **26**, 944–951.
- Pliego, G., Zazo, J. A., Blasco, S., Casas, J. A. & Rodríguez, J. J. 2012 Treatment of highly polluted hazardous industrial wastewaters by combined coagulation-adsorption and high-temperature Fenton oxidation. *Industrial & Engineering Chemistry Research* **51**, 2888–2896.
- Pliego, G., Zazo, J. A., Casas, J. A. & Rodríguez, J. J. 2013 Case study of the application of Fenton process to highly polluted wastewater from power plant. *Journal of Hazardous Materials* **252–253**, 180–185.
- Primo, O., Rueda, A., Rivero, M. J. & Ortiz, I. 2008 An integrated process, Fenton reaction-ultrafiltration, for the treatment of landfill leachate: pilot plant operation and analysis. *Industrial & Engineering Chemistry Research* **47**, 946–952.
- Puyol, D., Monsalvo, V. M., Mohedano, A. F., Sanz, J. L. & Rodríguez, J. J. 2011 Cosmetic wastewater treatment by upflow anaerobic sludge blanket reactor. *Journal of Hazardous Materials* **185**, 1059–1065.
- Tambosi, J. L., Di Domenico, M., Schirmer, W. N., Jose, H. J. & Moreira, R. F. P. M. 2006 Treatment of paper and pulp wastewater and removal of odorous compounds by a Fenton-like process at the pilot scale. *Journal of Chemical Technology and Biotechnology* **81**, 1426–1432.
- Zazo, J. A., Casas, J. A., Mohedano, A. F., Gilarranz, M. A. & Rodríguez, J. J. 2005 Chemical pathway and kinetics of phenol oxidation by Fenton's reagent. *Environmental Science and Technology* **39**, 9295–9302.

First received 10 December 2013; accepted in revised form 16 May 2014. Available online 28 May 2014