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Coagulation–Fenton coupled treatment for ecotoxicity reduction in highly polluted industrial wastewater

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ABSTRACT

A coupled coagulation–Fenton process was applied for the treatment of cosmetic industry effluents. In a first step, FeSO_4 was used as coagulant and the non-precipitated Fe^{2+} remaining in dissolution was used as catalyst in the further Fenton process. In the coagulation process a huge decrease in total organic carbon (TOC) was achieved, but the high concentration of phenol derivatives was not diminished. The decrease in TOC in the coagulation step significantly reduces the amount of H_2O_2 required in the Fenton process for phenol depletion. The coupled process, using a H_2O_2 dose of only 2 g l^{-1} , reduced TOC and total phenol to values lower than 40 and 0.10 mg l^{-1} , respectively. The short reaction period (less than 15 min) in TOC and phenol degradation bodes well for improving treatment in a continuous regime. The combination of both processes significantly reduced the ecotoxicity of raw effluent and markedly increased its biodegradability, thus allowing easier treatment by the conventional biological units in conventional sewage treatment plants (STPs).

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1. Introduction

During the last century, industrial activity increased the demand for fresh water, whereas generated wastewater was discharged into water bodies, thereby affecting the fragile aquatic ecosystem. Growing concern about these problems in both developed and developing countries is leading to more stringent regulations with regard to public and industrial wastewater disposal. One sector of special interest is the soap and cosmetic industry which generates wastewater characterized by high COD (chemical oxygen demand), mainly proceeding from the cleaning processes of batch reactors and mixers, which has to be washed before reuse. Cosmetics contain non-easily biodegradable xenobiotics including many toxic chemical compounds such as preservatives (normally phenol derivatives), mixtures of surfactants, dyes, fragrances and co-solvents which makes conventional biological treatment difficult [1,2]. Usual treatments of cosmetic industry effluents involve processes such as chemical oxidation [1,3], membrane technology [4], adsorption [5–7], flotation [8] or coagulation [9].

Among the currently used unit processes in wastewater treatment, coagulation has received considerable attention due to its high COD and TOC removal efficiency and cost effectiveness. The effectiveness of TOC removal by coagulation processes varies with the nature of the organic compounds as well as with water prop-

erties such as alkalinity or hardness [10,11]. Phenols in particular are hardly removed in the coagulation process and as a result these compounds exceed the discharge limits of local legislation [11]. In order to improve the efficiency of phenol removal, the use of Fenton followed by a coagulation process has been proposed [12–14]. This oxidation method is based on the use of a mixture of $\text{Fe}^{2+}/\text{H}_2\text{O}_2$ in acidic conditions that generates a high concentration of hydroxyl radicals, the particular feature which defines advanced oxidation process (AOP). Fenton processes have been widely studied in the degradation of phenol derivatives [15–17] and in the treatment of wastewater from the cosmetics industry [1,18,19]. The high COD concentration typically found in industrial cosmetic effluent requires the use of large amounts of H_2O_2 , an expensive chemical which would limit the practical application of the Fenton process.

As stated above, the presence of toxic substances in industrial wastewater would not only have a detrimental effect on aqueous ecosystems but also on the activated sludge process of conventional (STPs) [20]. Chemical analysis is still predominantly used to assess the degree of water pollution [21]. However, this traditional approach fails to provide an adequate interpretation of toxicity to biota due to mixture effects [22–24]. In fact, the ecotoxicity of a complex mixture of chemicals is influenced by the additive, synergic or antagonistic relations between components, which makes it a complex task to elucidate the toxicity of a mixture from that of individual chemicals [25]. Ecotoxicity bioassays provide a direct means of assessing the effect of wastewater on the aquatic environment by considering different issues such as metabolic variations, mortality, mobility, and the growing capacity or breathing rate of

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different microorganisms, invertebrates or higher organisms. Acute bioassays are characterized by a high rate of execution, low cost, easy manipulation and lack of ethical considerations.

This work reports the application of a coupled coagulation–Fenton process for the treatment of cosmetic industry effluents from an industrial facility located in Madrid (Spain). Contrary to other studies, in which H_2O_2 is added to the raw water together with the coagulant [26], the idea developed here was to use in a first step $FeSO_4$ as coagulant in order then to use the non-precipitated Fe^{2+} remaining in dissolution as catalyst in a Fenton process. The advantages of this coupled process are threefold: (i) the coagulation considerably reduces wastewater COD, thus leading to a lower requirement for H_2O_2 ; (ii) iron salt comes from the excess of coagulant, rendering unnecessary further additions and (iii) phenolic compounds that do not precipitate in the coagulation process could be removed in the subsequent Fenton process. The coagulation with $FeSO_4$ was optimized to achieve the best starting conditions for the Fenton process by leading to a low TOC and high Fe^{2+} concentration. The Fenton process was also optimized in terms of the amount of H_2O_2 used and the reaction time. TOC, total phenol and residual iron concentration were evaluated after treatment by paying special attention to the ecotoxicity of waste-streams.

2. Material and methods

Industrial wastewater was obtained from a cosmetic manufacturing facility located in Madrid (Spain). The industry wastewater parameters and the regionally permitted limits for industrial wastewater discharges to the municipal sewer system are summarized in Table 1.

The coagulation process was carried out with 400 ml of water samples in jar-test apparatus from Selecta. The coagulants used were: ferrous sulphate ($FeSO_4 \cdot 7H_2O$, $\geq 99\%$, Sigma–Aldrich) and calcium hydroxide ($Ca(OH)_2$, $\geq 90\%$, Panreac). The coagulant and the wastewater were vigorously mixed for 5 min at 200 rpm, followed by slow mixing for 30 min at 30 rpm and then allowed to settle for 10 min.

The Fenton process was carried out with aliquots of 50 ml of clarified water. The oxidation experiments were carried out in batch in 100 ml glass bottles placed in a Bunsen AO-400 orbital shaker. Each bottle was filled with 50 ml of clarified wastewater. Prior to the addition of H_2O_2 (33%, w/v, Panreac) pH was adjusted to 2.7 ± 0.2 with 1 M HCl. The initial concentration of hydrogen peroxide was established according to the theoretical stoichiometric amount from the initial COD value of $2.12 \text{ g } H_2O_2/\text{g COD}$ [1]. Each bottle was left to react for the prescribed reaction time (240 min) at room temperature and then pH was adjusted to 8.0 ± 0.5 and filtered with PVDF $0.45 \mu\text{m}$ filters (Millex GV). The fil-

Table 1
Main physico-chemical parameters of the industrial effluent and the permitted discharge limits.

Parameter	Industrial effluent value	Emission limit value ^a
pH	4.82	6–9
COD (mg l^{-1})	4150	1750
TOC (mg l^{-1})	1220	–
BOD ₅ (mg l^{-1})	12.90	1000
COD/TOC	3.4	–
BOD ₅ /COD	0.003	–
Conductivity ($\mu\text{S cm}^{-1}$)	894	5000
Total phenol (mg l^{-1})	21	2
Iron (mg l^{-1})	–	10
Ecotoxicity (equitox m^{-3})	200	25

^a Emission limit value for industrial wastewater discharges into the municipal sewer system according to Act 10/1993, passed by the Regional Community of Madrid.

trate was then analyzed for BOD (biochemical oxygen demand), TOC, COD, total phenol, iron and residual H_2O_2 as well as for the bioluminescence decay of marine Gram-negative bacterium *Vibrio fischeri*.

Analytical determinations were carried out using the methods approved by local legislation (Act 10/1993). COD was analyzed following the APHA standard methods [27] (Standard Method 5220 D). Total phenol, iron and H_2O_2 concentrations were determined colorimetrically by the 4-aminoantipyrine method (Standard Method 5530 D), fenantroline method (Standard Method 3500 Fe-B) and with titanium sulphate [28] respectively, with a Shimadzu UV-1800 spectrophotometer. TOC was determined using a TOC-V_{CSH} Shimadzu TOC analyzer. BOD₅ was measured after 5 days of incubation in line with the Standard Method 5210 B [27].

Bioassays with bioluminescent bacteria *V. fischeri* were carried out according to ISO 11348-3 standard protocol [29]. This bioassay measures, during the prescribed incubation period, the decrease in bioluminescence induced in the cell metabolism due to the presence of a toxic substance. *V. fischeri* reagent (*V. fischeri* NRRL-B 11177, a commercially available Biofix Lumi test from Macherey-Nagel, Germany) is supplied freeze-dried and was reconstituted and incubated at 3 °C for 5 min before use. The desired pH (7.0 ± 0.2) was set by using NaOH or HCl solutions. The analysis medium was 0.34 M NaCl (2%, w/v) and tests were performed at 20 °C. The testing was performed in 96-well, white polypropylene microplates and the measurements of light were made using a microplate luminometer Fluoroskan Ascent FL (Thermo Scientific). 100 μl of test solution was pipetted into each well, which was supplemented with 100 μl of bacterial suspension. Toxicity values were routinely obtained after 5, 15 (data reported here) and 30 min exposure. Phenol and $ZnSO_4 \cdot 7H_2O$ were used as toxicity standards and all tests were been replicated to ensure reproducibility. Although EC₅₀ (effective concentration of compound reducing the bioluminescence by 50%) is used to quantify the ecotoxicity of a compound, when the samples are complex IC_x is usually determined. This parameter is defined as the dilution percent of the sample that reduces by x% the intensity of light emitted by the microorganisms. Moreover, in order to compare the ecotoxicity of raw and treated wastewater with emission limit values in local legislation, equitox m^{-3} unit (1 equitox m^{-3} is defined as the reciprocal of the wastewater dilution (expressed in parts per one) resulting in 50% inhibition within 15 min under typical biotesting conditions) was determined.

3. Results and discussion

As can be seen in Table 1, there are various physico-chemical parameters of the industry wastewater giving values beyond the emission limit range (pH, COD, total phenol and ecotoxicity).

The main concern regarding industrial effluent is the high COD value reflecting a large amount of non-biodegradable organic matter. Although the legally permitted limit for organic compounds is expressed in terms of COD, in this study the evolution of this parameter was also monitored by TOC because it is a faster technique that gives a direct measure of carbon content without interference from other oxidizable inorganic substances present in the water. The ratio COD/TOC in untreated wastewater was 3.4, close to the value found by others authors dealing with similar systems [1]. The COD/TOC ratio after the treatments used in this work falls within the 2.9–3.1 range.

3.1. Coagulation process

The coagulation process using $FeSO_4 \cdot 7H_2O$ was evaluated in search of the optimum working pH and dose of Fe^{2+} (expressed

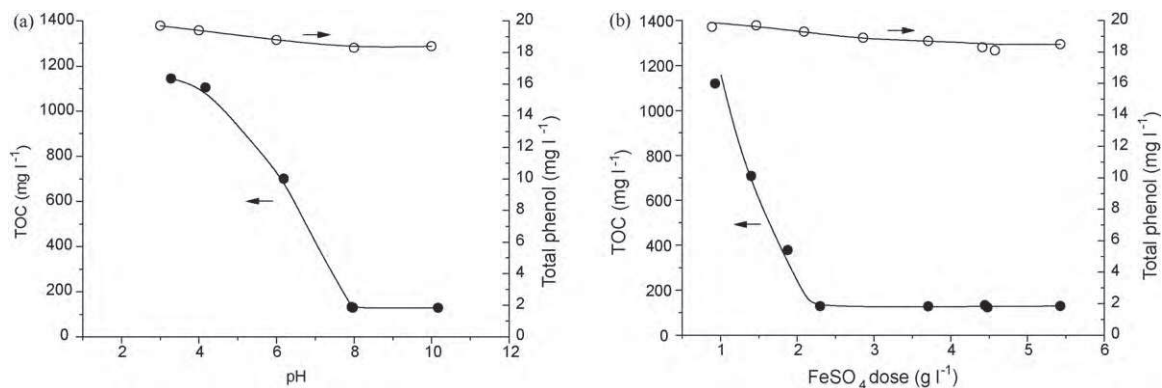


Fig. 1. Variation of TOC (solid symbols) and concentration of total phenol (empty symbols) with a) pH and b) FeSO₄ doses.

as FeSO₄). Fig. 1(a) shows (solid symbols) the variation of TOC with pH. In this set of experiments pH was adjusted using NaOH 1 M. The lowest TOC was achieved at pH ≥ 8, without significant differences in the 8–10 pH range. The final TOC in clarified effluent was lower than 200 mg l⁻¹ (COD = 680 mg l⁻¹), well below the emission limit established by local regulations. According to this, optimum coagulant doses were determined at pH 8. FeSO₄ doses between 1 and 6 g l⁻¹ were studied. These doses are high but frequently used to treat highly polluted wastewater [13,14,30,31].

Fig. 1(b) shows the evolution of TOC (solid symbols) with coagulant concentration. A significant improvement may be observed in TOC removal to around 2 g l⁻¹, with no further improvement at higher doses. Taking into account the COD/TOC ratio of 3.4, the TOC corresponding to the discharge limit for COD (1750 mg l⁻¹) would be 515 mg l⁻¹. A FeSO₄ dose of 1.33 g l⁻¹ would therefore fulfill the legal discharge limit (Fig. 1b). Nevertheless, a dose of 2.29 g l⁻¹ would optimize the TOC removal/coagulant dose ratio as shown in Fig. 2.

Fig. 1(a) and (b) (open symbols) also show the evolution of total phenol concentration in the coagulation process. No significant differences were found among the different working conditions, the working pH or the coagulant doses. The coagulation process was able to achieve enough organic load reduction to meet COD discharge limits, but only to decrease total phenol concentration as far as 18 mg l⁻¹, which is still significantly higher than the limit for discharge into the municipal sewer system. This low phenol removal using a coagulation process has been already reported by other authors [10,11].

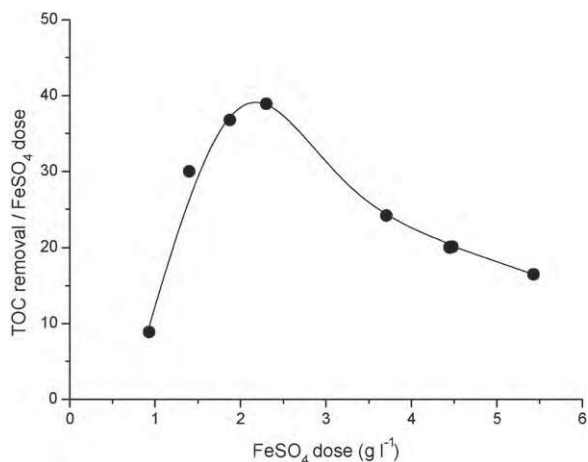


Fig. 2. Variation of TOC removal (mg l⁻¹) per gram with FeSO₄ doses.

3.2. Coagulation–Fenton process

In order to reduce the concentration of phenol derivatives in the effluent from the coagulation process, a Fenton oxidation system was implemented on the grounds of its great capacity for the removal of phenolic compounds [14,15,17].

Coagulation pH was adjusted by means of Ca(OH)₂, which is cheaper, more easily available and more frequently used than NaOH. The relative concentration of FeSO₄ and Ca(OH)₂ in the coagulant mixture had a great influence on the two main parameters for the subsequent use of Fenton's reagent: the remaining TOC and the dissolved iron. This relative concentration was adjusted from the previously optimized FeSO₄ values (2.29 g l⁻¹) and its corresponding theoretical Ca(OH)₂ concentration (1.76 g l⁻¹) [32]. In order to achieve the best conditions for Fenton oxidation, the coagulation process was intended to reduce TOC as much as possible to avoid interferences from other organic compounds and to reduce the dose of H₂O₂ required by maintaining a high concentration of dissolved iron. Table 2 shows that on increasing FeSO₄ concentrations, for a given Ca(OH)₂ dose, the final TOC decreases while dissolved iron increases due to the lower pH which restricts the formation of insoluble iron hydroxide. It is thought that organic matter decreases as a consequence of a higher concentration of both hydrated ions and polymeric molecules for the dose [33]. Increasing Ca(OH)₂ concentrations, for the same FeSO₄ concentration, caused a decrease in both TOC and dissolved iron concentration. This could be due to the enhanced formation of iron hydroxides which precipitate by sweeping organic matter. Ca(OH)₂ doses higher than

Table 2
Coagulation experimental conditions, final TOC and dissolved Fe values.

Experiment	Coagulator mixture doses (g l ⁻¹)		pH	TOC (mg l ⁻¹)	Dissolved Fe (mg l ⁻¹)
	Ca(OH) ₂	FeSO ₄			
C-1	1.23	2.06	8.95	223.2	121.1
C-2		2.29	8.62	196.2	174.5
C-3		2.74	7.00	177.8	296.2
C-4	1.40	1.83	10.79	195.1	9.9
C-5		2.06	9.18	176.3	33.1
C-6		2.29	8.80	162.6	86.2
C-7		2.74	8.58	158.1	157.7
C-8	1.58	1.83	11.49	182.5	2.3
C-9		2.06	10.91	178.6	3.6
C-10		2.29	9.97	169.5	11.3
C-11		2.74	8.74	147.0	102.4
C-12	1.76	1.83	12.19	190.0	0.1
C-13		2.06	11.91	176.6	0.1
C-14		2.29	10.58	168.8	0.1
C-15		2.74	9.07	144.1	0.1
C-16	2.11	2.74	10.70	161.3	0.1

Table 3
Main parameters after coagulation and coagulation–Fenton processes.

Experiment ^a (g l ⁻¹)	Coagulation				Coagulation–Fenton				X _{TOC} ^d (%)	X _{phenol} ^e (%)
	TOC (mg l ⁻¹)	Phenols (mg l ⁻¹)	Fe (mg l ⁻¹)	H ₂ O ₂ ^b (g l ⁻¹)	TOC (mg l ⁻¹)	Phenols (mg l ⁻¹)	Fe (mg l ⁻¹)	H ₂ O ₂ ^c (mg l ⁻¹)		
C-2 (1.23;2.29)	196.2	18.5	170.4	0.99	39.9	0.18	0.6	<0.1	96.7	99.1
C-3 (1.23;2.74)	177.8	18.4	294.4	0.91	44.4	0.91	1.5	<0.1	96.4	95.7
C-7 (1.40;2.74)	158.1	18.2	156.5	0.80	50.8	1.02	0.5	<0.1	95.8	95.1

^a Coagulator mix doses (Ca(OH)₂;FeSO₄).

^b H₂O₂ doses added in Fenton process.

^c Residual H₂O₂.

^d TOC removal efficiency.

^e Total phenol removal efficiency.

1.76 g l⁻¹ caused total iron depletion, thus avoiding the use of clarified water for the Fenton process. Therefore, three mixtures, named C-2, C-3 and C-7 in Table 2, were selected for the Fenton process.

Table 3 summarizes the main parameters after coagulation and coagulation–Fenton processes for experiments C-2, C-3 and C-7. In all three cases, TOC after coagulation was significantly below the discharge limit. However, iron and total phenol concentrations exceeded their respective limit values of 10 and 2 mg l⁻¹ notably. The coagulation–Fenton process yielded TOC values of 39.9, 44.4 and 50.8 mg l⁻¹, corresponding to TOC removal efficiencies of 96.7%, 96.4% and 95.8% for samples C-2, C-3 and C-7, respectively. The sample with the highest final iron content (C-3) had a concentration of 1.5 mg l⁻¹, considerably lower than its discharge limit, thus indicating that no further treatment would be necessary to reduce iron concentration. As for phenol derivatives, the Fenton process after coagulation significantly reduced their concentration to values as low as 0.18 mg l⁻¹, considerably below the discharge limit (2 mg l⁻¹). Total phenol removal efficiencies for samples C-2, C-3 and C-7 were 99.1%, 95.7% and 95.1%, respectively. In all cases, the residual H₂O₂ after the Fenton process was below the detection limit (<0.1 mg l⁻¹). Taking into account TOC reduction, final iron and final total phenol concentrations, as well as the amount of reagent used, sample C-2 was selected for further Fenton process optimization. It is well known that Fenton active specie Fe²⁺ is oxidized to less active Fe³⁺ by the dissolved oxygen present in water. In order to make use of the highest amount of iron Fenton active specie Fe²⁺, addition of H₂O₂ was carried out within few minutes after coagulation process to avoid iron oxidation. In the experiments when H₂O₂ was added 6 h after coagulation the total phenol removal efficiency dramatically decreased.

Besides pH and temperature, the main parameters affecting the efficiency of a Fenton process are reaction time and the concentration of hydrogen peroxide. Both have been taken into account in this work. First, the concentration of hydrogen peroxide was optimized as this is the main drawback of real Fenton application in terms of cost effectiveness [17]. Due to the initial TOC reduction carried out in the previous coagulation process, the initial H₂O₂ concentration (around 1 g l⁻¹) can be considered relatively low compared with other Fenton process studies carried out with highly polluted water [1,14,26]. Nevertheless, further dose optimization was carried out in an attempt to reduce this concentration even more. Fig. 3 shows the evolution of TOC (solid symbols) and total phenol concentration (empty symbols) for runs performed using different H₂O₂ doses. A significant improvement in TOC removal can be observed while the H₂O₂ dose was raised as far as 3 g l⁻¹, whereas little effect was noted thereafter. This behavior, previously observed by others [1,13], is due to the scavenger effect of excess H₂O₂. The Fenton process removed 90% of initial TOC, achieving a final value lower than 20 mg l⁻¹ in the overall process for the highest H₂O₂ dose (5.4 g l⁻¹). As can be seen in Fig. 3, the concentration of phenol derivatives steadily declined as the H₂O₂ concentration was increased. A final concentration of total phenol of 0.09 mg l⁻¹ was reached for a 2 g l⁻¹ dose of H₂O₂, before the scavenging effect became significant. The reference discharge value of total phenol (2 mg l⁻¹) was achieved using H₂O₂ concentration of 0.30 g l⁻¹, three times lower than the stoichiometric amount. H₂O₂ is an expensive reagent which limits the practical use of Fenton process.

The ratio phenolic compounds/H₂O₂ is a key parameter when it comes to determining both the H₂O₂ efficiency and cost effectiveness of the process [13]. Fig. 4 shows a maximum value at 0.30 g l⁻¹,

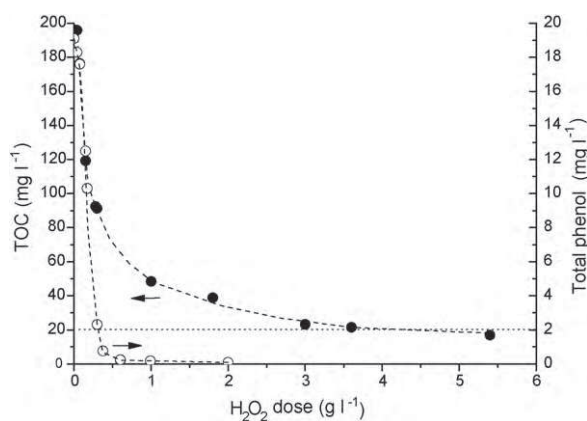


Fig. 3. Influence of H₂O₂ dose in TOC (solid symbols) and concentration of total phenol (empty symbols).

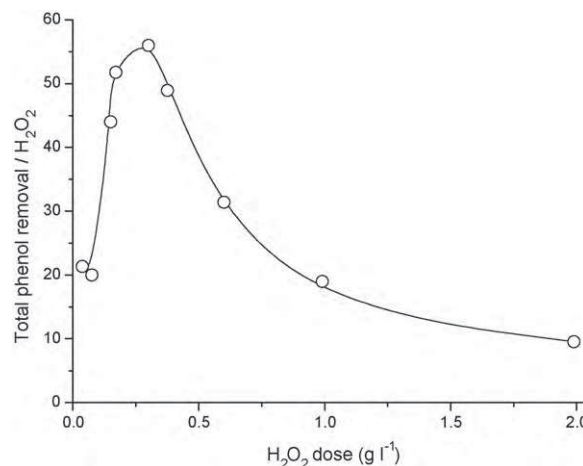


Fig. 4. Variation in total phenol removal per gram of H₂O₂.

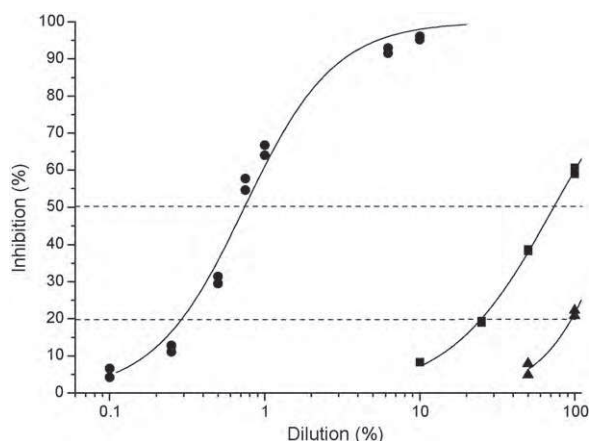


Fig. 5. Inhibition–dilution curve of the raw effluent (●) as well as the wastewater treated by coagulation (■) and coagulation–Fenton process (▲).

which is both the maximum efficiency and the minimum H_2O_2 dose required to meet the discharge limit for phenol concentration.

In a second step, the reaction time was optimized using a dose of 0.30 g l^{-1} as indicated before. TOC and total phenol were measured at 15, 30, 60, 120, 180 and 240 min. The reactions leading to TOC and phenol degradation came to an end within the first 15 min. This short reaction period has been cited by others [17].

3.3. Ecotoxicity and biodegradability

Fig. 5 shows the relation between effect (bioluminescence inhibition of *V. fischeri* after 15 min exposure) and percent dilution of raw effluent and treated wastewater (C-7 sample) by coagulation and coagulation–Fenton process. A similar trend was found for treated wastewater samples C-2 and C-3 (results not shown here).

The raw effluent showed a high ecotoxicity with values of $IC_{50} = 0.5\%$ (equivalent of $200\text{ equitox m}^{-3}$) and $IC_{20} = 0.1\%$. This ecotoxicity is significantly higher than the allowed emission limit (see Table 1) as well as compared with extremely polluted industrial wastewater (57 equitox m^{-3}) reported by others [26]. The high amount of toxicants present in cosmetics industry effluent (surfactants, dyes, preservatives, phenol derivatives, etc.) and the possible mixture effects (synergic or additive) among them may explain the high ecotoxicity of raw effluent. Moreover, due to the low biodegradability of samples (see below), no hormesis effect was observed.

The industrial effluent ecotoxicity was greatly reduced both by coagulation and the coagulation–Fenton process. The coagulation process led to an ecotoxicity reduction of up to $IC_{50} = 53.6\%$ (equivalent to $1.9\text{ equitox m}^{-3}$) and $IC_{20} = 18.6\%$, whereas the coagulation–Fenton process improved ecotoxicity reduction up to values of $IC_{20} = 75.3\%$; it was not possible to determine IC_{50} due to the low ecotoxicity of water after coupled treatment. As shown in Table 3, the amount of residual H_2O_2 after the coagulation–Fenton process was so low that its well-known high ecotoxicity did not interfere in the ecotoxicity evaluation. Zazo et al. [15] have shown that the neutralization step after carrying out the Fenton process for 240 min (the same conditions as used in this study) completely eliminates phenol degradation intermediates (hydroquinone and *p*-benzoquinone) with a high toxic potential. The very low ecotoxicity of coagulation–Fenton treated wastewater is a reflection of the elimination of these various sources of toxic effects (phenols, phenol degradation intermediates, H_2O_2).

As can be seen, after coagulation treatment the treated wastewater complies with the limit value for ecotoxicity emission, while the total phenol are still out of range. Treated wastewater after

coupled coagulation–Fenton process fulfilled all the emission limit criteria.

The biodegradability of the discharged water in a municipal sewer system is an important parameter because it is a rough indicator of the elimination in sewage treatment plants (STPs) of potentially bioaccumulative compounds. The ratio BOD_5/COD is commonly used as a biodegradability indicator because it expresses the amount of oxidizable matter that can be biologically degraded. The raw effluent was not biodegradable due to the presence of toxicants, a fact that may cause a failure in the activated sludge of STPs [34]. Biodegradability did not improve significantly ($BOD_5/COD = 0.03$) after the coagulation process in spite of the high TOC removal achieved (84%). However, the biodegradability of the effluent after the coupled coagulation–Fenton process attained a BOD_5/COD ratio of 0.37, close enough to consider the water to be biodegradable (0.4–0.6) [33,35].

4. Conclusions

A coupled coagulation–Fenton process proved to be a suitable treatment for dealing with cosmetics industry effluents. In a first step, coagulation using $Fe(SO_4)$ at $pH \geq 8$ reduced an initial TOC of 1220 mg l^{-1} to less than 200 mg l^{-1} . However, the concentration of phenol derivatives was not significantly lowered (18 mg l^{-1}) with regard to the initial value of 21 mg l^{-1} . The coupled coagulation–Fenton process was undertaken using the dissolved Fe^{2+} present after coagulation as Fenton catalyst. The coupled process, using a H_2O_2 dose of 2 g l^{-1} , reduced TOC and total phenol to values lower than 40 mg l^{-1} and 0.10 mg l^{-1} , respectively. The latter was well inside the limit value for discharge into the municipal sewer system established by local regulations (2 mg l^{-1}). An optimized H_2O_2 dose could be established at 0.30 g l^{-1} for the initial concentration of phenol (21 mg l^{-1}). The short reaction period (less than 15 min) in TOC and phenol degradation augurs well for improving treatment in a continuous regime. The combination of both processes significantly reduced the ecotoxicity of raw effluent and sharply increased its biodegradability, thus permitting easier treatment by the conventional biological units in conventional STPs.

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