



Treatment of wastewater from an alkaline cleaning solution by combined coagulation and photo-Fenton processes



Alejandro M. Senn^{a,b}, Yamila M. Russo^c, Marta I. Litter^{a,b,d,*}

^a Comisión Nacional de Energía Atómica, Avenida General Paz 1499, San Martín, Provincia de Buenos Aires, Argentina

^b Consejo Nacional de Investigaciones Científicas y Técnicas (CONICET), Av. Rivadavia 1917, Ciudad Autónoma de Buenos Aires, Argentina

^c Universidad Tecnológica Nacional, Medrano 951, Ciudad Autónoma de Buenos Aires, Argentina

^d Instituto de Investigación e Ingeniería Ambiental, Universidad de Gral. San Martín, Campus Miguelete, Av. 25 de Mayo y Martín de Irigoyen, San Martín, Provincia de Buenos Aires, Argentina

ARTICLE INFO

Article history:

Received 6 September 2013

Received in revised form 1 June 2014

Accepted 4 June 2014

Available online 13 June 2014

Keywords:

Advanced oxidation processes

Coagulation

Fenton

Photo-Fenton

Industrial wastewater

ABSTRACT

A coupled coagulation and photo-Fenton treatment has been applied to an industrial wastewater coming from the use of an alkaline cleaning solution. The real wastewater contained anionic and nonionic surfactants, tripolyphosphate, soda ash, metasilicate and oil residuals. After the proposed treatment, the wastewater fulfilled Argentine regulations for sewage discharge (10 mg/L total phosphorus, 0.7 g/L COD). First, phosphorous was eliminated by coagulation with FeSO₄ and then COD was removed by a photo-Fenton treatment. The dark Fenton treatment was also effective to remove COD but it did not allow achieving the discharge regulations, and the application of light was needed. The photo-Fenton treatment showed to be very effective to treat this particular wastewater in 2 h and with a high efficiency of H₂O₂ consumption. The experiments performed at bench scale allowed to propose a scheme for the *in situ* treatment of the alkaline cleaning solution wastewater, which could be extended to other similar wastewaters.

© 2014 Elsevier B.V. All rights reserved.

1. Introduction

Alkaline cleaners present a particular use as metal degreasers during manufacturing or finishing [1]. This cleaning process has three basic steps consisting of the application of the cleaner (by immersion at elevated temperature or spray washing), rinsing and drying. The cleaning solution has a limited lifetime and its quality can be monitored by different methods [2]. Once the solution is spent, it must be treated as a hazardous waste. The contaminants present in the effluent depend on the dirty removed (mainly oil and grease) and on the chemical components of the cleaner.

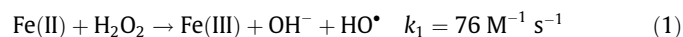
Generally, the alkaline cleaners are composed of alkaline and silicate builders, anionic and nonionic surfactants, complexing agents [3] and polyphosphates. Surfactants are the main contributors to the biochemical oxygen demand (BOD) of the effluent and they can be toxic to some aquatic organisms; the eventual production of foam can interfere in water oxygenation. Different phosphorus species promote the eutrophication of a water body, and the high pH of the cleaner must also be corrected. The grease and oil coming from the cleaning process are considered hazardous components.

* Corresponding author at: Comisión Nacional de Energía Atómica, Avenida General Paz 1499, San Martín, Provincia de Buenos Aires, Argentina. Tel.: +54 11 6772 7016; fax: +54 11 6772 7886.

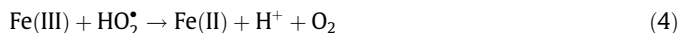
E-mail address: litter@cnea.gov.ar (M.I. Litter).

Conventional treatments including neutralization, coagulation or chemical treatments have been applied to spent alkaline cleaning solutions to break stable oil–water emulsions, and gravity separators were used to remove the oil; in some cases, biological treatments were applied at the end of the treatment [4]. However, these treatments are not suitable to discharge the effluents to municipal sewage treatment plants because they do not reach actual regulation values. Incineration has also been applied in especial facilities, but this alternative is expensive and ecologically arguable. Another alternative is to recycle the solution by filtration, but some problems arise from premature membrane fouling or removal of useful cleaner components [5].

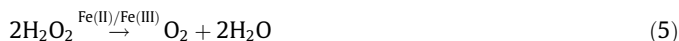
The application of advanced oxidation processes (AOPs) has been evaluated as a possible solution for industries related to surfactants [6]. In particular, the Fenton and photo-Fenton processes have been extensively studied and applied, due to the relative low cost and easy operation [7–9]. Briefly, the Fenton reaction is initiated by mixing aqueous iron with peroxide hydrogen to generate hydroxyl radicals (HO•) and other reactive oxygen species (ROS, like HO₂• and O₂^{-•}), and radical chain reaction is promoted [8,10]:



In the absence of organic matter, the termination of the radical chain reaction is favored and the process is unproductive:



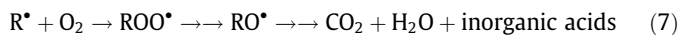
Therefore, cycles between Fe(II) and Fe(III) oxidation states take place and the net reaction is the iron catalyzed disproportionation of H_2O_2 :



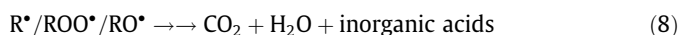
ROS are potent oxidants for organic matter; for example, HO^\bullet can induce hydrogen abstraction or other reactions (addition to double bonds, electron transfer, etc.):



By reaction with O_2 , peroxy (ROO^\bullet) or oxyl radicals (RO^\bullet) can be produced:

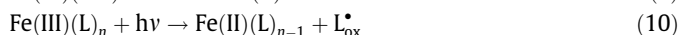


These intermediates may react further with HO^\bullet and O_2 , with the overall process leading eventually to mineralization [8]:



Evolution of CO_2 is slower than disappearance of the initial compound and ordinarily decreases in rate with time as the products become less and less reactive with HO^\bullet .

As widely known, the Fenton process is enhanced by light [8], allowing to reduce BOD and to achieve the complete mineralization of the organic components [11]. The enhancement of the Fenton reaction by light is due to the photolysis of Fe(III) hydroxo complexes (e.g., Eq. (9)) and the ligand-to-metal charge transfer excitation of Fe(III) chelates (Eq. (10)). Both processes provide an additional source for Fe(II) that complements the slow reaction (2).



The Fenton process has been successfully applied as a pretreatment for surfactants, the main result being the increase of the effluent biodegradability [9,12].

In order to reduce the chemical oxygen demand (COD), coagulation processes have been proposed as classical treatments. Both Fe^{2+} and Fe^{3+} ions are common coagulants; hence, the Fenton process can have a dual function in the whole treatment processes, namely oxidation and coagulation. Moreover, iron is a highly abundant and non-toxic element, and H_2O_2 is easy to handle environmentally. However, H_2O_2 represents the main cost of a Fenton treatment, and the amount needed depends on the COD content of the effluent.

The coupled coagulation–Fenton treatment has been proposed before as a process for the treatment of industrial wastewaters containing hazardous chemicals such as pesticides, cosmetics and inks [13–15]. The present work evaluates the possibility of the treatment of a different kind of wastewater coming from a real spent alkaline cleaning solution by using this combined technology. The samples were obtained from an industrial metal finishing process, where the cleaning process was performed by immersion of the metal in a warm alkaline degreaser. Until now, AOPs were not extensively studied for this type of effluent, whose matrix has very particular features considering the high concentration of surfactants combined with phosphorus and carbonate, which makes the effluent very difficult to be treated by conventional methods.

2. Experimental section

2.1. Wastewater description

The spent alkaline cleaning solution was obtained from an industrial metal finishing process. The samples were taken just before the cleaning solution was going to be replaced by a new one. The washing pools contained 10 m^3 of alkaline cleaning solution that was changed each month. The original washing solution (12% w/v) was prepared by the company from Truedene 602 provided by Química True (Argentina). The preliminary experiments and the final optimized experiment were performed with two different batches of the effluent provided by the company after the use. The components of the powder declared by the provider were: sodium hydroxide (CAS 1310-73-2), soda ash (CAS 497-19-8), sodium metasilicate (CAS 13517-24-3), anionic surfactants (not specified), nonylphenol ethoxylate (CAS 9016-45-9) and sodium tripolyphosphate (CAS 7758-29-4). The main parameters of the wastewater were determined in our laboratory and they are shown in Table 1.

2.2. Chemicals

The analytical reagents ammonium metavanadate, *o*-phenanthroline and methylene blue were provided by Mallinckrodt. The other chemicals were reagent grade and provided by Biopack (Argentina). Hydrogen peroxide (30% H_2O_2) was added without dilution in the amount needed to get the final concentration informed in each case. Sulfuric acid (95–98% H_2SO_4) was diluted 1:2 before being used. Iron was added as solid iron(II) sulfate heptahydrate ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$). Sodium hydroxide was 4 M. When indicated, drops of a technical silicone anti-foaming agent were applied.

2.3. Coagulation by acidification and by Fe(II) addition and filtration procedures

All the experiments were performed in bakerys with magnetic stirring at ambient temperature. For the coagulation tests, 20 mL samples of the cleaner solution were stirred for 1 h after: (1) addition of H_2SO_4 (varying concentrations from 1.5 to 4.4% v/v corresponding to pH 9.6 to 1.8), and (2) Fe(II) (varying concentrations from 8 to 40 mM). As the system was relatively stable after 1 h of treatment and the solution was homogenous, the reaction was allowed to continue for more time (all night) to see a change in the parameters. Then, the samples were allowed to settle down overnight in test tubes. The parameters needed to follow the treatment such as pH, total organic carbon (TOC), and inorganic carbon (IC) were measured in the supernatant.

In all the other experiments, coagulation was directly carried out adjusting the pH to 8 with H_2SO_4 and adding 40 mM Fe(II). The solution was stirred for 30 min.

In all cases, the solutions were filtered using a vacuum system with a nylon filter (Osmonics), 0.22 μm pore size and 47 mm diameter.

Table 1
Main parameters of the wastewater used for the experiments.

Anionic surfactants (g/L)	7
Total phosphorus (g/L)	0.4
Inorganic carbon (g/L)	5.2
pH	>13
COD (g/L)	35
TOC (g/L)	13

In the following sections, different experimental conditions are described for the Fenton and photo-Fenton treatments.

2.4. Fenton treatment with different initial concentrations of H_2O_2

A sample (100 mL) coming from the coagulation and filtration stages was acidified to pH 2.8 with H_2SO_4 ; it contained 18 mM of total dissolved Fe (13 mM Fe(II) and 5 mM Fe(III)) remaining from the coagulation process. The total volume was divided into four beakers, each one containing 25 mL of sample. H_2O_2 was added to each beaker at different initial concentrations ($[H_2O_2]_0$): 0.4, 0.8, 1.1 and 1.4 M. The system was magnetically stirred for 1 h and then left overnight in contact with the reagent without stirring. Samples were taken at different times in order to quantify the different parameters.

2.5. Photo-Fenton treatment

In the photo-Fenton experiments, two different irradiation setups were used: (a) a 50 mL cylindrical jacketed Pyrex glass reactor with an external UV lamp (Philips HPA 400S, maximum emission at 365 nm, 400 W) placed laterally at 10 cm from the reactor wall, thermostatted at 25 °C; (b) a UV lamp (MP 3U shape energy saving Blacklight lamp, 15 W) partially immersed in a similar reactor of greater size (300 mL capacity), also thermostatted at the indicated temperature. Temperature was controlled by recirculating water through the jacket using a Polyscience 9106 Circulator. The concentration of the reagents (H_2O_2 and Fe) varied according to the experiments and are described in the following sections.

2.6. Photo-Fenton in tandem with Fenton treatment

The effluent was treated overnight with the Fenton reagent as described in Section 2.4 ($[H_2O_2]_0 = 1.1$ M). After that, 0.2 M H_2O_2 remained in the system. Then, the lamp (setup (a)) was switched on. H_2O_2 concentration was followed during time and one supplementary addition of the reagent (0.5 M final concentration) was made when depletion of the reagent was observed.

2.7. Photo-Fenton treatment under optimized conditions

A 200 mL sample submitted first to the coagulation–filtration process (Section 2.3), and where 17 mM total iron remained, was irradiated using setup (b), switching on the lamp after addition of 1.2 M H_2O_2 . Initial pH was adjusted to 3 with H_2SO_4 . At the beginning, the system was not thermostatically controlled and it began to warm up. After 30 min, the temperature reached 68 °C, and then it was controlled at 45 °C using a thermostat. H_2O_2 was totally consumed several times during the process and four additions of 5 mL of 9.1 M H_2O_2 (i.e. 0.23 M final concentration in the reactor) were made.

2.8. Analytical techniques

COD was determined by the close reflux colorimetric method at 600 nm [16]. Anionic surfactants were measured by reaction with methylene blue at 650 nm using sodium lauryl sulfate as the calibration standard [17]. H_2O_2 was determined spectrophotometrically with a method using ammonium metavanadate, measuring the absorbance at 450 nm [18]. Fe^{2+} determination was carried out by the *o*-phenanthroline method at 508 nm, and total iron was determined by previous reduction to Fe^{2+} using hydroquinone [19]. The Fe^{3+} concentration was obtained by difference. Dissolved oxygen was determined in percentage of saturation using an oxygen sensor (Hach Sens Ion 156 Multiparameter Meter) equipped

with a Hach DO meter electrode. Phosphate was quantified by the ascorbic method measuring the absorbance at 820 nm [20] and total phosphorus was also quantified as phosphate after acid hydrolysis of the sample [21]. TOC and IC were determined with a Shimadzu 5000-A TOC analyzer.

3. Results and discussion

3.1. General considerations

As indicated in Section 2.1, the cleaning powder was composed of alkaline constituents, silicates, anionic and neutral surfactants and sodium tripolyphosphate. As phosphate forms complexes with ferrous and ferric ions that inhibit the Fenton reaction [22], they have to be removed first. The strategy for the treatment involved three main processes: (I) an acid coagulation step up to pH 8 to partially eliminate the anionic surfactants; (II) the coagulation and filtration of phosphate and tripolyphosphate with $FeSO_4$ at pH 8, which additionally provided enough Fe for the Fenton reaction without further addition; (III) a Fenton or photo-Fenton reaction at pH 3 to eliminate the rest of organic matter (anionic and neutral surfactants and other minor organic residuals).

3.2. Preliminary experiments

3.2.1. Coagulation of the effluent by acidification. Partial removal of surfactants

The spent alkaline cleaning solution was a highly caustic solution with pH above 13. A first addition of 1 mL 5.5 M H_2SO_4 was made to bring the solution to pH 9.6, to facilitate the measurement of the parameters needed to follow the treatment. After this initial addition, continuous H_2SO_4 addition was performed up to pH 1, and this process gave rise to events defining three stages: (1) first coagulation (white flocs), (2) CO_2 evolution and (3) second coagulation (Fig. 1). Additionally, separate experiments were performed at different pH values in order to quantify the events above described. Some parameters, described in Table 2, were measured in the supernatant after overnight sedimentation. In Exp. 1, there was not visible sedimentation.

Stage 1: At the beginning, addition of the H_2SO_4 solution caused a sharp decrease of pH from 13 to 8 without any apparent change in the solution. The composition of the solution at this

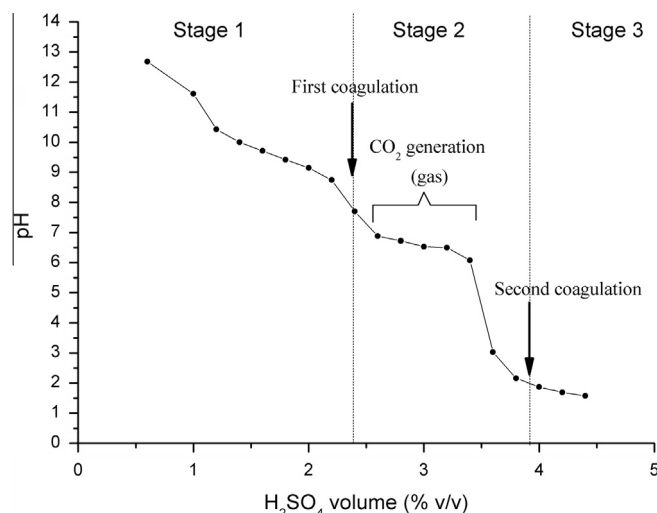


Fig. 1. pH adjustment of the alkaline cleaning solution with H_2SO_4 . The arrows indicate the amount of acid that produces each coagulation.

Table 2
Parameters measured after the coagulation tests by H₂SO₄ addition.

Exp. ^a	Stage	Acid% v/v	pH	TOC (g/L)	IC (g/L)	Anionic surfactants (mM)	Phosphate (mg/L)	Total phosphorus (mg/L)
1	1	1.5	9.6	10.2	5.2	7.0	135	400
2	1	2.3	8.0	8.6	3.6	1.8	n.d.	473
3	2	3.1	8.0	7.9	1.3	1.6	n.d.	463
4	3	4.4	1.8	6.0	0.0	1.0	n.d.	407

n.d.: not determined.

^a Separated coagulation experiments.

stage was considered similar to the original effluent, and the parameters measured after H₂SO₄ addition up to pH 9.6 were used for further comparisons (Table 2, Exp. 1). At pH 8, a visible coagulation started to take place, with formation of a white sludge. The coagulation tests indicated that, during this Stage 1, mainly anionic surfactants precipitated, as their concentration dropped from 7.0 to 1.8 mM, with a concomitant TOC removal from 10.2 to 8.6 g/L. The acid coagulation did not remove phosphorus, which remained above 400 mg/L (Table 2, Exp. 2). The fluctuation of the concentration in the different experiments 1–4 near 400 mg/L was assigned to errors in the method of determination.

Stage 2: Further addition of acid promoted the formation of an important amount of gas, with the consequent production of bubbles and foam. The evolved gas was generated from carbonates initially present in the sample, and consequently, pH was buffered close to 8 (for carbonic acid, $K_{a1} = 4.45 \times 10^{-7}$). The evolution of CO₂ was confirmed by the partial removal of inorganic carbon (IC) during this stage (Table 2, Exp. 3) and the complete IC elimination after this stage (Table 2, Exp. 4). To avoid foam formation, drops of a silicone anti-foaming agent were added in further experiments during this second stage.

Stage 3: After the elimination of carbonates, pH continued to drop with the acid additions, and a second coagulation (white flocs) was observed below pH 2, which produced a TOC removal from 7.9 to 6.0 g/L (Table 2, Exp. 4). This correlated with the removal of an additional quantity of anionic surfactants from 1.6 to 1.0 mM. The remaining TOC would correspond then to anionic and neutral surfactants and minor organic components.

3.2.2. Coagulation of the effluent by addition of iron. Removal of phosphates and polyphosphates

Although the original Truedene 602 contained sodium tripolyphosphate, the sample of the initial spent cleaning solution to be treated contained 400 mg/L total phosphorus and 135 mg/L phosphate, attributed to the hydrolysis of tripolyphosphate during the cleaning process (Table 2, Exp. 1). As said, neither H₂SO₄ addition nor the surfactant coagulation eliminated the content of phosphorus (Table 2, Exps. 2–4). Therefore, in separate experiments, addition of FeSO₄ at different concentrations was tested to attempt phosphorus removal by coagulation. The addition was carried out at pH 8, after the first coagulation of surfactants by H₂SO₄ addition and before the second stage (see Fig. 1). In this way, it was not necessary to adjust the pH after the addition of Fe(II) that otherwise tends to acidify the solution. The buffering of the solution between pH 7 and 8, due to bicarbonate formation, gave the optimum pH for phosphate removal by Fe(II), as reported in the literature [23].

In Table 3 are presented the values of the parameters measured in the runs with addition of different concentrations of Fe(II). It is observed that the phosphorus removal increased with the increasing Fe(II) concentrations (Table 3, Exps. 5–7). With 40 mM Fe(II), the total phosphorus concentration in the supernatant dropped to 10 mg/L, which is the limit for local sewage discharge [24]. Moreover, comparing Exp. 2 of Table 2 (coagulation by acidification

without Fe(II) addition) with Exp. 7 of Table 3 (coagulation by Fe(II) addition), it can be observed that this operation helped to go further in the removal of TOC (from 8.6 to 7.2 g/L) and anionic surfactants (from 1.8 to 1.1 mM). The overall TOC removal by Fe(II) addition was 30%, i.e., from 10.2 to 7.2 g/L (Table 3, Exps. 1 and 7), indicating still the presence of organic compounds in the system.

3.2.3. Properties of solids obtained by coagulation

As indicated, after H₂SO₄ addition at pH near 8 (end of Stage 1, Fig. 1 and Table 2, Exp. 2), a white sludge appeared. A sedimentation step was attempted at this point, but the solid produced presented unsatisfactory settling properties. The sedimentation process, being of *hindered* (zone) settling type [25], took more than one day, rendering a clarified volume less than the half of the total volume.

In separated experiments, the coagulated particles were removed by filtration instead of using sedimentation. The solid obtained after filtration at pH 8 (end of Stage 1, Fig. 1) had a white gel-like appearance (Fig. 2A). After drying the solid at ambient temperature, a white powder was obtained, which was stable and had a relatively small volume, being suitable for storage and final disposal (Fig. 2B). The amount of this solid waste was 0.65 g in the 50 mL of solution used in the coagulation process, i.e. 13 g (dry weight) per liter of wastewater. The mixed coagulation process (H₂SO₄ addition plus Fe(II) addition, Section 2.3), where surfactants and phosphorus were eliminated, did not improve the settling properties, which were very similar to those described before (Fig. 2C). When the solid obtained after this coagulation was filtered, a gel-like green solid was obtained (Fig. 2D), transformed to a green powder after drying, indicative of green rusts, reported to be formed under reducing and weakly acid to weakly alkaline conditions as intermediate phases in the formation of Fe oxides [26,27].

3.2.4. Fenton process

As said before, the coagulation–filtration sequence allowed removal of phosphorus to the limits required by the regulations [24], together with the partial elimination of TOC and anionic surfactants. Further removal of TOC and COD was attempted by testing the Fenton and photo-Fenton processes in order to achieve local regulations for these parameters and to eliminate other possible organic components.

The amount of iron remaining after the coagulation was 18 mM from the initial 40 mM Fe; this concentration was assumed to be enough for the Fenton reaction, avoiding the addition of an extra amount of the salt. pH was adjusted to 2.8 and different initial H₂O₂ concentrations were tested to find the optimal condition. The temporal evolution of H₂O₂ concentration during the Fenton treatment using different H₂O₂ concentrations is presented in Fig. 3. TOC and COD evolution were also measured (Fig. 4).

Fig. 4 clearly shows two stages: (a) a fast reaction before the first 63 min, yielding high COD and TOC removal; (b) a slower reaction with a lower decrease of the parameters during the following 8 h. In accordance to the velocity of COD and TOC removal, H₂O₂ consumption was faster in the first stage than in the second stage

Table 3

Parameters measured after the coagulation tests by addition of Fe(II) (Stage 1 of Fig. 1).

Exp. ^a	Acid (% v/v)	pH	Fe(II) (mM)	TOC (g/L)	IC (g/L)	Anionic surfactants (mM)	Phosphate (mg/L)	Total phosphorus (mg/L)
1	1.5	9.6	–	10.2	5.2	7.0	135	400
5	2.3	8.0	8	8.5	4.1	1.7	n.d.	457
6	2.3	8.0	14	7.6	3.7	1.7	120	232
7	2.3	8.0	40	7.2	3.8	1.1	4	10

n.d.: not determined.

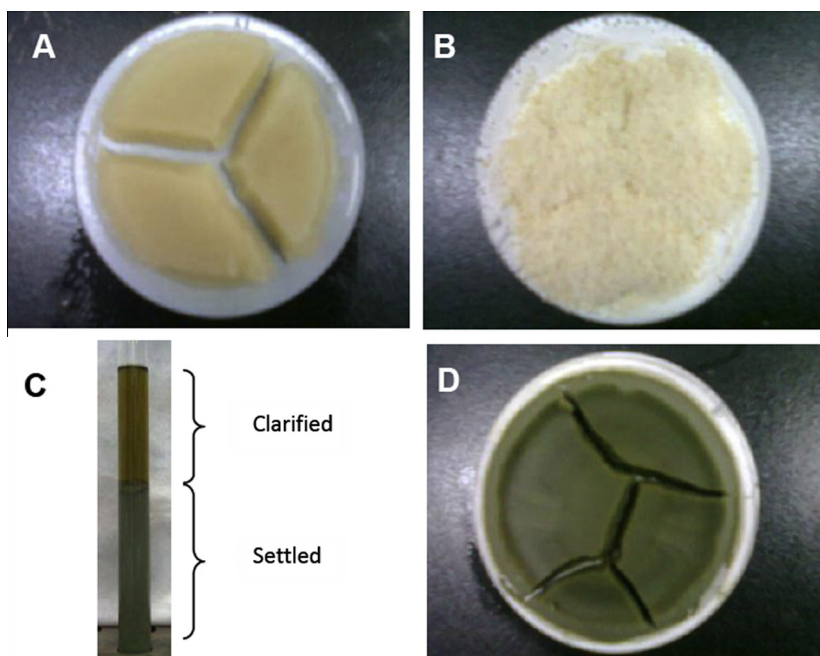
^a Separated coagulation experiments.

Fig. 2. Aspect of solids obtained from the effluent after coagulation and filtration. (A) Solid obtained after filtration of a 50 mL sample after H_2SO_4 addition up to pH 8 (end of Stage 1). (B) Solid obtained (0.65 g) after drying solid A at ambient temperature (13 g/L of solid waste). (C) The pH of the sample was adjusted to 8 as in A, and then 40 mM $\text{Fe}(\text{SO}_4)$ was added and the solution allowed to settle down in a test tube for 3 days. (D) Solid obtained after filtration of the sample treated as in C but without settling.

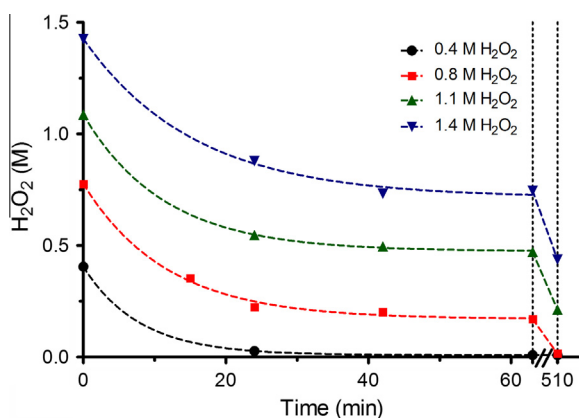


Fig. 3. Temporal evolution of H_2O_2 concentration during the Fenton treatment of the spent cleaning solution with different initial H_2O_2 concentrations. Conditions: effluent previously coagulated with 40 mM FeSO_4 and filtered, pH 2.8, $[\text{Fe}_{\text{total}}] = 18$ mM.

(Fig. 3). With initial H_2O_2 concentrations equal or higher than 0.8 M, COD and TOC removal were similar: COD dropped in average from 19 to 7 g/L in the first stage and from 7 to 5.5 g/L in the second stage, while TOC dropped from 6.4 to 3.2 and then to 2 g/L (Fig. 4).

Table 4 shows the COD/TOC final ratio and the percentage of efficiency of H_2O_2 consumption for the two stages of the Fenton reaction, using different initial H_2O_2 concentrations. The efficiency of H_2O_2 consumption was calculated as the COD removed/ H_2O_2 consumed ratio. The highest efficiency of H_2O_2 consumption was reached in the first stage of the Fenton treatment when using 0.8 M H_2O_2 . In this case, 12 g/L of COD were removed and 21 g/L ($\equiv 0.62$ M) of H_2O_2 were consumed (see Figs. 3 and 4): the ratio (12 g/L/21 g/L = 0.6) was taken as reference (100%) for the rest of the measurements. This efficiency was very high and similar (96–100%) in the first stage, independently of the initial H_2O_2 concentration. However, an initial 0.4 M H_2O_2 concentration was not enough to produce important COD and TOC removals because the reagent was totally consumed before finishing the first stage, and the reaction stopped.

The initial COD/TOC ratio was 3 and it decreased to ca. 2.5 after 1 h, independently of the initial H_2O_2 concentration. As TOC assesses the mass of mineralizable total organic carbon present in the sample, while COD provides a measure of the oxygen-demanding substances, this diminution of the COD/TOC ratio after the first stage indicated the partial oxidation of compounds recalcitrant to final mineralization by the dark Fenton process. On the other hand, during the second stage, the COD/TOC ratio remained constant, indicating that no changes on the relative amount of recalcitrant products were produced.

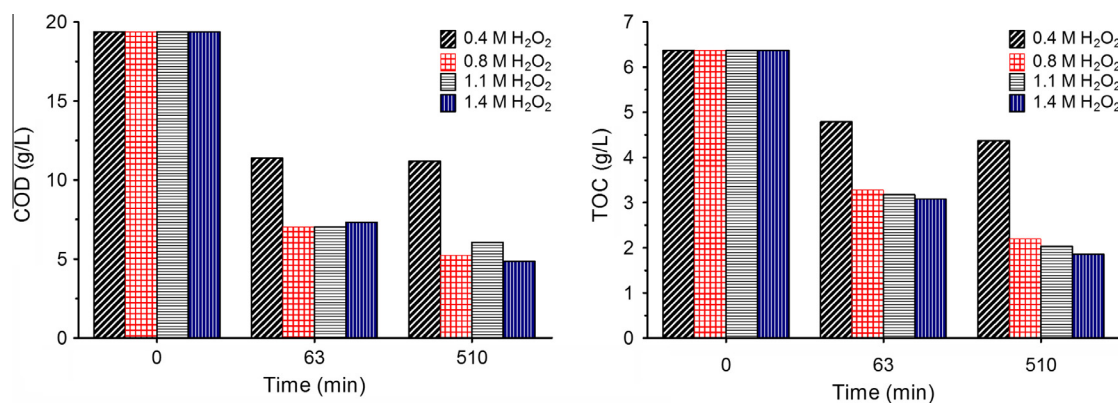


Fig. 4. COD and TOC temporal evolution during the Fenton treatment of the spent cleaning solution with different initial H_2O_2 concentrations. Conditions of Fig. 3.

Table 4

COD/TOC final ratio and efficiency of H_2O_2 consumption during different time intervals of the Fenton experiments and for different initial H_2O_2 concentrations (conditions of Figs. 3 and 4).

[H_2O_2] (M)	0–63 min		63–510 min	
	(COD/TOC) ^a	H_2O_2 consumption efficiency (%)	(COD/TOC) ^a	H_2O_2 consumption efficiency (%)
0.4	2.4	96	2.6	^b
0.8	2.1	100	2.4	56
1.1	2.2	98	3.0	18
1.4	2.4	97	2.6	39

^a Ratio measured at the end of the time period.

^b H_2O_2 is totally consumed before this stage.

In the second stage, the efficiency dropped significantly. The difference between both stages can be explained considering that the speed of organic oxidation depends on the amount of HO^\cdot generated mainly by Eq. (1). In order to sustain the reaction, the principal way of Fe(II) reformation is reduction of Fe(III) by H_2O_2 (Eq. (2)) but, as said, this reaction is several orders of magnitude slower than reaction (1) (cf. k_1 and k_2). On the other hand, 20 g/L (≈ 0.6 M) H_2O_2 was consumed in average in the first stage, whereas the initial total Fe concentration was relatively low (18 mM). Therefore, several cycles of Fe(II)/Fe(III) redox conversion (Eqs. (1) and (2)) were expected to have happened in order to consume that amount of H_2O_2 and to produce enough concentration of ROS for the removal of COD. The reaction in the second stage was slower, which is in agreement with the formation of recalcitrant compounds less reactive to the Fenton reagent such as low-molecular-weight acids (e.g., oxalic acid, etc. [8]), coming from the oxidation of the surfactants. This is also supported by the decrease of the COD/TOC ratio from 3 at the beginning to around 2.3 at the end of the first stage. Besides, the lower concentration of the organic matter and the lower reactivity of the remaining compounds could lead to a decreased scavenging of HO^\cdot . This more available HO^\cdot concentration could enhance the propagation and termination of the basic Fenton chain reaction, ending in the disproportionation of H_2O_2 (Eq. (5)), which constitutes a waste of the oxidant when occurring in excess.

According to the literature, the presence of oxygen can lead to a greater mineralization of the pollutant [8]. In these experiments, there was not aeration and the only source of new O_2 was the decomposition of H_2O_2 mentioned above (Eq. (5)). Before the addition of H_2O_2 to start the Fenton reaction, the dissolved O_2 concentration was 70%. When the starting H_2O_2 concentration was ≥ 0.8 M, the measured O_2 concentration was always higher than the supersaturation value (i.e., higher than 100%), and bubbles were observed. When the initial concentration was 0.4 M, the

Fenton reaction consumed much of the dissolved O_2 (final concentration less than 20%) as well as the H_2O_2 , and the COD and TOC removal was arrested as already shown. This O_2 depletion can be explained by the reaction with organic radicals depicted by Eq. (7) [8].

3.2.5. Photo-Fenton process

The minimum COD achieved by the Fenton process above described was 5.5 g/L after 510 min (Figs. 3 and 4), a value still higher than the value required by the regulations (0.7 g/L [24]). In an attempt to further decrease COD concentration and to speed up the process, irradiation with UV light was tested. The irradiation setup (a) (Section 2.5) was used. The same experiment of Figs. 3 and 4 with 1.1 M H_2O_2 was continued after 510 min switching on the lamp at this time. This initial H_2O_2 concentration was chosen because, according to Fig. 3, it was the lowest value of reagent that was not totally consumed in the dark reaction. Figs. 5 and 6 show the temporal evolution of the H_2O_2 concentration and COD and TOC decays during the consecutive Fenton and photo-Fenton treatment.

At 510 min, H_2O_2 remaining from the Fenton process was 0.2 M, which under irradiation was totally depleted in 30 min (Fig. 5). Fig. 6 shows that COD and TOC decreased from 6 to 3 g/L and from 2 to 0.9 g/L, respectively, in the same time (Fig. 6). The efficiency of H_2O_2 consumption (71%) was higher than that observed in the second stage of the previous Fenton reaction (18%), but lower than that of the fast first stage (98%) (cf. Table 4). After the addition of supplementary 0.5 M H_2O_2 at 550 min, COD continued to drop up to 1.3 g/L and TOC up to 0.08 g/L at 600 min. The oxidant was quickly consumed again but with a lower efficiency (16%).

Further removal of COD and better efficiencies were achieved by optimizing the photo-Fenton process as follows. A new sample of the effluent (200 mL) was used, where H_2SO_4 addition and coagulation–precipitation procedures were applied (Section 2.3). Then,

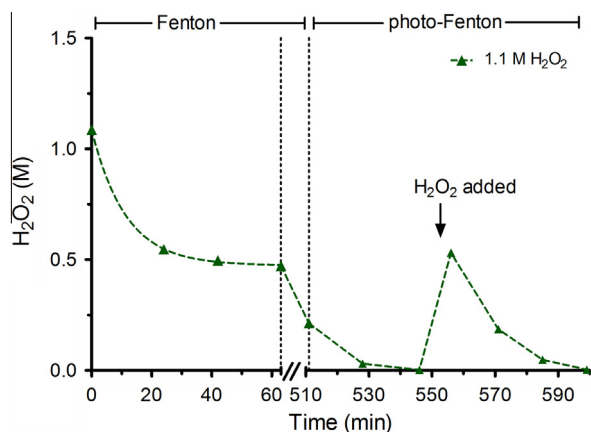


Fig. 5. Temporal evolution of H_2O_2 concentration during the consecutive Fenton and photo-Fenton treatment of the spent cleaning solution. Conditions: effluent previously coagulated and filtered, pH 2.8, $[\text{Fe}_{\text{total}}] = 18 \text{ mM}$, $[\text{H}_2\text{O}_2]_0 = 1.1 \text{ M}$.

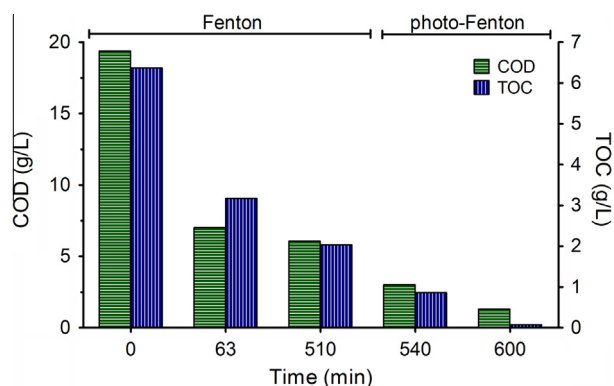


Fig. 6. COD and TOC during the consecutive Fenton and photo-Fenton. Conditions of Fig. 5.

the lamp of setup (b) was switched (Section 2.5) in order to test a system more similar to those available at industrial scale. Initial conditions of the photo-Fenton step were pH 3, $[\text{Fe}_{\text{total}}] = 17 \text{ mM}$ and $1.2 \text{ M H}_2\text{O}_2$ (added). The system was thermostatted at 45°C . H_2O_2 was periodically added as soon as its depletion was noticed. Fig. 7 shows the results of H_2O_2 consumption and COD depletion. It can be seen that COD continuously dropped up to 0.92 g/L , in 120 min. Besides, the photo-Fenton reaction proved to be a very

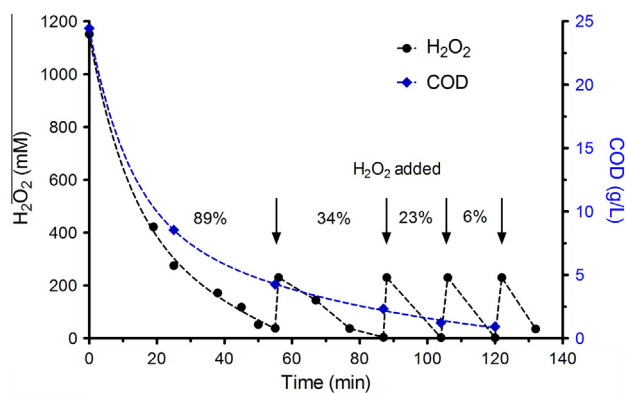


Fig. 7. H_2O_2 consumption and COD removal during a photo-Fenton treatment of the wastewater under optimized conditions. Conditions: effluent previously coagulated and filtered (Section 2.3), pH 3, $[\text{Fe}_{\text{total}}] = 17 \text{ mM}$, $[\text{H}_2\text{O}_2]_0 = 1.2 \text{ M}$, $T = 45^\circ\text{C}$. Extra additions of H_2O_2 are indicated by arrows. The efficiency (%) of H_2O_2 consumption is informed for each time interval.

powerful treatment for this matrix taking into account that 97% of the organic carbon content of the sample was mineralized (TOC removal from 7.6 to 0.21 g/L) in only 2 h.

Fig. 7 shows that the efficiency of H_2O_2 consumption was very high at the beginning (89%) and similar to that obtained in the first stage of the Fenton reaction (Table 4, between 0 and 63 min). The efficiency decreased after each H_2O_2 addition and was very low (6%) at the end because the speed of COD removal decreased with time whereas the speed of H_2O_2 consumption was always high due to the operation of Eq. (5). In this experiment, the COD removed was 24 g/L and the total H_2O_2 consumed was 63 g/L during the whole experiment. Therefore, a 63% of overall efficiency can be calculated.

In this case, although recalcitrant compounds such as oxalic acid can be produced, as said before, they can form complexes with Fe(III) (Fe(III)-L) that can be further degraded under UV-light according to Eq. (10) [28], providing an additional source for Fe(II) that complements the slow reaction (2).

During the experiments, the samples were supersaturated with O_2 due to the H_2O_2 decomposition, similarly to that indicated in the case of the Fenton reaction.

3.2.6. Effect of temperature and pH on Fenton and photo-Fenton reactions

Other experiments under similar conditions but without temperature control showed that both Fenton and photo-Fenton reactions promoted a great liberation of heat during the first stage that rose the system temperature up to 70°C . The photo-Fenton was also performed at 25°C under comparable conditions (15 mM total Fe, $1 \text{ M H}_2\text{O}_2$). The concentration of Fe used in these experiments was not exactly the same as in the case of the experiments of Section 3.2.5 because it corresponded to the Fe remaining from the previous coagulation. The amount of added H_2O_2 was accordingly diminished in order to maintain a similar Fe/ H_2O_2 ratio.

The whole process was much slower because a COD value of 1.7 g/L was reached in 230 min, whereas at 45°C the same value was reached just in 100 min (Fig. 7). On the other hand, a slightly greater efficiency of H_2O_2 consumption in order to obtain the same COD value was observed at 25°C (82%) compared with the value at 45°C (70%). Therefore, the working temperature will depend on the operation conditions and the time available for the wastewater treatment. For example, the heat generated by the highly exothermic reaction could be profited in the scaling up of the system.

In order to test the effect of the working pH range (important for practical considerations), photo-Fenton experiments at 45°C were performed at other two pH values (3.6 and 2.5) in addition to pH 3 described in Fig. 7. After 75 min of reaction, COD dropped from 24 g/L to 3.4 , 3 and 3.3 g/L for pH 3.6, 3 and 2.5, respectively, indicating almost no differences and that a rather wide pH range can be used without inconvenience.

3.3. Overall treatment under optimized conditions

The whole treatment was performed in just one experiment and described straightforward step by step, based on the results and optimal conditions obtained before. A fresh 200 mL sample of a spent alkaline cleaning solution (Section 2.1) was used. The analysis of the sample indicated that it contained 35 g/L COD and 400 mg/L total phosphorus, pH higher than 13. Table 5 shows the initial and final values of selected parameters.

The steps for the treatment were the following (Fig. 8):

- (1) Sulfuric acid was added to obtain pH 8 (2.8 % v/v). This neutralization promoted a visible coagulation with the formation of a white solid, associated mainly to the coagulation of anionic surfactants (see Section 3.2.1).

Table 5
Main parameters of the wastewater before and after the proposed treatment.

	Before treatment	After treatment	Local regulation values ^a
COD (g/L)	35	0.28	0.70
TOC (g/L)	13	0.14	n.e.
Total phosphorus (mg/L)	400	0.93	10
pH	>13	8.5	7–10
H ₂ O ₂ (mM)	–	0.1	n.e.
Total Fe (mg/L)	–	0.56	10

n.e.: not established.

^a Ref. [24].

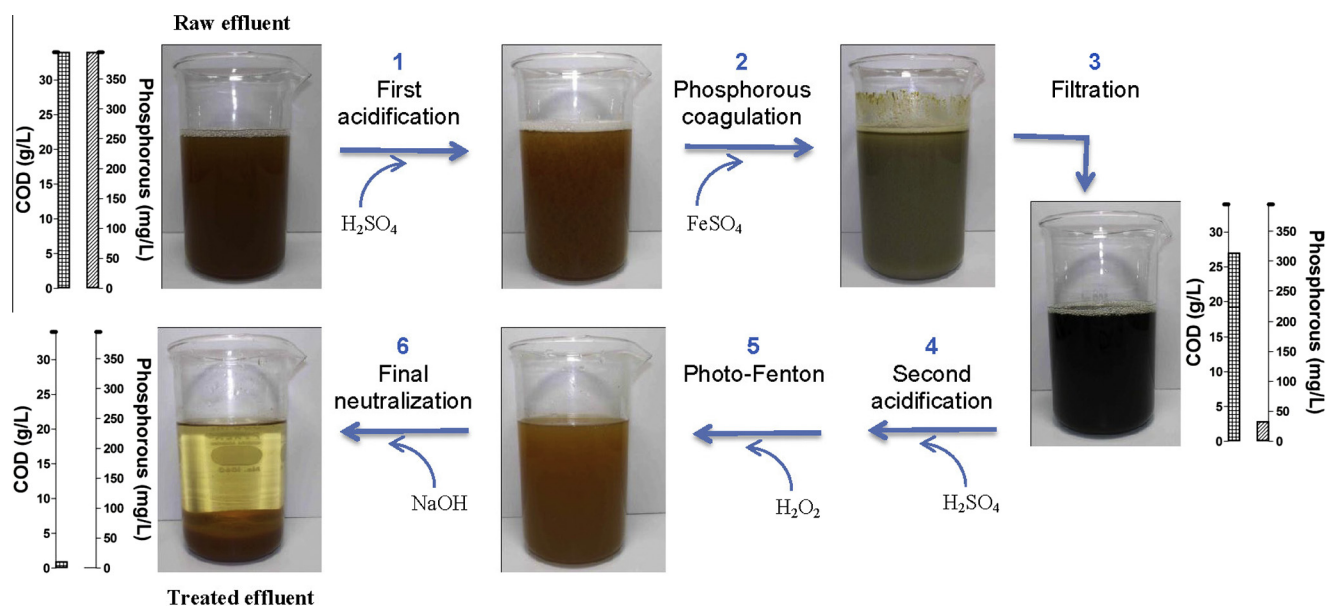


Fig. 8. Overall treatment proposed for the treatment of the alkaline cleaning solution. The numeration corresponds to the description made in Section 3.3. The left and right scales show evolution of selected parameters during the treatment.

- (2) Fe(II) was added as 1.1% w/v FeSO₄·7H₂O, and the solution was stirred for 30 min.
- (3) The coagulated solid was filtered and, in the solution, total phosphorus dropped to 33 mg/L and COD to 27 g/L.
- (4) Sulfuric acid (1% v/v) was added again, getting a final pH of 3. Drops of the anti-foaming agent were added after the appearance of foam generated by the large amount of gas (CO₂) released during the acidification process.
- (5) H₂O₂ was added to reach 1.1 M and the irradiation was started immediately using the irradiation setup (b). The system was thermostatically controlled at 45 °C. H₂O₂ was supplemented four times (0.23 M final concentration in the reactor) after each observed depletion. After the third H₂O₂ addition, foam was abundantly formed and some drops of the anti-foaming agent had to be added again. This addition was repeated each time that an intense foam was observed. After this photo-Fenton treatment, COD drastically diminished from 24 to 0.56 g/L.
- (6) At the end of the photo-Fenton step, neutralization was performed by adding 1% v/v NaOH (4 M) up to pH 8.5. The iron precipitated immediately, with an excellent settlement after approximately 2 h (Fig. 8, treated effluent). In this step, iron was removed and this helped also to further remove phosphorus. The obtained concentrations of total phosphorus (0.93 mg/L), COD (0.28 g/L) and Fe (0.56 mg/L) were in agreement of local regulations [24] (Table 5). Concerning H₂O₂ remaining after the treatment (0.1 mM, Table 5), no

regulations for discharge have been found in the literature. However, it would be advisable to use a lower amount than in the present work in the last addition before NaOH precipitation. The addition of a quenching agent to destroy H₂O₂ excess could be another alternative.

4. Conclusions

A real effluent from a metal finishing process, characterized by a strong dark color and alkaline pH was treated by a very simple process of two stages, i.e., a coagulation step followed by a photo-Fenton reaction. This process can be a general treatment suitable to be applied to liquid wastes coming from the cleaning of metallic parts employed in industrial processes. The initial coagulation step removed mainly the phosphorus content (which is an inhibitor of the following photo-Fenton reaction), decreased the pH and provided the enough Fe content for the further photo-Fenton reaction. In this way, total phosphorus dropped from 400 to 0.98 mg/L (99.8%) at the end of the process, whereas COD dropped from 35 to 0.28 g/L (99.2%) yielding a transparent effluent. These values were in agreement with the local regulations for sewage discharge (10 mg/L and 0.7 g/L respectively) [24]. The solid dry residue obtained after the coagulation (13 g/L) was relatively small compared with the amount of the solid powder used to prepare the cleaning solution (120 g/L). The treatment presented is simple and economical. For the particular detergent (12% w/v) here treated, 2.8% v/v sulfuric acid, 11 g/L FeSO₄·7H₂O, 63 g/L H₂O₂ and

1.6 g/L NaOH were needed. The proposed method allows the possibility of the *in situ* treatment of the spent alkaline cleaning solution and presents an alternative to other more expensive methods.

Acknowledgement

This work was supported by CONUAR S.A. (Combustibles Nucleares Argentinos S.A.) with the project PAT 804 – SAT 460.

References

- [1] R.W. Bird, Aqueous alkaline cleaners: a better alternative, *Met. Finish.* 93 (1995) 10–20.
- [2] M. Menta, J. Frayret, C. Gleyzes, A. Castetbon, M. Potin-Gautier, Development of an analytical method to monitor industrial degreasing and rinsing baths, *J. Clean. Prod.* 20 (2012) 161–169.
- [3] T.W. Burnett, H.W. Krebs, Theories of Alkaline Cleaners, in: *Proceedings of the 51st Porcelain Enamel Institute Technical Forum: Ceram. Eng. Sci. Proc.*, John Wiley & Sons Inc, 2008, pp. 443–448.
- [4] R.W. Bird, B.A. Donahue, Aqueous alkaline cleaners: an alternative to organic solvents, US Army Corps of Engineers, Construction Engineering Research Laboratory, [Champaign, Ill.], Springfield, Va., 1993.
- [5] A.S.C. Chen, N. Stencel, D. Ferguson, Using ceramic membranes to recycle two nonionic alkaline metal-cleaning solutions, *J. Membr. Sci.* 162 (1999) 219–234.
- [6] P.R. Gogate, A.B. Pandit, A review of imperative technologies for wastewater treatment I: oxidation technologies at ambient conditions, *Adv. Environ. Res.* 8 (2004) 501–551.
- [7] P. Bautista, A.F. Mohedano, J.A. Casas, J.A. Zazo, J.J. Rodriguez, An overview of the application of Fenton oxidation to industrial wastewaters treatment, *J. Chem. Technol. Biotechnol.* 83 (2008) 1323–1338.
- [8] J.J. Pignatello, E. Oliveros, A. MacKay, Advanced oxidation processes for organic contaminant destruction based on the Fenton reaction and related chemistry, *Crit. Rev. Environ. Sci. Technol.* 36 (2006) 1–84.
- [9] L. De La Fuente, T. Acosta, P. Babay, G. Curutchet, R. Candal, M.I. Litter, Degradation of nonylphenol ethoxylate-9 (NPE-9) by photochemical advanced oxidation technologies, *Ind. Eng. Chem. Res.* 49 (2010) 6909–6915.
- [10] R. Chen, J.J. Pignatello, Role of quinone intermediates as electron shuttles in fenton and photoassisted fenton oxidations of aromatic compounds, *Environ. Sci. Technol.* 31 (1997) 2399–2406.
- [11] M. Dopar, H. Kusic, N. Koprivanac, Treatment of simulated industrial wastewater by photo-Fenton process. Part I: the optimization of process parameters using design of experiments (DOE), *Chem. Eng. J.* 173 (2011) 267–279.
- [12] R.C. Martins, A.M.T. Silva, S. Castro-Silva, P. Garção-Nunes, R.M. Quinta-Ferreira, Advanced oxidation processes for treatment of effluents from a detergent industry, *Environ. Technol.* 32 (2011) 1031–1041.
- [13] G. Pliego, J.A. Zazo, S. Blasco, J.A. Casas, J.J. Rodriguez, Treatment of highly polluted hazardous industrial wastewaters by combined coagulation-adsorption and high-temperature Fenton oxidation, *Ind. Eng. Chem. Res.* 51 (2012) 2888–2896.
- [14] J.A. Perdigón-Melón, J.B. Carbajo, A.L. Petre, R. Rosal, E. García-Calvo, Coagulation-Fenton coupled treatment for ecotoxicity reduction in highly polluted industrial wastewater, *J. Hazard. Mater.* 181 (2010) 127–132.
- [15] M.I. Badawy, M.E.M. Ali, Fenton's peroxidation and coagulation processes for the treatment of combined industrial and domestic wastewater, *J. Hazard. Mater.* 136 (2006) 961–966.
- [16] Method 5220 D. Closed reflux, colorimetric method, in: APHA, AWWA, WEF (Eds.), *Standard methods for the examination of water and wastewater*, 2005.
- [17] D 2330-02. Standard Test Method for Methylene Blue Active Substances, in: ASTM, 2002.
- [18] R.F.P. Nogueira, M.C. Oliveira, W.C. Paterlini, Simple and fast spectrophotometric determination of H₂O₂ in photo-Fenton reactions using metavanadate, *Talanta* 66 (2005) 86–91.
- [19] S.L. Bandemer, P.J. Schaible, Determination of iron: a study of the o-phenanthroline method, *Ind. Eng. Chem.* 16 (1944) 317–319.
- [20] Method 4500-P E. Ascorbic acid method, in: APHA, AWWA, WEF (Eds.), *Standard methods for the examination of water and wastewater*, 2005.
- [21] Method 4500-P B. Sample preparation, in: APHA, AWWA, WEF (Eds.), *Standard methods for the examination of water and wastewater*, 2005.
- [22] M.C. Lu, J.N. Chen, C.P. Chang, Effect of inorganic ions on the oxidation of dichlorvos insecticide with Fenton's reagent, *Chemosphere* 35 (1997) 2285–2293.
- [23] M. Ghassemi, H.L. Recht, Phosphate Precipitation with Ferrous Iron, *Water pollution control research series* (Ed.), U.S. Environmental Protection Agency, 1971.
- [24] Administración General de Obras Sanitarias de la Provincia de Buenos Aires (AGOSBA) resolution 389/1998 Annex II.
- [25] L.D. Mackenzie, *Water and Wastewater Engineering*, McGraw-Hill, 2010.
- [26] R. Guilbaud, M.L. White, S.W. Poulton, Surface charge and growth of sulphate and carbonate green rust in aqueous media, *Geochim. Cosmochim. Acta* 108 (2013) 141–153.
- [27] U. Schwertmann, H. Fechter, The formation of green rust and its transformation to lepidocrocite, *Clay Miner.* 29 (1994) 87–92.
- [28] N. Quici, M.E. Morgada, G. Piperata, P. Babay, R.T. Gettar, M.I. Litter, Oxalic acid destruction at high concentrations by combined heterogeneous photocatalysis and photo-Fenton processes, *Catal. Today* 101 (2005) 253–260.