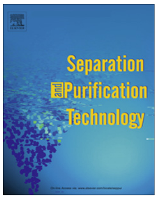
Separation and Purification Technology 132 (2014) 552–560

Contents lists available at ScienceDirect

Separation and Purification Technology

journal homepage: www.elsevier.com/locate/seppur



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

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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 $FeSO_4$ 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 H_2O_2 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.

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.

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 ($HO^{\cdot}$) and other reactive oxygen species (ROS, like $HO_2^{\cdot}$ and $O_2^{\cdot-}$), and radical chain reaction is promoted [8,10]:

$$Fe(II) + H_2O_2 \rightarrow Fe(III) + OH^- + HO^{\bullet} \quad k_1 = 76\ M^{-1}\ s^{-1} \tag{1}$$

$$Fe(III) + H_2O_2 \rightarrow Fe(II) + H^+ + HO_2^{\bullet} \quad k_2 = 0.01\ M^{-1}\ s^{-1} \tag{2}$$

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http://dx.doi.org/10.1016/j.seppur.2014.06.006
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In the absence of organic matter, the termination of the radical chain reaction is favored and the process is unproductive:

$$HO^{\bullet} + Fe(II) \rightarrow Fe(III) + OH^{-} \quad (3)$$

$$Fe(III) + HO_2^{\bullet} \rightarrow Fe(II) + H^{+} + O_2 \quad (4)$$

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:

$$2H_2O_2 \overset{Fe(II)/Fe(III)}{\rightarrow} O_2 + 2H_2O \quad (5)$$

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

$$RH + HO^{\bullet} \rightarrow R^{\bullet} + H_2O \quad (6)$$

By reaction with O_2, peroxyl ($ROO^{\cdot}$) or oxyl radicals ($RO^{\cdot}$) can be produced:

$$R^{\bullet} + O_2 \rightarrow ROO^{\bullet} \rightarrow\rightarrow RO^{\bullet} \rightarrow\rightarrow CO_2 + H_2O + \text{inorganic acids} \quad (7)$$

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

$$R^{\bullet}/ROO^{\bullet}/RO^{\bullet} \rightarrow\rightarrow CO_2 + H_2O + \text{inorganic acids} \quad (8)$$

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 $HO^{\cdot}$.

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).

$$Fe(III)(OH)^{2+} + h\nu \rightarrow Fe(II) + HO^{\bullet} \quad (9)$$

$$Fe(III)(L)_n + h\nu \rightarrow Fe(II)(L)_{n-1} + L_{ox}^{\bullet} \quad (10)$$

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 ($FeSO_4 \cdot 7H_2O$). 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 bakers 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