Iron recovery from the Fenton's treatment of winery effluent using an ion-exchange resin

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Pedro J.M. Martins, Patrícia M. Reis, Rui C. Martins, Licínio M. Gando-Ferreira *, Rosa M. Quinta-Ferreira

Chemical Processes and Forest Products Research Centre (CIEPQPF), GERST, Group on Environment, Reaction, Separation Engineering and Thermodynamics, Department of Chemical Engineering, Faculty of Sciences and Technology, University of Coimbra, Pólo II – Rua Sílvio Lima, 3030-790 Coimbra, Portugal

ABSTRACT

A new sludge free Fenton's process for wastewater treatment is proposed. Fenton's reagent is an interesting oxidation treatment for organic matter removal from liquid effluents. However, its main drawback is the iron sludge produced at the end of the reaction. An integrated methodology is recommended involving the application of ion exchange resins that recover dissolved iron without the need of sludge production. The results reveal high iron removal efficiencies (~100%). On the other hand, this strategy is able to fulfill iron removal requirements even if some iron precipitation occurs during Fenton's peroxidation. In fact, sludge dissolution is promoted and the resulting dissolved iron is then adsorbed by the resin. Langmuir model was able to satisfactorily describe the experimental results leading to a $q_m = 56$ mg/g. A design of experiments approach allowed concluding that pH is a key parameter for ion-exchange. This combined strategy overcomes Fenton's main shortcoming and will boost the industrial application of this interesting wastewater treatment approach.

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1. Introduction

The Fenton's process is an interesting advanced oxidation process (AOP) for the treatment of biorefractory effluents. This methodology, based on the oxidant potential of hydrogen peroxide catalyzed by iron ions, involves simple operating and instrumental procedures [1]. Fenton's oxidation can be easily carried out at room conditions of pressure and temperature not requiring sophisticated equipment [2]. Moreover, it involves easy to handle and low cost reactants. In this context, several studies involving this procedure can be found for the treatment of industrial effluents. Particular relevance is given to agro-wastewaters [2,3]. These streams usually contain phytotoxic compounds that unable the application of biological treatment approaches.

However, one of the main drawbacks of the Fenton's peroxidation relies on the application of an iron homogeneous catalyst, since at the end of the oxidation there is a large amount of dissolved iron in the treated water. Metals can lead to toxic consequences above certain concentrations [4]. Thus, environmental legislation establishes a maximum limit for wastewater discharge into the natural watercourses and for public water supply as well. Fenton's treatment must therefore be followed by an iron separation technology before the effluent disposal. The most common procedure involves precipitation by alkalinization. Nevertheless, this procedure, besides requiring the addition of further chemicals (for rising pH), embraces a quite serious environmental

problem due to the large amounts of iron sludge that are produced, requiring thus further management [5]. In a previous work from our research group the direct reutilization of iron sludge as Fenton's catalyst was attempted [6]. However, their high alkaline characteristics reduce Fenton's efficiency.

Bearing this issue in mind, seeking for iron removal techniques at the end of the Fenton's treatment is a highly important scientific and industrial challenge. Ion exchange is recognized as an alternative for removal/recovery of inorganic pollutants, in particular heavy metals [7]. This technology of easy handling is characterized by low operational costs associated with low reactants requirements [8]. Therefore, coupling Fenton's process with ion exchange (IE) seems to be an interesting approach enabling iron recovery for reuse and wastewater purification before discharge.

Although some works deal with this integrated strategy in specialized literature, ion exchange was applied only after that the iron precipitation step was carried out at the end of the Fenton's process, aiming solely at removing the residual iron still remaining in the liquid phase after separation of the produced iron sludge. This way, this procedure also requires the highly environmentally costly iron sludge management that is the most serious drawback for the industrial application of the Fenton's technology. In this context, Víctor-Ortega et al. [9] tested a strong-acid cation Dowex Marathon C resin only for the removal of the iron left on the supernatant liquid resulting from the sludge removal of the precipitated iron at the end of the Fenton's oxidation of an olive mill wastewater (OWM). Therefore, only quite low iron feeds to IE were studied involving iron concentrations solely up to 5 mg/L, being

* Corresponding author.
E-mail address: lferreira@eq.uc.pt (L.M. Gando-Ferreira).

reported a final effluent with iron concentration (200 μg/L) below the limit for water reuse. In other works of the same authors, Dowex Marathon C (strong-acid cation) coupled with Amberlite IRA-67 (weak-base anion) resin were tested for the removal of sodium, chloride, iron and phenols from a simulated OMW coming from a chemical treatment that also involved Fenton's peroxidation and iron precipitation [10]. Further studies confirmed that this procedure, involving cationic followed by anionic exchange resin, was able to lead to water suitable for drinking from OMW [11,12].

However, the iron sludge resulting from the precipitation step was not avoided in this approach. Contrarily, our study focuses this cumbersome issue that has been associated to the restrictions on the application of the highly industrially attractive Fenton's unless for the iron precipitation step. Our target was then clearly directed towards the design of a treatment approach able to avoid the production, separation and management of the undesirable iron sludge at the end of the Fenton's oxidation. For this, an ion exchange system was innovatively tested for the direct removal of iron from wastewaters treated by Fenton's. Therefore, this is the first work dealing with the integration of Fenton's process with IE aiming to avoid sludge iron generation. These results will surely boost the application of this interesting treatment process at the industrial scale by overcoming its most important shortcoming. This integrated methodology was here applied on the treatment of a synthetic winery wastewater. In fact, these effluents, due to their seasonal features, sometimes require the application of an advanced oxidation process to overcome the difficulties of biological treatment on reaching the environmental regulations [2].

2. Materials and methods

2.1. Resin and chemicals

Weak-acid cation exchange Lewatit TP 207 resin provided by Sigma-Aldrich was used in this study. Its main characteristics are reported in Table 1. Lewatit TP 207 is usually used for the removal of trace heavy metals from effluents of metal industry or from contaminated ground water for potable water production.

The chemicals heptahydrate iron sulfate, monohydrate iron nitrate, chloridric acid, sulphuric acid and nitric acid were obtained from VWR while hydrogen peroxide and sodium hydroxide were acquired from Panreac and EKA, respectively.

A synthetic winery wastewater was prepared by diluting commercial red wine (1:200) with distilled water.

2.2. Experimental procedures

2.2.1. Oxidation with Fenton's reagent

Fenton's process was carried out in a batch stirred reactor and the effluent pH was set at 3 using H_2SO_4. The iron catalyst was added at the form of $FeSO_4.7H_2O$ and the reaction started when the required amount of hydrogen peroxide was slowly added. After reaction, in some tests, NaOH was introduced until pH reached 7 and whenever needed some

drops of catalase solution were added to promote the remaining hydrogen peroxide removal since this reactant interferes with the determination of some parameters such as COD.

2.2.2. Ion-exchange

Before the experiments, the resin was conditioned in a fixed-bed column by cyclic washings with 1.0 M HCl, and 1.0 M NaOH for removing solvents and other impurities. The last step of the conditioning consisted in percolating a solution of 1.5 M HCl through the resin in order to convert it into H^+ form.

2.2.2.1. Equilibrium experiments.
Equilibrium isotherms were determined through batch tests by contacting 40 or 80 mL of iron solutions of known concentration with different conditioned resin amounts (from 0.1 to 5 g). The flasks were sealed and were continuously stirred in a thermostatic bath during 24 h until equilibrium was reached. At the end of this period, the resin was separated by filtration and the liquid was further analyzed for iron content and pH. To check the effect of pH and temperature over removal efficiency of iron ions, tests involving different temperatures (25 °C and 50 °C) and pH values (pH 1–4) were performed. Experimental data were fitted to Langmuir and Freundlich isotherm models.

2.2.2.2. Experimental design.
A 2^3 full factorial design, including two replicates at central point, was performed in order to evaluate the effect of the factors pH, liquid-solid ratio (L/S) and contact time on the removal efficiency of iron (response variable, Y). The levels studied for each factor are indicated in Table 2.

The analysis of variance (ANOVA) and 3 D response surface were carried out using the software Statistica 7. The multivariable regression for predicting the Y(%) values, which includes 2-way and 3-way interactions, was based on the following equation:

$$Y = \beta_0 + \beta_1 X_1 + \beta_2 X_2 + \beta_3 X_3 + \beta_{12} X_1 X_2 + \beta_{13} X_1 X_3 + \beta_{23} X_2 X_3 + \beta_{123} X_1 X_2 X_3 \tag{1}$$

2.3. Analytical techniques

Chemical and biochemical oxygen demand (COD and BOD_5, respectively) were determined according to the standard methods [13]. The COD determination involved the sample digestion (1 mL) with 1.2 mL and 2.8 mL of digestion and acid solution respectively in an ECO 25 thermoreactor during 2 h at 150 °C. After cooling down, the resulting mixture absorbance at 605 nm was measured by a Photolab S6 WTW photometer. A calibration curve was prepared using potassium hydrogen phthalate standard solutions. Dissolved oxygen before and after 5 days of the effluent samples contact with activated sludge coming from an agro-industrial wastewater treatment plant were measured with an INOLab 740 WTW automatic apparatus for BOD_5 determination. pH was assessed by an automatic pH meter (Crison micropH 2002). Flame atomic absorption spectrophotometry (Perkin Elmer 3300) was used for iron quantification in the liquid phase.

3. Results and discussion

A winery wastewater (WW) was mimicked by diluting commercial red wine (1:200) in distilled water. Some ion exchange (IE)

Table 1
General characteristics and properties of resin.

Item	Property
Type	Crosslinked polystyrene
Functional group	Iminodiacetic acid
Structure	Macroporous
Particle size	0.40–1.25 mm
Ionic form as shipped	Na^+
Total exchange capacity	2.2 eq/L
Effective pH range	0–14
Shipping weight	720 g/L

Table 2
Parameters and factor levels.

Factor	Level		
	Low (−1)	Central (0)	High (+1)
X_1 – pH	1.5	2.5	3.5
X_2 – L/S	20	30	40
X_3 – Time (h)	4	6	8