



Nanofiltration and Fenton's process over iron shavings for surfactants removal

Rui C. Martins, Marta Nunes, Licínio M. Gando-Ferreira & Rosa M. Quinta-Ferreira

To cite this article: Rui C. Martins, Marta Nunes, Licínio M. Gando-Ferreira & Rosa M. Quinta-Ferreira (2014) Nanofiltration and Fenton's process over iron shavings for surfactants removal, *Environmental Technology*, 35:18, 2380-2388, DOI: [10.1080/09593330.2014.906507](https://doi.org/10.1080/09593330.2014.906507)

To link to this article: <https://doi.org/10.1080/09593330.2014.906507>



Published online: 29 Apr 2014.



Submit your article to this journal [↗](#)



Article views: 92



View Crossmark data [↗](#)



Citing articles: 3 View citing articles [↗](#)

Nanofiltration and Fenton's process over iron shavings for surfactants removal

Rui C. Martins, Marta Nunes, Licínio M. Gando-Ferreira* and Rosa M. Quinta-Ferreira

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

(Received 10 October 2013; accepted 14 March 2014)

The presence of surfactants in wastewater composition tends to jeopardize the efficiency of the traditional aerobic treatment processes. In this regard, the application of Fenton's reaction and nanofiltration as single processes and integrated (nanofiltration followed by Fenton's process) was investigated on the abatement of a solution containing two surfactants usually found in effluents coming from detergent industry (dodecylbenzene – DDB and sodium lauryl ether sulphate – SLES). The potential of a solid waste (iron shavings) as catalyst in the Fenton's process was evaluated and the reaction system was optimized regarding the key operating parameters (iron and hydrogen peroxide concentration and pH). The highest chemical oxygen demand (COD) degradation (66%) was attained for pH 3, $[H_2O_2] = 32$ mM and 50 g/L of iron shavings. Besides, it was concluded that oxidation was due to hydroxyl radicals adsorbed on the metal surface even if bulk interaction between hydrogen peroxide and dissolved iron cannot be neglected. The main variables ruling nanofiltration were evaluated (pH, temperature and cross-flow rate). Eighty-four percent of COD rejection was determined at pH 7.5, cross-flow 14.4 cm³ s⁻¹, 20°C and 15 bar of pressure drop. Finally, nanofiltration followed by Fenton's process under the best conditions was integrated; however, no significant improvement was attained with 85% of COD being globally removed.

Keywords: Fenton's process; nanofiltration; processes integration; surfactants; detergent industry wastewater

1. Introduction

Nowadays, mankind starts to concern with environment protection related with the excessive resources consumption and pollution. The industrial activity has an important responsibility spending a large amount of assets to satisfy the needs and producing a large quantity of solid, liquid and gaseous residues that must be treated before final release to the surroundings.

The presence of surfactants in the effluents jeopardize the efficiency of the traditional biological aerobic systems once these compounds confer biorefractory character and difficult the reactors aeration. Besides, these substances tend to bio-accumulate threatening the ecosystems.[1] The impact of these compounds is important not only on the analysis of the treatment of detergent industry wastewaters but also on the depuration of municipal effluents once the release of these substances into the domestic sewage interferes in the efficiency of the municipal wastewater treatment plants.[2] This highlights the importance of investigating and optimizing technologies capable of removing surfactants from the water streams. The application of advanced oxidation processes (AOPs) and/or membrane separation technologies (MSPs) can overcome these fragilities of the classic depuration systems. Among the AOPs, Fenton's process is arising as industrially interesting due to the easiness

on reactants handling and low-cost operation.[3] This technology is based upon the hydrogen peroxide oxidant power enhanced by ferrous salts.[4,5] However, the high amount of iron sludges produced at the end of the treatment constitutes the main drawback of this technique when operated under homogeneous liquid systems. Therefore, some studies have been conducted trying to select a suitable solid catalyst able to be applied in Fenton's peroxidation.[6–8] Recently, some investigation efforts were performed to analyse the ability of iron wastes (such as iron shavings) to be used as low-cost catalyst in this treatment.[9] MSPs, such as nanofiltration, use semipermeable membranes to separate the feeding mixture into two streams, permeate and retentate.[10] Nanofiltration is characterized by operating pressures within the range 5–40 bar and membrane pore sizes between 0.5 and 2 nm. These membrane technologies present the advantages of not requiring chemical addition besides the moderately low-energy consumption and the mild conditions needed for separation.

There are some studies in literature regarding the depuration of detergents containing effluents. Mensah and Foster [11] analysed the performance of an anaerobic digester on the treatment of a simulated surfactant mixture; however, it was verified that high concentrations provoked the disruption of the biological filter. A solution of sodium dodecyl

*Corresponding author. Email: lferreira@eq.uc.pt

sulphate was treated by ultrafiltration using a polysulfone membrane with a cut-off of 5 kDa with a global chemical oxygen demand (COD) removal within 65–85%. [12] Fenton's process was analysed by various authors on the depuration of surfactant effluents. [13–16] Bautista et al. [2] and Naumczyk et al. [17] conducted studies with the classic Fenton's process for the treatment of a real cosmetic wastewater. Trying to overcome the drawback associated with the iron sludge production in the homogeneous process, Martins et al. [16] tested the applicability of a solid catalyst (Fe–Ce–O) to enhance hydrogen peroxide action for the degradation of an actual detergent industry effluent and enhance its biodegradability. Integrated systems such as Fenton's process followed by aerobic digestion [18] were also evaluated to maximize the depuration and biodegradability enhancement of this kind of wastewater. Nanofiltration was applied with good results for surfactants removal from water. [19,20]

Within this scope, the aim of the present research was to analyse the possibility of using a low-cost catalyst (iron shavings, which are wastes from iron processing industry) for the degradation of a simulated mixture of surfactants. Besides, nanofiltration was also optimized for the same effluent. The final goal was to integrate both processes (nanofiltration followed by Fenton's process) to promote water reuse.

2. Experimental

2.1. Oxidation procedure

Fenton's process was carried out in batch reactors stirred in an orbital shaker. First, the effluents' pH (measured with a Crison micro pH) was set at the desired value using either sulphuric acid (0.1 M) or sodium hydroxide (0.1 M) and a certain load of iron shavings was added. The reaction started when hydrogen peroxide (industrial, 50%) was introduced. At the end of each experiment, the samples withdrawn were filtrated to remove the catalyst and alkalized to eliminate the remaining H_2O_2 , which interferes with the analytical techniques.

2.2. Nanofiltration procedure

Nanofiltration was performed in batch mode in a flat-sheet laboratory scale, cross-flow membrane filtration apparatus encompassing a membrane module, a diaphragm pump, a reservoir, valves and sensors as described elsewhere. [21] A Desal 5 DK (GE OSMONICS) membrane consisting of a thin-film of polyamide composite (140 cm² of filtration area) was tested. The molecular weight cut-off of the Desal 5 DK lies between 200 and 300. First, the membrane was wetted with distillate water during 30 min at 10 bar. Preliminary experiments were carried out to assess the time required for the system to reach steady state (which was concluded to be 15 min) and the hydrodynamic membrane resistance

(R_m). This process performance on removing surfactants was evaluated by changing the key operating parameters, pH, drop pressure, cross-flow rate and temperature.

2.3. Wastewater preparation, catalyst and analytical techniques

The effluent was prepared using two of the most significant surfactants present in the real wastewater from a detergent industry nearby, namely dodecylbenzene (DDB) and sodium lauryl ether sulphate (SLES). The average molecular weight of these surfactants is higher than 300 g/mol. According to the stakeholder, the maximum total concentration on surfactants of the actual stream is around 2 g/L, thus the simulated mixture was prepared, using equal concentrations of each substance until fulfilling this threshold.

The catalyst consisted in iron shavings (zero-valent iron, ZVI) are wastes from iron processing industry. Once ZVI was very difficult to mill, the particles were used at their original size (0.814–1.140 mm). The ZVI composition in N, C, H and S was determined by elemental analysis using a Fisons Instruments EA 1108 CHNS-O while its content in metals was assessed after acid digestion by atomic absorption spectrophotometry (Perkin-Elmer 3300). The specific surface area (S_{BET}) was obtained with an accelerated surface area equipment (ASAP 2000, Micromeritics). Finally, the crystalline structure was inferred by X-ray diffraction (Philips PW 3040/00 X'Pert Analyser).

The COD was determined according to the closed reflux colorimetric Standard Method 5220D, [22] where the samples were digested during 2 h at 150°C in a WTW CR3000 instrument and the COD was directly read in a WTW MPM3000 photometer at 605 nm. Biochemical oxygen demand (BOD_5) was obtained by measuring the dissolved oxygen concentration (WTW INOLab 740) before and after 5 days of incubation of microorganisms coming from garden soil. [22]

The critical micelle concentration (CMC) of the surfactants was determined according to the procedure described by Kertész et al. [20] Briefly, solutions with different concentrations were prepared and their conductivities at different temperatures (20, 30 and 40°C) were determined (Multi-Parameter Analyser CONSORT C86); this parameter is directly proportional to concentration and the point where the formation of the micelles starts is indicated by a breaking point on this dependence.

3. Results and discussion

3.1. Effluents and catalyst characterization

The synthetic effluent comprising two surfactants that are commonly present in detergent industry wastewaters was prepared to present a COD value around the one determined for the actual wastewater (2255 ± 180 mg O_2 /L) and

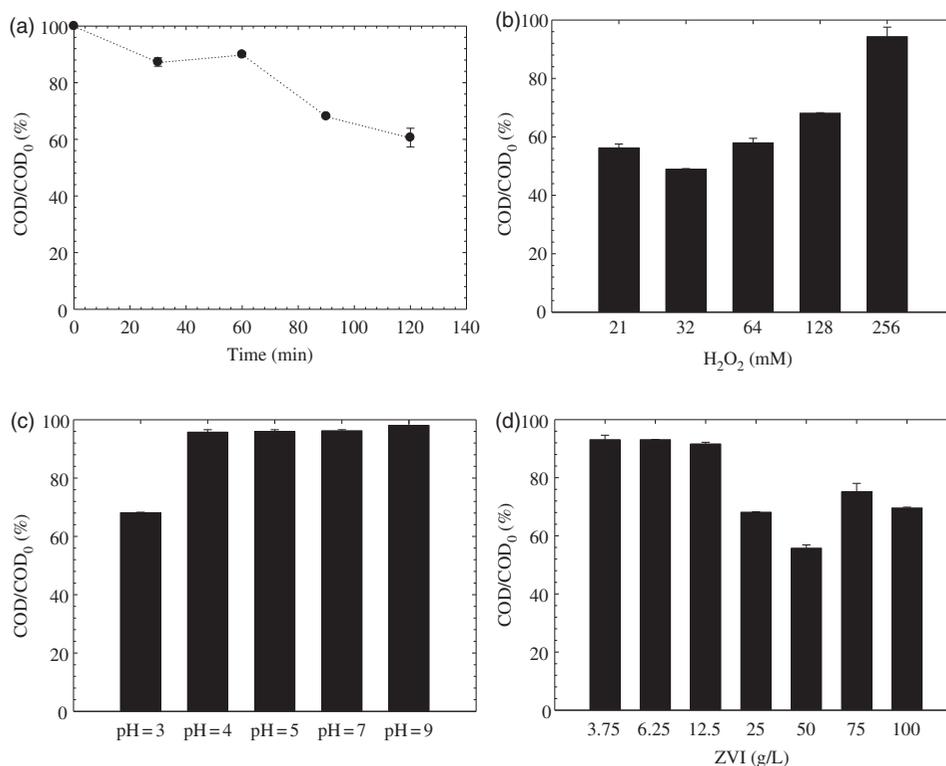


Figure 1. (a) COD abatement trend along time during Fenton's peroxidation over iron shavings (pH 3, $[\text{H}_2\text{O}_2] = 128$ mM and 25 g/L of catalyst). (b) Effect of hydrogen peroxide concentration on the efficiency of Fenton's process regarding COD removal (25 g/L of iron shavings, pH 3 and 90 min of reaction). (c) Effect of pH on the efficiency of Fenton's process regarding COD removal ($[\text{H}_2\text{O}_2] = 128$ mM, 25 g/L and 90 min of reaction). (d) Effect of iron shavings load on the efficiency of Fenton's process regarding COD removal ($[\text{H}_2\text{O}_2] = 128$ mM, pH 3 and 90 min of reaction).

a global surfactant concentration of 2 g/L (the maximum value reported by the industrial plant). Moreover, an initial BOD_5 of 1400 ± 280 mg O_2/L was also determined; this leads to a BOD_5/COD ratio of 0.6, which is above the threshold commonly accepted to consider a stream to be completely biodegradable (0.4 according to Esplugas et al. [23]). However, the application of activated sludge treatments is usually unsuccessful for this kind of effluent. This is due to the presence of large amounts of surfactants that difficult the reactors aeration. On the other hand, the strong variability of the wastewater composition (function of the kind of product being processed) would entail continuous microorganism adaptation. In addition, this solution presented a pH of 3.0.

According to Archer et al., [24] in nanofiltration of surfactants, the rejection values tend to increase in the CMC region. In our experiments, the mixture concentration always presents values below the CMC.

3.2. Fenton's process

In this section, the results regarding the application of Fenton's process over iron shavings for the degradation of the simulated mixture encompassing the surfactants DDB and SLES are presented and discussed. The amount of hydrogen peroxide theoretically required for the complete oxidation

of the effluent (128 mM) was determined according to the initial COD. [25]

3.2.1. Effect of operation time

The treatment operation time is an important factor since it will influence the volume of the reactors required for the process. In this context, the COD abatement of the simulated effluent was followed up through time when Fenton's process was applied using 128 mM of hydrogen peroxide, pH 3 and 25 g/L of iron shavings. This load of catalyst was selected due to the previous results attained on the depuration of landfill leachate by this system. [9] Figure 1(a) depicts the temporal trend of COD during the depuration process.

The results show a decrease in COD along time with about 32% depleted after 60 min and 40% after 120 min, which corresponded to a final value of 1335 mg O_2/L . It should be noticed that the deviations between trials was always around 3%. The following experiments were performed for a fixed reaction time of 90 min.

3.2.2. Effect of hydrogen peroxide concentration

Hydrogen peroxide concentration is a key operating parameter that may determine both the process efficiency and cost.

With this ambit, the effect of $[H_2O_2]$ was evaluated within a range 21 (1/6 of the stoichiometric value)–256 mM (the double of the theoretical amount required for total oxidation) using 90 min of reaction, 25 g/L of ZVI and pH 3. The results regarding COD abatement at the end of oxidation are shown in Figure 1(b) revealing that an increase in the oxidant load from 21 to 32 mM enhanced the depuration with COD abatement increasing from 46% to 52%. However, for higher concentrations the opposite effect is evident. In fact, for 256 mM COD, removal is below 10%. This is explained by the radical scavenger effect of hydrogen peroxide, which when in excess promotes the production of hydroperoxide radicals with much lower oxidant power than hydroxyl, inhibiting, this way, the treatment efficacy.[26]

3.2.3. Effect of pH

The effect of pH over the process efficiency was also assessed within the range 3–9. The iron shavings and hydrogen peroxide concentration were fixed in 25 g/L and 128 mM, respectively. Figure 1(c) shows the COD abatement after 90 min of reaction. It is clear that pH 3 is the most favourable one for this process as already reported in literature.[27] At these conditions, COD removal reaches 32%, whereas for higher pH values a strong inhibition occurred with depuration barely grasping 5%. This behaviour may be attributed to the enhanced decomposition of hydrogen peroxide in water and oxygen for high pH values, which reduces the amount of oxidant available for the production of hydroxyl radicals.[28] On the other hand, it was observed that with the pH decrease the iron sludge produced at the end of the experiment increased. This is probably related with the augment in Fe leached [29] for acidic conditions. Somehow, this fact may also be an explanation for the lower efficiency of this catalytic system when more alkaline solutions were used if the hydroxyl radicals are mainly produced in solution due to the interaction between hydrogen peroxide and dissolved ferrous ions and not by the direct reaction of the oxidant over the Fe^0 surface. This will be further discussed in a following section.

3.2.4. Effect of ZVI concentration

The effect of the load of iron shavings over the oxidation process efficiency was evaluated using amounts within the range 3.75–100 g/L. The selected operation time was 90 min, the pH was fixed in 3 and the concentration of hydrogen peroxide in 128 mM. The COD removal percentages at the end of the reaction are represented in Figure 1(d) as a function of ZVI load.

As it can be observed, for low catalyst concentrations (below 12.5 g/L) COD degradation does not reach 10% in 90 min. Nevertheless, a high improvement is observed afterwards with the maximum depuration being reached for 50 g/L of iron shavings with 45%. The further increase in

the ZVI amount introduced in the reactor decreased the efficiency, which may be related to the scavenger effect due to an excess of iron leading to a reduction in the quantity of hydroxyl radicals available for reaction.

3.2.5. Optimal conditions

To refine the optimal conditions, several iron shavings' loads were tested (25–100 g/L) together with different hydrogen peroxide concentrations (32–128 mM) at a fixed pH of 3 since it is well known that there is a strong interaction between these two variables. The COD abatement results attained after 90 min of Fenton-like reaction are reported in Figure 2(a).

As it can be observed, whichever may be the catalyst load introduced in the reactor, the highest COD depuration is attained when $[H_2O_2] = 32$ mM with degradation ranging within the values 52–66%. Therefore, to establish the best iron shavings amount one can observe the behaviour of COD depleted in this case. It is obvious that there was an improvement when that quantity was changed from 25 to 50 g/L, as COD abatement increases from 52% to 61%. Nevertheless, for higher concentrations (50–100 g/L) organic matter abatement oscillates between 61% and 66% representing a difference of 5%, which is within the experimental error associated with the technique as referred before. Therefore, the criterion for selecting the best iron shavings load has into account the operating costs for a future industrial plant; thus, the 50 g/L was chosen.

An important aspect of using AOPs is related with their ability to enhance the effluents biodegradability so that a subsequent and inexpensive biological process may be applied afterwards to refine the wastewater, generally in municipal treatment plants. In this context, the ratio BOD_5/COD was evaluated for the raw stream after being subjected to the Fenton's process over 50 g/L of iron shavings, pH 3 during 90 min at different hydrogen peroxide concentrations. As it can be observed in Figure 2(b), biodegradability increases relatively the raw effluent's characteristics when $[H_2O_2] = 21, 64$ and 256 mM leading to BOD_5/COD values of about 0.8 when compared with 0.6 initially determined. Contrarily, for the optimum hydrogen peroxide concentration, 32 mM, which reached the maximum COD removal, a biodegradability decrease was observed to around 0.30. It seems thus that the organic matter removed at these conditions results in an effluent with more bio-refractory characteristics than the original mixture, which is not the case for the other hydrogen peroxide loads that were tested.

3.2.6. Effect of the presence of radical scavengers

The role of ZVI (which is the case of our iron shavings) on Fenton's like treatment efficiency is not clear. If some authors refer that this process is mainly heterogeneous, with hydroxyl radicals being produced due to the decomposition

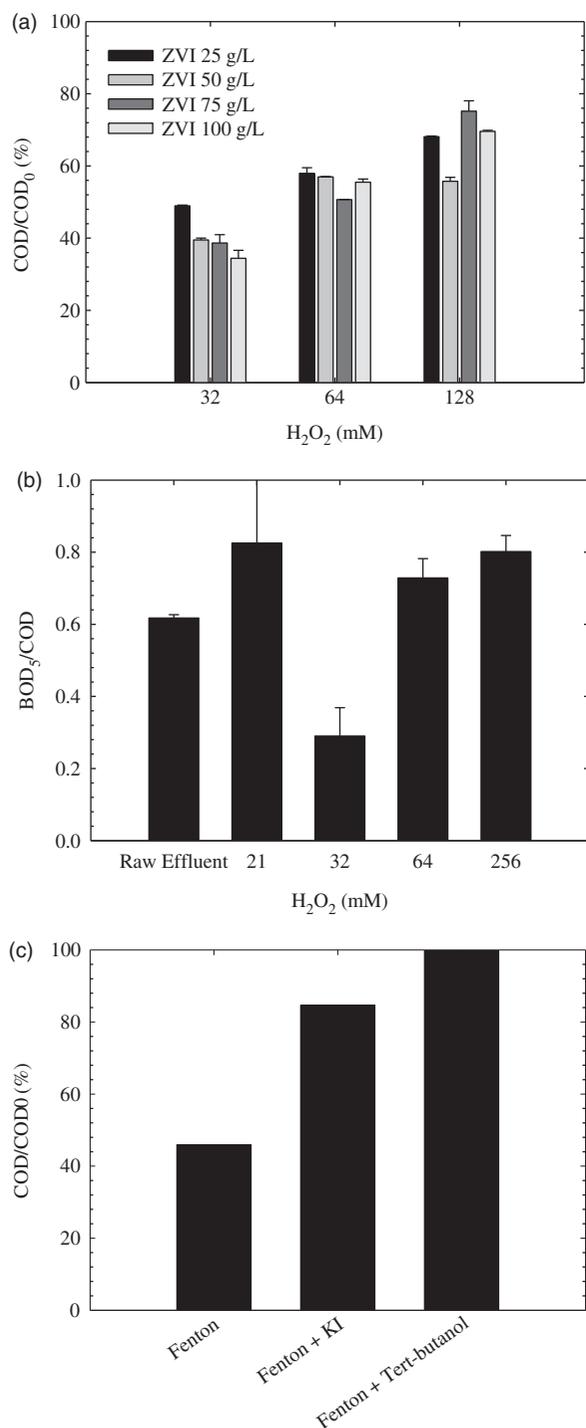


Figure 2. (a) Final COD removal for several hydrogen peroxide and iron shavings concentrations (pH 3). (b) Effect of hydrogen peroxide load over the effluents biodegradability measured as BOD₅/COD ratio (50 g/L, pH 3 and 90 min). (c) Comparison between COD removal after Fenton's process at the absence and presence of radical scavengers ([H₂O₂] = 32 mM, 50 g/L, pH 3 and 90 min of reaction).

of hydrogen peroxide over the catalyst followed by the surface reaction between the adsorbed radicals and pollutants, on another hand, others do not discard the possibility of

the formation of HO• in the bulk due to the interaction of H₂O₂ with dissolved iron ions, which will oxidize the organic compounds in the liquid.[30]

In the first approach, the amount of carbon adsorbed in the iron shavings collected after the treatment was evaluated to determine if the COD abatement is truly due to oxidation or by adsorption over the solid surface. A negligible quantity of carbon (below the detection limit of the apparatus) was observed revealing that COD is really eliminated by chemical reaction. Afterwards, the heterogeneity of this system was assessed. For this, the COD removal after 90 min of Fenton's reaction (50 g/L of catalyst, [H₂O₂] = 32 mM and pH 3) in the absence and presence of two radical scavengers (*tert*-butanol and potassium iodide) was compared. While the first compound traps both free and surface-bounded hydroxyl radicals, the second is only able to inhibit those adsorbed in the catalyst.[30] The results attained are shown in Figure 2(c). It is clear that the surfactants degradation is due to hydroxyl radicals, since in the presence of *tert*-butanol, the treatment is completely repressed with negligible COD abatement after 90 min when compared with up to 66% when no scavenger compound is added. When analysing the effect of KI, one can observe that <16% of COD was removed in 90 min. It seems, thus, that the reaction mainly occurs at the catalyst surface with the hydroxyl radicals bounded in the iron shavings; nevertheless, the occurrence of oxidation in the liquid bulk may not be neglected.

3.3. Nanofiltration

3.3.1. Membrane characterization

Nanofiltration was optimized for the depuration of the surfactant mixture (50:50 in DDB and SLES), being evaluated the effect of pressure drop, pH, temperature and flux of permeated effluent.

The commercial membrane applied for nanofiltration was a DK Osmonics consisting of a thin polyamide composite film with a molecular cut-off range of 150–300 Da and an active filtration area of 140 cm². While for low pH values, its surface is positively charged, for alkaline conditions it is negatively charged presenting an isoelectric point at pH 3.9.[31]

To determine the hydrodynamic resistance (membrane permeability), pure water was used and the permeate flux (J_v) was evaluated for different pressure drop values (ΔP). A linear behaviour was found for these two variables and the following relation was attained by linear regression (Equation 1):

$$J_v = 1 \times 10^{-6} \Delta P. \quad (1)$$

The hydrodynamic resistance of the membrane (R_m) determined by the Darcy equation was $2.5 \times 10^{15} \text{ m}^2 \text{ m}^{-3}$.

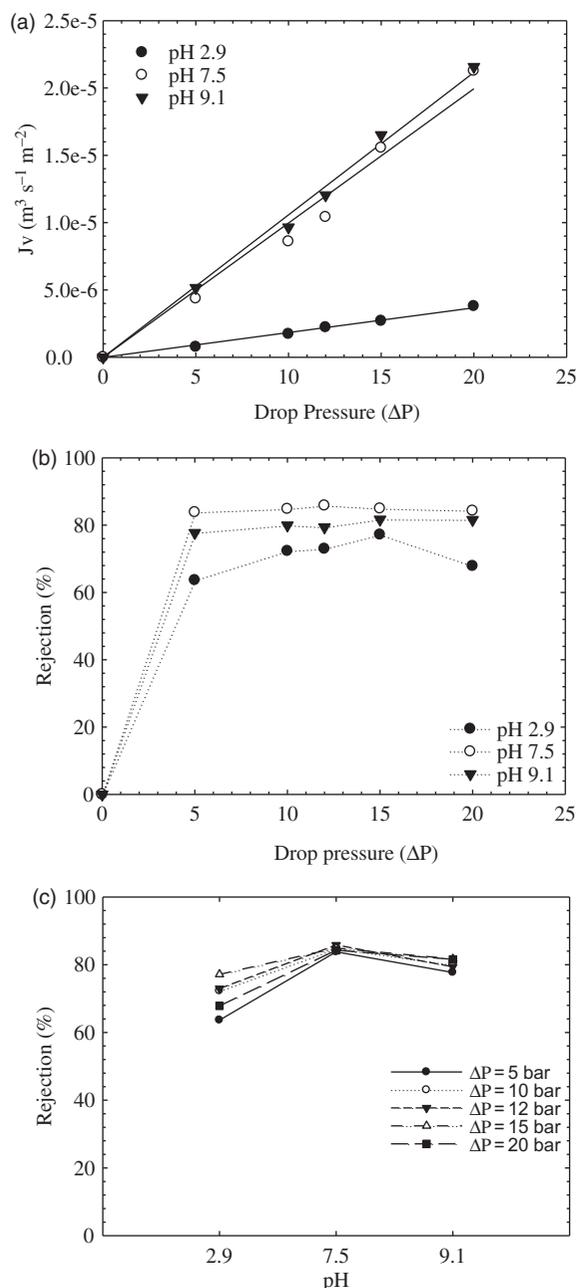


Figure 3. (a) Permeate flux against pressure drop for several pH values; (b) rejection regarding COD for different pH values as a function of pressure drop and (c) rejection achieved for different pressure drops as a function of the solution pH.

3.3.2. Effect of pH

The pH of the solution is an important parameter affecting the electrostatic interaction between membrane and organic compounds. Thus, the behaviour of the nanofiltration system at different pH values was analysed in the range 3–9.

As it can be observed in Figure 3(a), the permeate flux reveals a linear behaviour against pressure drop whichever pH is used. Moreover, when pH increases from 2.9 to

7.5 a strong improvement is observed in what regards J_v , which also slightly augments for pH 9.1. The relative fluxes, defined as the ratio between the flux of solute (surfactant) and flux of water, were close to 100% at pH 7 and 9.1, suggesting that under these conditions it is possible to conclude a lower fouling tendency of the membrane. However, a reduction in 18.3% in the relative flux was found for the filtration at pH 2.9. In this case, it is likely that the adsorption of the surfactant in the pores occurs due to the electrostatic interactions of the solute with the membrane surface hence anticipating more membrane fouling at low pH values. High rejection levels were attained for all the range of pH studied (Figure 3(b)). Even so, the lowest values ($\sim 70\%$) were observed for pH 2.9, whereas for 7.5 an increase to around 84% was detected followed by a small decrease to 80% at pH 9.

The key parameter for these results is the isoelectric point of the membrane (3.9). At pH values lower than the isoelectric point, electrostatic attraction between the anionic surfactants and the positively charged membrane occurs. On the other hand, for high pH, both membrane and organic compounds are negatively charged and repulsion is dominant.[19] Figure 3(c) shows that pH 7.5 is clearly the optimum regarding rejection whichever the pressure drop; besides, the performance profile of this membrane initially increases with pH reaching a maximum value and then decreases for extremely alkaline conditions.

To determine a characteristic parameter (B) of the solute/membrane under study, at different pH levels, an equation for describing the flux of the solute through the NF membrane was considered as follows:

$$J_s = B(C_m - C_p) \quad (2)$$

where J_s is the diffusive flux of the solute, C_m the solute concentration on the membrane surface and C_p the solute concentration in the permeate. The permeate flux, J_v , can be calculated using the following equation:

$$J_s = J_v C_p. \quad (3)$$

Combining Equations (2) and (3) and using the definition of intrinsic rejection, we obtain the following equation:

$$R_i = \frac{J_v}{J_v + B}. \quad (4)$$

Using the film theory, the relationship between the apparent (R_{app}) and intrinsic rejection (R_i) is given by the following equation:

$$R_i = \frac{R_{app} e^\alpha}{1 - R_{app}(1 - e^\alpha)} \quad (5)$$

where $\alpha = J_v/k$, being k the mass transfer coefficient for which was assumed the value of 1.24×10^5 m/s estimated by Gomes et al.[21] The Excel platform was used

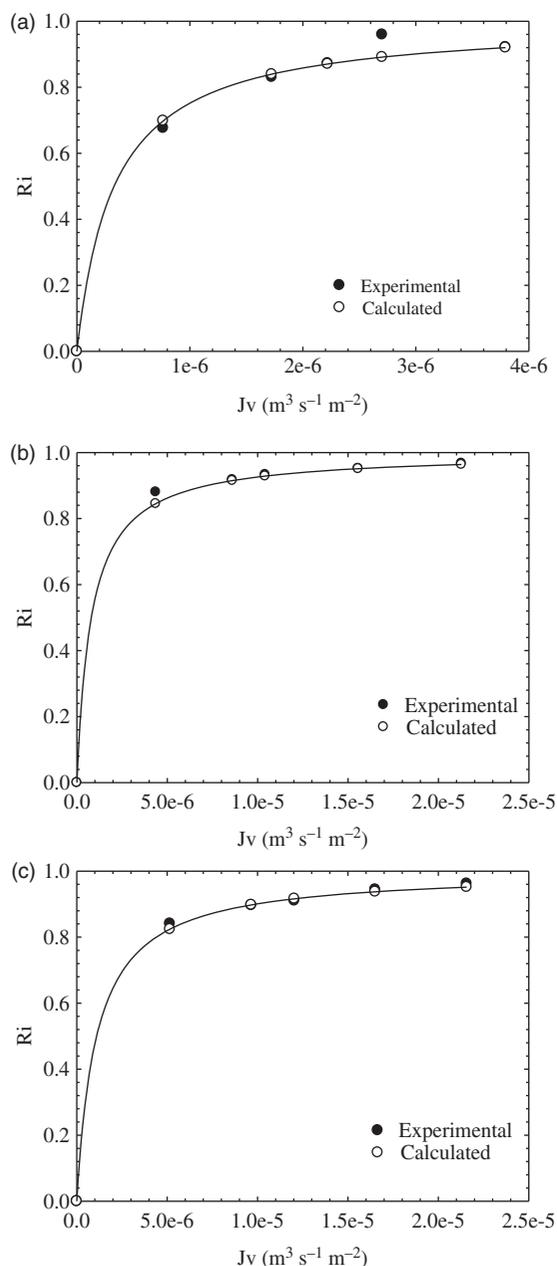


Figure 4. Experimental and modelled intrinsic rejection values as a function of the permeate flux for pH (a) 2.9, (b) 7.5 and (c) 9.1.

to obtain the B that minimizes the sum of the squares of the deviations between the calculated (Equation (4)) and the experimental (Equation (5)) R_i values. Figure 4(a)–(c) shows a good agreement between the calculated and experimental intrinsic rejection values for the three pH values under study.

The B values estimated for pH 2.9, 7.5 and 9.1 were 3.3×10^{-7} , 9×10^{-7} and $11.0 \times 10^{-7} \text{ m s}^{-1}$, respectively. Therefore, there is an increase in the B parameter with the pH. Like it was previously discussed, the affinity between the membrane and the solute depends on the magnitude of

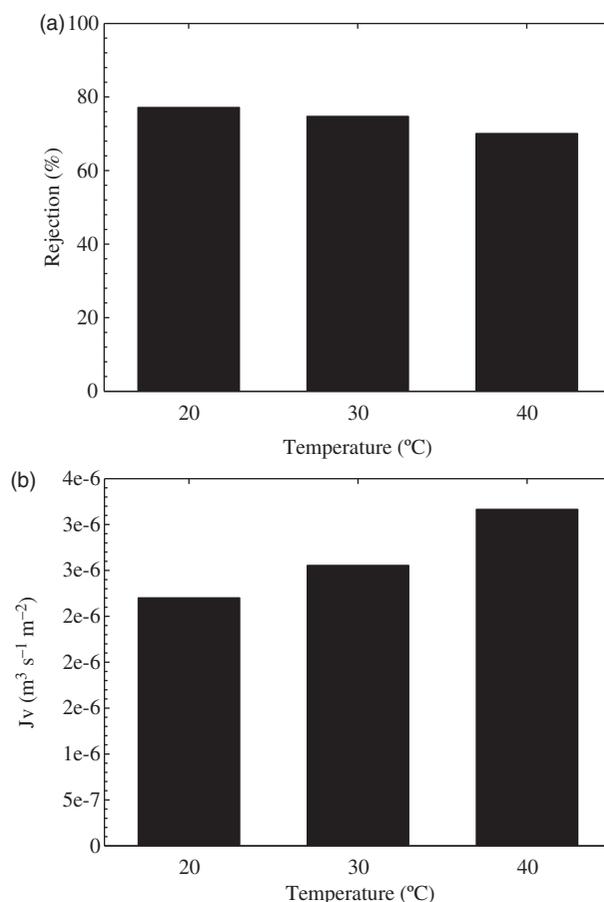


Figure 5. Effect of temperature over (a) COD rejection and (b) permeate flux.

their charges, which are directly associated with the pH of the solution.

3.3.3. Effect of temperature

Temperature is another key variable influencing the NF membrane performance. To evaluate its effect, nanofiltration experiments were conducted at 20, 30 and 40°C keeping constant the following parameters: $P = 15$ bar, pH 2.9 (original pH of the simulated effluent) and cross-flow rate = $14.36 \text{ cm}^3 \text{ s}^{-1}$.

Figure 5(a) shows that the temperature increase causes a decrease in rejection once the diffusion coefficients of the solutes rise with temperature, so that surfactants can pass through the membrane more easily resulting in lower rejection values. Besides, the permeate flow rate increased with temperature (Figure 5(b)), which can be explained by the expansion of the membrane.[19]

3.3.4. Effect of cross-flow rate

The tangential flow rate velocity also influences NF performance. To evaluate this effect, the effluent at pH 2.9 was filtrated at two different cross-flow rates (14.4 and

$11.4 \text{ cm}^3 \text{ s}^{-1}$) using a pressure drop of 15 bar and temperature of 25°C .

It was observed that with the increasing flow rate the permeate flow rate decreases while the rejection coefficient increases. Unfortunately, due to technical problems, it was not possible to operate with a wider range of cross-flow rates.

Gathering up all the former results, the following operating conditions seem to be optimal for the nanofiltration of the synthetic effluent: pH 7.5; cross-flow rate $14.4 \text{ cm}^3 \text{ s}^{-1}$, temperature 20°C and pressure drop 15 bar, leading to a rejection of 84% correspondent to about $360 \text{ mg O}_2 \text{ L}^{-1}$ of COD, which is still above the legal limit for wastewater discharge throughout the natural water courses.

3.4. Processes integration: nanofiltration followed by Fenton's process

Trying to improve the treatment of this simulated effluent, the permeate obtained from nanofiltration at the optimal conditions referred before was subjected to Fenton's peroxidation over iron shavings (50 g/L of catalyst, $[\text{H}_2\text{O}_2] = 32 \text{ mM}$ and pH 3). Nevertheless, it was verified that the integration did not bring significant advantage for the wastewater treatment once barely 85% of COD removal was reached at the end of the depuration, with about 84% being obtained by nanofiltration.

The biodegradability of the resulting mixture was still analysed to infer about the applicability of a subsequent aerobic system. A low BOD_5/COD ratio of about 0.1 was detected, which may be attributed to the high amount of iron leached at the end of the Fenton's process (193 mg Fe L^{-1} , the concentration of iron detected in the samples coming from Fenton's process), which may have a negative impact over biomass.

Even if the integration of Fenton's with nanofiltration did not significantly improve the effluents treatment, the individual processes lead to a significant removal of the tested surfactants. In fact, the optimization of Fenton's and nanofiltration allowed abating 66% and 84% of COD of the analysed surfactants. These data are important not only for the treatment of detergent industry wastewater but also to improve domestic effluents depuration once the daily use of surfactants that will end up in the municipal wastewaters treatment plants may jeopardize their efficiency and eventually reach the natural water courses.

4. Conclusions

The aim of the present research was to study the application of Fenton's process catalysed by iron processing industries wastes (iron shavings) and nanofiltration for the removal of surfactants from a simulated wastewater composed by DDB and SLES.

In what regards the Fenton's process, it was concluded that waste management can be successfully integrated with

effluents treatment once the iron shavings were able to promote hydrogen peroxide action over pollutants. It was verified that the system was more efficient under acidic conditions. Moreover, the increase in H_2O_2 and catalyst concentration improved COD abatement until a certain point above which the excess on reactants acted as radical scavengers. In this context, the best COD (66%) removal was attained for $[\text{H}_2\text{O}_2] = 32 \text{ mM}$ and 50 g/L of iron shavings. The effect of the presence of two radical scavengers (KI and *tert*-butanol) permitted to settle that oxidation mainly occurred through hydroxyl radicals bounded to iron metal, but the production of these moieties in the bulk due to the reaction between hydrogen peroxide and dissolved iron may not be neglected.

Nanofiltration showed high potential on COD removal. The effect of the key operating conditions was analysed, and it was concluded that COD abatement was higher for pH values near neutrality (pH 7.5). On the other hand, the increase in temperature reduced efficiency and the same behaviour was found when the effect of cross-flow rate was analysed. In this regard, 84% of COD rejection was attained for pH 7.5, cross-flow $14.3 \text{ cm}^3 \text{ s}^{-1}$, 20°C and 15 bar of pressure drop.

The integration scheme involving nanofiltration followed by Fenton's over iron shavings under the optimal conditions was analysed; however, no significant improvement was observed. Even so, both treatment systems seem individually to have potential on the abatement of surfactants from wastewater.

Funding

Rui C. Martins gratefully acknowledges the *Fundação para a Ciência e Tecnologia*, Portugal, for the financial support under the Pos-Doc grant [BPD/72200/2010].

References

- [1] Silva S, Chiavone-Filho O, Neto E, Mota A, Foletto E, Nascimento C. Photodegradation of non-ionic surfactant with different ethoxy groups in aqueous effluents by the photo-Fenton processes. *Environ Technol.* 2014;35:1556–1564.
- [2] Kaleta J, Elektorowicz M. The removal of anionic surfactants from water in coagulation process. *Environ Technol.* 2013;34:999–1005.
- [3] Bautista P, Mohedano A, Gilarranz M, Casas J, Rodriguez J. Application of Fenton oxidation to cosmetic wastewater treatment. *J Hazard Mater.* 2007;143:128–134.
- [4] Neyens E, Baeyens J. A review of classic Fenton's peroxidation as an advanced oxidation technique. *J Hazard Mater.* 2003;98:33–50.
- [5] Rodrigues C, Boaventura R, Madeira L. Technical and economic feasibility of polyester dyeing wastewater treatment by coagulation/flocculation and Fenton's oxidation. *Environ Technol.* 2014;35:1307–1319.
- [6] Martins RC, Amaral-Silva N, Quinta-Ferreira RM. Ceria based solid catalysts for Fenton's depuration of phenolic wastewaters, biodegradability enhancement and toxicity removal. *Appl Catal B.* 2010;99:135–144.

- [7] Rossi A, Amaral-Silva N, Martins RC, Quinta-Ferreira RM. Heterogeneous Fenton using ceria based catalysts: effects of the calcination temperature in the process efficiency. *Appl Catal B*. 2012;111:254–263.
- [8] Jiang C, Xu Z, Guo Q, Zhuo Q. Degradation of bisphenol A in water by the heterogeneous photo-Fenton. *Environ Technol*. 2014;35:966–972.
- [9] Martins RC, Lopes DV, Quina MJ, Quinta-Ferreira RM. Treatment improvement of urban landfill leachates by Fenton-like process using ZVI. *Chem Eng J*. 2012;192:219–225.
- [10] Zhou H, Smith D. Advanced technologies in water and wastewater treatment. *J Environ Eng Sci*. 2002;1:247–264.
- [11] Mensah K, Foster C. An examination of the effects of detergents on anaerobic digestion. *Bioresour Technol*. 2003;90:133–138.
- [12] Kowalska I, Majeswaska-Nowak K, Kabsch-Korbutowicz M. Influence of temperature on anionic surface active agent removal from a water solution by ultrafiltration. *Desalination*. 2006;162:33–40.
- [13] Lin S, Lin C, Leu H. Operating characteristics and kinetic studies of surfactant wastewater treatments by Fenton oxidation. *Water Res*. 1998;33:1735–1741.
- [14] Perkowski P, Józwiak W, Kos L, Stajszyk P. Application of Fenton's reagent in detergent separation in highly concentrated water solutions. *Fibres Text East Eur*. 2006;14:114–119.
- [15] Pagano M, Lopez A, Mscolo G, Cionarella R. Oxidation of nonionic surfactants by Fenton and H_2O_2/UV processes. *Environ Technol*. 2008;29:423–433.
- [16] Martins RC, Silva A, Castro-Silva S, Garção-Nunes P, Quinta-Ferreira R. Advanced oxidation processes for treatment of effluents from detergent industry. *Environ Technol*. 2011;32:1031–1041.
- [17] Naumczyk J, Bogacki J, Marcinowski P, Kowalik P. Wastewater treatment by coagulation and advanced oxidation processes. *Environ Technol*. 2014;35:541–548.
- [18] Wang X, Song Y, Mai J. Combined Fenton oxidation and aerobic biological processes for treating a surfactant wastewater containing abundant sulfate. *J Hazard Mater*. 2008;160:344–348.
- [19] Kaya Y, Barlas H, Arayici S. Nanofiltration of cleaning-in-place (CIP) wastewater in a detergent plant: effects of pH, temperature and transmembrane pressure on flux behaviour. *Sep Purif Technol*. 2009;65:117–129.
- [20] Kertész S, László Z, Horváth Z, Hodúr C. Analysis of nanofiltration parameters of removal of an anionic detergent. *Desalination*. 2008;221:303–311.
- [21] Gomes S, Cavaco SA, Quina MJ, Gando-Ferreira LM. Nanofiltration process for separating Cr(III) from acid solutions: experimental and modelling analysis. *Desalination*. 2010;254:80–89.
- [22] Greenberg A, Clesceri L, Eaton A. Standard methods for the examination of water and wastewater. Washington, DC: American Public Health Association; 1985.
- [23] Esplugas S, Contreras S, Ollis D. Engineering aspects of the integration of chemical and biological oxidation: simple mechanistic models for the oxidation treatment. *J Environ Eng*. 2004;130:967–974.
- [24] Archer A, Mendes A, Boaventura R. Separation of anionic surfactant by nanofiltration. *Environ Sci Technol*. 1999;33:2758–2764.
- [25] Eckenfelder W. Industrial water pollution control. 3rd ed. Singapore: McGraw-Hill; 2000.
- [26] Pignatello J. Dark and photoassisted Fe^{3+} -catalyzed degradation of chlorophenoxy by hydrogen peroxide. *Environ Sci Technol*. 1992;26:944–951.
- [27] Martins RC, Rossi AF, Quinta-Ferreira RM. Fenton's oxidation process for phenolic wastewater remediation and biodegradability enhancement. *J Hazard Mater*. 2010;180:716–721.
- [28] Kallel M, Belaid C, Mechichi T, Ksibi M, Elleuch B. Removal of organic load of phenolic compounds from olive mill wastewaters by Fenton oxidation with zero-valent iron. *Chem Eng J*. 2009;150:391–395.
- [29] Ramirez J, Costa C, Madeira L, Mata G, Vicente M, Rojas-Cervantes M, López-Peinado A, Martín-Arada R. Fenton-Like oxidation of Orange II solutions using heterogeneous catalysts based on sepiolite clay. *Appl Catal B*. 2007;71:44–56.
- [30] Xu L, Wang J. A heterogeneous Fenton-like system with nanoparticles zero-valent iron for removal of 4-chloro-3-methyl phenol. *J Hazard Mater*. 2011;186:256–264.
- [31] Al-Amoudi A, Williams P, Mandale S, Lovitt R. Cleaning results of new and fouled nanofiltration membrane characterized by zeta potential and permeability. *Sep Purif Technol*. 2007;54:234–240.