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Study of kinetic parameters related to the degradation of an industrial effluent using Fenton-like reactions

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Abstract

In the present work, some parameters (temperature, pH, concentration of Fe^{2+} and initial concentration of H_2O_2) were evaluated aiming to find the optimal conditions to promote the efficient degradation of the organic matter present in the effluent from a chip board industry, using Fenton's reactions and artificial illumination. The optimal conditions involve to upkeep the pH of the reaction medium around 3.00, a H_2O_2:Fe^{2+} molar ratio between 98:1 and 295:1, and Fe^{2+} concentration around 10 mg L^{-1}. The temperature of the reaction medium and the suitable use of the high photonic flux from the lamp are important parameters to improve the degradation rate.

The possibility of a two-step effluent treatment, combining Fenton's reactions and a biological treatment step is suggested.

Keywords: Fenton's reactions; Degradation; Organic matter; Industrial effluent

1. Introduction

The elimination of pollutants in wastewaters can be considered a great challenge, especially when the question is how to warrant potable water for an increasing population, in an environment more and more rich in non-biodegradable contaminants, and above all when it is known that potable water is scanty and badly distributed in our planet.

The conventional technologies for removal of pollutants, excluding the biological processes, decisively does not solve the problem since they are based on the phase transfer of these substances, passing the buck of the problem solution for future generations. The biological treatment is often the most cost-effective conventional alternative for treatment of wastewaters since is possible to degrade the pollutants. However, industrial effluents are known to contain toxic and/or non-biodegradable organic substances for which biological treatment is not efficient.

The treatment of wastewaters using sequential advanced oxidative processes (AOP) treatment followed by a biological one has been evidenced by many researchers to promote the oxidation of biorecalcitrant wastewaters [1–16], and is justified considering that the most hazardous and biorecalcitrant components can suffer chemical transformation, resulting in less or non-toxic species, warranting a drastic reduction of the global time of treatment. Several coupled systems, in general characterized by the use of sequencing batch reactors, have been proposed to treat different kinds of industrial wastewaters

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Abbreviations: AOP, advanced oxidative processes; BOD_5, amount of oxygen consumed biologically in 5 days; CONAMA, Conselho Nacional do Meio Ambiente; CPSC, U.S. Consumer Product Safety Commission; COD, chemical oxygen demand; FEAM, Fundação Estadual do Meio Ambiente; HSE, Health & Safety Executive (U.K.); IDLH, immediately dangerous to life and health; NCI, National Cancer Institute (U.S.); NIOSH, National Institute for Occupational Safety and Health; OSHA, U.S. Occupational Safety and Health Administration; TWA, time weighted average; USEPA, U.S. Environmental Protection Agency

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[4,5,8–10,13–16]. The key characteristic of the AOP is the generation of hydroxyl radicals ($HO^{\bullet}$), extremely reactive, possessing an oxidation potential of 2.8 V, suitable to promote the oxidation of a great variety of organic compounds [17–19].

Between the sequential systems, the association of an AOP based on Fenton's reactions and an aerobic biological stage is a promising methodology [1,4,5,9,11,13,14]. Pulgarin and co-workers, for example, have shown that photoassisted AOP and aerobic biological processes are a good combination to degrade biorecalcitrant, non-biodegradable and/or toxic pollutants. In this case, the biological step consists in immobilized activated sludge culture [1,2,12].

In this work, we explore Fenton's reactions based on the use of artificial radiation, to perform efficiently the degradation of the organic matter present in the effluent of a chip board industry. The role of a set of selected parameters on degradation performance was evaluated. Evidences based in biodegradability measurements suggest that this kind of effluent can be treated the using Fenton's reactions coupled to a biological stage.

2. Experimental

2.1. General

The effluent used in this work was provided by SATIPEL S.A., a chip board industry. The samples were collected immediately before its destination to the effluent treatment unit. They were not coloured, possessing a strong odour of formaldehyde at the moment of the collect, and some particulate material. After transport to the laboratory, the samples were filtered and stored for the assays.

The chemical oxygen demand (COD) of these samples is usually high, presenting a large variance, ranging between 2000 and 8000 mg L^{-1}, depending on the production conditions. The pH of these effluents lie around 4. Previously to each assay, the COD of the stored effluent was measured, and an aliquot was diluted with ultra pure water, so that the initial COD of the effluent was around 2000 mg L^{-1}.

The amounts of the principal organic constituents (formaldehyde, melamine, urea, wood extractives, lignin fragments, resin fragments—urea/formaldehyde and melamine/formaldehyde) in the collected samples are quite variable and strongly dependent on production conditions, resulting in unsafe data to be reported. With the packing, transport, filtration and hoard, the amount of formaldehyde in the effluent tends to decrease. However, this is not sufficient to reduce significantly the COD previously measured for these effluents.

The amount of extractives and lignin fragments in the effluent can be considered insignificant since the process used for the production of wood chip boards is not capable to promote an extensive delignification of the start material. By a simplified way, in this process woodchips are defibrated under heating using pressurized hot water. Under this condition, there is a softening of the lignin that facilitates fibre separation along the middle lamella.

The wood boards are then prepared by pressing of a mixture of defibrated material with urea/formaldehyde resin. In SATIPEL, melamine/formaldehyde resin is applied in the finish of part of the final product.

Based on these considerations, we can consider that formaldehyde, melamine, urea, urea/formaldehyde and melamine/formaldehyde resin fragments are the main constituents of the organic matter present in the effluent. Formaldehyde, melamine and the cited resins are known to be dangerous to life, even at low concentrations [20–24]. This can be considered as indication of the hazardous character of these components. The presence of these compounds in the effluent certainly will impair a direct biological treatment.

2.2. The photochemical reactor

The photochemical reactor consists in a cylindrical borosilicate glass jacket with a path length of 1.0 cm and a 400 W high-pressure mercury lamp coaxial to it. Being of borosilicate glass, the radiation cut-off occurs at 300 nm.

The lamp emission spectrum was measured using a setup consisting in a monochromator aligned to a photomultiplier, connected to an oscilloscope. The intensity of the emitted radiation at a wavelength range between 300 and 560 nm was measured at 10 nm steps.

The irradiance measurements were done using a Solar Light PMA2100 photometer/radiometer, equipped with a UV-A detector. The solution containing the photocatalyst and the material to be degraded was pumped into the jacket, being circulated in front of the lamp, at a constant rate of 0.142 $m^3 h^{-1}$. A cooler, mounted between the reservoir and the pump was used to control the temperature of the reaction medium during the experiments. The experiments were performed in a batch regimen.

Fig. 1 shows the emission spectrum of the lamp, expressed in terms of relative intensity.

The lamp emission profile in the range between 300 and 560 nm possesses around 18% of the emitted photons between 300 and 400 nm (Fig. 1), which can be considered an advantage over solar irradiation, since for the radiation emitted by the sun only a small fraction in this range (less than 8%) is available on the biosphere [25]. Besides, artificial illumination is capable to furnish high doses of radiation in any region of the electromagnetic spectrum. The average UV-A irradiance in

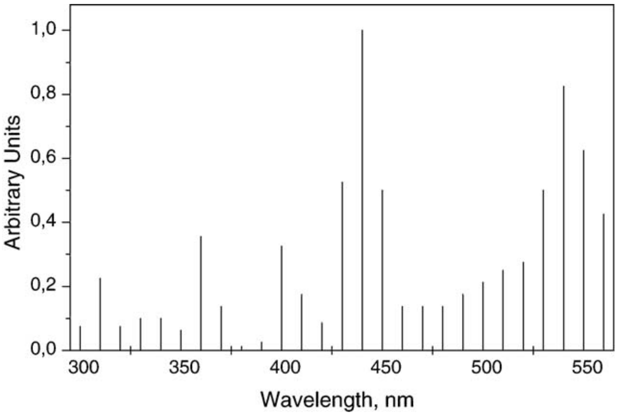

Fig. 1. Emission spectrum of the high-pressure mercury lamp.

our experiments was, for example, of 1100 W/m^2, whereas the maximum irradiance in experiments using solar irradiation, was limited to 66 W/m^2 [26].

The difficulty in the use of artificial radiation is in the high cost of energy, mainly in regions poor in renewable resources. However, this difficulty can be certainly minimized by the optimization of the reaction parameters.

2.3. Chemical analysis

The degradation of the organic matter was monitored in terms of COD. Aliquots of the effluent were collected at different reaction times, and treated using a USEPA (United States Environmental Protection Agency) approved method [27,28], in which aliquots of the effluent react under heating and closed reflux, at 423 K during 2 h, reducing dichromate ions to chromic ions in a strongly acid medium. From absorbance measurement, done at 620 nm using a Hach DR-4000U spectrophotometer and a resident program, the COD of the samples was determined.

The biochemical oxygen demand (BOD$_5$) of dilutions of the effluent was determined after an incubation time of 5 days at 293.0 ± 0.1 K, in the dark, following a classical method recommended by Brazilian Environmental Agencies [29]. The dilutions of the samples were done using buffered solution (pH 7.2), prepared with ultrapure water, containing the suitable nutrients for the living organisms during the incubation period. The dissolved oxygen was titrimetrically determined using Winkler's method.

2.4. Evaluation of kinetic parameters related to the degradation performance

The following parameters were evaluated aiming to find the optimal conditions to promote the degradation of the organic matter present in the effluent: temperature, pH, concentration of Fe^{2+} and H_2O_2.

For these assays, initial values were arbitrated for temperature, pH and concentration of Fe^{2+}. The guess for temperature was based on previous studies involving solar irradiation, in which the temperature of the reaction medium usually reaches a stationary point between 313 and 323 K [30,31]. The selected value was the average temperature (318 K). The pH in the initial assays was defined as being 3, since it has been reported that Fenton's reactions occur efficiently at pH in a range between 2.9 and 3.5 [32–36]. The guess for concentration of Fe^{2+} was based on the limits defined by Brazilian environmental laws (the maximum limit is 5 mg L^{-1} of soluble iron for class 3 waters, which corresponds to 8.95×10^{-5} mol L^{-1}) [29].

To evaluate the role of H_2O_2 concentration on reaction kinetics, pH (3.00 ± 0.10), concentration of Fe^{2+} (50 mg L^{-1} $FeSO_4{\cdot}7H_2O$, corresponding to 0.18 mM or 10 mg L^{-1} Fe^{2+}), and temperature of the reaction medium (318 ± 2 K) were maintained constant.

The role of Fe^{2+} concentration on the reaction kinetics was evaluated considering constant values for pH (3.00 ± 0.10) and temperature (318 ± 2 K) of the reaction medium. The initial concentration of H_2O_2 was 53 mM, added from 30% (w/w) stock solution, and defined in the above experiment.

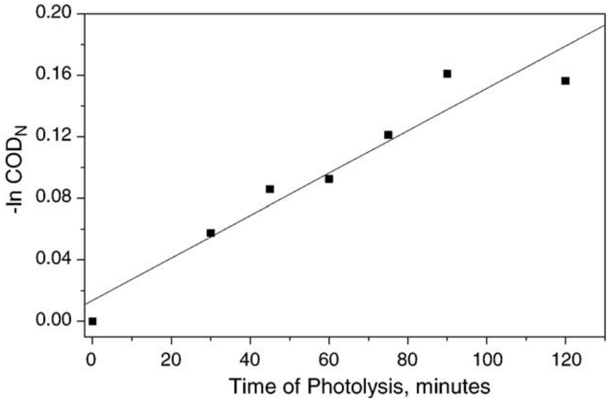

Fig. 2. Typical kinetic profile for the degradation of the effluent from SATIPEL S.A., at pH 3 and 318 K. The apparent rate constant is $1.38(\pm 0.17) \times 10^{-3}$ min^{-1}, $r = 0.9636$.

In the evaluation of the influence of pH, the concentration of Fe(II) salt (0.18 mM) and the temperature of the reaction medium (318 ± 2 K), were maintained constant. The initial concentration of H_2O_2 was 53 mM, added from 30% (w/w) stock solution.

The role of the temperature was evaluated maintaining constant the following parameters: pH 3.00(±0.10) and 50 mg (0.18 mM) of $FeSO_4{\cdot}7H_2O$ per litre of solution. The initial concentration of H_2O_2 was 53 mM. The ratio between temperature and apparent rate constant was described in terms of Arrhenius equation plot.

Considering that the concentration of generated reactive species must reach quickly a stationary-state regimen during the photocatalytic process, the rate law for the degradation process was treated as being a pseudo-first order, in terms of consumption of the organic matter. The degradation of the organic matter was monitored in terms of COD considering that this parameter reflects the remaining concentration of the organic matter, we have

$$-[\ln(\mathrm{COD}) - \ln(\mathrm{COD})_0] = k_{\mathrm{app}}t \quad \text{or} \quad -\ln(\mathrm{COD})_{\mathrm{N}} = k_{\mathrm{app}}t \tag{1}$$

where $(\mathrm{COD})_0$ is the chemical oxygen demand of the untreated effluent.

Fig. 2 presents a typical profile of the kinetic treatment of a data set, indicating that the degradation kinetics can be safely treated using a pseudo-first order rate law, based on the steady-state approximation.

For all experiments, the maximum irradiation time was limited to 2 h. All experiments were done at least in triplicate.

3. Results and discussion

3.1. Evaluation of kinetic parameters related to the degradation performance

It is known that Fenton's reactions can be triggered by thermal and/or photochemical pathways [37]. These reactions can

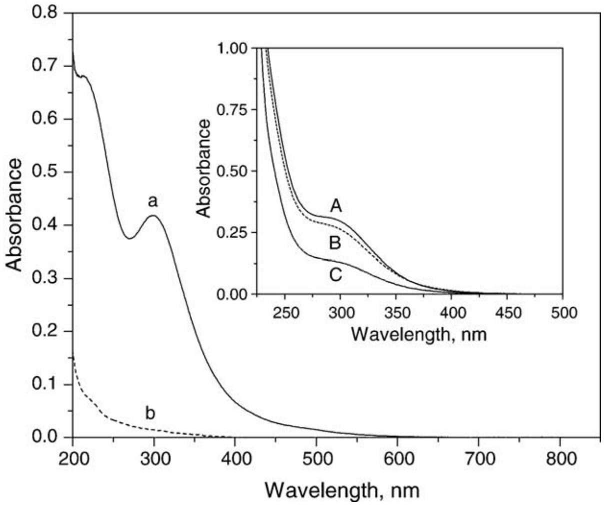

Fig. 3. UV/vis spectrum of aqueous solutions of: (a) Fe(III) sulphate (10 mg L^{-1} Fe^{3+}); (b) Fe(II) sulphate (10 mg L^{-1} Fe^{2+}), at pH 2.86. (Inset) Absorption spectrum of an effluent sample previously filtered and diluted (1:5, v/v) with ultrapure water, submitted to Fenton's reactions: (A) before; (B) 60 min of reaction; (C) after 120 min of reaction.

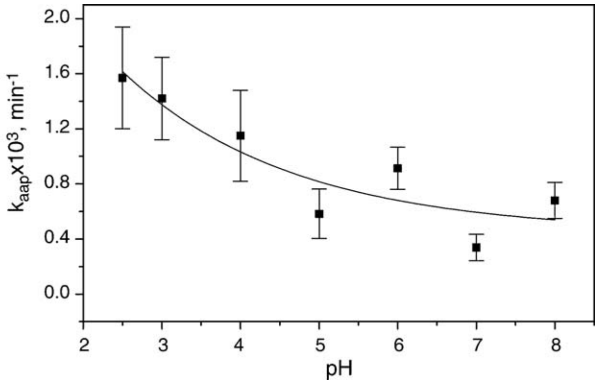

Fig. 4. Apparent rate constant vs. pH for the degradation of the effluent under study.

be considered as being founded on the synergism between photochemical and thermal processes.

Fig. 3 suggests that the thermal reactions induced by Fe(II) must exert an important role in the initiation of the studied process, since the considerable initial absorbance of the effluent (Fig. 3, inset) can cause a "filter effect" on the photochemically induced processes, minimizing the photocatalytic action of the Fe^{3+} ions formed in the beginning of the reaction.

Besides the low molar absorptivity of the Fe^{2+} solution, evidences are not known on the direct involvement of this species in photochemical processes. On the other hand, the formation of the hydrated Fe(II)–H_2O_2 complex is thermodynamically favoured [38], resulting in a steady-state concentration of Fe^{2+} bound to H_2O_2. Ensing, using density functional theory calculations and Car–Parrinello molecular dynamics simulations have demonstrated the occurrence of O–O lysis of hydrogen peroxide when coordinated to hydrated iron(II), being the homolysis the most favourable process [39], suggesting that this route can be the main responsible by the generation of hydroxyl radicals in the thermal process.

Although known at more than a century, the mechanism of Fenton's reactions is not yet completely cleared. Recent results have demonstrated that Haber and Weiss reaction (Eq. (1)) is not thermodynamically favourable, since the formation of the intermediate $H_2O_2^{-}$ is not viable [41,42]. Despite this, many researchers have based their discussions in the Haber and Weiss mechanism [43,44], probably based on the fact that hydroxyl radicals are produced [32,38,40]:

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + H_2O_2^{-} \rightarrow Fe(OH)^{2+} + HO^{\bullet} \qquad (2)$$

Being oxidized to Fe(III) during the thermal reactions, the Fe(II) is recovered [32,38,40] in the photochemical processes [32,34–36]:

$$Fe(OH)^{2+} \xrightarrow{h\nu} Fe^{2+} + HO^{\bullet} \quad (\mathrm{pH}\ 2.9\text{–}3.5) \qquad (3)$$

$$Fe^{3+} + H_2O \xrightarrow{h\nu} Fe^{2+} + HO^{\bullet} + H^{+} \qquad (4)$$

in reactions which result in more hydroxyl radicals, giving the conditions to upkeep the degradation at a desirable level of efficiency. Fig. 3 (inset) shows the decrease in the absorbance of the effluent, suggesting an increasing participation of the photochemical reaction in the global process.

The UV/vis spectrum of an aqueous solution of Fe(III) sulphate, at pH 2.8, shows that Fe^{3+} is capable to do a good UV-A photon pick up (Fig. 3). Many authors have reported that $Fe(OH)^{2+}$ is the main specie for photo-Fenton reactions at a pH near 3 [36], possessing expressive molar absorption coefficient in the wavelength range between 280 and 370 nm [45]. Its photochemical dissociation results in hydroxyl radicals, with expressive quantum yield ($\Phi_{(HO^{\bullet})} = 0.195 \pm 0.033$ at 310 nm) [46], which increases when Fe(III) is complexed with an organic ligand [1,47]. This iron-complex is also able to oxidize organic molecules by electron transfer [48].

Evidences about other reactions without the direct action of hydroxyl radicals, capable to influence positively the degradation of the organic matter, have been presented. The photochemical reaction involving Fe(III) under acidic pH in the presence of O_2 as electron acceptor, has proven to be an important pathway, mainly if Fe(III) is complexed with an organic ligand [1,49]. Bossmann et al. have presented evidences on the occurrence of an electron transfer mechanism for the degradation of 2,4-dimethylaniline [38].

3.1.1. The role of pH

Fig. 4 presents the profile obtained for the degradation rate at different pHs.

The curve points to an optimal degradation rate at pH lower than 3. A pH around 2.8 has been proposed as fundamental for the efficient photodegradation of organic matter, since the presence of Fe^{3+} and $Fe(OH)^{2+}$, formed during the reactions, will improve the production of hydroxyl radicals [32,33–36].

However, considering the costs involved for pH adjustment in large-scale processes, we established the work pH as being around 3, since the usual pH of this effluent before treatment is around 4.

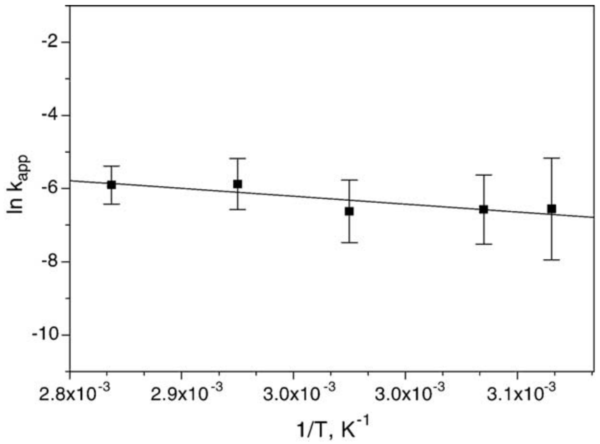

Fig. 5. Arrhenius correlation between temperature and apparent rate constant.

The pH control, restricted to a range around 3, during the course of the reaction, will avoid the formation of Fe(III) complexes capable to reduce the reaction performance.

3.1.2. The role of temperature

Fig. 5 shows the dependence of the reaction rate with the temperature, expressed in terms of Arrhenius equation.

As can be seen, temperature has a positive impact on reaction rate, although our results suggest that the photochemical process mediated by artificial irradiation, most probably due to the high photonic flux of the lamp, tends to mask the role of temperature at mean and low temperatures. An estimate of the ratio between the reaction rate for the photo-Fenton and the purely thermal Fenton's process, both performed at 318 K under similar conditions (0.18 mmol L^{-1} Fe^{2+} and 26 mmol L^{-1} H_2O_2 added in the beginning of the reaction, and initial pH of the reaction medium adjusted to 2.89), reveals that photo-Fenton process is at least three to four times more efficient (Fig. 6).

A criterious analysis of the rate constants at different temperatures suggests that the increase in the temperature of the reaction medium possesses a positive effect on the degradation. The comparison of the rate constants at 318 and 342 K shows that k_{app} at 342 K is practically twice the value at 318 K (from 1.42×10^{-3} to 2.79×10^{-3} min^{-1}). An estimate on the participation of the thermal process in k_{app} suggests that it must correspond to, at least, 62% at this temperature.

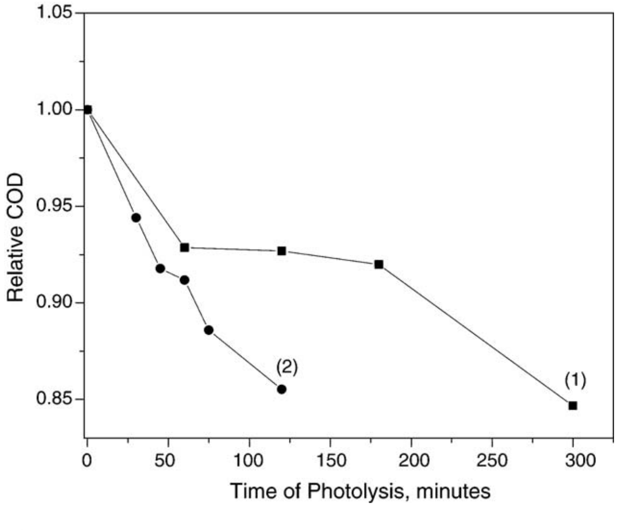

Fig. 6. Degradation of the organic matter present in the effluent by thermal Fenton's (1) and Fenton-like (2) reaction both performed under the same conditions.

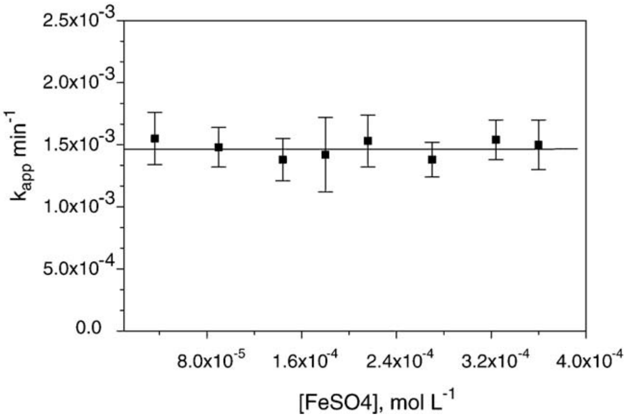

Fig. 7. Ratio between the apparent rate constant and concentration of Fe^{2+} for the degradations made using the laboratorial setup.

In virtue of the nature of photochemical processes, the initiation stages must be very fast and not dependent on temperature of the reaction medium. Despite the photonic flux has been very high in these experiments, the performance obtained in the reactions using artificial radiation was lower to that observed in the tests using a prototype of CPC reactor, despite in the reactions induced by solar radiation the maximum irradiance reached in our studies has been 66 W m^{-2} [30,31]. This is probably related to the lower residence time of the effluent in the annular reactor, 6.8 s, whereas in the prototype of CPC reactor this value is 22 s.

3.1.3. The role of Fe^{2+} concentration

An apparently unexpected result was obtained for the degradation rate when the concentration of Fe(II) salt was varied. The apparent degradation constant, measured for a range of Fe(II) concentration between 3.6×10^{-5} and 3.6×10^{-4} mol L^{-1}, practically did not vary, presenting a rate constant around 1.46×10^{-3} min^{-1}. This must be related to the high photonic flux during the reaction, enabling the efficient synergism between photochemical and thermal processes (Fig. 7).

Considering this, our option was to use low Fe(II) concentration approximately twice the limit for class 3 waters [29]. Thus, it is possible to avoid expensive stages to reduce the concentration of soluble iron to a level acceptable by environmental laws, after the effluent treatment.

3.1.4. The role of H_2O_2 concentration

Hydrogen peroxide is a very suitable font of reactive species for these reactions. Fig. 8 shows the ratio between H_2O_2 concentration and the apparent reaction rate under our experimental conditions.

Several studies have proposed the existence of an optimum H_2O_2 concentration to perform efficient Fenton's reactions. However, there still no agreement on the [HOOH]/[Fe^{2+}] molar ratio that gives the best results. Different ratios have been pro-

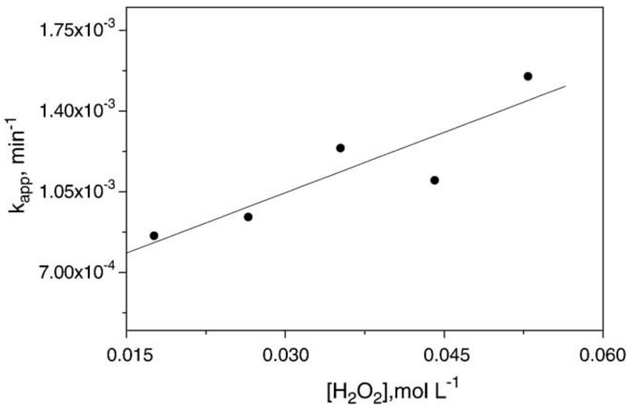

Fig. 8. Ratio between the apparent rate constant and concentration of hydrogen peroxide in the photolysed solution. $k_{app} = 5.23 \times 10^{-4} + 0.018$ [H_2O_2]; $r = 0.892$.

posed, covering a range between 1:1 and 400:1 [47,50–57]. In this study, we observed an increasing performance for the degradation working in a range between 98:1 and 295:1.

It is known that excessive amounts of this reactive could act as $HO^{\bullet}$ scavenger, reducing the degradation efficiency [32,45]. Particularly, in our case, the concentration of hydrogen peroxide only seems to be high, since [Fe^{2+}] is considerably small. Due to this, the concentration range of hydrogen peroxide used in this study is not detrimental for the good course of the process.

In assays using solar light irradiation to treat large amounts of effluent, our option was by the use of 50 mg L^{-1} of $FeSO_4 \cdot 7H_2O$ per litre of effluent, which corresponds to 10 mg L^{-1} Fe(II) (or 1.80×10^{-4} mol L^{-1})—two times the cited limit, with excellent results [30]. In these assays, we worked with a H_2O_2:Fe^{2+} molar ratio in the range between 92:1 (16.00 mg L^{-1} soluble iron) and 147:1 (10.05 mg L^{-1} of soluble iron). A COD reduction around 70% was reached for a UV-A dose of almost 1000 kJ m^{-2}. In both cases, the concentration of H_2O_2 was limited to 27 mM. In another essay in which we worked with a molar ratio of 92:1, but using a combination of Fe(II) and Fe(III), in a Fe^{2+}:Fe^{3+} mass ratio of 1.29, the COD reduction was of about 80%, for a UV-A dose of 760 kJ m^{-2}, corresponding to no more than two hours of reaction in a sunny day in Uberlândia [31].

3.2. *Biodegradability assays*

The BOD_5/COD ratio for the effluents prior Fenton's reactions is considerably low, despite it presents a large variability. For one of the lots of effluent we worked, the measured BOD_5/COD ratio was equal to 0.09, indicating a very low biodegradability [3–5]. Being this effluent composed by biorecalcitrant organic components, this explains its very low biodegradability. After 2 h of photo-Fenton reaction, the biodegradability of the cited effluent changed to 0.33, reflecting an increase of 267% in this parameter. This value is near the established as being the quantitative index for organic matter complete biodegradability [6]. This result suggests that Fenton's reactions could be used as previous treatment of chip board effluents, followed by a biological stage in the moment in which the biodegradability of the effluent indicate the feasibility for the biological treatment.

4. Conclusions

The present study dealt with the development of a process for treatment of effluent from a chipboard industry, using AOP based on Fenton reactions, induced concomitantly by thermal and light-induced processes.

The studied effluent usually presents very high COD, ranging between 2000 and 8000 mg L^{-1} and very low biodegradability, most probably due to the high COD and presence of strongly biohazardous components.

The temperature of the reaction medium has an important role over the efficiency of the global process. The results show the importance of the thermal process, mainly in the beginning of the degradation, when the considerable absorbance of the effluent tends to cause a "filter effect" on the photochemically induced processes, minimizing the photocatalytic action of the ions Fe^{3+} eventually formed.

In virtue of the high photonic flux furnished by mercury lamp, the photochemical component of the rate constant is between three and four times the thermal component, at 318 K. However, at 342 K the importance of thermal processes on rate constant increases significantly since k_{app} is almost two times the value at 318 K.

The optimal conditions, to perform the photodegradation using artificial irradiation, in terms of H_2O_2:Fe^{2+} molar ratio, were defined as values between 98:1 and 295:1.

The optimum pH for the reaction medium was established in 3, since the usual pH of the untreated effluent is around 4. Although our results show that a pH of at least 2.5 should improve the degradation, for large volumes of effluent the correction and pH upkeep at low set point during the treatment can be an expensive procedure.

Probably a combined system using artificial and solar radiation can be advantageous to reduce the costs and considering the possibility to promote the degradation of the organic matter in the absence of solar radiation or in periods of low solar irradiance.

As suggest the biodegradability assays, the Fenton's reactions can be used as pre-treatment in a two-step process involving a biological stage, for the treatment of this kind of effluent.

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References

[1] V. Sarria, M. Deront, P. Péringer, C. Pulgarin, Appl. Catal. B: Environ. 40 (2003) 231.
[2] M. Rodriguez, V. Sarria, S. Esplugas, C. Pulgarin, J. Photochem. Photobiol. A: Chem. 151 (2002) 129.

[3] A. Marco, S. Esplugas, G. Saum, Water Sci. Technol. 35 (1997) 321.
[4] F. Al-Momani, Combination of photo-oxidation processes with biological treatment, Doctoral Thesis, Universitat de Barcelona, Spain, 2003.
[5] M. Rodríguez, Fenton and UV-vis based advanced oxidation processes in wastewater treatment: degradation, mineralization and biodegradability enhancement, Doctoral Thesis, Universitat de Barcelona, Spain, 2003.
[6] J.P. Scott, D.F. Ollis, Environ. Prog. 14 (1995) 88.
[7] J.P. Scott, D.F. Ollis, J. Adv. Oxid. Technol. 2 (1997) 374.
[8] R. Krull, C.C. Hempel, Water Sci. Technol. 44 (2001) 85.
[9] V. Sarria, S. Parra, M. Invernizzi, P. Péringer, C. Pulgarin, Water Sci. Technol. 44 (2001) 93.
[10] S. Ledakowicz, M. Solecka, R. Zylla, J. Biotechnol. 89 (2001) 175.
[11] G. Bertanza, C. Collivignarelli, R. Pedrazzani, Water Sci. Technol. 44 (2001) 109.
[12] S. Parra, S. Malato, C. Pulgarin, Appl. Catal. B: Environ. 36 (2002) 131.
[13] G. Vidal, J. Nieto, H.D. Mansilla, C. Bornhardt, Water Sci. Technol. 49 (2004) 887.
[14] F. Torrades, J.G. Montaño, J.A.G. Hortal, X. Domènech, J. Peral, Solar Energy 77 (2004) 573.
[15] I.O. Koh, X.C. Hamacher, K. Hicke, W. Thiemann, J. Photochem. Photobiol. A: Chem. 162 (2004) 261.
[16] Fahmi, W. Nishijima, M. Okada, Chemosphere 50 (2003) 1043.
[17] R. Andreozzi, V. Caprio, A. Insola, R. Marotta, Catal. Today 53 (1999) 51.
[18] M.R. Hoffmann, S.T. Martin, W. Choi, D.W. Bahnemann, Chem. Rev. 95 (1995) 69.
[19] A. Legrini, E. Oliveros, A.M. Braun, Chem. Rev. 93 (1993) 671.
[20] The IDLH is defined as the concentration below which an individual could escape within 30 min without experiencing any escape-impairing irreversible health effect, NTIS Publication No. PB-94-195047, May 1994.
[21] The TWA is the exposure limit, based on an 8 h workday.
[22] CPSC report: http://www.cpsc.gov/cpscpub/pubs/pub_idx.html.
[23] HSE report: http://www.hse.gov.uk/lau/lacs/37-9.htm.
[24] NCI report: http://www.nci.nih.gov.
[25] J.B. Galvez, S.M. Rodriguez, World Solar Programme 1996–2005, UNESCO, 2002.
[26] D.R. Souza, Degradação da matéria orgânica proveniente de efluente de indústria de madeira, empregando fotocatálise e radiação solar, M.Sc. Dissertation, Universidade Federal de Uberlândia, Brazil, 2004.
[27] A.M. Jirka, M.J. Carter, Anal. Chem. 47 (1975) 1397.
[28] USEPA, Federal Register, April 21, 47 (1980) 26811.
[29] CONAMA (http://www.mma.gov.br), Resolution no. 20, Brasília, Brazil, 18 June 1986; http://www.feam.br.
[30] A.E.H. Machado, T.P. Xavier, D.R. Souza, J.A. Miranda, E.T.F.M. Duarte, R. Ruggiero, L. Oliveira, C. Sattler, Solar Energy 77 (2004) 583.
[31] E.T.F. Mendonça Duarte, T.P. Xavier, D.R. Souza, J.A. Miranda, A.E.H. Machado, C. Jung, L. Oliveira, C. Sattler, Quim. Nova 28 (2005) 921.
[32] J.J. Pignatello, Environ. Sci. Technol. 26 (1992) 944.
[33] J.L. Acero, F.J. Benítez, F.J. Real, A.I. Leal, Water Sci. Technol. 44 (2001) 31.
[34] M. Pérez, F. Torrades, J.A. Garcia-Hortal, X. Domènech, J. Peral, Appl. Catal. B: Environ. 36 (2002) 63.
[35] R.F.P. Nogueira, J.R. Guimarães, Water Res. 34 (2000) 895.
[36] O. Bajt, G. Mailhot, M. Bolte, Appl. Catal. B: Environ. 33 (2001) 239.
[37] A. Safarzadeh-Amiri, J.R. Bolton, S.R. Cater, J. Adv. Oxid. Technol. 1 (1996) 18.
[38] S.H. Bossmann, E. Oliveros, S. Gob, S. Siegwart, E.P. Dahlen, L. Payawan Jr., M. Straub, M. Worner, A.M. Braun, J. Phys. Chem. 102 (1988) 5542.
[39] B. Ensing, Chemistry in water—first principles computer simulations, Ph.D. Thesis, Vrije University, Amsterdam, 2003.
[40] J.J. Pignatello, D. Liu, P. Houston, Environ. Sci. Technol. 33 (1999) 1832.
[41] S. Goldstein, G. Czapski, D. Meyerstein, Free Radic. Biol. Med. 15 (1993) 435.
[42] M. Marsarwa, H. Cohen, D. Meyerstein, D.L. Hickman, A. Bakac, J.H. Espensen, J. Am. Chem. Soc. 110 (1988) 4293.
[43] F. Haber, J. Weiss, J. Proc. Roy. Soc. London, Ser. A 147 (1934) 332.
[44] J.H. Merz, W.A. Waters, Discuss. Faraday Soc. 2 (1949) 179.
[45] A. Fujishima, T.N. Rao, D.A. Tryk, J. Photochem. Photobiol. C: Photochem. Rev. 1 (2000) 1.
[46] H.-J. Benkelberg, P. Warneck, J. Phys. Chem. 99 (1995) 5214.
[47] M. Pérez, F. Torradez, X. Domènesch, J. Peral, Water Res. 36 (2002) 2703.
[48] M.R. Enriquez, N. Shahin, C.D. de-Bazúa, J. Lang, E. Oliveros, S.H. Bossmann, A.M. Braun, Solar Energy 77 (2004) 491.
[49] P. Mazellier, M. Bolte, Chemosphere 42 (2001) 361;
H.-J. Benkelberg, P. Warneck, J. Phys. Chem. 99 (1995) 5214.
[50] G. Ruppert, R. Bauer, G. Heisler, Chemosphere 28 (1994) 1447.
[51] W.Z. Tang, P. Huang, Environ. Technol. 18 (1997) 13.
[52] N.H. Ince, G. Tezcanli, Water Sci. Technol. 40 (1999) 183.
[53] M. Neamtu, A. Yediler, I. Siminiceanu, A. Kettrup, J. Photochem. Photobiol. A: Chem. 161 (2003) 87.
[54] M.M. Kondo, M.A.S.V. Arcos, M.T. Grassi, Brazil. Arch. Biol. Technol. 45 (2002) 81.
[55] C.P. Huang, C. Dong, Z. Tang, Waste Manage. 13 (1993) 361.
[56] M. Kitis, C.D. Adams, G.T. Daigger, Water Res. 33 (1999) 2561.
[57] R. Bauer, H. Fallmann, Res. Chem. Intermed. 23 (1997) 341.