



The effect of operational parameters on electrocoagulation–flotation process followed by photocatalysis applied to the decontamination of water effluents from cellulose and paper factories

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ABSTRACT

Cellulose and paper pulp factories utilize a large amount of water generating several undesirable contaminants. The present work is a preliminary investigation that associates the electrocoagulation–flotation (EC) method followed by photocatalysis to treat such wastewater. For EC, the experiment with aluminium and iron electrodes showed similar efficiency. Iron electrodes (anode and cathode) were chosen. By applying 30 min of EC/Fe⁰, 153 A m⁻² and pH 6.0, the COD values, UV–vis absorbance and turbidity underwent an intense decrease. For the subsequent UV photocatalysis (mercury lamps) TiO₂ was employed and the favourable operational conditions found were 0.25 g L⁻¹ of the catalyst and solution pH 3.0. The addition of hydrogen peroxide (50 mmol L⁻¹) highly increased the photo-process performance. By employing the UV/TiO₂/H₂O₂ system, the COD reduction was 88% compared to pre-treated effluents and complete sample photobleaching was verified. The salt concentration on EC (iron electrodes) showed that the electrolysis duration can be reduced from 30 to 10 min by the addition of 5.0 g L⁻¹ of NaCl. The biodegradability index (BOD/COD) increased from 0.15 (pre-treated) to 0.48 (after EC) and to 0.89 (after EC/photocatalysis irradiated for 6 h), showing that the employed sequence is very helpful to improve the water quality. This result was confirmed by biotoxicity tests performed with microcrustaceous *Artemia salina*.

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1. Introduction

The Brazilian Association of Cellulose and Paper (BRACELPA) estimates that 155 million tons of wooden pulp are produced per year and foresees an increment of 67% on this value up to 2010 [1]. Cellulose and paper factories generate a high amount of contaminated water to produce paper pulp [2]. Among the constituents of wood, in addition to cellulose fibres, there are other natural substances such as tannins, resins and lignins; the latter act as adhesive substances for cellulose fibres in the wood [3]. Additionally, other pollutants are created during the stages of pulping, bleaching and paper production (chlorinated lignins, acid resins, phenols, dioxins, furans) – xenobiotic compounds. Several of these compounds remain in the water effluents and are severe water pollutants, notably polychlorinated dibenzodioxins and dibenzofurans, which are recalcitrant to the degradation and are classified as persistent organic pollutants [4]. As an example, the cellulose paste presents

an intense brown color caused by the lignin presence, color that has to be removed. In this pulp bleaching process, chlorine was widely used in the past [3], however the elementary chlorine reaction with lignin and other organic substances generates toxic chlorinated products. In order to minimize the generation of pollutants, other bleaching processes have been developed; processes using chlorine dioxide, oxygen, ozone, and hydrogen peroxide are used nowadays [5]. The major part of the residues resulted from the bleaching process (around 90%) is used as energy source because such residues are constituted by rich organic materials – known as black liquor; however the other 10% of residues remain in the water as severe pollutants.

1.1. Brazilian Environmental Legislation

Brazilian authorities admit that aqueous effluents from any polluting sources can be launched (directly or indirectly) in natural water receptors (rivers, lakes, seas, etc.) after adequate treatment established by the legislation. Despite the high number of varied harmful substances produced daily by factories, the Brazilian Environmental Regulation pointed out only a limited number of these pollutants (and even fewer environmental parameters), eventually

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restricted only to compounds that are recognized as highly harmful to the human health. According to the Brazilian National Council for the Environment (CONAMA) through the Resolution No. 357/2005, it is forbidden to launch persistent organic pollutants (POP) and more importantly all processes that produce dioxins and furans should be avoided [6]; therefore some industrial processes have been replaced by other technologies in order to diminish or eliminate this kind of pollutants.

Rio de Janeiro State (Brazil) by the Directive 205 R – 5 No. 2491/1991 regulates the quality of the dischargeable water from paper and cellulose factories [7]. It determines that the chemical oxygen demand (COD) of the effluents must be inferior to 200 mg L⁻¹. The same legislation describes the importance of the biochemical oxygen demand (BOD) control, which establishes that for the BOD/COD ratio (biodegradability index) inferior to 0.25 it is mandatory either to implement less pollutant technologies on production procedures or it is necessary to perform effluent treatment to control non-biodegradable organic loads. According to the literature, in order to reach complete biodegradation, the effluent must present a biodegradability index of at least 0.40 [8].

1.2. Wastewater treatments

Two very interesting wastewater treatments are the physical–chemical processes of electrocoagulation–flotation (EC) and the heterogeneous photocatalysis with titanium dioxide. In the EC process coagulant agents are generated in situ by the electrochemical dissolution (oxidation – anode) of the sacrificial electrode, mostly using aluminium and iron metals as anodes and cathodes. Within some specific pH range, the generated cationic metal creates metallic hydroxide compounds of low water solubility (hydrolysis process, $M(OH)_n^{z+}$). Usually these metallic products present positive charged residues that interact with negative particles or negative groups of organic compounds promoting the coagulation. The water treatment is enhanced by the flotation step of the coagulate flakes promoted by hydrogen bubbles generated in the cathode (from water reduction: $H_2 + OH^-$) [9]. However for the EC, it is not possible to discard the direct electrolysis of pollutants or production of oxidant compounds (as chlorine); these electrochemical reactions occur specially applying EC with high potentials, whose processes help the water treatment [10–12].

The heterogeneous photocatalysis methods are based on the absorption of light by semiconductor particles, such as titanium dioxide. This species absorbs ultraviolet light ($\lambda < 380$ nm), whose energy is equal or superior to the bandgap (3.2 eV), leading one electron from the valence band (producing a positive charged hole, h_{VB}^+) to the conduction band (forming a e_{CB}^-) [13]. Many advantages are associated to the TiO₂ use such as low costs, low toxicity and high photochemical stability [14]. The performance of h_{VB}^+ and e_{CB}^- in the degradation of organic materials is largely known including several pathways that lead the adsorbed water and hydroxide ions at TiO₂ surface to produce hydroxyl radicals, HO•, the most relevant oxidant species formed [15]. However, according to [16], for this process to succeed the chemical oxygen demand (COD) must be lower than 800 mg L⁻¹.

In order to improve the final water quality a combined treatment seems very interesting and some of the experimental parameters of these processes are investigated in the present work (preliminary studies): the EC operational conditions are examined and in sequence the samples are submitted to heterogeneous photocatalysis using TiO₂ as catalyst. The wastewater investigated was obtained after the pulp ozonization from the industrial bleaching step.

2. Material and methods

2.1. Reagents

TiO₂ was kindly supplied by Degussa Co. (P-25, 80% anatase and 20% rutile, with 50 m² g⁻¹ of specific surface area, it was used without previous treatment). H₂O₂ (30%, v/v from Synth Co.) and other reagents were analytical grade and they were used as received. Solutions of HCl and NaOH (0.10 mol L⁻¹) were employed for pH adjustments.

2.2. Effluent characterization

Three samples were collected in a paper and cellulose factory located in Paraná state, Brazil, in September of 2005 (sample 1), in December of 2005 (sample 2), and a third one in March of 2006 (sample 3); all samples were specifically collected after the pulp bleaching process unit stage (ozone treatment). The physical–chemical analysis of the samples was performed following standard analytical methods [17]. The software Statistic 5.0 was used applying the Tuckey test and $P < 0.05$ as confident parameter. After this characterization the samples were stored in a ventilated place protected from light.

2.3. Electrocoagulation–flotation (EC) treatment

Studies of EC were executed with both cathodes and anodes composed by aluminium electrodes and iron electrodes (commercial plates). The electrode dimensions were 12.50 cm × 2.50 cm with 0.10 cm of thickness that corresponds to total area of 6.6×10^{-3} m², at a distance of 2.0 cm between themselves, in 500 mL of sample (bathwise). The EC was performed with a power supply of continuous current of 1 A and 12 V (HAYAMA, 1212), whose current density (cd) was 153 A m⁻². After the EC the sample was left to rest (approximately 1 h) and the resulted water was withdrawn and filtered (paper filter). The effect of initial pH was studied at pH 4.0, 5.0, 6.0, 7.0 and 10.0. At the desired pH, the EC time was determined. At the desired experimental conditions, physical–chemical analyses have been determined in order to evaluate the performance of the treatment. The surfaces of the electrodes were cleaned with diluted nitric acid solution.

2.4. Heterogeneous photocatalysis treatment

The photocatalysis methods were applied to samples previously treated by the EC technique. The photoreactor consisted of a wooden box with dimensions of 80 cm × 80 cm and 50 cm of depth with all walls covered by aluminium foil, with light source composed by three mercury lamps of 250 W without the glass bulbs (Brazil General Electric Co.) fixed on the top side approximately 15 cm away from the samples. The light power was measured by a light meter apparatus (Newport Optical Power Meter Model 1830-C), positioned at the same place of the sample (wavelength set at 400 nm). The samples have been irradiated in borosilicate erlenmeyers (bathwise) under a magnetic mixer. In order to reduce the heat, four fans were fixed in the photoreactor sidewalls. After the illumination, the samples were filtered (Millipore, 0.22 μm). In the UV/TiO₂/H₂O₂ system the effect of initial pH (at 3.0, 5.0, 7.0 and 10.0) was studied. The effect of TiO₂ concentrations (0.25, 0.50 and 0.75 g L⁻¹) and of H₂O₂ concentrations (2, 10 and 50 mmol L⁻¹) was analyzed.

2.5. Toxicity investigations of the effluent

The existence of biotoxic substances in the effluent was evaluated by the *Artemia salina* tests. This species of aquatic microcrustaceous (*Artemia* spp.) survives in salted aqueous solutions and

Table 1

Analytical characteristics of the collected effluents (pre-treated) from cellulose and paper factory

Parameter	Sample 1	Sample 2
pH	9.6 ^a	9.8 ^a
Conductivity (mS cm ⁻¹)	1.63 ^b	2.08 ^b
Turbidity (NTU)	12 ^a	10 ^a
O _D (mg L ⁻¹)	– ^c	7.8
COD (mg L ⁻¹)	1313 ± 7 ^a	1302 ± 25 ^a
BOD ₅ (mg L ⁻¹)	163 ± 11 ^a	148 ± 5 ^a
SO ₄ ²⁻ (mg L ⁻¹)	590.1 ± 9.1 ^a	677.6 ± 7.2 ^b
PO ₄ ²⁻ (mg L ⁻¹)	582.8 ± 56.4 ^a	871.6 ± 2.3 ^b
N _{NH3} (mg L ⁻¹)	ND	1.7 ± 0.0
N _{org} (mg L ⁻¹)	ND	108 ± 0.0
NO ₂ ⁻ (mg L ⁻¹)	56.3 ± 0.8 ^a	44.8 ± 0.3 ^b
NO ₃ ⁻ (mg L ⁻¹)	112.9 ± 0.8 ^a	168.5 ± 13.5 ^b
Cl ⁻ (μg L ⁻¹)	– ^c	80.1 ± 1.2

Samples analyzed $n = 3$. Different superscript letters (a or b) in the line implies values statistically different ($P < 0.05$ by Tuckey tests). –^c Analysis not performed. ND, below detection limits.

it is very sensitive to the water environment [18]. The adopted methodology [19] is described as follows: eggs of *A. salina* were hatched in water (NaCl 3.8 g L⁻¹); volumes of 0.5, 1.0, 1.5, 2.0 and 2.5 mL of effluents were added to test tubes and the volume was filled up to 3.0 mL of saline water (17, 33, 50, 67, 83% (v/v) of effluent at pH~7); 20 mature crustaceans were transferred to the tubes. After 24 h the number of live animals was counted. Assays were performed in triplicate.

3. Results and discussion

The analytical and physical–chemical characterization of the pre-treated effluent (original samples as collected at the factory) is shown in Table 1.

As it is observed in Table 1 both samples, despite having been collected in a time interval of 3 months, presented similar characteristics, fact which is not so usual for industrial effluents. The values of pH are higher than the ones allowed by Brazilian authorities for the discharge of water effluents (the acceptable top limit is pH 9.0, [6]). However no buffering effects were observed so that a small amount of HCl/NaOH was necessary to modify the pH of the effluent. The COD value, around 1310 mg L⁻¹, is more than six times the permitted by the environmental legislation (200 mg L⁻¹). The biodegradability indexes (BOD/COD ratio) for sample 1 and 2 were, respectively, 0.12 and 0.11, indexes that require water treatment according to the Brazilian Legislation (acceptable limit 0.25, [7]). Studies of biodegradability [3] carried out in six effluents of paper and cellulose factories presented BOD/COD ranging from 0.015 to 0.072, which are more biorefractory than the samples investigated in the present work.

Biological treatment is widely used for the treatment of cellulose pulping water effluents [5], however the investigated samples show biorefractory characteristics that are not recommended for this technology (low BOD/COD ratio). As mentioned in Section 1 the biodegradability indexes should be higher than 0.40 in order to undergo complete biodegradation [8], which is not the present case. Additionally the amount of sulphate (from Kraft technology) and phosphate ions detected was high whereas the nitrite and nitrate ions concentrations were reasonable. Therefore the application of other decontamination methods became necessary [20], procedure that would permit the water re-use or the discharge of water as free pollutant.

3.1. The electrocoagulation–flotation process

The nature of the metal used as electrode (anode and cathode) in the EC efficacy were aluminium and iron metals, which are the most

cited in the literature because of their largest viability for industrial application [11,21].

For samples submitted to 60 min of electrolysis with aluminium electrodes (EC/Al⁰) the results were high reduction of the UV–vis absorption (several analytical wavelengths were monitored) and of COD values at pH ranging from 4.0 to 7.0. This result is similar to that obtained with fresh olive mill samples treated by EC/Al⁰ [10]. The predominant chemical species at pH 2.0–3.0 are the Al³⁺ and Al(OH)²⁺. At pH in the range of 4.0–9.0, polymeric species such as Al₁₃O₄(OH)₂₄⁷⁺ were formed and precipitated as Al(OH)₃. At pH greater than 10.0, a monomeric anion Al(OH)₄⁻ prevails [22]. Thus at initial pH around 4.0–9.0, the coagulated Al(OH)₃, an amorphous flake, exhibits high superficial area that leads to a quick adsorption process of organic compounds, colloidal particles, and salts. The flakes formed were removed naturally from the solution through flotation by the generated H₂(g) in the cathode region [23]. The EC/Al⁰ treatment at fixed pH 5.0 was carried out at several electrolysis times. Its efficiency was analyzed by COD results: after 30 min an average reduction of 55% was obtained whereas after 60 min the reduction was 56%. As a consequence the electrolysis/Al⁰ was performed up to 30 min of duration.

For the EC/iron electrodes experiments (EC/Fe⁰), the pH range of 4.0–7.0 resulted in COD values that were statistically equal, whose average decay was approximately 52%. However the most significant UV–vis absorbance decrease occurred at pH 6.0, result that is attributed to the generation of Fe(OH)₂⁺ (prevalent species at pH 5) or Fe(OH)₃ (prevalent species at pH 8) [24] both presenting low solubility and high aggregation tendency by surface effects caused by London forces and electrostatic charge neutralization (against compounds with negative charge and/or with substances presenting negative electronic density) [23,25]. This flake leads the organic and inorganic materials of the effluent to coagulate and to float. However, during the EC the pH raised (from 6.0 to 9.6 after 30 min and to 10.5 at 80 min), due to the hydroxide ions generation from water reduction in the cathode. Despite this, the literature [26] pointed out that the Fe(III) sustains its coagulant efficiency until pH 11.

For the experiments at initial pH 6.0 the values of absorbance intensity were monitored during the EC/Fe⁰ at four different wavelengths (Fig. 1 at 284, 310, 350, and 500 nm). The radiation at 500 nm is a characteristic of light absorption of colored substances presenting high level of resonance; at 350 nm the compounds exhibit conjugated aromatic rings with reasonable level of resonance; 310 nm corresponds to restrained conjugated aromatic rings and 284 nm is related to aromatic groups such as phenols, which

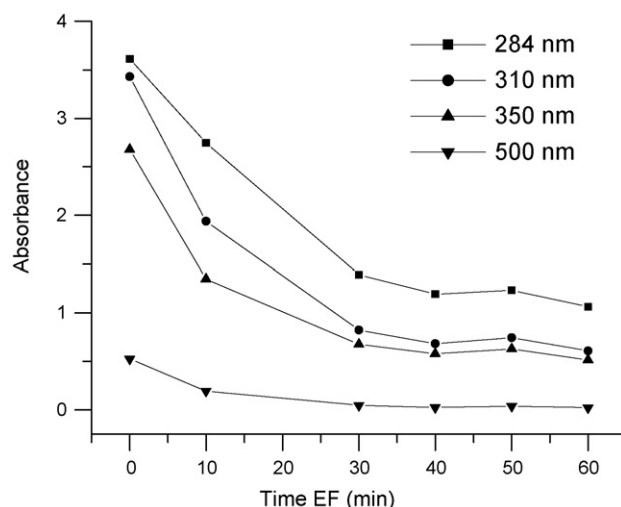


Fig. 1. Absorbance decrease during the EC performed with iron electrodes at pH 6.0. The intensity at 0 min corresponds to the pre-treated effluent.

are usually present in this kind of wastewater. In the present work these wavelengths were chosen as representative to pollutants that usually are found in this kind of wastewater (dioxins, furans, lignin, cellulose, hemicellulose, quinoid, dyes, and other derivative compounds), some of them highly toxic and refractory. Additionally the absorbance intensity at wavelengths in UV region is suitable to detect colloidal particles in the effluent by the light scattering phenomenon.

As it is possible to observe in Fig. 1, at all monitored wavelengths the absorbance intensity during the EC/Fe⁰ decreased significantly and after approximately 30 min it remained almost constant; the treated water became almost colorless. The strong absorbance decrease evidences the quality of the EC method that is reinforced by the reduction of COD values of approximately 55% after 30 min of electrolysis.

The data illustrated in Fig. 2 permit to compare the aluminium and iron electrodes regarding the efficacy of organic substances and suspended particle separation in water effluents.

Again the results of both electrodes indicate that 30 min of electrolysis is enough EC time for the reduction of COD and the turbidity. The COD reductions are statistically equal for iron and aluminium, however for the turbidity, iron electrodes presented higher efficiency (90%) than aluminium (75%). The comparative studies found in the literature pointed out that the efficiency of each electrode depends on the composition of the effluent matrix treated; for example, in the treatment of textile wastewater, the iron electrodes present lower operational costs and similar efficiency compared to aluminium [12]. Although both metals are abundant in Brazil, aluminium is more expensive and may be hazardous to the human health [27,28]. Therefore in the subsequent EC experiments, iron (as cathode and anode) was employed at initial pH 6.0 during 30 min of electrolysis. For the experiment at this operational condition, the results of COD and inorganic compounds are shown in Fig. 3.

COD decayed from 1310 to 589 mg L⁻¹ (approximately 55%). The removal of phosphate ion was complete, whereas the decontamination for nitrite, sulphate and N-ammoniac reached high levels (Fig. 3). These data indicate that the flakes formed during EC (which adsorb the colloidal and dissolved materials) drag the ions and other molecular species, even if they are soluble in water. Although it was observed the removal of ions, the solution conductivity increased from ~2 mS cm⁻¹ (average value of the pre-treated sam-

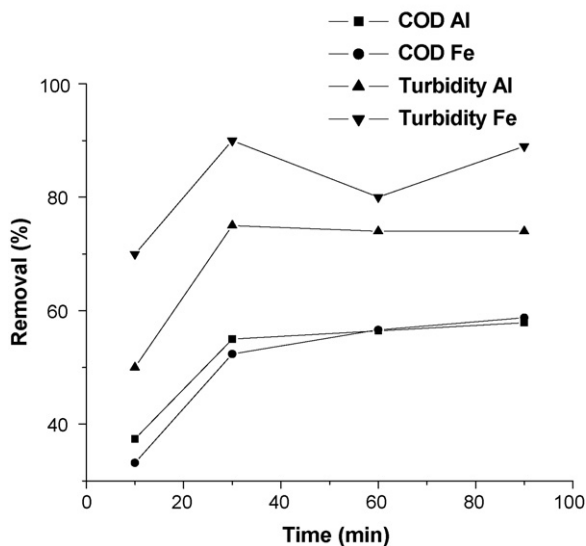


Fig. 2. Effects of the EC processes on the wastewater samples evaluated by percentage reduction of the turbidity and COD values: iron electrodes at pH 6.0 and aluminium electrodes at pH 5.0.

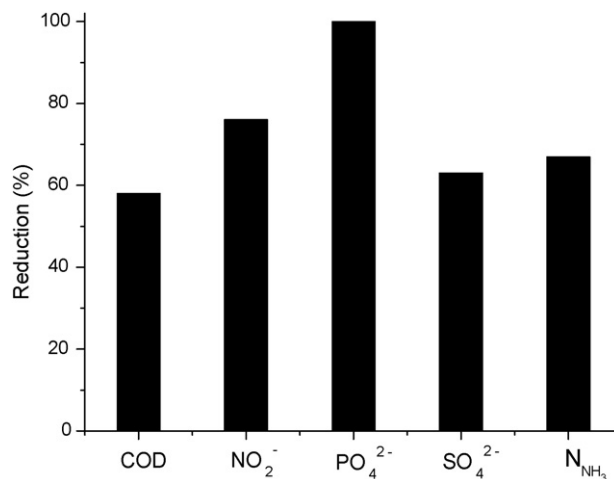


Fig. 3. Percentage of COD and inorganic ions reductions after 30 min of EC employing iron electrodes at initial pH 6.0.

ples 1 and 2) to ~3 mS cm⁻¹ after EC due to hydroxide formation (as aforementioned, the pH increases).

Additionally, although high saline concentrations can be undesirable for subsequent biological treatments [29], salt presence in EC/Fe⁰ increases the electrolysis performance by increment of the solution conductivity diminishing the internal resistance [22]. NaCl is the most usual salt employed in this kind of process due to its high efficiency and low environmental impact [30,22]. In fact, with the addition of 5.0 g L⁻¹ of NaCl to the effluent, the electrolysis leads to absorbance decrease superior to 80% (at all four wavelengths monitored) after 10 min of electrolysis. In this experimental condition the COD reduction was approximately 50% (10 min of electrolysis), performance that is similar to 30 min of EC without extra NaCl addition – note that this process saves electric energy and time [1,21]. Chlorine generation was not detected, even with NaCl addition (Cl₂ eventually generated from direct Cl⁻ ions oxidation [10,31]), which means that the applied anode potential is not high. Higher NaCl concentrations of 10, 15 and 20 g L⁻¹ were evaluated as equal effect to 5.0 g L⁻¹.

Regarding current density (cd) the high value of this physical parameter should increase the electrochemical reactions [30]. It was expected that in EC this parameter would modify the coagulant production, the velocity and quantity of hydrogen bubbles formation and the flakes' characteristics [23]. However a test employing higher cd (763 A m⁻² instead of 153 A m⁻², both with power supply of 12 V) did not significantly increase the EC efficiency. This unexpected result favours the present EC treatment because keeping this parameter at low values provides energy saving and low consumption of the sacrificial electrode (Fe⁰ – anode). It is known that a too large cd can waste electric energy in heating up the water [11]. Future studies on current density and the use of low NaCl concentrations have already been planned.

3.2. The photocatalysis process

All these subsequent experiments of photocatalysis were performed in samples previously treated by EC/Fe⁰, except for the study of pH. The assays were not affected by the temperature elevation inside the photoreactor (not shown). The light source irradiance was measured as 8.9 mW cm⁻².

The pH effect on the photocatalysis was carried out in an original effluent (pre-treated sample) with a previous sample dilution (1:1, v/v, in water). This procedure was necessary due to the high organic material concentration, which is inappropriate for heterogeneous photocatalysis. In accordance to the literature [16], for this process

the effluent should present COD values below 800 mg L^{-1} ; the COD of the pre-treated sample was more than 1300 mg L^{-1} (Table 1).

At 0.5 g L^{-1} of TiO_2 (constant for all samples) and the initial pH studied: 3.0, 5.0, 7.0, and 10.0, the highest performance on the photobleaching process was observed at pH 3.0 independently of the analytical wavelength. At 254 and 284 nm, regions where chromophores present aliphatic and single aromatic rings such as phenol [32], the absorbance reductions were 57% and 60%, respectively. In 500 nm it was possible to observe the most intense absorbance reduction: 89% (the sample became almost colorless). The similar effect was observed in acid solution on COD values (resulting on 565 mg L^{-1} after correction for the dilution factor, whose value corresponds to 57% COD reduction). The efficiency verified in pH 3.0 is caused by positive charges acquired by the TiO_2 surface in acid solutions permitting the adsorption of negatively charged contaminants [33].

The irradiations have been carried out in an open system due to the presence of atmospheric oxygen, which is an important factor in the TiO_2 photo-system. The adsorbed oxygen on TiO_2 surface reacts with the e_{CB}^- , forming the superoxide radical ($\text{O}_2^{\bullet-}$) according to Eq. (1) [34]. The oxygen as electrons acceptor prevents the recombination of the $e_{\text{CB}}^-/h_{\text{VB}}^+$ pair, turning TiO_2 photocatalyzed reactions viable in industrial scale [35].



The photolysis reaction (UV/effluent without catalyst) is quite slower than the photocatalysis (TiO_2 presence). The effect of the TiO_2 concentration in the photodegradation was performed in samples previously treated by EC/ Fe^0 . The efficiency was evaluated through the remaining UV–vis absorbance intensity and COD values. The UV irradiation on TiO_2 was conducted during 4 h at pH 3.0. In the range of the catalyst concentration investigated, statistically significant differences (among 0.25, 0.50 and 0.75 g L^{-1} of TiO_2) were not observed. At illumination of 0.25 g L^{-1} of TiO_2 , the absorbance reduction percentage (at 350 nm) was around 60% and the COD reduction was 8% compared to the sample treated by EC (after EC: 589 mg L^{-1} and after photocatalysis: 542 mg L^{-1}). The lack of direct correspondence between the photocatalysis efficiency and the amount of TiO_2 utilized is not usual. Usually as the added TiO_2 quantity increases, more pollutants' molecules are adsorbed, which implies in degradation increment [36]. However, the excess of semiconductor can make the passage of light more difficult through the solution (high turbidity) due to light scattering effects [16,37], fact that would explain this result. With the purpose of performing environmentally responsible experiments allied to cost saving and focusing on industrial application, the TiO_2 amount was kept at 0.25 g L^{-1} in the subsequent experiments.

One very interesting result on the photocatalysis was obtained by the employment of hydrogen peroxide as photooxidant auxiliary. After 4 h of irradiation at pH 3.0 and TiO_2 0.25 g L^{-1} it was possible to observe that the addition of 2, 10 and 50 mmol L^{-1} of H_2O_2 reduces the COD values to 545, 521 and 211 mg L^{-1} , respectively. At 50 mmol L^{-1} of H_2O_2 (largest decrease of UV–vis absorbance), the COD reduction was 84% (compared to the pre-treated samples) and 64% (compared to the samples after EC).

Hydrogen peroxide is either a strong oxidant agent added in photo-oxidation treatments or it can be generated during the photocatalysis (small amounts). The H_2O_2 can prevent the recombination of the $e_{\text{CB}}^-/h_{\text{VB}}^+$ pair (Eq. (2)), increasing the degradation of the contaminants. Additionally, hydrogen peroxide can react with superoxide radicals (formed as stated in Eq. (1)) increasing the amount of hydroxyl radicals, as described in Eq. (3) [38–42].

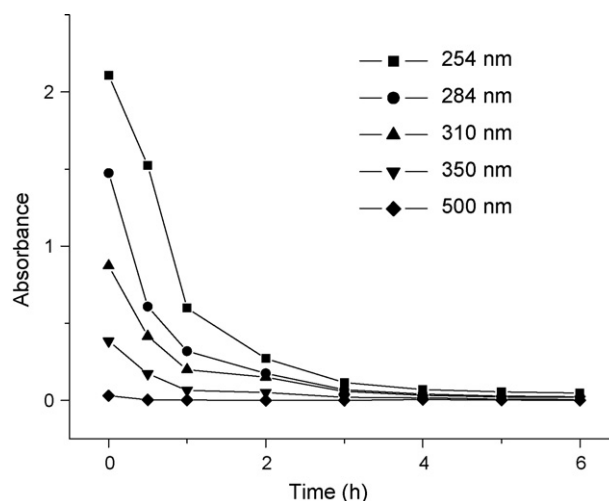
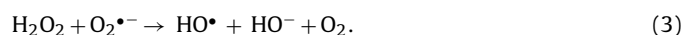


Fig. 4. Effects of photocatalysis with 0.25 g L^{-1} of TiO_2 and 50 mmol L^{-1} of H_2O_2 on water samples previously treated by EC. Residual absorbance intensity followed at several analytical wavelengths.

High concentrations of hydroxyl radicals in the lignin oxidation lead to phenolic intermediates that undergo aromatic ring rupture producing acids of small molecular size, such as carboxylic acids [43]. Therefore hydrogen peroxide can significantly increase the efficacy of the photodegradation, however its use should be controlled due to the remaining peroxide in the wastewater, whose presence causes damages to the environment. At these experimental conditions, after 3 h of illumination the peroxide was completely eliminated from the solution. Additionally some authors [38] pointed out that the excess of hydrogen peroxide may be an obstacle to the photocatalysis because: (i) light absorption competition between H_2O_2 and TiO_2 would decrease the catalyst photo-excitation and (ii) the fact that part of the hydroxyl radical is annihilated by the excess of H_2O_2 , converting it to hydroperoxyl radical (HO_2^\bullet), which is suppressed by other hydroxyl radicals producing $\text{H}_2\text{O} + \text{O}_2$. However this is not the present case, in which results show higher efficacy by oxygen peroxide addition (50 mmol L^{-1}).

In order to investigate the photocatalysis duration, Fig. 4 presents the absorbance decrease during the illumination at pH 3.0, 0.25 g L^{-1} TiO_2 and 50 mmol L^{-1} of H_2O_2 . The data show that the chromophores monitored at all wavelengths decreased to zero absorbance intensity in 5–6 h. The COD decreased to almost 210 mg L^{-1} after 3 h of irradiation.

The literature reports [40] that for a mixture of samples collected at different stages of a paper factory (initial COD around $400\text{--}500 \text{ mg L}^{-1}$), the photolysis employing 0.050 g L^{-1} of TiO_2 , pH 3.0 and 1 h of light in a reactor of internal re-circulation, reached 60% of COD reduction. This value is slightly lower than that one obtained in the present work (64% using 0.25 g L^{-1} , pH 3.0, 4 h of irradiation and 50 mmol L^{-1} of H_2O_2 in the bathwise system). It seems that photo-reactors with re-circulating water effluents require lower TiO_2 concentration than bathwise reactors to reach similar efficiency.

Additionally the pre-treated sample presented sulphate ions concentration of $523 \pm 9 \text{ mg L}^{-1}$. After 30 min of EC its amount was reduced to $183 \pm 4 \text{ mg L}^{-1}$, which corresponds to 65% removal; probably the sulphate is dragged by the organic particles in the adsorption step. However after UV/ TiO_2 / H_2O_2 photocatalysis during 30 min, the sulphate concentration was $202 \pm 12 \text{ mg L}^{-1}$ (an increment of 10%) and after 4 h it was $231 \pm 10 \text{ mg L}^{-1}$, which means 26% of increment. The sulphate ion formation and all other param-

Table 2
Biodegradability index of samples pre-treated, after EC and after photocatalysis treatments (sample 3)

Sample	BOD (mg L ⁻¹)	COD (mg L ⁻¹)	BOD/COD
Pre-treated	172 ± 1	1162 ± 14	0.15
EC	171 ± 4	357 ± 10	0.48
EC + Photocat. (2 h)	80 ± 2	148 ± 1	0.54
EC + Photocat. (4 h)	123 ± 1	138 ± 5	0.89

eters of the photocatalyzed sample suggest that the mineralization of the organic materials in the effluent is taking place. To reinforce such hypothesis, the solution conductivity increased from 3.0 mS cm⁻¹ (sample after EC) to 4.2 mS cm⁻¹ (after 6 h of photocatalysis).

The kinetic profile data (Fig. 4) evaluated through the absorbance decrease as a function of the irradiation time obeyed the first-order kinetic law (TiO₂, H₂O₂, and constant light irradiance). The rate constants calculated at 254, 284, 310 and 350 nm resulted in almost the same value, approximately 0.8 h⁻¹ ($r=0.99$).

Summing up, for the sake of comparison, the efficiency and the rate of absorbance intensity reduction obeyed the following order: photolysis (without catalyst) < photolysis (with peroxide) < photocatalysis (TiO₂ without peroxide) < photocatalysis (TiO₂/H₂O₂).

3.3. The biodegradability results (EC and photocatalysis)

For the specific analysis of the biodegradability index (COD and BOD), sample 3 was employed. The data of the effluent submitted to EC (30 min, pH 6.0, and iron electrodes), followed by photocatalysis (UV, pH 3.0, 0.25 g L⁻¹ of TiO₂, and 50 mmol L⁻¹ of H₂O₂ for 4 h) – all parameters at the best operational conditions obtained in the present work, have the BOD and COD results summarized in Table 2.

The data in Table 2 show that the COD of pre-treated sample 3 is slightly lower than that COD obtained previously with samples 1 and 2 (~1.310 mg L⁻¹). This variation is normal because in the industrial pulp production there are several parameters which are hard to control in the pipeline: (1) wood type, quality, size, age, and conditions; (2) reactants (quality and quantity); (3) process parameters (time duration, temperature, pressure, and others); and all other experimental conditions that are involved in large scale production. After EC the COD reduction of sample 3 was around 69%, which is higher than the reduction obtained for samples 1 and 2 (~55%) at the same EC conditions. Probably sample 3 presented pollutants' conditions that favoured the EC. For this sample 3 submitted to EC and photocatalysis, the COD reduction (compared to the pre-treated sample) was 88%, which is not so different from samples 1 and 2, whose average decay was 84%.

The biodegradability index of the effluent before and after EC/Fe⁰ treatment changed from 0.15 to 0.48 (Table 2). This process eliminates part of the organic substance in suspension and in colloidal form. The biodegradability index of 0.48 (EC/Fe⁰) means that the effluent submitted to biological treatment would suffer complete degradation, however a reasonable amount of organic materials still remained in the solution. This sample after 2 h of photocatalysis improved the water quality (to 0.54 index) whereas

after 4 h the result was excellent (index of 0.89). These data show that the photocatalysis method promotes an efficient elimination of the remaining organic pollutants (represented by COD values) either adsorbing or transforming them into biodegradable species (represented by BOD values). These results showing the photocatalysis capacity to treat wastewater are endorsed by the literature [44].

Sample 3 submitted to EC (Fe⁰ electrodes, 30 min of electrolysis and pH 6.0) can be compared to the same collected sample submitted to the coagulation–flocculation (CF) process [32] using FeCl₃·6H₂O (0.50 g L⁻¹) at pH 6.0. The COD decrease were 69% to EC and 56% to CF, which mean higher EC performance than CF in these experimental conditions. Additionally, sample 3 after EC/photocatalysis (0.25 g L⁻¹ of TiO₂, pH 3.0, 50 mmol L⁻¹ of H₂O₂, and 4 h of irradiation) and CF/photocatalysis (0.50 g L⁻¹ of TiO₂, pH 3.0, 10 mmol L⁻¹ of H₂O₂, and 6 h of irradiation), all at desirable operational conditions, resulted in 64% and 60% COD decay, respectively (percentage calculated from coagulated samples – by EC and by CF). This small difference means that the photocatalysis efficiency is not so dependent on the previous coagulation process (EC or CF treatments).

The combined water purification of EC or CF, as pre-treatment, followed by the photocatalysis, seems very efficient however it is difficult to compare these combined methods with others because all the studies (even about residues from paper factories) have used different effluents (from different wood types, seasons of the year, pulp fabrications, bleaching processes, operating parameters and all other factories' conditions). However, associated with the pre-treatment with iron (as metallic electrodes or salt), an interesting second treatment is Fenton or photo-Fenton processes, which employ Fe²⁺ and H₂O₂ and require light of low energy (photons with wavelength around 400 nm or absorption up to 550 nm for Fe³⁺/H₂O₂ – photo-Fenton-like reactions) [45].

3.4. Water toxicity experiments by *Artemia salina* microcrustaceous

The fact that water presents colorlessness, high transparency, high biodegradability index (BOD/COD ratio), small ions presence, and all other parameters investigated do not permit us to assure that the water is free from pollutants and harmful substances. Therefore biotoxicity assays with *A. salina* were performed. There was investigated the pre-treated samples, samples treated by EC and treated by EC/photocatalysis at experimental conditions, EC/Fe⁰: initial pH 6.0 during 30 min, and photocatalysis: 0.25 g L⁻¹ of TiO₂, initial pH 3.0, and 50 mmol L⁻¹ of H₂O₂ irradiated for 2 and 6 h. The results are shown in Table 3 for different solutions (samples with different effluent percentages).

As can be seen the pre-treated samples are highly toxic to the microcrustaceous. The first treatment, EC, promoted the most intense toxicity reduction. Although the photocatalysis performed during 2 h exhibited proportionally small toxicity decay (in comparison to the sample after EC), the irradiation during 6 h revealed to be very efficient. After the treatments the water effluent seems to contain low levels of toxic compounds such as phenol, residual hydrogen peroxide and others.

Table 3
Death percentage of *Artemia salina* submitted to treatments with different amount of effluents

Effluent (%)	Pre-treated (%)	EC (%)	EC/Photocat. 2 h (%)	EC/Photocat. 6 h (%)
83	97	33	30	19
67	82	22	20	12
50	76	20	17	8
33	40	15	15	4
17	34	10	11	0

4. Conclusions

The preliminary results obtained in this work present evidences that the combined techniques electrocoagulation–flotation followed by UV/TiO₂/H₂O₂ photocatalysis system are efficient to reduce organic and inorganic contaminants in wastewater from the cellulose pulp bleaching process. The EC removed the greatest part of the organic substances (colloidal and suspended materials), mainly by using iron as anode and cathode electrodes, which permits to apply the heterogeneous photocatalysis. With the association of this process, the remaining pollutants were transformed into more single substances towards mineralization. These facts are suggested mainly by the absorbance intensity, COD reductions, and sulphate ion formation. The biological tests using *A. salina* confirmed that the investigated treatments produce water containing lower levels of harmful substances. The pre-treatment by EC method previous to photocatalysis revealed to be necessary. Finally, the resulting water quality evidenced the high performance of these methods in wastewater treatment of effluents from paper and cellulose factories.

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