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Combined electrocoagulation and TiO_2 photoassisted treatment applied to wastewater effluents from pharmaceutical and cosmetic industries

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ABSTRACT

The treated wastewater consists of refractory materials and high organic content of hydrolyzed peptone residues from pharmaceutical factory. The combination of electrocoagulation (EC) followed by heterogeneous photocatalysis (TiO_2) conditions was maximized. The EC: iron cathode/anode (12.50 cm × 2.50 cm × 0.10 cm), current density 763 A m^{-2}, 90 min and initial pH 6.0. As EC consequence, the majority of the dissolved organic and suspended material was removed (about 91% and 86% of the turbidity and chemical oxygen demand (COD), respectively). After EC, refractory residues still remained in the effluent. The subsequent photocatalysis: UV/TiO_2/H_2O_2 (mercury lamps), pH 3.0, 4 h irradiation, 0.25 g L^{-1} TiO_2 and 10 mmol L^{-1} H_2O_2 shows high levels of inorganic and organic compounds eliminations. The obtained COD values: 1753 mg L^{-1} for the sample from the factory, 160 mg L^{-1} after EC and 50 mg L^{-1} after EC/photocatalyzed effluents pointed out that the combined treatment stresses this water purification.

1. Introduction

Water is an essential natural resource for human beings and for all life forms. Its protection is guaranteed by the Brazilian legislation, however, in addition to having precarious inspection, there are thousands of residues generated by several factories. As a consequence there are no specific rules or regulations for many industrial effluents, including the residues investigated in the present work. Increasing efforts to provide treatment to liquid, solid and gaseous residues have stimulated the development of new technologies.

In the present research studies were carried out with aqueous effluents collected from a pharmaceutical and cosmetic factory. The employed enzymatic process of this factory produces chondroitin sulfate, a type of medication used to fight arthritis illnesses; however the effluent generated by this process contains fragments of hydrolyzed proteins named peptones, which are a culture medium for microorganism development. This aqueous effluent is released into the equalization lagoon (first step of the biological treatment) and, besides peptones residues, it contains surfactants compounds, chlorides and others. It should be emphasized that there is no citation on the Brazilian's legislation about this kind of industrial waste and also there is no methodology describing any specific treatment to this kind of effluent.

The electrocoagulation process (EC) using metallic electrodes is a technique used to remove organic and suspended materials from several types of effluent matrix [1–5]. The fundament of the EC/metallic electrodes is the generation of M^{n+} species in the metallic anode, which can suffer hydrolysis or form polymeric compounds; these species can adsorb organic materials by charge or surface effects, leading the contaminants to coagulate. Depending on the formed flocks characteristics, the hydrogen bubbles formed by water reduction in the cathode can promote the flotation of the aggregated pollutants [6]. The EC process is highly dependent on physical–chemical characteristics of the effluent (nature, composition and concentration of the pollutants [7], solution conductivity [8], pH, electrolysis cell design (size/area and electrodes distance), electrolysis time, current and electrodes material). Several advantages are attributed to EC such as the contaminants removal rate, small apparatus size, easy maintenance and low equipment operation costs [9]. Furthermore, there is no need of adding chemical agents, which can generate secondary pollution [10].

Another wastewater treatment is the heterogeneous photocatalysis, an advanced oxidation process (AOP) involving the conversion of organic pollutants to short species and even to their complete mineralization through the generation of highly reactive free radical oxidants. This treatment can be performed using mercury lamps and a metal oxide as catalyst. Titanium dioxide is one of the most

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[1] In memoriam.

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useful catalysts showing several advantages compared to others, due to its high photochemical stability, low toxicity and reduced costs [11]. The heterogeneous photocatalysis systems are based on the absorption of photons with energy greater than 3.2 eV (which corresponds to wavelengths lower than ~390 nm) to initiate the excitation, related to a charge separation event (gap band), *i.e.* one electron promotion at the conductive band (e_{CB}^-) and a positive hole at valence band (h_{VB}^+), as represented in Eq. (1) (bands formed by the evolvement of molecular orbitals of TiO_2 as it is packed into a lattice). The h_{VB}^+ can oxidize H_2O molecules and OH^- ions adsorbed at the particle surface (TiO_2) producing $^{\bullet}OH$ radicals [12] (Eqs. (2) and (3)). The hydroxyl radical is a short-lived and extremely powerful agent in the organic substances oxidation, degrading and mineralizing them to CO_2, H_2O and inorganic ions [13].

$$TiO_2 + h\nu \rightarrow e_{CB}^- + h_{VB}^+ \quad (1)$$

$$H_2O_{(ads)} + h_{VB}^+ \rightarrow {}^{\bullet}OH + H^+ \quad (2)$$

$$OH_{(ads)}^- + h_{VB}^+ \rightarrow {}^{\bullet}OH \quad (3)$$

On the other hand, e_{CB}^- can react with O_2 forming the anion radical superoxide as represented in Eq. (4) [14]. Subsequent reactions can lead to hydrogen peroxide and, once again, to the hydroxyl radical [12].

$$O_2 + e_{CB}^- \rightarrow O_2^{\bullet -} \quad (4)$$

The presence of such dissolved oxygen is very important for heterogeneous photocatalysis because it can make the recombination process on TiO_2 (h_{VB}^+/e_{CB}^-) more difficult and maintain the electroneutrality of the TiO_2 particles. This condition makes the treatment practicable for industrial scale application in the environment conditions [15]. However, according to literature [16], for the TiO_2 photocatalysis process to succeed, the chemical oxygen demand (COD) must be lower than 800 mg L^{-1}.

Several studies on effluents treatment have shown the advantages of associating different techniques, such as: heterogeneous photocatalysis combined prior to or after the biological treatment of textile wastewater [17]; ozonation prior to the biological treatment for wastewater from paper and cellulose factories [18]; and biological treatment followed by membrane filtration from paper and cellulose industry effluents [19]. In this work the electrocoagulation using iron electrodes (as cathode and anode) followed by photocatalysis in $UV/TiO_2/H_2O_2$ was applied to treat effluents from a pharmaceutical and cosmetic factory. The optimized experimental conditions were obtained for each treatment.

2. Material and methods

2.1. Materials

The effluent was obtained from a pharmaceutical and cosmetic factory located in northwestern Parana State, Brazil. It was collected at various baths in an equalization tank of the last stage of the biological treatment. Titanium dioxide (TiO_2 P25, *ca.* 80% anatase and 20% rutile; BET area, *ca.* 50 $m^2\,g^{-1}$) was kindly supplied by Degussa Co. and it was used as received. All of the reagents used in this work were analytical grade and were used without any further purification.

2.2. Electrocoagulation study

The EC apparatus used in this investigation (Fig. 1) consists of a pair of iron electrodes (dimensions: 12.50 cm × 2.50 cm × 0.10 cm of thickness), area approximately 31.25 cm^2, with the electrodes distanced by 2.0 cm. Electrodes were connected to a dc power supplier of 5 A and 12 V (Hayama 1-212), operating with current density of 763 A m^{-2}.

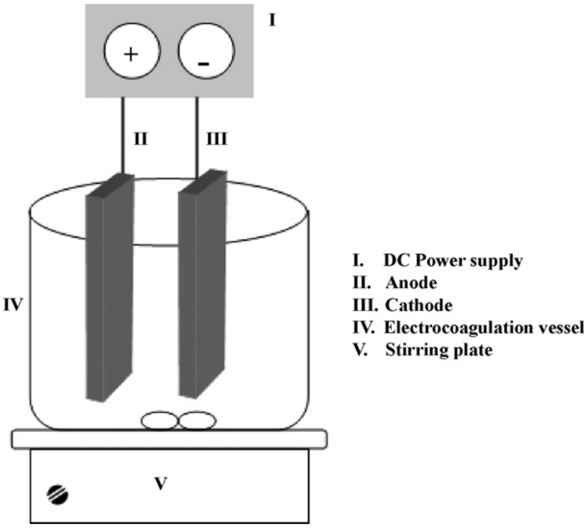

Fig. 1. Electrocoagulation apparatus diagram.

The investigation of the desirable electrocoagulation time was carried out on a batch-type system by using 500 mL of original samples (as collected from the factory) at pH of 4.0, 5.0, 6.0, 7.0 and 10.0. All pH adjustment realized in the present work was done by HCl and NaOH addition under stirring. After EC, part of the coagulated flocks settled down at the bottom of the vessel and part of the coagulated flocks flowed carried by hydrogen bubbles; these coagulated materials were separated.

2.3. Photocatalytic studies

The effluent after EC treatment executed at optimized operational conditions was submitted to the photocatalysis with UV artificial irradiation provided by 250 W low-pressure mercury lamps without bulbs (Brazilian General Electric), using a photoreactor system described as follows: 300 mL of effluent into 500 mL of borosilicate glass Erlenmeyer, in a wooden made box as a photoreactor (80 cm × 50 cm) fit with three mercury lamps on the top side 15 cm away from the samples. The light power was measured by a light meter apparatus (Newport Optical Power Meter Model 1830-C), with the wavelength set at 400 nm. All solutions were kept on the magnetic stirring instrument during irradiation to avoid TiO_2 deposition. Four fans set on the box side walls were used to reduce the heat caused by the lamps. Experiments were conducted in order to establish optimum photocatalysis conditions such as pH, time, catalysts and hydrogen peroxide concentration. The last one was employed as auxiliary catalyst. Aliquots of a photo-reacted sample taken from the photo-reactor were immediately filtered by a cellulose ester membrane filter (Millipore®, pore diameter of 0.45 μm) followed by all the analyses such as absorbance measurement and mineralization extent. For pH optimization, experiments were conducted in 0.25 g L^{-1} of TiO_2 without H_2O_2. At pre-set pH, experiments were carried out in 0.25, 0.50 and 0.75 g L^{-1} of TiO_2 without H_2O_2. After pH and TiO_2 optimization, irradiations were taken in the presence of 2, 10 and 50 mmol L^{-1} of H_2O_2. The necessary time of irradiation was investigated at optimum conditions of pH, TiO_2 and H_2O_2. The thermal effect on the sample was checked keeping the solution in the dark (erlenmeyers covered by aluminum foil) inside the photo-reactor with the lamps switched on. All experiments were conducted in triplicate and average values reported as follows.

2.4. Analytical measurements

Measurements of pH, conductivity, turbidity, dissolved oxygen, chemical oxygen demand (COD), biochemical oxygen demand (BOD), organic and ammonia nitrogen, sulfate, phosphate, nitrite, nitrate and chloride of effluents samples were performed following the Standard Methods of Examination of Water and Wastewater. A Varian UV–vis model Cary 50 spectrophotometer was used for absorbance monitoring at 254, 284, 310, 350 and 500 nm, using quartz cuvets of 10 mm optical path. These wavelengths represent several chromophore groups: 254 nm corresponds to the aliphatic region; 284 nm is related to aromatic groups such as phenols; 310 nm corresponds to conjugated aromatic rings; and 500 nm represents visible light-absorbing molecules.

3. Results and discussion

3.1. Characterization of the original sample (as collected from the factory)

The physical and chemical characteristics of the collected effluent from the pharmaceutical and cosmetic factory are shown in Table 1. The calculated biodegradability index (taken as BOD/COD ratio) is 0.11, caused by the high COD value. Such low index indicates the presence of refractory substances, probably stable organic compounds, which can hardly undergo biological degradation [20]. Reports have shown that at biodegradability index below 0.3 the sample is not adequate for biological treatment [21]. Moreover, the high COD value (1753 mg L^{-1}) implies that the TiO_2 photocatalysis of this effluent is not convenient (must be lower than 800 mg L^{-1} [16]), therefore it was proposed the EC as preliminary method.

Additionally data in Table 1 shows the presence of high quantities of nitrogen compounds and sulfate ions whose presence can cause rivers and lakes eutrophication [18]. The concentration of Cl^- ions is also high.

3.2. Electrocoagulation study of the collected effluents

3.2.1. Effect of the pH

The effect of the initial pH on the EC treatment using iron electrodes (as cathode and anode) was investigated at constant 763 A m^{-2} current density and 30 min of electrolysis (Fig. 2).

According to this data, the COD removal percentage oscillates between 78% and 82%, showing relative standard deviations ranging from 2% to 6%; the Tuckey test ($P < 0.05$) confirmed the absence of the initial pH influence on these COD results. However, the turbidity removal percentage ranges between 85% and 95%, with a relative standard deviation ranging from 3% to 5%; according to the Tuckey test ($P < 0.05$), there are no differences in those extraction efficacy percentages at initial pH 5.0–7.0 (region corresponding to the highest turbidity removal). The pH 6.0 was taken as optimum initial pH, which is employed for all subsequent EC experiments. At pH 6.0 the main Fe^{n+} species formed in solution is $Fe(OH)_2^+$ [22], which can neutralize organic substances and suspended materials (usually presenting negative charge density) [8] leading them to aggregation process. At higher pH (alkaline medium), instead of $Fe(OH)_2^+$ (prevalent species at pH 5) other species prevail, such as $Fe(OH)_3$ (prevalent species at pH 8) [23], a hydrophobic compound which can form polymeric entities [22] leading the contaminants to aggregate. At a pH higher than 10, the $Fe(OH)_4^-$ species is the main product; this species is not an effective coagulant agent. This effect is important once the experimental pH increases during the EC application (Fig. 3) mainly due to the hydroxide ions produced in the cathode, from water reduction (forming H_2 and OH^-). After 60 min the pH exceeded 10 reaching approximately 10.5 after 100 min. Despite this, it is considered that iron derivatives sustain their coagulant efficiency until pH 11 [24].

Table 1
Chemical characteristics of the original effluent as received from the factory

Parameter	Value
pH	7.3
Conductivity (mS cm^{-1})	20.0
Dissolved oxygen (mg L^{-1})	8.10
Turbidity (FTU)	25.50
COD (mg L^{-1})	1753
BOD_5 (mg L^{-1})	200
BOD_5/COD (biodegradability)	0.11
Sulfate (mg L^{-1})	893.7
Phosphate (mg L^{-1})	17.0
N-Ammoniac (mg L^{-1})	220.4
Organic nitrogen (mg L^{-1})	344.0
Nitrite (mg L^{-1})	383.9
Nitrate (mg L^{-1})	7.9
Chloride (g L^{-1})	4.2

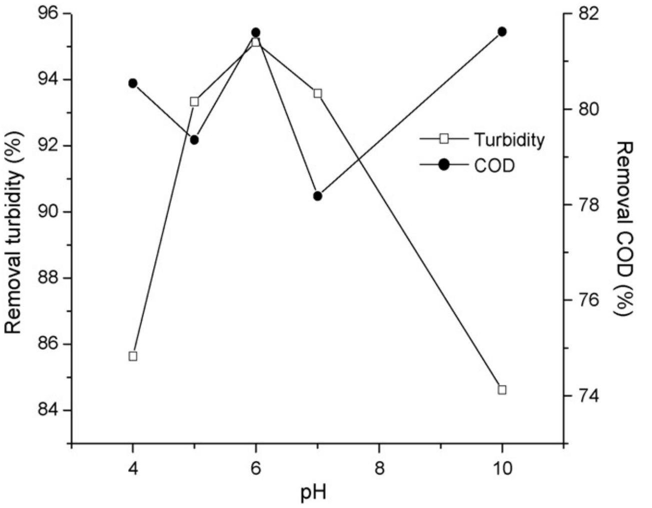

Fig. 2. COD (●) and turbidity (□) removals of EC-treated water at several initial pHs. Applied by 30 min and 1600 A m^{-2}.

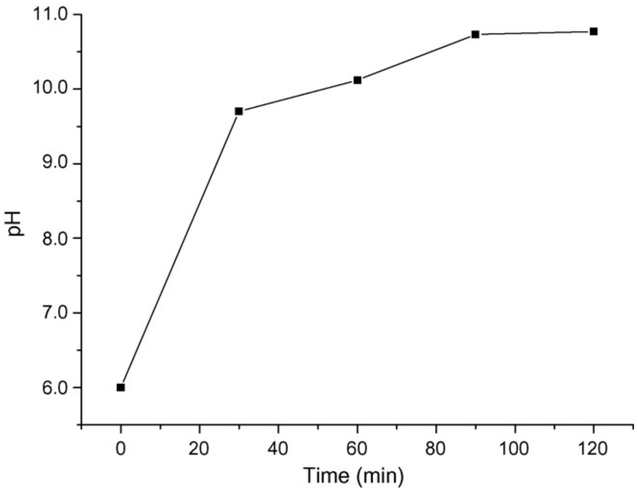

Fig. 3. pH values evolution during EC times. Initial pH 6.0.

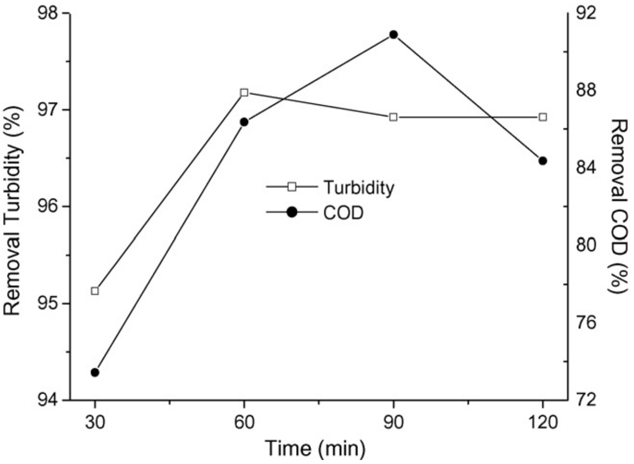

Fig. 4. COD (●) and turbidity (□) removals of water during EC. Initial pH 6.0.

3.2.2. *Study of the electrocoagulation time*

The efficiency of contaminant reduction depends on Fe(III) production by the anode [8] so that high electrolysis duration would cause higher production of these iron hydroxides which are in turn responsible for the coagulation process [25]. The reduction of the turbidity and COD values was compared during the EC at initial pH 6.0. According to Fig. 4 and the Tuckey test ($P < 0.05$), the best COD reduction is observed at 90 min of the EC (from original sample with 1750 to 160 mg L^{-1}). On the other hand, the optimum efficiency for turbidity extraction is reached at about 60 min; no efficacy changes are observed (Tuckey test) as the EC duration is increased. After ~90 min of EC the effectiveness of organic matters removal underwent a small decrease, which suggests that the coagulated flocks can be partially re-dissolved; this effect maybe resulted from pH elevation during the EC (Fig. 3).

The analysis of nitrogen compounds is an interesting parameter on the EC efficiency because the effluent contains high level of protein residues as indicated in Table 1. During the EC, the quantity of nitrogen species decreased (Table 2).

The adsorption of colloids and organic materials by the generated coagulant probably drag ions and other soluble substances as the EC is performed. These results illustrate the efficiency of the process.

Additionally, it is necessary to emphasize that the original effluent from the factory presents high ions content. It is reported that the NaCl increases the EC efficiency because of the enhancement of the solution conductivity, providing a greater level of contaminants extraction while the applied voltage cell is reduced, saving electric energy [26]. Even during the EC the conductivity increased (mainly promoted by hydroxide ions electro-generated at the cathode as mentioned previously), which is convenient for the process. This effect is mainly observed after 90 min of EC.

Table 2
Removal percentage of nitrogen species during the EC employing iron electrodes at initial pH 6.0

Time (min)	NO_2^-	NO_3^-	Norg	N_{NH_3}
30	75 a	10 a	0 a	20 a
60	99 b	36 b	45 b	31 b
90	100 b	58 c	24 c	55 c
120	100 b	69 d	24 d	45 d

Different letters in the same column imply values statistically different ($P < 0.05$ by Tuckey test). $n = 3$ samples analyzed.

3.2.3. *EC current efficiency*

The efficacy of the current is related to the electrode lifetime; consequently, the mass consume of the anode (iron) would give us information about such efficiency [26]. For the treatment in optimized conditions, initial pH 6.0, 90 min and 5 A current, the efficiency of current is calculated by Eqs. (5) and (6).

$$m = \frac{I \times t \times M}{Z \times F} \qquad (5)$$

where I is the current (A), t is the time of EC, M is the molar mass (g mol^{-1}), F is the Faraday constant (96485 C mol^{-1}), Z represents the number of electrons whose value is 3 (present case) and the losing mass ($m_{theoretical}$), which is theoretically estimated by Eq. (5). The empirical value ($m_{experimental}$) was obtained according to the difference between the electrode mass prior to and after the EC process. Eq. (6) provides information about the process efficacy (ρ).

$$\rho = \frac{m_{experimental}}{m_{theoretical}} \times 100 \qquad (6)$$

For the effluent employed in this study at optimized conditions (iron electrodes, initial pH 6.0, 90 min and 763 A m^{-2}) we obtained current efficiency of 92%, which is a good result. This high ρ value could be increased employing pure iron metal as electrode.

3.3. *Photocatalysis studies*

The light source power inside the photo-reactor (3× 250 W, mercury lamps) was measured with a light meter probe placed at the same position of the sample, resulting in irradiance of approximately 8.9 mW cm^{-2}.

3.3.1. *Effect of the pH on the UV/TiO_2 system*

For electrocoagulated effluents (COD of 160 mg L^{-1}) at the optimized operational conditions, the UV/TiO_2 photocatalysis evaluated at pH 3.0, 7.0, and 10.0 showed that the best pH for absorbance intensity diminution occurs in acid and neutral media. After 4 h of irradiation, for example, absorbance reduction at 254 nm using pH 3.0 was 75%, while at pH 7.0, 63% (percentages calculated from the electrocoagulated effluent). For the same samples (EC/photocatalysis), quantities of nitrite and nitrate at pH 7.0 were 2.56 ± 0.02 mg L^{-1} (original sample: 383.9 mg L^{-1}) and 10.06 ± 0.58 mg L^{-1} (original sample: 7.9 mg L^{-1}), respectively. At pH 3.0, it was not possible to detect nitrite (under detection limit), while nitrate was 12.40 ± 0.01 mg L^{-1}. All these results suggest that at pH 3.0, the strong photo-oxidative environment causes nitrite oxidation to nitrate ions. It seems that the mineralization at pH 3.0 would be more efficient than at other pH. Significant changes in pH samples after photocatalysis were not observed.

The pollutants adsorption at the TiO_2 surface is an important step in photocatalysis [27]. It is well known that the TiO_2 charges are dependent on the pH, making such variable control crucial to the process. At alkaline medium, the TiO_2 is negatively charged, allowing the catalytic photodegradation of the cationic pollutants. However, at low pH values, TiO_2 is positively charged whereas the negatively charged pollutants can undergo easier degradation. The treatment of the investigated wastewater at acid medium was favored because these effluents present particles with negative charge density due to the anions adsorption in the suspended materials and the presence of oxygen, carboxylate and other negatively charged groups in these organic molecules. The point zero charge of the TiO_2 occurs near pH 6.5 [11].

After the catalyst photo-activation, generating hydroxyl radicals as the main active species (via Eqs. (2)–(4)), the undesirable organic pollutant present on the catalyst surface is degraded.

Table 3
Effect of TiO_2 on COD for samples electrocoagulated (initial pH 6.0 and 90 min) and photocatalyzed (pH 3.0 and 4 h of irradiation)

TiO_2 ($g\,L^{-1}$)	COD reduction (%) compared to original effluent
0.0	10
0.25	98
0.50	99
0.75	97

Table 4
Values of rate constants (k) and kinetic correlation coefficient (CC) for photocatalysis monitored at different wavelengths and several H_2O_2 concentrations

[H_2O_2] ($mmol\,L^{-1}$)	254 nm	284 nm	310 nm	350 nm
0				
k (h^{-1})	0.35	0.45	0.53	0.60
CC	0.998	0.998	0.996	0.993
2				
k (h^{-1})	0.41	0.53	0.66	0.91
CC	0.987	0.977	0.969	0.971
10				
k (h^{-1})	0.54	0.70	0.80	1.25
CC	0.996	0.989	0.990	0.999
50				
k (h^{-1})	–	0.71	0.86	–
CC	–	0.988	0.992	–

$0.25\,g\,L^{-1}$ of TiO_2, pH 3.0 and 4 h of irradiation.

3.3.2. Study of catalyst concentration: UV/TiO_2 system

Experiments performed using 0.0, 0.25, 0.50 and $0.75\,g\,L^{-1}$ of TiO_2 as catalyst showed that TiO_2 presence is necessary to obtain high level of decontamination. Data of COD at Table 3 pointed out that $0.25–0.75\,g\,L^{-1}$ permits approximately 98% of COD reduction (compared to collected effluents), whereas the efficacy without catalyst (direct UV application) is low. For the obtained absorbance decrease, the data at $0.25\,g\,L^{-1}$ exhibit slightly lower effect than that at $0.50\,g\,L^{-1}$ of TiO_2, respectively: 80% and 85% at 254 nm; 87% and 91% at 284 nm; 91% and 93% at 310 nm.

The lack of higher efficiency using more than $0.25\,g\,L^{-1}$ of TiO_2 can be explained: as the catalyst concentration increases, the photodegradation should increase because of the enhancement of the available photoactive sites. However, highest quantities of the solid catalyst can make light penetration more difficult through this heterogeneous solution, causing a light scattering phenomenon, which diminishes the photo-excitation [27].

3.3.3. Study of hydrogen peroxide and photocatalysis duration: UV/TiO_2/H_2O_2 system

The effect of H_2O_2 concentration, an auxiliary oxidant catalyst, on the TiO_2 photocatalyzed system (pH 3.0 and $0.25\,g\,L^{-1}$ of TiO_2) was studied in the range of $0–50\,mmol\,L^{-1}$ (results are shown in Fig. 5). It was noticed, for all the monitored wavelengths, that, as H_2O_2 concentrations increase, the percentage of removal absorbance undergoes a small increase, reaching similar values at 10 and $50\,mmol\,L^{-1}$ proved by Tuckey test ($P < 0.05$), Fig. 5a. The TiO_2 photocatalysis, even without H_2O_2, shows high efficacy, although it is lower than in the presence of peroxide (absorbance monitored at 350 nm, approximately 88% against 98%); besides it, the velocity of the photo-treatment adding this auxiliary oxidant is faster (see kinetic studies). For the subsequent studies, $10\,mmol\,L^{-1}$ was adopted, having considered the smaller environmental impact caused by both lower concentrations of chemicals and costs. After 3 h of photocatalysis, H_2O_2 was completely consumed, so that all COD analysis performed was not affected by peroxide presence.

For studies on irradiation time on the effluent quality (after combined, EC + photocatalysis), according to data in Fig. 5b, the absorbance in all UV wavelengths reach a maximum reduction after 5 h of illumination. For the visible region (500 nm), the absorbance was not monitored, because after the EC process, such intensity was near zero.

3.3.4. The kinetics of photocatalysis process: UV/TiO_2/H_2O_2 system

Samples that have been electrocoagulated and submitted to photocatalysis showed absorbance intensity decrease as illumination was taking place. Samples submitted to UV/TiO_2 at pH 3.0, 4 h and various hydrogen peroxide concentrations were followed at 254, 284, 310 and 350 nm. For the resulted data, the kinetic treatment of first-order law was applied successfully (see Table 4).

As it can be seen, the observed rate constant (k) obeys the following order: $k_{350\,nm} > k_{310\,nm} > k_{284\,nm} > k_{254\,nm}$. The oxidation process preferentially occurs at the highest electronic density positions, like the conjugated aromatic groups that absorb at 350 nm, for example.

On the other hand, although the experiments carried out with or without hydrogen peroxide have not showed significant difference on the total absorbance decrease, the rate constant was magnified by twofold in $10\,mmol\,L^{-1}$ of these compound. The H_2O_2 can prevent the recombination of e_{CB}^-/h_{VB}^+ pair by electron acceptance [28] and can react with superoxide radicals [29]; both reactions

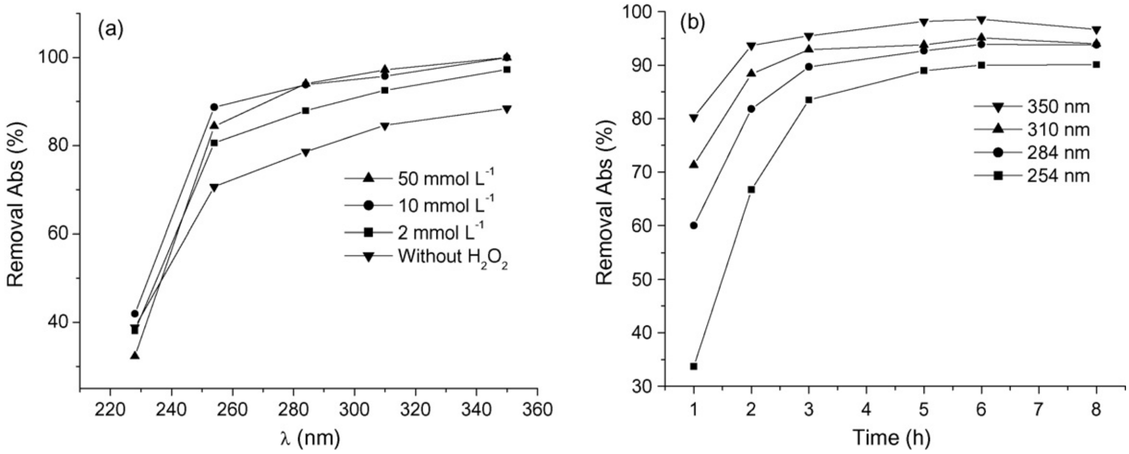

Fig. 5. Absorbance variation of the effluent photocatalyzed at: (a) several H_2O_2 concentrations monitored at various wavelengths (4 h-irradiation) and (b) monitored at several wavelengths analyzed at various irradiation times ($10\,mmol\,L^{-1}$ H_2O_2). All experiments were performed at pH 3.0 and $0.25\,g\,L^{-1}$ of TiO_2.

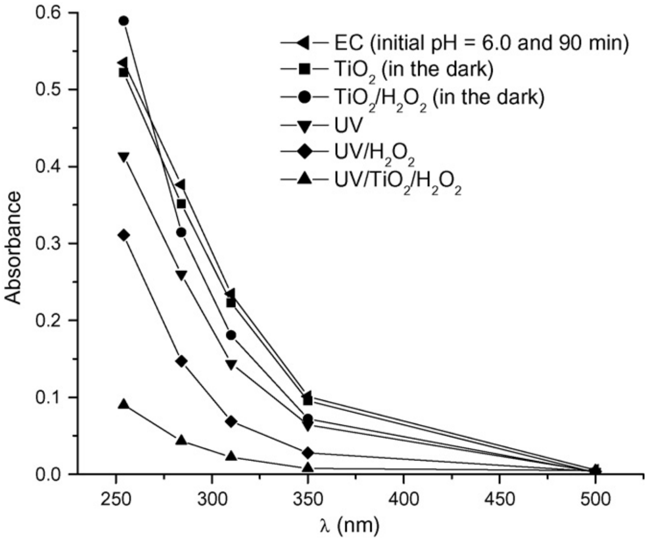

Fig. 6. Absorbance behavior at several wavelengths for samples submitted to different methods.

increase the amount of $^{\bullet}OH$ radicals. This result shows the importance of the hydrogen peroxide in the velocity of this process.

3.3.5. Systems comparison

Fig. 6 shows the results obtained in the treatment of effluents from the pharmaceutical and cosmetic industry (aqueous peptones residues) evaluated according to absorbance changes using optimized experimental conditions for each system investigated. The experiments carried out on the covered reaction vessel by aluminum foil (sample in the dark, 55 °C—the averaged temperature in the photo-reactor), allow us to understand the thermal effect on the pollutants (TiO_2 without and with H_2O_2). Furthermore, there is a comparison among the EC results with different UV systems: only UV; UV/H_2O_2 and UV/TiO_2/H_2O_2. The optimized conditions are: for photocatalysis pH 3.0, 4 h of illumination, 0.25 mg L^{-1} of TiO_2 and 10 mmol L^{-1} of H_2O_2. All photolyzed samples were previously submitted to EC (initial pH 6.0, 90 min and 763 A m^{-2} using iron electrodes).

By comparison (Fig. 6), the sample kept in TiO_2 in the dark showed that the thermal reaction after 4 h is almost insignificant and even samples protected from UV light in TiO_2 and H_2O_2 presence shows small degradation effect. The level of the degradation increases in the following order of the systems: EC < TiO_2 (in the dark) < TiO_2/H_2O_2 (in the dark) < UV < UV/H_2O_2 < UV/TiO_2/H_2O_2. Similar performance we obtained in the wastewater treatment of cellulose and paper factories using these methods [30]. As it is shown, the photolysis with TiO_2, particularly with hydrogen peroxide presence, is the most efficient tested clarification method, however a previous treatment should be performed because of the high COD value of the collected wastewater. For the chosen EC method, the iron electrodes are suitable because of the high efficiency and low costs (specially in Brazil). The oxygen (O_2) presence in the photocatalysis, increasing the hydroxyl radical formation by electron (e_{CB}^-) acceptance, permits to use this process in environmental conditions, which is convenient for industrial scale.

All these results and the obtained COD values, 1753 mg L^{-1} for original sample, 160 mg L^{-1} for electrocoagulated (91% of reduction), and 50 mg L^{-1} for EC/photocatalyzed effluents (97% of reduction), pointed out that the combined treatment stresses the water purification.

4. Conclusions

The results showed that the combination of electrocoagulation followed by catalyzed photo-oxidation improves the quality of the effluent with peptides residues, such as peptone fragments. The electrocoagulation removed the majority of the colloidal organic substances and suspended materials; however, refractory compounds still remained in this water effluent. In the sequence, by employing the heterogeneous photocatalysis, these refractory compounds were degraded up to mineralization (or at least to small and simple molecules). Such combined process of electrocoagulation and photocatalysis proved to be efficient and presents potential application in industrial scale.

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