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Polishing of Water Treated by a Biological Process with Heterogeneous Photocatalysis

G. Giovanni, José Pedro S. Valente, Pedro M. Padilha, Sônia M.A. Jorge,
Margarida J. Saeki and Ariovaldo O. Florentino
Department of Chemistry and Biochemistry-IB/UNESP,
C. Postal 510, 18618-000 Botucatu, SP, Brazil

Abstract: Effluent from a vegetal extraction plant situated in the region of Botucatu, state of São Paulo, Brazil was treated by combining a biological process and heterogeneous photocatalysis. The biologically pretreated effluent was polished by heterogeneous photocatalysis on a laboratory scale, using TiO_2 in suspension as catalyst. The heterogeneous photocatalysis experiments were carried out with natural pH (~ 7.5) and pH adjusted to 3 and 4. An analysis was made to ascertain how the addition of potassium persulfate inhibited the recombination of the e^-/h^+ pair and incremented the generation of hydroxyl radicals. Coagulation-flocculation to remove the catalyst in suspension reduced the effluent's initial turbidity of more than 4000 NTU to 2 NTU in 30 min. The photocatalysis reduced the sample's initial TOC (Total Organic Carbon) from about 40 mg L^{-1} (in O_2 demand) to approximately 3 mg L^{-1} in 180 min, rapidly removing the odors from the sample and disinfecting the water.

Key words: Heterogeneous photocatalysis, vegetal extraction, coagulation-flocculation, TiO_2 , combined process, biological treatment

INTRODUCTION

Wastewaters produced by vegetal extraction plants for pharmaceutical purposes constitute a particular type of effluent, comprising wastes from raw materials and from extraction processes. It is known that active principles are extracted by pressing the vegetable, followed by the use of solvents. The type of solvent depends on the vegetable and the desired active principle. The effluent is a mixture produced by several processes, including the water used to wash equipment, bathrooms, facilities, etc. In addition to these residues, the wastes from this type of plant usually contain biologically active material that can contaminate wastewater originating from the washing and cleaning of mixing tanks, of manufacturing and weighing areas and of machinery in general (Braile and Cavalcanti, 1993).

After separation of the fibers, the biological treatment of wastewater from this type of plant is relatively efficient, allowing for the reduction of Total Organic Carbon (TOC) and thus satisfying environmental regulations. However, the treated water may contain persistent organic compounds and the total quality attained does not allow for reuse of the water. The treatment of industrial wastewater aiming at its reuse by the plant itself or for irrigation, provided it meets the prerequisites of quality, reduces the contamination of water resources and the

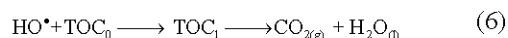
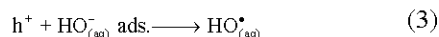
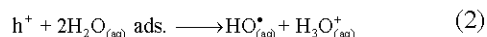
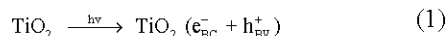
consumption of water, a resource which tends to become increasingly scarce and expensive.

Heterogeneous catalysis has been pointed out as an Advanced Oxidation Process (AOP) for degrading persistent organic compounds and eliminating microorganisms that are present in water. Another advantage of this process is that it is a sustainable technology because it uses solar energy and mineralizes the contaminants, be they simple or complex molecules (Valente *et al.*, 2006; Augugliaro *et al.*, 2006; Araújo *et al.*, 2006; Cristante *et al.*, 2007). Heterogeneous photocatalysis, in turn, does not suffice to treat concentrated effluent prior to its biological treatment. This is the reason for the importance of combining processes, using biological treatment to reduce the concentration of organic matter, followed by photocatalysis to degrade the organics most resistant to biological treatment, thus attaining the proper quality standard for the water's reuse.

The mechanism of heterogeneous photocatalysis is based on the activation of a semiconductor, usually TiO_2 , by sunlight or artificial light (UV radiation) (Quorzal *et al.*, 2006). The interaction of light with the semiconductor excites electrons in the valence band to the conduction band. This excitation produces holes (h^+) in the valence band, that act as oxidizing sites, while the photogenerated electrons (e^-) combine with the dissolved oxygen, reducing the recombination of the electron-hole pair

(h^+/e^-) (Augugliaro *et al.*, 2006; Rajeshwar *et al.*, 2008; Malato *et al.*, 2009; Wallois *et al.*, 1996; Minero *et al.*, 1996; Khuanmar *et al.*, 2007). In addition, the oxygen reduced by electrons of the conduction band initially forms the superoxide radical ion ($O_2^{\cdot-}$) and thereafter peroxides (Augugliaro *et al.*, 2006). The latter can react with photogenerated electrons (or superoxide radical ions), forming HO^{\cdot} radicals (Augugliaro *et al.*, 2006). By this mechanism, the water adsorbed in the semiconductor acts in the catalytic process and both molecular and dissociated water (OH^- groups bound to the TiO_2 surface) reacts with the photogenerated h^+ holes (Eq. 1 to 3) to form highly oxidizing HO^{\cdot} hydroxyl radicals ($E^{\circ} = 2.8$ V) that degrade the organic matter into carbon dioxide (CO_2 gas) and water (H_2O).

Thus, the efficiency of the photocatalytic process depends on the competition between the formation of hydroxyl radicals (Eq. 2 and 3) and the recombination of the electron-hole pair, which results in the release of heat (Eq. 4).



In this scheme, TOC_0 indicates the initial organic carbon content and TOC_1 the carbon content of possible intermediary chemical species.

Most studies use the TiO_2 semiconductor as a photocatalyst due to its nontoxicity, photostability and chemical stability within a wide range of pH (Araújo *et al.*, 2006; Cristante *et al.*, 2007; Rajeshwar *et al.*, 2008; Malato *et al.*, 2009). The addition of small amounts of potassium persulfate to the sample containing the TiO_2 , when exposed to UV light, accelerates the degradation by inhibiting the recombination and increasing the concentration of HO^{\cdot} radicals during the photodegradation (Grätzel *et al.*, 1990). It should also be noted that hydroxyl radicals are bactericidal, killing the bacteria that damage cell tissue or even mineralizing the bacteria (Dunlop *et al.*, 2002; Robert and Malato, 2002; Guimarães *et al.*, 2001; Huang *et al.*, 2000).

The most efficient procedure for treating contaminated waters uses suspensions of titanium dioxide (TiO_2). However, the recovery or separation of this oxide makes the large scale use of this technique difficult. To overcome this difficulty, many researchers have attempted to immobilize the TiO_2 on supports, in the form of films, but have encountered the obstacle of reduced process efficiency due to the reduction of mass transport to the surface of the catalyst. The separation of TiO_2 particles from the suspension by conventional filtration is slow, expensive and inefficient, so studies are needed to devise improved conditions of sedimentation to enhance the separation performance.

In this study, we studied the combination of the biological process and heterogeneous photocatalysis to polish biologically pretreated wastewater, enabling it to be reused. The semi-treated wastewater utilized came from a vegetal extraction plant (for pharmaceutical purposes) located in the municipality of Botucatu, SP, Brazil. The photocatalyst used was Degussa's TiO_2 P25 and the photodegradation experiments were carried out as a function of pH and the addition of potassium persulfate as an aid for the degradation of organic matter. A study was also made to increase the efficiency of the separation of TiO_2 from the suspension by coagulation-flocculation.

MATERIALS AND METHODS

Physicochemical determinations: The physicochemical parameters were determined according to the Standard Methods for the Examination of Water and Wastewater (Eaton *et al.*, 1995).

Heterogeneous photocatalysis: The photodegradation experiments were carried out in a 12 cm tall cylindrical borosilicate glass photoreactor with 11 cm external diameter and 7 cm internal diameter, under external illumination. A cylindrical reactor was chosen because the lamps were on the outside, simulating a reactor illuminated by sunlight. Varying the distance of the lamps enabled us to use a flow of artificial radiation similar to sunlight on a sunny day (measured with a Solar Light Co. 2100 radiometer). According to Galvez *et al.* (2001), with this type of reactor one can obtain a maximum velocity of photodegradation with a low concentration of TiO_2 . Two hundred and fifty milliliter of water semi treated by the biological process were used, with natural pH of 7.5-7.9 or adjusted to 4.0 with nitric acid. TiO_2 (Degussa P25, surface area of 51.7 ± 0.2 m² g⁻¹), precalcined at 400°C for 24 h to eliminate any possible trace of adsorbed organic compounds, was then added in sufficient quantity to obtain a concentration of 0.5 g L⁻¹. The resulting

suspension was kept under stirring and irradiated with four 15 W (5.11 mW cm^{-2}) lamps with a peak wavelength of 365 nm. At given intervals, 10 mL aliquots were removed from the reactor and filtered through $0.22 \mu\text{m}$ pore membranes (Millipore), after which the remaining TOC concentration was determined in a TOC-V_{CPH} Shimadzu analyzer.

Up to a given limit, the initial velocity of a photocatalytic reaction is directly proportional to the mass of the catalyst used. This limit corresponds to the concentration at which all the particles of the catalyst are exposed to light. A concentration of 0.5 g L^{-1} normally meets this requirement. Higher concentrations produce an occultation effect, i.e., some of the particles of the catalyst that are blocked from light remain hidden. This limit also depends on the type of organic substrate and the reactor's diameter and geometry (Cardona, 2001). Mills and Wang (1998) recommend a concentration of 0.5 g L^{-1} as the standard for the heterogeneous photocatalysis of aqueous samples. This concentration was therefore used.

Addition of potassium persulfate as an aid for photocatalysis: An evaluation was made of the effect of adding potassium persulfate ($\text{K}_2\text{S}_2\text{O}_8$) to inhibit recombination of the h^+/e^- pair and increment hydroxyl radicals in order to hasten photodegradation. The concentrations added varied from 0.1 to 0.3 g L^{-1} .

Coagulation-flocculation tests of the TiO_2 of the suspension: The wastewater treated by heterogeneous photocatalysis was subjected to coagulation-flocculation to separate the TiO_2 from the suspension. After the study, the coagulation-flocculation procedure was carried out by adding 0.05 g L^{-1} of aluminum sulfate ($\text{Al}_2(\text{SO}_4)_3 \cdot 10\text{-}14\text{H}_2\text{O}$) to a jar test (Milan JT 101) and stirring at 120 rpm for 1 min, 60 rpm for 9 min, 25 rpm for 4 min and 10 rpm for 2 min. Finally, the stirrer was turned off and the suspension allowed to rest and to settle for 30 min. The turbidity of the supernatant was then determined using a HACH 2100P turbidimeter.

RESULTS AND DISCUSSION

Table 1 shows the average results of the physicochemical parameters determined in the effluent after the biological treatment. The high electrical conductivity indicated a high concentration of ions resulting from degradation products of the treated wastewater. The high alkalinity at pH 7.55 was likely due to a high concentration of bicarbonate, a degradation product of organic matter and a possible inhibitor of heterogeneous photocatalysis. The hardness revealed the

Table 1: Average results of the physicochemical determinations obtained from three samples collected on different days at the exit of the stabilization pond

Parameters	Results
TOC (O_2 demand)	$33.7 \text{ (mg L}^{-1}\text{)}$
Sulfate	$21.0 \text{ (mg L}^{-1}\text{)}$
Phosphate (P)	$<0.05 \text{ (mg L}^{-1}\text{)}$
Chloride	$30.6 \text{ (mg L}^{-1}\text{)}$
Total hardness (CaCO_3)	$280.0 \text{ (mg L}^{-1}\text{)}$
Alkalinity (CaCO_3)	$267.7 \text{ (mg L}^{-1}\text{)}$
Electric conductivity	$535.6 \text{ (}\mu\text{S cm}^{-1}\text{)}$
Turbidity	5.3 (NTU)
pH	7.55

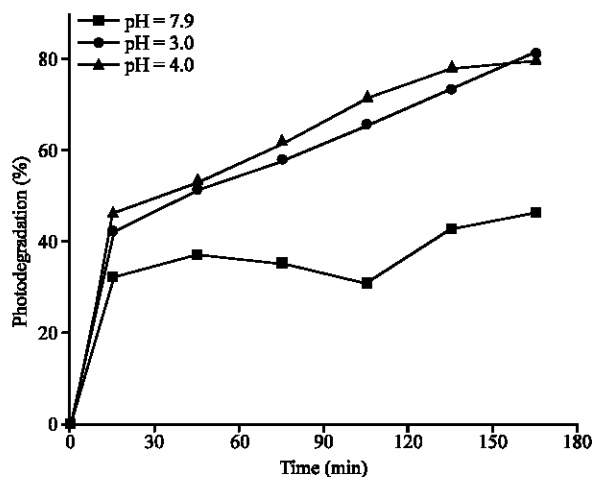


Fig. 1: Effect of pH on the photodegradation of organic matter remaining after the biological treatment with a TOC of 43 mg L^{-1} in O_2

significant presence of divalent ions. The concentration of organic matter indicated by the TOC was still too high to allow for the water's reuse.

Figure 1 shows the photodegradation profile of organic matter in the effluent from the biological treatment as a function of the radiation time at different pHs, in a sample with an initial TOC of 43 mg L^{-1} (in oxygen demand). It was found that after 15 min of radiation at pH levels of 3.0 and 4.0, 45% of the organic matter was degraded, compared with 30% of the sample at pH 7.9, without adjustment, before the addition of TiO_2 . After 3 h of radiation there was an 80% reduction in the organic load when working within a pH range of 3 to 4.

A similar behavior was observed when the sample containing a TOC of 27 mg L^{-1} was used, as indicated in Fig. 2. It should be noted, however, that although the profiles of the degradation curves are similar, the degradation rate is lower. This experiment required 75 min to degrade the same 45% as in the experiment with the more concentrated sample. At a pH of close to 7.6 after

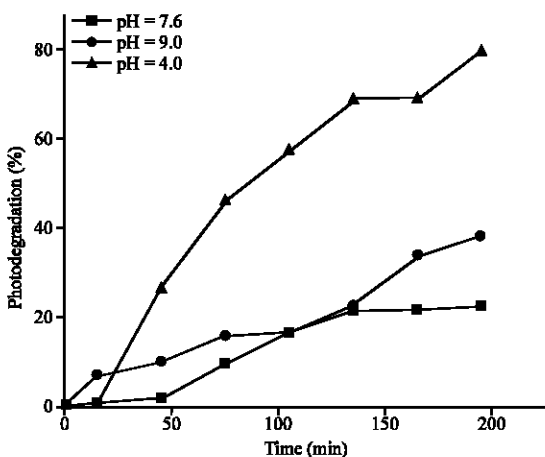


Fig. 2: Effect of pH on the photodegradation of organic matter remaining after the biological treatment with a TOC of 27 mg L⁻¹ in O₂

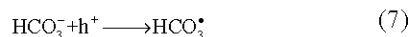
Table 2: Percentage of photodegradation after 3 h of photocatalysis at different pHs and initial TOCs in samples collected on different days at the exit of the stabilization pond

pH	Initial TOC (mg L ⁻¹ O ₂)		
	27	31	43
4.0	85%	67%	83%
7.5-7.6	73%	32%	53%

3 h, only 20% of the organic load was degraded, while at pH of 4.0, photodegradation was higher than 80%.

Table 2 shows the percentage of degradation after 3 h of radiation as a function of the pH for samples with different initial TOCs. Note that photodegradation is more efficient at a pH of 4.0 and that slower at pH levels close to 7.5.

The low performance at basic pH is probably due to the alkalinity of the bicarbonates in the sample. Bicarbonate ions compete with the organic substrate for h⁺ oxidizing sites, as indicated by Eq. 7, reducing the efficiency of the photocatalytic process (Bekbölet *et al.*, 1996).



In acid pH, bicarbonate is decomposed into CO₂ and the h⁺ are more readily available to oxidize the water and hydroxyl groups at the surface of the TiO₂, forming OH radicals, or even to oxidize organic matter directly, according to Eq. 2, 3 and 5 (Daneshvar *et al.*, 2003).

Moreover, acid pH levels favor the formation of superficial OH[•] groups via reactions with photogenerated electrons (e_{cb}⁻) in the conduction band. The mechanism that increments the formation of this radical in acid medium can be illustrated by the following set of reactions:

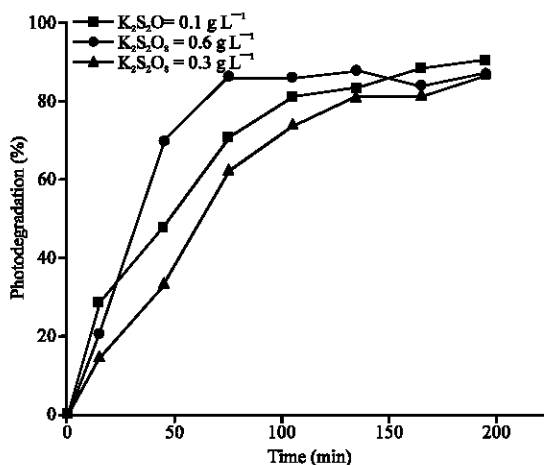
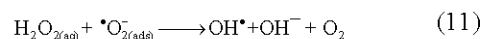
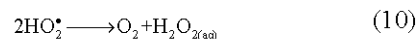
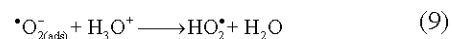
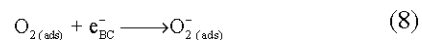


Fig. 3: Effect of the addition of persulfate on the sample treated biologically at pH 4.0 and TOC of 27 mg L⁻¹ in O₂



The samples under study presented an initial alkalinity of about 270 mg CaCO₃ L⁻¹ and pH of around 7.5. At the end of the photocatalysis the pH increased to 8.5. When the pH was adjusted to around 4.0, the bicarbonate ions decomposed into CO₂ and this was naturally reflected in an increase in the catalyst's performance.

Figure 3 shows the effect of the addition of potassium persulfate to the solution. Note the 75% reduction in the organic load after the first 60 min of radiation, when 0.6 g L⁻¹ of potassium persulfate was added. Note, also, that more than 90% of the organic load can be degraded after 3 h of reaction, even when only 0.1 g L⁻¹ of potassium persulfate is added to the suspension. One should keep in mind that although this value is only 5% higher than the best result obtained without the addition of persulfate, it is nonetheless significant because it indicates the process is more effective in degrading the most persistent species, which are the ones that resist 3 h of radiation in the samples with pH 4.0

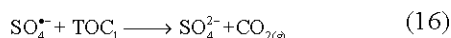
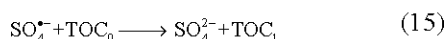
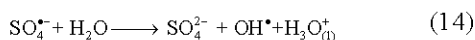
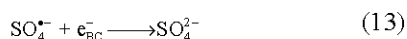
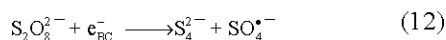
This improved performance can be explained by the mechanism of action of potassium persulfate (K₂S₂O₈) in acid medium (Malato *et al.*, 2000). Initially, the persulfate is reduced by the photogenerated electron, forming the

Table 3: Turbidity after coagulation-flocculation of the suspension with the catalyst: pH 4.0, aluminum sulfate 0.2 g L⁻¹, TiO₂ 0.5 g L⁻¹ and initial turbidity of >4000 NTU

Time (min)	Turbidity (NTU)-sample of industrial effluent	
	Without aluminum	With aluminum
1	222	220
15	94.0	5.0
30	30.0	2.0

SO₄^{•-} radical (Eq. 12) and inhibiting the recombination of the e⁻/h⁺ pair. The SO₄^{•-} is reduced by the water, increasing the formation of HO[•] radicals (Eq. 14), or directly oxidizing the organic matter (Eq. 1 and 16). This radical combines with the water, forming the HO[•] radical with greater oxidizing potential and favoring the oxidation of the organic matter contained in the reactional medium. The fact that the addition of persulfate lowered the pH of the sample from 4.0 to 2.9 further favored the decomposition of the bicarbonate ions into CO₂.

These results are in agreement with those reported by other researchers (Rajeshwar *et al.*, 2008; Malato *et al.*, 2000; Pelizzetti, 1995), who studied the effect of the addition of persulfate on the photodegradation of phenol:



The results of this study indicate that the addition of persulfate, even in minor quantities, favors the degradation rate of the most persistent pollutants remaining in pretreated effluents and even of intermediaries formed during photocatalysis.

Coagulation-flocculation of the suspension used in the heterogeneous photocatalysis: Table 3 shows the turbidity values after polishing of the water by photocatalysis. In this study, the sedimentation time of material in suspension the sample containing added aluminum sulfate was 30 min. The final turbidity of the treated effluent was 2 NTU, i.e., lower than that of the biologically treated effluent, which was 5.3 NTU (Table 1).

Table 4: Mean results of the physicochemical determinations of three samples polished by heterogeneous photocatalysis after coagulation-flocculation, for separation of the catalyst

Parameters	Results
TOC (in O ₂)	2.5 (mg L ⁻¹)
Sulfate	18.0 (mg L ⁻¹)
Phosphate (P)	<0.05 (mg L ⁻¹)
Chloride	64.0 (mg L ⁻¹)
Total Hardness (CaCO ₃)	288.0 (mg L ⁻¹)
Alkalinity (CaCO ₃)	7.9 (mg L ⁻¹)
Electrical conductivity	968.5 (μS cm ⁻¹)
Turbidity	2.0 (NTU)

The coagulation-flocculation process for separating material in suspension was about 70-fold faster than that of vacuum filtration (pressure of about 650 mmHg) through a filtration membrane (47 mm diameter and 0.22 μm pore size) of one liter of the suspension. The material that settled by coagulation-flocculation was separated from the water by siphoning.

Table 4 shows the results of the physicochemical determinations of the water polished for 3 h by heterogeneous photocatalysis, followed by coagulation-flocculation with aluminum sulfate.

The final turbidity of the effluent treated by photocatalysis and coagulation-flocculation was 2.0 NTU, which is lower than that of water supplied by public water networks (approximately 3.0 NTU). The concentrations of sulfate, phosphate and total hardness remained practically unchanged. The chloride concentration doubled, indicating the possible existence of an organochlorine compound in the effluent prior to the photocatalytic treatment. The bicarbonate alkalinity declined sharply due to the destruction of the bicarbonate at low pH levels, while the electrical conductivity increased due to mineralization of the sample.

CONCLUSIONS

Heterogeneous photocatalysis is an efficient process for reducing the concentration of organic compounds in wastewaters from vegetal extraction processes after pretreatment by a biological process. The efficiency of TOC removal from the effluent studied here was considerable in 3 h, as was the removal of odors and disinfection of the water. The photodegradation of organic matter was highest after 3 h at pH 4.0, with or without the addition of 0.1 g L⁻¹ of potassium persulfate. The removal of TiO₂ from the suspension through the coagulation-flocculation process indicated, in principle, the feasibility of separation in large volumes of water. In a 30 min period, the semi-treated water with a turbidity level of 5 NTU, which rose to >4000 NTU in response to the introduction of TiO₂, was reduced to 2 NTU after the

catalyst was separated by coagulation-flocculation. In this type of effluent, the combination of heterogeneous photocatalysis and biological treatment allows for the reuse of the water, provided the official regulations are followed.

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