

Sequential Use of Bentonites and Solar Photocatalysis to Treat Winery Wastewater

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The sequential use of low-cost adsorbent bentonites and solar photocatalysis to treat winery wastewater has been studied. Three commercial sodium-bentonites (MB-M, MB-G, and MB-P) and one calcium-bentonite (Bengel) were characterized and used in this study. These clay materials were useful to totally remove turbidity (90–100%) and, to a lesser extent, color, polyphenols (PPh), and soluble chemical oxygen demand (COD_s) from winery wastewater. Both surface area and cation exchange capacity (CEC) of bentonite had a positive impact on treatment efficiency. The effect of pH on turbidity removal by bentonites was studied in the 3.5–12 pH range. The bentonites were capable of greatly removing turbidity from winery wastewater at pH 3.5–5.5, but removal efficiency decreased with pH increase beyond this range. Settling characteristics (i.e., sludge volume index (SVI) and settling rate) of bentonites were also studied. Best settling properties were observed for bentonite doses around 0.5 g/L. The reuse of bentonite for winery wastewater treatment was found not to be advisable as the turbidity and PPh removal efficiencies decreased with successive uses. The resulting wastewater after bentonite treatment was exposed to solar radiation at oxic conditions in the presence of Fe(III) and Fe(III)/H₂O₂ catalysts. Significant reductions of COD, total organic carbon (TOC), and PPh were achieved by these solar photocatalytic processes.

KEYWORDS: Bentonite; environmental remediation; solar photocatalysis; winery wastewater

INTRODUCTION

Production of wines is a commercial activity with a consolidated marketplace that greatly contributes to the economical development of many regions in the world (1). However, a serious environmental drawback of winemaking is the seasonal generation of large volumes of wastewater from the processing and cleaning operations in wineries. As an average figure, the amount of wastewater produced in a winery is about 1.2 times greater than that of wine (2). Winery wastewater is typically characterized by low pH of 3–4, large turbidity, and COD values up to 25 g/L (3). Major constituents of winery wastewater are the same as those of wine (organic acids, sugars, alcohols, proteins, and polyphenols) in addition to others coming from washing water (4). Release of winery wastewater into natural aquatic environments leads to dissolved oxygen consumption, bad odors, and decrease of natural photoactivity because of turbidity, color, and so forth. Therefore, remediation technologies have to be applied to winery wastewater before disposal.

The treatment of winery wastewater by photocatalytic methods seems to be a promising alternative to traditional biological methods such as activated sludge systems, UASB reactors, sequencing batch reactors, rotating contactors, or biofilters. Biological methods require rigorous pH control, and micro-

organisms are also quite sensible to seasonal overloads, deficit of N and P sources, and the presence of high concentrations of polyphenols (5). Moreover, COD reductions achieved by biotreatment are not usually high enough for effluent reuse. These drawbacks can be overcome by advanced oxidation technologies (AOT) such as the photocatalytic systems UV/H₂O₂, UV/TiO₂, UV/H₂O₂/TiO₂, UV/O₃/TiO₂, and UV/H₂O₂/clay materials (6–8). The high COD removal efficiencies usually achieved by these AOTs are primarily due to the generation of hydroxyl radicals (HO•) and other free radicals, which unselectively oxidize the organic matter present in water (9). Photocatalytic AOT systems typically incur large costs, which can be greatly reduced by using eco-friendly and low-cost solar photocatalysis methods (e.g., using sunlight and cheap catalysts, for example, iron salts). Solar photocatalysis has already been successfully applied to degrade specific priority pollutants of water (e.g., pesticides, pharmaceuticals, and personal care products) and to treat real wastewater as a stand-alone method or combined with biotreatment (10). Recently, Mosteo et al. have suggested a solar photo-Fenton process combined with an activated sludge treatment to treat winery wastewater (11).

Prior to the photocatalytic treatment of winery wastewater, removal of turbidity is recommended to increase COD removal efficiency. Some coagulants and coagulant aids can be used to achieve this goal. Bentonite, a clay material mainly constituted

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Table 1. Characterization of the Winery Wastewater Used in This Work

parameter	mean value \pm SD
pH	3.5 \pm 0.1
total acidity (g/L) ^a	0.5 \pm 0.1
suspended solids (mg/L)	145 \pm 52
turbidity (NTU)	100 \pm 32
COD _T (g/L)	12.4 \pm 0.7
COD _S (g/L)	10.4 \pm 0.6
TOC (g/L)	4.2 \pm 0.4
PPh _T (mg/L) ^b	99 \pm 29
PPh _S (mg/L) ^b	86 \pm 15
color	
absorbance 420 nm	0.25 \pm 0.03
absorbance 520 nm	0.31 \pm 0.08
absorbance 620 nm	0.08 \pm 0.01

^a As tartaric acid. ^b As gallic acid.

of montmorillonite, is characterized by high specific surface and high cation exchange capacity, which both make it an attractive material for the treatment of winery wastewaters with the aim of removing turbidity, dissolved organic matter (e.g., polyphenols), and metal species. As in wines, turbidity in winery wastewaters is mainly due to the presence of proteins, though polysaccharides and polyphenols might also have an impact (12, 13). At a typical winery wastewater pH of 3–4, net positively charged proteins can be retained electrostatically by negatively charged surfaces of bentonite, producing their flocculation and thereby removing turbidity. Bentonites might also be useful as adsorbents to remove polyphenols and other dissolved organic compounds as well as metal species typically present in wastewater (14, 15). Recently, Eroglu et al. have shown that a pretreatment with clays is advisable prior to a photofermentation treatment of olive mill wastewater (16).

This article presents results from an experimental study on the treatment of winery wastewater by the sequence of clarification with bentonite followed by solar photocatalysis using Fe(III) and H₂O₂ as catalysts. The results are focused on the removal of turbidity by different types of bentonites and the further removal of COD and TOC by the photocatalytic treatment.

MATERIALS AND METHODS

Winery Wastewater. Winery wastewater was taken from an experimental winery at the Faculty of Sciences of the University of Extremadura (Badajoz, Spain). This facility is designed to produce, on a pilot-plant scale, various red and white table wines. At the winery, the grapes are pressed into juice and stored for later fermentation. The wastewater for this study was taken from various small temperature controlled fermenters and mixed with washing water. After collection, wastewater samples were analyzed for pH, total acidity, suspended solids, turbidity, COD, TOC, polyphenols (PPh), and color. **Table 1** shows the characterization of this wastewater. The pH was analyzed by means of a Radiometer Copenhagen pH-meter (HPM82). Total acidity was determined by mass titration and expressed as equivalent concentration of tartaric acid. Suspended solids were analyzed gravimetrically according to Standard Methods (17). Turbidity was measured with a Neurtek NTP 8801 turbidity-meter. Total and soluble COD (COD and COD_S, respectively) were analyzed on nonfiltered and filtered (0.45 μ m membrane) samples, respectively, by the colorimetric dichromate Standard Method (17). A TOC-V_{CSH} Shimadzu carbon analyzer was used to measure TOC. Polyphenols were analyzed on nonfiltered and filtered samples by the Folin–Ciocalteu method to obtain the total and soluble polyphenol concentration, respectively (PPh_T and PPh_S, respectively), which were expressed as equivalent gallic acid concentrations (18). Absorbances of aqueous samples at 620, 520, and 420 nm were determined with an UV–visible Thermo Spectronic Helios α spectrophotometer and used to provide a measure of wastewater color.

Table 2. Some Characteristics of the Bentonites Used in This Work

	MB-G	MB-P	MB-M	Bengel
swelling index (mL/g)	24	37	48	27
CEC (meq/100 g)	44	47	79	83
exchangeable Na ⁺ (meq/100 g)	31.3	35.9	54.7	17.6
exchangeable K ⁺ (meq/100 g)	2.4	1.8	2.5	1.4
exchangeable Ca ²⁺ (meq/100 g)	12.5	16.4	16.9	55.9
exchangeable Mg ²⁺ (meq/100 g)	1.6	1.8	2.3	3.8
BET surface area (m ² /g)	35	41	69	74
particle size (μ m)	>200	100–200	20–100	70–80
pH (in H ₂ O)	9.7	9.8	10.2	9.1
% SiO ₂	>70	>70	57.5	62
% Al ₂ O ₃	<20	<20	21.2	22.5
% Na ₂ O	<3	<3	3.1	2.8
% K ₂ O	<3	<3	<0.2	0.7
% CaO	<1	<1	<1	2.1
% MgO	<3	<3	<3	4.5
% Fe ₂ O ₃	<2	<2	<3.5	3.5
% TiO ₂	<0.3	<0.3	<0.3	0.6
% MnO	<0.05	<0.1	<0.1	0.1
% P ₂ O ₅	<0.1	<0.15	<0.05	0.2
% loss on ignition	4.6	4.6	7.5	5.5

Bentonites. Four bentonites of enological interest (MB-G, MB-P, MB-M, and Bengel), supplied by Agrovin S.A. (Spain) in dry form, were characterized and used in this work. Some properties of these materials are given in **Table 2**. Swelling index was measured by soaking 2 g of dry bentonite into 100 mL of ultrapure water (Milli-Q, Millipore) and subsequent reading of the total volume of the column of solid after equilibrium. Surface area of bentonite samples was determined by the BET method from the first part of the N₂ adsorption isotherm at 77 K (P/P⁰ < 0.3) obtained with an Autosorb-1 (Quantachrome Corp.) gas adsorption apparatus. Cationic exchange capacity (CEC) and the amount of exchangeable Na⁺, K⁺, Ca²⁺, and Mg²⁺ were determined by the methylene blue standard method and the ammonium acetate method, respectively, following the procedures described elsewhere (19). Metals in solution were measured by atomic absorption using a Varian AA140 spectrometer. To determine the pH of bentonites in water, 100 mg of clay sample were mixed with 100 mL of deionized water, and the mixture was shaken for 24 h. After centrifugation, the pH of the supernatant was measured. Particle size and chemical composition data of bentonites were provided by the supplier. Before use in winery wastewater treatment, the bentonites were swollen in ultrapure water (Milli-Q, Millipore) for 24 h.

Clarification of Winery Wastewater with Bentonite. Swollen bentonites at dosages up to 2 g/L were used in jar-test experiments at room temperature. The required amount of bentonite was placed in glass bottles containing 50 mL of wastewater. After mixing for 10 min, the suspension was left to settle for 24 h. Then, a sample of the supernatant was taken to be analyzed for pH, turbidity, PPh, COD_S, and color. As the wastewater pH is thought to be a key variable affecting the process, a series of jar-test experiments were carried out at varying aqueous pH in the 3.5–12 range. Prior to these experiments, the pH of winery wastewater was adjusted to the desired value by adding the required amount of NaOH.

Additional experiments aimed to determine settling characteristics of bentonites were also carried out in standard 1 L settling graduate cylinders. Each cylinder was filled with winery wastewater, and the required amount of bentonite was then added. The mixture was vigorously agitated for 1 min and left to settle. From the test results, the settling rate and the sludge volume index after 24 h (SVI, that is, the volume in mL occupied by 1 g of a suspension after settling) were analyzed according to Standard Methods (17).

Photocatalytic Treatment of Winery Wastewater. The solar photo-oxidation experiments were carried out in Badajoz (Spain) (North Latitude, 38° 53' and West Length, 6° 58') from 10 a.m. to 5 p.m. during the summer of 2007 (June–July) under clear skies. The intensity of solar radiation at 365 nm during the experimental period was measured with a UVA-365HA Lutron UV meter. The average value of this variable was determined to be 2.2 mW/cm². The photocatalysts used were H₂O₂, Fe(III), and mixtures of Fe(III) and hydrogen peroxide

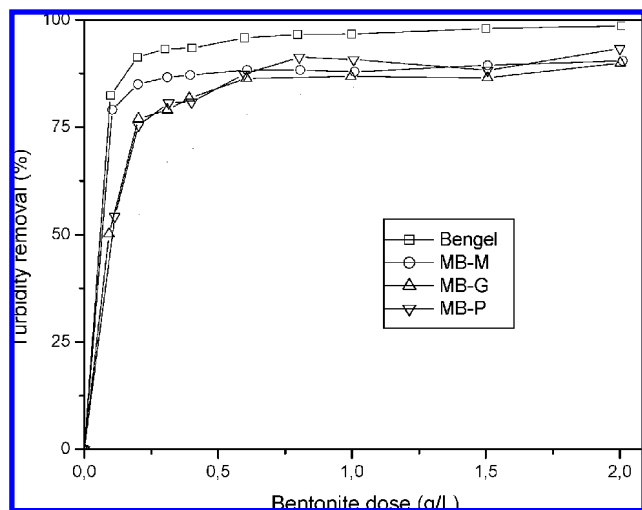


Figure 1. Removal of turbidity achieved by bentonite treatment at pH 3.5.

(i.e., photo-Fenton system). Fe(III) stock aqueous solutions were prepared from $\text{Fe}(\text{ClO}_4)_3$ as reported elsewhere (20). A hydrogen peroxide stock solution was also prepared from a reagent grade 30% solution (Merck). Winery wastewater degradation experiments were conducted batch-wise in a 250 mL borosilicate glass jacketed reactor provided with an inlet for gas feeding and exit ports for gases and liquid sampling. The reactor was placed on a 40° platform to optimize sunlight absorption. The reactor was first fed with winery wastewater previously treated with bentonite, and thereafter, amounts of catalysts (i.e., Fe(III) and/or hydrogen peroxide) were added at convenience to attain the desired catalyst concentration. To check for catalyst concentration, hydrogen peroxide concentration was determined iodometrically, and the ferrozine and 1–10 phenantroline methods were used to measure the concentration of total iron and Fe(II) species, respectively (21, 22). The aqueous solution was continuously agitated by bubbling air, and the reaction temperature was controlled at 27–30 °C. Samples were withdrawn from the reactor during the course of the process and analyzed for pH, COD, TOC, and PPh. For TOC analysis, sodium thiosulfate was added to sample vials immediately after withdrawal to quench oxidant species. The other parameters were analyzed immediately after withdrawal.

RESULTS AND DISCUSSION

Bentonite Treatment. Removal of Turbidity. Figure 1 shows the percentage of turbidity removal as a function of the type and dose of bentonite used in jar-test experiments carried out on unmodified-pH winery wastewater. As can be seen from this figure, all of the bentonites behaved in the same fashion: turbidity removal increased as the bentonite dose increased to reach a maximum percentage removal level in the range 90–100%. Although sodium-bentonites are usually more efficient than calcium-bentonites for removal of proteins from wines (23), we found that the turbidity removal capacity of the calcium-bentonite Bengel was somewhat higher than the capacity of the sodium-bentonites used in this work. From the results of Figure 1, the following turbidity removal efficiency order can be assigned to bentonites: Bengel > MB-M > MB-P ~

MB-G. This order is in agreement with the greater surface area and CEC of Bengel and MB-M materials (see Table 2). It is also noteworthy that the bentonites Bengel and MB-M were useful to effectively remove turbidity (>85% removal) even at a dose as low as 0.2 g/L, well below the range used in the bentonite fining treatment of wines, which is typically 0.8–1.0 g/L (13).

Removal of COD, Color, and Polyphenols. The treatment of winery wastewater with bentonite led not only to the removal of turbidity but also to reductions in color (i.e., absorbance values at 420, 520, and 620 nm), PPh_T , PPh_S , and COD_S to some extent. As an example, Table 3 shows the results obtained with the four bentonites at a dose of 0.2 g/L. As can be seen, reductions of these parameters were quite similar for all of the bentonites used (notice that average removal percentages and standard deviation values are presented in the last row of Table 3). As presented in this table, only small fractions of polyphenols and COD_S of winery wastewater were adsorbed onto bentonites. In contrast, the disappearance of color was more significant. Removal of target pollution parameters did not rise significantly with increasing doses of bentonites within the range 0.2–2.0 g/L. For example, from a test carried out with 2.0 g/L dose of the bentonite Bengel, the removal percentages of PPh_T , PPh_S , and COD_S were 21.5%, 15.3%, and 14.1%, respectively, which are not much higher than those achieved with a dose of 0.2 g/L. It should be stated here that the adsorption of organic compounds from winery wastewater, especially polyphenols, could be enhanced by using organo-bentonites, in which organic cations (e.g., quaternary ammonium organic cations) have replaced the native inorganic exchangeable cations (i.e., Na^+ or Ca^{2+}) of the bentonite (24).

The organic cations make the bentonite organophilic, and its capability to remove organic compounds from aqueous solutions may be greatly increased. However, in this work bentonites were used with the intention of primarily removing turbidity. This goal was effectively achieved by the lower-cost unmodified bentonites. Further removal of soluble wastewater pollutants was attained by solar photocatalysis as shown in the Solar Radiation Photocatalytic Treatment section.

Influence of pH on Turbidity Removal. Figure 2 shows the turbidity of the wastewater before bentonite addition and after a bentonite treatment as a function of pH. It can be observed that turbidity of winery wastewater was clearly pH dependent. The decrease of turbidity with increasing pH is likely mainly due to the solubilization of proteins as no precipitate but a slight increase of COD_S was observed when raising the pH of winery wastewater from 3.5 to 12. As can be seen in Figure 2 for the case of bentonite MB-M, the turbidity of the wastewater after bentonite treatment increased with increasing pH, slightly from pH 3.5 to 9 and more sharply from pH 9. At pH 12, the turbidity removal efficiency of bentonite was negligible. This behavior can be explained by the isoelectric point (pI) of proteins of winery wastewater and the pH in water of the bentonite. Proteins in wines have pI typically ranging from 3.1 to 9.2, though most of them have it in the narrower range (i.e., 4.2–6.5) (25). At

Table 3. Percentage of Removal of COD_S , Polyphenols, and Color of Winery Wastewater by Treatment with Various Bentonites at 0.2 g/L

bentonite	PPh_T	PPh_S	A_{420}	A_{520}	A_{620}	COD_S
MB-G	12.6	8.6	24.4	27.2	32.3	6.5
MB-P	17.8	9.7	27.7	29.9	36.8	6.0
MB-M	18.9	11.3	28.0	33.9	35.6	8.0
Bengel	18.2	11.3	22.8	34.2	35.2	8.8
average values	16.9 ± 2.5	10.2 ± 1.1	25.7 ± 2.2	31.3 ± 2.9	35.0 ± 1.7	7.3 ± 1.1

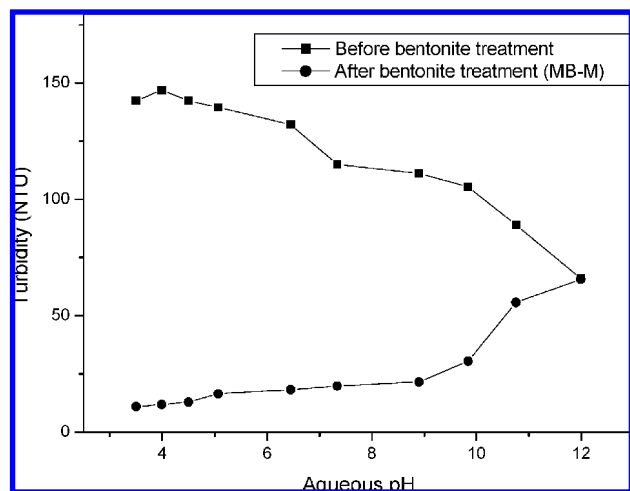


Figure 2. Variation of winery wastewater turbidity as a function of pH before and after bentonite treatment. Conditions: bentonite, MB-M; bentonite dose, 0.5 g/L.

pH above the pI and below the pH of bentonite, the net surface charge of proteins is negative and can not be retained by negatively charged adsorption sites of bentonites. Further experiments showed that all of the four bentonites tested have their highest turbidity removal capacities at pH 3.5–5.5.

Bentonite Sludge Formation. A series of experiments were conducted to determine settling characteristics of the bentonites MB-M and Bengel. **Figures 3A** and **B** show the effect of bentonite dose on the SVI and the settling rate, respectively. **Figure 3A** shows that there is an increasing settling volume of bentonite sludge with the increase of the dose. Good SVI values (i.e., <75 mL/g) were obtained for a bentonite dose lower than 0.5 g/L. From **Figure 3B**, it is apparent that the highest settling rate was achieved at 0.5 g/L bentonite dose, regardless of the bentonite used. However, at any dose used, the Na-bentonite MB-M showed a much higher settling rate than the Ca-bentonite Bengel.

Reuse of Bentonite. To make the wastewater treatment process more inexpensive and to minimize the bentonite waste disposal problem, it is desirable to reuse the bentonite sludge in winery wastewater treatment. **Figure 4** shows the results of turbidity and PPh_T removals within three consecutive experiments reusing sludge from bentonites MB-M and Bengel. As a general behavior, the increase in the number of uses led to a decrease in the efficiency of bentonites to remove turbidity and PPh. However, the SVI values (not shown) were maintained throughout the experimental series below 80 mL/g for the two bentonites tested. Loss of turbidity removal efficiency can be attributed mainly to the fact that the use of bentonite for wastewater treatment lowers its pH in water. Thus, after the fourth use of bentonites MB-M and Bengel the pH in water was found to be 4.1 and 4.7, respectively. Accordingly, as far as bentonite is reused its surface becomes less negatively charged, and therefore, its ability to remove proteins by a cation-exchange process based on electrostatic interactions decreases to a great extent.

Solar Radiation Photocatalytic Treatment. Prior to solar radiation experiments, winery wastewater was subjected to bentonite treatment under the following conditions: bentonite MB-M, bentonite dose = 0.2 g/L, aqueous pH 3.5. The resulting wastewater was mixed with washing water, and it showed turbidity below 5 NTU, PPh_S concentration of about 8 mg/L, and COD_S of about 1 g/L. A series of preliminary experiments were carried out to ascertain the effect of only sunlight and

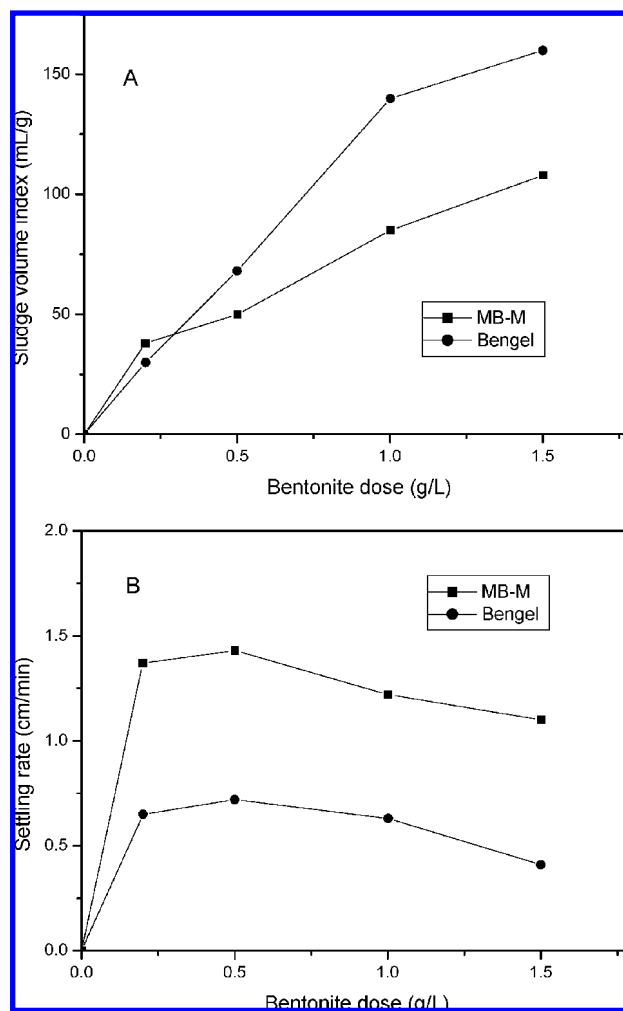


Figure 3. Effect of bentonite dose on settling parameters. Conditions: bentonites, MB-M and Bengel; winery wastewater pH 3.5.

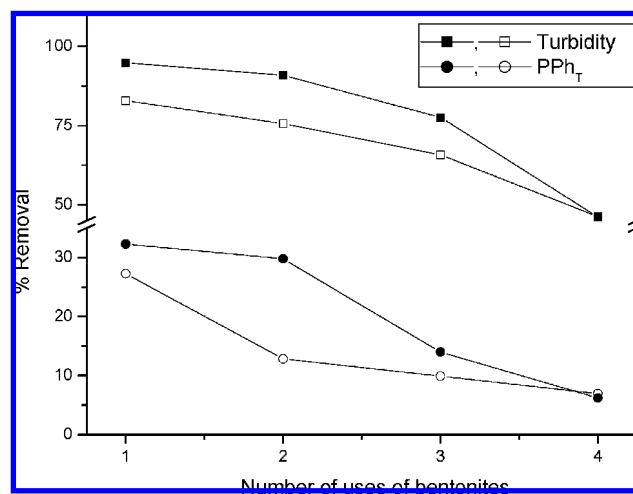


Figure 4. Effect of bentonite sludge reuse on turbidity and polyphenol removal efficiency. Conditions: ■, ●, bentonite Bengel; ○, □, bentonite MB-M. Bentonite dose = 0.5 g/L; winery wastewater pH 3.5.

aeration (no catalyst added) on the performance of winery wastewater depollution. **Figure 5** shows the percentage of COD removal achieved during these noncatalytic experiments. It can be observed that in the experiment carried out in darkness and without gas bubbling there was no COD depletion at all. A negligible COD removal was also obtained in the presence of sunlight but the absence of gas bubbling. This means that

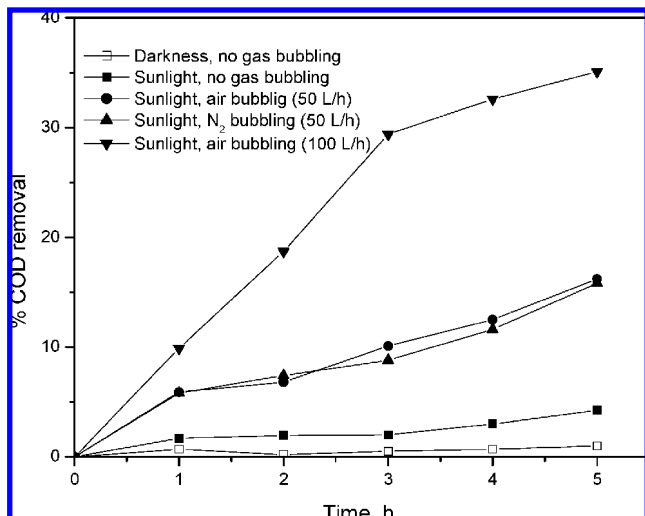


Figure 5. Removal of COD from winery wastewater previously treated with bentonite. Nonadded catalyst processes. Effects of sunlight and gas bubbling. Conditions: pH 3.5; temperature = 27–30 °C; reaction volume = 250 mL; solar radiation intensity at 365 nm (average) = 2.2 mW/cm².

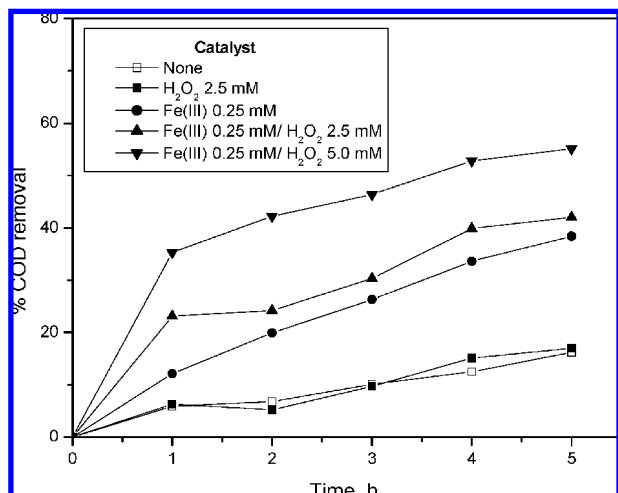


Figure 6. Removal of COD from winery wastewater previously treated with bentonite. Photocatalytic processes. Conditions: pH 3.5; temperature = 27–30 °C; reaction volume = 250 mL; solar radiation intensity at 365 nm (average) = 2.2 mW/cm².

compounds in winery wastewater are not appreciably directly photolyzed by solar radiation. The COD removal was much greater when either air or nitrogen was bubbled through wastewater. Moreover, the higher the gas flowrate, the higher the COD removal rate. This suggests the stripping of volatile compounds of winery wastewater, which is mainly composed of ethanol (~0.3–1% vol/vol) (26).

Figure 6 shows the evolution of the COD of the winery wastewater during various solar radiation experiments carried out under the same air-flowrate of 50 L/h. From this figure, it is observed that the presence of only hydrogen peroxide does not have appreciable effect on the process performance (i.e., COD removal). In contrast, the use of Fe(III) and Fe(III)/H₂O₂ photocatalysts greatly enhances the COD removal rate. Thus, the use of the 0.25 mM Fe(III) homogeneous catalyst led to about 40% COD removal after 5 h of treatment. This catalytic process is based on the photolysis of Fe(III)-hydroxo complexes to yield hydroxyl radicals (HO•), which can further oxidize most of the organic compounds in water (27). In the particular case

Table 4. Percentage of Removal of COD, TOC, and PPh_T of Winery Wastewater after 5 h of Exposition to Solar Radiation

catalyst	% COD removal	% TOC removal	% PPh _T removal
none ^a	2.1	1.3	
none	16.2	2.7	10.4
H ₂ O ₂ , 0.25 mM	17.0	2.9	9.7
Fe(III), 0.25 mM	40.3	48.2	40.0
Fe(III) 0.25 mM, H ₂ O ₂ 2.5 mM	43.7	58.9	44.0
Fe(III) 0.25 mM, H ₂ O ₂ 5 mM	58.2	66.5	48.4

^a No aeration.

of winery wastewater, the formation of HO• is also favored by the presence of tartaric acid and citric acid. These organic acids, naturally occurring in winery wastewater, form Fe(III) complexes that easily absorb solar radiation to decarboxylate themselves and generate hydroxyl radicals with high quantum yields (28). From **Figure 6**, it is apparent that the solar photo-Fenton process was even more efficient than the Fe(III)-mediated photodegradation, as after only 1 h of treatment a COD conversion of 24–38% was reached depending on the amount of hydrogen peroxide added. In this type of oxidation process, the formation of hydroxyl radicals comes in addition from the reaction between hydrogen peroxide and Fe(II) species (29).

A comparison of the performance of the solar radiation processes used in this work is presented in **Table 4**. It can be seen that the photocatalytic systems led not only to higher COD removal but also to a large disappearance of PPh_T and a great level of mineralization (i.e., TOC removal).

CONCLUSIONS

In this study, it has been shown that winery wastewater can be effectively treated by the sequential use of bentonite (low-cost adsorbent) and solar radiation photocatalysis. Bentonites were useful to remove turbidity and to a lesser extent color, polyphenols, and COD₅ from winery wastewater. The performance of the process was greatest at pH 3.5–5, which is within the typical pH of winery wastewater. The bentonites tested showed good settling characteristics, with a maximum settling rate at a dose of 0.5 g/L. The reuse of bentonite was not advisable as the loss of ability to remove turbidity and PPh_T was observed. The solar radiation post-treatment of winery wastewater is effective in the presence of either Fe(III) or Fe(III)/H₂O₂ homogeneous catalysts as high level of COD, PPh_T and TOC removals can be achieved. The depollution mechanism can be ascribed to stripping of volatile compounds and simultaneous oxidation of soluble organic compounds through a free-radical mechanism involving the hydroxyl radical. Experimental conditions of solar photocatalytic processes have not been optimized in this work, and studies are now in progress in this field due to its potential benefits.

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