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Chemical Engineering Journal 135 (2008) 151–156

Chemical Engineering Journal

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Treatment of winery wastewater using a photocatalytic/photolytic reactor

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Received 12 September 2006; received in revised form 1 July 2007; accepted 7 July 2007

Abstract

In this study, an annular photocatalytic/photolytic reactor system was designed to investigate remediation of winery wastewater. The performance of the reactor was studied as a functional of various operating variables, such as gas flow rate, pH and catalyst loading. It was found that the optimum gas flow rate was 6 L/min whereas the optimum pH value is 6.5. The highest photodegradation rate and the maximum COD removal were achieved at zero catalyst loading with COD removal of about 84%. Lower rates of chemical reaction in photocatalysis compared to photolysis were possibly because of the shielding of UV light by titania particles. This hypothesis was confirmed by conducting further experiments with inert glass beads where the reaction rate decreased with particle loading in an identical manner.

Keywords: Photocatalytic; Wastewater treatment; Photolysis; Winery wastewater; pH; TiO_2 catalyst

1. Introduction

Winery wastewater is the waste product of many independent processing and cleaning operations in wineries. Wineries and other grape processing industries annually generate a large volume of wastewater. This mainly originates from various washing operations during the crushing and pressing of grapes, as well as rinsing of fermentation tanks, barrels and other equipment or surfaces [1]. The unique combination of wine styles, processing operations and cleaning practices result in each winery generating wastewater with unique characteristics, especially during vintage. Vintage is a 6–20-week period in which harvesting and crushing of wine grapes and fermentation of grape juice to wine take place. The remainder of the year is non-vintage. As the numbers of wineries are rapidly multiplying, concern about wastewater treatment from this industry has grown.

Winery wastewater is characterized by large seasonal fluctuations in volume and composition and is often discarded with little or no treatment. In general, the regulatory bodies dictate that treated wastewater should have a pH of 5.5–7.5 and chemical oxygen demand should not exceed 75 mg/L before discharging into the environment. However, winery wastewater typically has a pH of 3–4, with a COD of 800–12,800 mg/L [2]. Furthermore, the COD can increase to 25,000 mg/L depending on the harvest load and processing activities. The organic carbon compositions of wastewater produced by wineries are tartaric, lactic and acetic acids, also found are glucose, fructose, glycerol and ethanol. So it is clear that sugars, organic acids and alcohols dominate the organic carbon composition of wastewater produced by wineries [3]. The chemical analyses of winery wastewater indicate that the organic acids play a more prominent role in the acidity of the wastewater, whereas the high concentration of sugars contributes largely to COD [4].

These sugars are easily dissolved in wash-down water, and are measured in the effluent as biochemical oxygen demand (BOD). The BOD levels associated with grape crushing, barrel washing and bottling may be as high as 5000 (ppm or mg/l). Wastewater with high levels of BOD combined with chlorine from chlorinated water sources may produce a known cancer-causing disinfection by-product, trihalomethanes (THMs), which can contaminate the ground water [5]. Thus it is essential to treat the wastewater appropriately before discharging it to the environment.

There are three common techniques presently employed by wineries to reduce BOD level: septic tank leach field, ponding, and bioreactor systems [5]. Each has various degrees of failure. The septic tank leach field quickly plugs with the high solid loading rate. The ponding system usually requires several hectares of land, often located on valuable vine land, and often fails to achieve acceptable level of BOD apart from odour problems coming out of the ponds. In the bioreactor systems, a number of biological systems have been evaluated for winery wastewa-

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doi:10.1016/j.cej.2007.07.063

ter, such as activated sludge reactors [1,2,6], that are efficient in BOD removal, but require long retention times. The bioreactor systems are often associated with high capital and operational costs. Consequently, there has been no general agreement on the most suitable method for the treatment of winery wastewater.

Recently, the photocatalytic action has provided a promising potential alternative method for wastewater treatment. A comprehensive review of synergistic effect of photocatalysis and ozonation on wastewater treatment has been done by the present authors [7]. Several previous studies [8,9] have reported application of this technique for the degradation of almost all types of organic and inorganic substances including aliphatic compounds, inorganic compounds, aromatic compounds, surfactants, dyes, herbicides, pesticides, fungicides, amides, and also sulphides. In the presence of oxygen, many types of semiconductor powders have been used as photocatalysts to promote the oxidation of chemical contaminants. When illuminated with light of energy higher than the band gap, electrons and holes are formed on the surface of semi-conductors that are capable of initiating chemical reaction. The method of the oxidizing reaction associated with the holes can be used to hydroxylate various compounds.

The aim of this work is to conduct a feasibility and experimental study on the treatment of winery wastewater using a photocatalytic/photolytic reactor. The performance of the reactor was studied with respect to various process parameters such as gas flow rate, initial pH of solution and catalyst loading.

2. Experimental

2.1. Chemicals and materials

Winery wastewater (WW) was obtained from a commercial wine company located in the Swan Valley in Western Australia. A typical assay of winery wastewater has been provided in Table 1. Titanium dioxide (≥99.0%) was obtained from Aldrich Chemicals. It is almost pure anatase with almost no rutile, as confirmed by X-ray crystallography studies. As per the manufacturer's specifications, the particle size was approximately 325 mesh (<44 μm), with the specific surface area (BET) 40–150 m^2/g. Ambient compressed air was used as the feed gas for the reactor. Continuous pH monitoring was conducted using a TPS Digital pH meter.

Table 1
An example of the organic carbon composition of wastewater produced by wineries

	Vintage	Non-vintage
Organic acids		
Tartaric	530	350
Lactic	250	120
Acetic	100	50
Sugars		
Glucose	2500	230
Fructose	2500	270
Alcohols		
Glycerol	190	120
Ethanol	2400	2900

Units are in mg/L [3]. Samples may also contain butyric acid, which co-elutes with ethanol.

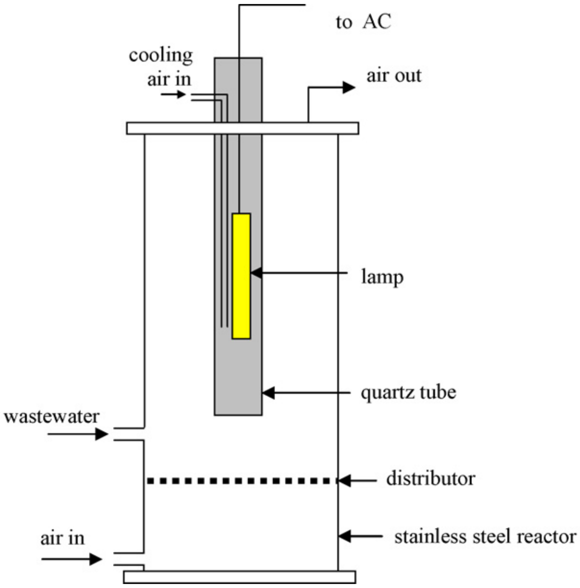

Fig. 1. Schematic of photocatalytic reactor.

2.2. Experimental procedure

Experiments were carried out in batch operation in an annular type reactor as shown in Fig. 1. Reactor capacity is 60 L with an irradiated volume of 38.5 L. The outer chamber is a stainless steel vessel (i.d. = 30 cm, height = 60 cm), fitted with a UV lamp enclosed in a cylindrical quartz tube (i.d. = 5 cm). This gave an effective L/D ratio of about 3 (because about 30% of the cross-section was occupied by the annular lamp assembly) which corresponds to the lower limit of the recommended values for this quantity for bubble columns. The low L/D value used in this work was an outcome of a trade-off between typical requirements for a bubble column (i.e., L/D > 3) and results from our previous study [10] where it was found that in order to keep the light intensity distribution uniform, the length of the UV lamp should be as close to the photoreactor height as possible. Since a longer lamp costs significantly higher and is expensive to operate, we used a 30 cm (length) lamp. To keep the light intensity distribution uniform in at least in the half of the reactor volume, the reactor height was limited to 60 cm. The lamp used in this study was a medium pressure mercury arc UV lamp (Primarc Ltd., PM2326) emitting in the wavelength range 310–435 nm, with a maximum emission at 365 nm.

The reactor was thoroughly cleaned before each of the experimental runs. The pH meter was calibrated periodically. The winery wastewater was appropriately diluted with water while adding sulphuric acid or sodium hydroxide to adjust the pH; then the wastewater was mixed with a measured amount of TiO_2 (anatase) powder to give uniform slurry in 60 L supply tank. The air supply was turned on and the annular photoreactor was filled with solid–liquid slurry (winery wastewater + catalyst powder) using a pump while continuously stirring the slurry in the supply tank to avoid the settling of the catalyst. Air from the flow controller was passed upwards through the slurry solution via a 1 mm stainless mesh distributor. The UV light was illuminated after the solution was aerated with air. The reaction temperature was maintained between 25 and 30°C by adjusting the flow rate of the cooling water.

2.3. *Analytical method*

Samples were taken periodically for analysis of total organic carbon (TOC) and chemical oxygen demand (COD). TOC was determined using a Shimadzu TOC 5000 analyzer and COD was measured through a titrimetric method. Before analysis each sample was passed through a 0.45 μm Whatman filter to eliminate the TiO_2 particles.

3. Results and discussion

Industrial winery wastewaters consist of a matrix of a large number of organic pollutants. In this situation, the TOC measurement gives a more realistic estimate of total organic carbon than either biochemical oxygen demand (BOD), assimilable organic carbon (AOC), or COD [11,12] measurements. Therefore, the organic concentration in this study was characterized in terms of TOC.

3.1. *Effect of gas flow rate*

When the electrons and holes are generated on the TiO_2 surface, the electrons should be effectively removed to prevent the recombination of electrons and holes and thereby keeping the holes to promote the oxidation process. Although some metal ions are effective in scavenging electrons, the use of oxygen or air is preferred for wastewater treatment, as oxygen does not introduce other pollutants into the system. Moreover, three components must be present in line for the heterogeneous photocatalytic reaction to take place: an emitted photon (in appropriate wavelength), a catalyst surface (usually a semi-conductor material) and a strong oxidizing agent which in most cases is oxygen [13]. In this experiment, compressed air was used as additional oxidizing agent and to promote better mass transfer between the catalyst particle and the solution.

Fig. 2 shows the effect of gas flow rate on the photodegradation rate of wastewater. It is clear that the average reaction rate increases with increasing gas flow rate. However, as the gas flow rate exceeds 6 L min^{-1}, reaction rate decreases with gas flow rate. Although, for the gas flow rates investigated in this study (0–10 L min^{-1}), the superficial gas velocities in the column were in the range 0–0.24 cm s^{-1}, which in 30 cm diameter ordinary bubble column should correspond to homogenous bubbly flow regime (with bubbles of almost equal size). However, even at these relatively low gas velocities, the presence of annular glass assembly resulted in a significant bubble break-up and coalescence which was clearly noticed during the experiment. Therefore, it is believed that the decrease in reaction rates can be attributed to relatively unfavourable gas–liquid hydrodynamic conditions at higher gas glow rates. When the flow rate is greater than a critical value, the fine bubbles in solution had more tendencies to collapse together and form large bubbles. As a result, the total contact area between the gas and liquid was reduced. Furthermore, the residence time of large bubbles is shorter than that of fine bubbles. The decreased gas–liquid interface and shortened residence time of oxygen retard the oxidation rate. However, to ascertain the exact cause of this apparently reverse trend from those obtained by other researchers [13], more investigations such as measurements on dissolved oxygen should be carried out.

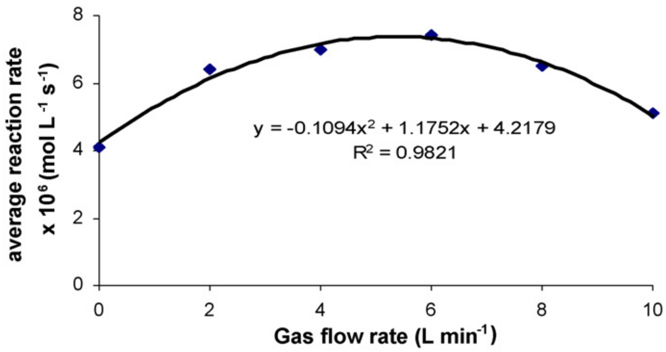

Fig. 2. Effect of gas flow rate on photodegradation rate. Experimental conditions: residence time 5 h, catalyst loading 1 g L^{-1}, and average reaction temperature 25 °C.

3.2. *Effect of initial pH solution*

The pH may affect the surface charge on the photocatalyst and also the state of ionization of the substrate and so adsorption of the substrate [8,14]. Also, industrial effluents may be basic or acidic and therefore pH effect must be considered.

Fig. 3 illustrates the dependence of photodegradation rate on the pH value. It indicates that increasing the pH from 4 promoted the degradation rate but it reaches a maximum rate at pH 6.5. As the pH value increased further, the degradation rate dropped rapidly. Subramanian et al. [15] found a similar effect in their study on pH. They showed that in the case of *p*-hydroxy benzoic acid, adsorption and degradation attained a maximum close to the zero point charge of TiO_2 catalyst at pH 7 (approx.) and then decreased again as the pH was further increased.

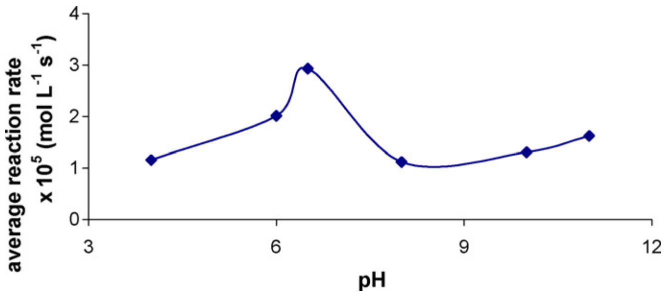

Fig. 3. Effect of pH on photodegradation rate. Experimental conditions: air flow rate 6 L min^{-1}, catalyst loading 0.5 g L^{-1}, average reaction temperature 25 °C, and reaction time 60 h.

Furthermore, when the pH value was above 10, the average reaction rate increased again. This is because when solution is sufficiently alkaline (pH values more than 10), the increased the concentration of $OH^•$ radicals increases the degradation rate. Wei and Wan [16] reported the same propensity of pH effect in their study on the photocatalytic oxidation of phenol. They found that at acidic conditions (with pH values less than 2) did not favour the photocatalytic oxidation of phenol but with less acidic solutions phenol degradation increased and reached a maximum at pH ∼6.5. As the pH value increased further, the removal percent is reduced rapidly. However, when the pH value is above 11, the phenol oxidation rate increased again. In their explanation, they mentioned that when the pH increased, the active hydroxyl groups on TiO_2 surface increased too. Consequently, a faster generation of $OH^•$ radicals accelerated the phenol oxidation. As the pH increased further to 6.5, the phenoxide ions induced by the increasing pH value tend to replace the OH^- ions on the TiO_2 surface and result in the elimination of the $OH^•$ generation. However, when the pH value reached 11, the OH^- ions are concentrated enough to compete with the phenoxide ions for adsorption on the TiO_2 surface. Therefore, the generation of $OH^•$ is enhanced again.

3.3. Effect of catalyst loading

The effect of the amount of catalyst on the photodegradation rate was investigated. Experiments were conducted with various amounts of catalyst powder (0–3 g L^{-1}). Fig. 4 shows the effect of TiO_2 loading on average reaction rate. It indicates that the degradation could occur without TiO_2 (photolysis condition) and the degradation rate decreased with increasing catalyst loading. It is obvious that in this case, the TiO_2 has a shading effect on the light. Furthermore, the TOC removal is highest when the experiments were conducted without photocatalyst as demonstrated in Fig. 5.

Sabate et al. [17] studied the photolysis of polycyclic aromatic hydrocarbons in aqueous phase by UV irradiation. They found that photolysis degradation of fluorene was more efficient than sensitized photolytic oxidation in the presence of TiO_2 suspensions. The photolytic elimination kinetics is faster than photocatalytic and is dependent on molecular size and the presence and type of substrates. Beltran at al. [18] examined the various oxidation processes for the removal of phenols from water. They reported that the addition of TiO_2 gives negative effect since the rate constant clearly decreased with respect to that with photolysis system. Different factors are likely to be responsible for the negative effect of TiO_2 compared with photolysis alone such as different pH values (the reactions were not buffered) and the presence of intermediates at varying concentration. Several studies showed that photolysis and photocatalysis involve the same pathway, and the difference in the reaction rates between the two processes is due to the hydroxyl radical concentration [19–21].

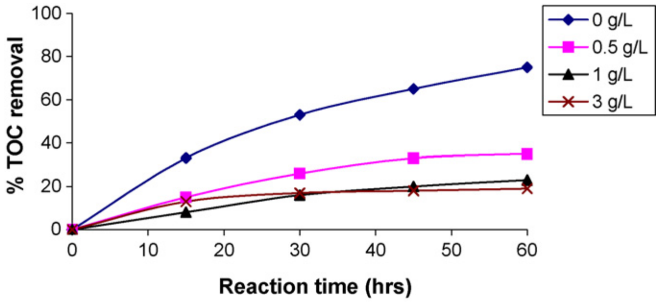

Fig. 5. Effect of catalyst loading on TOC degradation. Experimental conditions: air flow rate 6 L min^{-1} initial solution pH 6.5, and average reaction temperature 25 °C.

Fig. 6 shows extents of COD and TOC removals for reaction time of 60 h with other experimental conditions indicated. It shows that the highest COD and TOC removals were in the absence of any catalyst, with removals of 84% and 75%, respectively. This proves that the photolysis process is better than the photocatalysis process for the treatment of winery wastewater. The probable reason for this behaviour is that the contaminants in the wastewater are photosensitive and the presence of TiO_2 tended to block some of the UV light reaching the organic contaminants and thus reducing the TOC removal rates. However, to confirm this notion that light shielding is responsible for decreased reaction rates in the presence of TiO_2 catalyst, further experiments on photolysis were conducted to ascertain the effect of pH and inert particles having similar physical properties to TiO_2 were conducted as below.

Fig. 7 shows the effect of initial solution pH in the absence of any catalyst. It is clear that the average reaction rate increased on increasing the initial solution pH. These results are in agree-

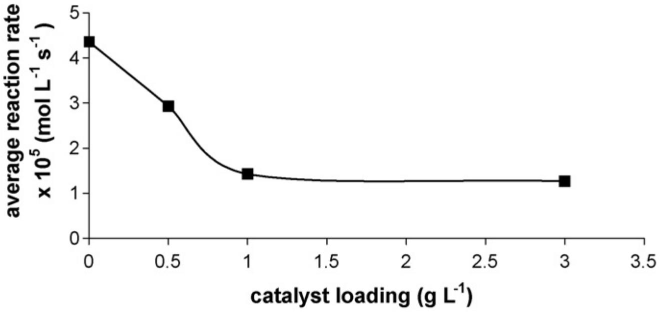

Fig. 4. Effect of catalyst loading on photodegradation rate. Experimental conditions: air flow rate 6 L min^{-1}, initial solution pH 6.5, average reaction temperature 25 °C, and reaction time 60 h.

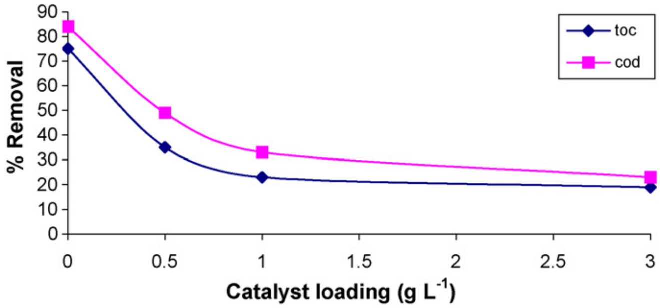

Fig. 6. Effect of catalyst loading. Experimental conditions: air flow rate 6 L min^{-1}, initial solution pH 6.5, and average reaction temperature 25 °C. Reaction time 60 h.

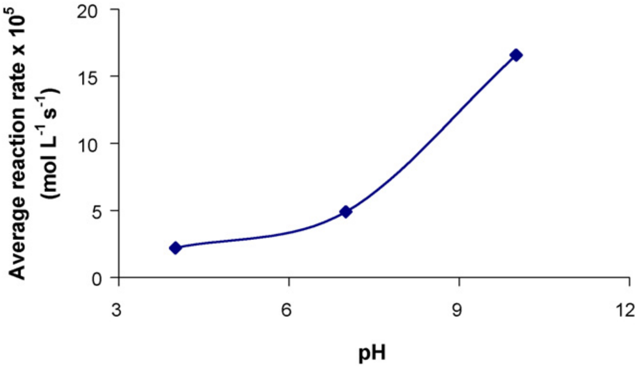

Fig. 7. Effect of initial solution pH on average reaction rate in photolysis. Experimental conditions: air flow rate 6 L min^{-1}, reaction time 60 h, and average reaction temperature 28 °C.

ment with Ku et al. [22], who in their investigation on the effect of solution pH on the hydrolysis and photolysis of diazinon in aqueous solution, found that the photolytic rate constant for the decomposition of diazinon by photolysis decreased under acidic condition. Lipczynska-Kochany and Bolton [23] also reported that photochemical removal of phenol under alkaline conditions is more efficient than under neutral and acidic ones. These results could be due to inhibition of reaction rates by high proton (H^+) concentration in acidic solutions. Furthermore, under the alkaline condition, the addition of hydroxide ions (OH^-) could neutralize acidic products generated from the photolysis, and therefore improved the photosentitization process [24]. A comparison between Figs. 7 and 3 reveals that throughout the range of pH studied, photolysis always gave higher reaction rates. Therefore, results in Figs. 4 and 5 could not simply be because of associated pH values in photocatalysis and photolysis.

Finally, in order to establish that the decreased reaction rate in photocatalysis was indeed because of the shading effect of TiO_2, a study was conducted by replacing TiO_2 with glass beads. The size distribution of glass beads used was equal to that of TiO_2 powder. As shown in Fig. 8, the percentage TOC removal decreased consistently on increasing the glass beads loading. Thus, it is proven that the catalyst loading (TiO_2) could be responsible for shielding UV light in photocatalysis.

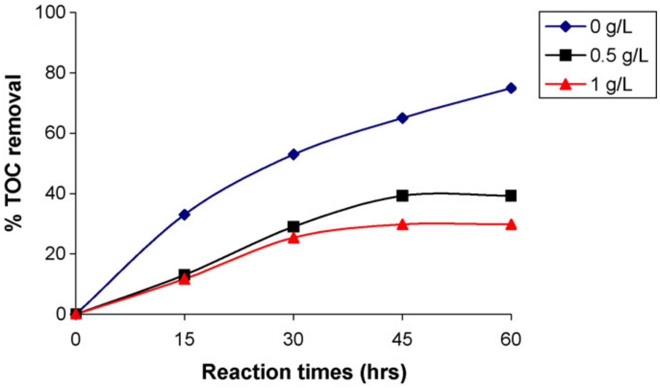

Fig. 8. Extent of TOC degradation with glass beads. Experimental conditions: air flow rate 6 L min^{-1}, initial wastewater pH 6.5, and average reaction temperature 25 °C.

4. Conclusions

The treatment of winery wastewater using a photocatalytic reactor was studied. The effects of gas flow rate, initial solution pH and catalyst loading on the photodegradation rate were investigated. It was found that the optimum gas flow rate was 6 L min^{-1} while the optimum pH value is 6.5. On the other hand, the photodegradation rate decreased with increasing catalyst loading. The highest photodegradation rates, measured as COD or TOC removals, were attained in the absence of any catalyst. This study shows that for winery wastewater, TiO_2 had a shading effect on the light reaching the organic contaminants in the reactor. Thus the study proved conclusively that photolysis is superior to photocatalysis as a treatment alternative for winery wastewater.

Acknowledgement

Tuty Agustina greatly appreciates the partly financial support given to her by Technological Professional Skill Development (TPSDP) Project, ADB Loan no. 1792-INO, Ministry of National Education of Republic of Indonesia.

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