Desalination and Water Treatment
www.deswater.com
47 (2012) 295–299
September

doi: 10.1080/19443994.2012.696413
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Chemical and biological treatments to clean oily wastewater: optimization of the photocatalytic process using experimental design

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Received 24 August 2011; Accepted 19 March 2012

ABSTRACT

The remediation efficiency of oil containing wastewater was evaluated employing an integrated photocatalytic and biological treatment. Both the photocatalytic and biological treatments were carried out in batch reactors using TiO_2 as the photocatalyst. The effects of TiO_2 concentration, pH, and reaction time were optimized by the experimental design, achieving 90.0% of oil removal in 30 min of reaction time at pH = 5.0, with a reaction rate constant of 0.027 min^{-1} ($R^2 = 0.71$). For biological treatment, we used the bacteria *Pseudomonas aeruginosa* in biofilms. The biological treatment alone achieved 66.5% of oil removal in just 45 min of treatment, with a reaction rate constant of 0.018 min^{-1} ($R^2 = 0.99$). To augment the process efficiency, we integrated both the chemical and biological treatments, achieving 99.0% of oil and 78.6% total organic carbon (TOC mg L^{-1}) removal. The concept of experimental design adopted to optimize the photocatalytic process saved time and generated adequate estimates of the experimental variables, which were validated by the reaction kinetics.

Keywords: Biodegradability; Oily wastewater; Photocatalysis; *Pseudomonas aeruginosa*; TiO_2

1. Introduction

Photocatalysis is based on the irradiation of a semiconductor to the conduction band (CB), with specific wavelength, triggering off an electron transfer from the valence band (VB), producing electron–hole (e^-/h^+) pairs. If the charge separation were maintained, then the electron and the hole may migrate to the catalyst surface where are involved in redox reactions with the adsorbed species (Eq. (1)). On the catalyst surface, the oxygen acts as an electron acceptor generating superoxide radical anions as indicated in Eq. (2) [1,2]:

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

$$O_2 + e^-_{CB} \rightarrow O_2^{\bullet -} \quad (2)$$

In aqueous systems, the hole species may react with the adsorbed species to produce hydroxyl radicals, which are highly oxidizing species that promote the rapid in situ degradation of organic matter as indicated in the following Eqs. (3)–(5) [3,4]:

$$H_2O + h^+_{VB} \rightarrow {}^{\bullet}OH + H^+ \quad (3)$$

$$OH^- + h^+_{VB} \rightarrow {}^{\bullet}OH \quad (4)$$

$$R\text{–}H + {}^{\bullet}OH \rightarrow R^{\bullet} + H_2O \quad (5)$$

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The properties of TiO_2 are of great help in efficiently treating the wastewater containing a high concentration of oil. This process in turn acts to improve the effluent's biodegradability. The intermediates thus produced are easily degradable by the microorganisms with further biological treatment [5,6]. They are many oxidation processes that are applicable for treating the bio-refractory molecules, and for achieving a complete mineralization of the contaminants or at least converting the organics into less harmful compounds [7–12]. Similar processes have been applied to the phenolic compounds generated from the olive mill wastewater or for the petroleum refinery effluents using the UV/TiO_2 and Fenton oxidation [13–15]. The aim of this work is to present studies on the degradation of organic pollutants in fishmeal wastewater prior to biological treatment, using the UV/TiO_2 process.

2. Experimental

The removal of oil and any other organic matter from the fishmeal processing wastewater was carried out using both chemical and biological treatments. The chemical treatment was performed using heterogeneous photocatalysis with the $TiO_2/UV/O_2$ systems, in a spherical reactor with TiO_2 Degussa P-25 in suspension. The solution was irradiated with a Philips UV-C lamp (254 nm, 120 W). Prior to biodegradation, the photocatalytic effluent was filtered through a Millipore filter (0.45 μm) to remove the titanium dioxide particles. The biological treatment was carried out using *Pseudomonas aeruginosa* bacteria in a capacity glass reactor (30 cm high × 5.0 cm diameter; 1.3 L). The bacteria were prepared inside the reactor forming biofilms on polyethylene sheets (21.5 cm length × 2.0 cm width). The removal of organic matter was observed at 530 nm using a Spectronic 20 Genesys spectrophotometer. For determining the oil concentration in the effluent, the samples were digested with 1 mL of concentrated sulfuric acid in a water bath for 1 min, then cooled, 2.5 mL of phosphovanillin acid was added, and the mixture was incubated for 1 min at 37°C. The reaction of the oils with the phosphovanillin acid resulted in a pink chromogen that absorbed at 530 nm, whose color intensity was directly proportional to the oil concentration in the sample. The chemical oxygen demand (COD) was determined using spectrophotometry at 593 nm, with Spectroquant NOVA 60 Merck, Standard Methods 5220 D-ISO 15705. For the TOC analysis, the samples were filtered in cellulose 0.22 μm filters, then acidified with hydrochloric acid and injected into a TOC analyzer (Shimadzu 5000).

3. Results and discussion

To optimize the oil removal from wastewater, an experimental design was built incorporating all the three variables given below: pH, reaction time (in minutes), and TiO_2 concentration. The combination between minimum and maximum values of the variables resulted in a full quadratic experimental matrix of 17 experiments (Table 1). The first eight experiments correspond to initial scanning, Experiment 14 corresponds to the star experiments, and the last three experiments correspond to the central points. Each experiment was performed in the order given by the experimental matrix, as is described in Table 1, and carried out in a photocatalytic reactor (Fig. 1). After obtaining the experimental response for each experiment, measured as the percentage of oil removed, the values were entered into the model to obtain the response surface of the experimental design (Fig. 2), where the red area indicates the optimal response zone. As is observed, the contour plot gives the values of those experimental variables which achieved the removal of organic matter to the maximum. The optimal experimental values of the variables were: 30 min of reaction time at pH = 5.0 with 1.0 mg L^{-1} TiO_2 concentration. To corroborate the experimental design, the

Table 1
Experimental design for the removal of oil from fishmeal wastewater

Experiment	Order run	TiO_2 (mg L^{-1})	pH	Reaction time (min)
1	8	0.5(−1)	3(−1)	30(−1)
2	17	1.5(+1)	3(−1)	30(−1)
3	3	0.5(−1)	10(+1)	30(−1)
4	12	1.5(+1)	10(+1)	30(−1)
5	10	0.5(−1)	3(−1)	120(+1)
6	11	1.5(+1)	3(−1)	120(+1)
7	14	0.5(−1)	10(+1)	120(+1)
8	16	1.5(+1)	10(+1)	120(+1)
9	1	0.293 (−1.41)	6.5(+1)	75(+1)
10	9	1.707 (+1.41)	6.5(+1)	75(+1)
11	7	1(+1)	1.551 (−1.41)	75(+1)
12	15	1(+1)	11.449 (+1.41)	75(+1)
13	4	1(+1)	6.5(+1)	11.37(−1.41)
14	6	1(+1)	6.5(+1)	138.63(+1.41)
15	5	1(0)	6.5(0)	75(0)
16	13	1(0)	6.5(0)	75(0)
17	2	1(0)	6.5(0)	75(0)

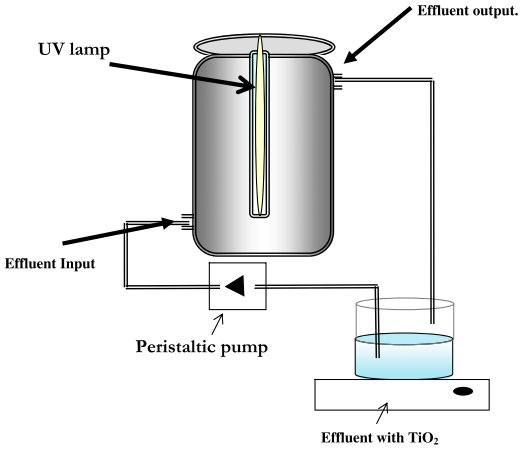

Fig. 1. Photoreactor used in the photocatalytic process with HRT of 1.7 min.

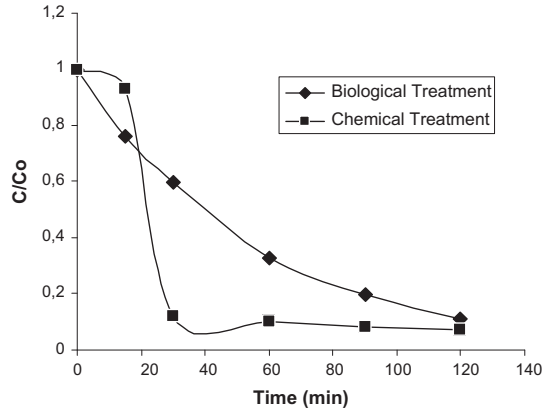

Fig. 3. Oil removal from fishmeal wastewater as a function of reaction time at optimal values of the experimental variables.

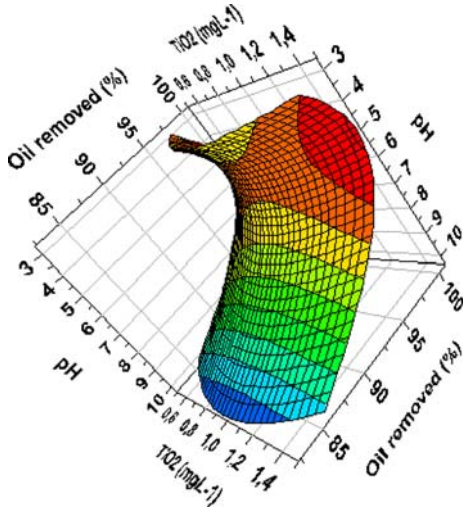

Fig. 2. Contour plots for the optimization of oil removal from wastewater.

Fig. 4. Bioreactor with *P. aeruginosa* in biofilm.

optimal values of the variables were used to follow the kinetics (Fig. 3). During the first 30 min, the oil concentration decreased by 90.0%, remaining constant over time, coinciding with the values estimated by the experimental design. To observe whether the oils present in the chemically treated effluent can be submitted to any further biological treatment (i.e. to demonstrate that the effluents are not toxic), we implemented a biological reactor with *P. aeruginosa* bacteria in biofilms (Fig. 4). Prior to biological treatment, the pH was adjusted to 6.0, given that this is the condition under which the bacteria grow the best [16].

We also compared the efficiency of the chemical and biological treatments, both separately and as an integrated system. The biological process is slower than the chemical treatment (Fig. 3), requiring a longer time to reach the same removal value as the photocatalytic treatment. Similar results were obtained by other authors too who had also studied the bioremediation of olive mill wastewater, whose characteristics were high chemical oxygen demand and dark color, requiring days of treatment to obtain complete mineralization [17–19]. In this study, the fishmeal wastewater initially contained 3,300 mg L^{-1} COD and 854. 8 mg L^{-1} TOC, which were reduced by 74.6 and

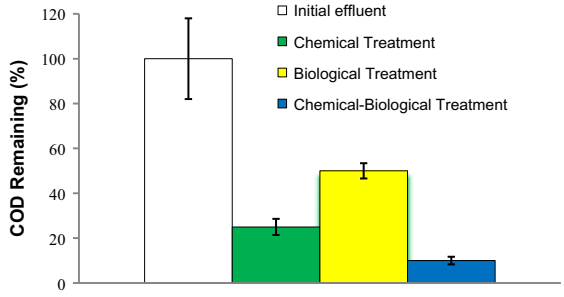

Fig. 5. COD remaining from fishmeal wastewater with the optimized integrated chemical and biological treatments (average ± standard deviation).

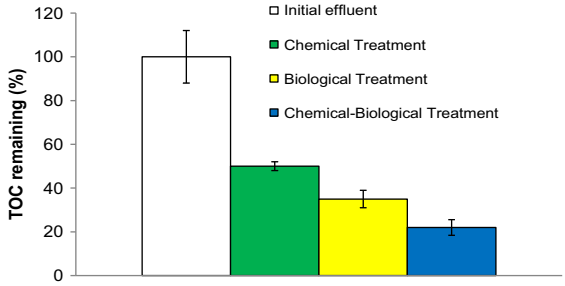

Fig. 6. TOC removal from fishmeal wastewater with the optimized integrated chemical and biological treatments (average ± standard deviation).

50.2%, respectively, with the photocatalytic treatment. To enhance the removal efficiency, the chemical and biological treatments were integrated, achieving 99.0% of oil removal, 88.3% COD removal, and 78.6% TOC removal. The results showed a better overall COD removal with the combined treatment resulting in organic matter, which is easily consumed by microorganisms [20,21]. The efficiency of each treatment in COD and TOC removal is shown (Figs. 5 and 6). It is important to emphasize that after the photocatalytic treatment, the effluent was filtered to eliminate the TiO_2 prior to the biological treatment.

According to the mathematical model retrieved from the experimental data, with a 95.0% confidence interval, $F_{exp.}$=1.1 and $F_{crit.9.7}$ = 4.2; thus, the model is correct because the experimental F is lower than the critical *F*. To analyze the error $F_{exp.}$ = 87.5 and $F_{crit.5.2}$ = 8.4; therefore, the model can be validated, due to the non-significance of the errors.

4. Conclusion

Oil oxidation by photocatalysis using TiO_2 as a photocatalyst was highly efficient, achieving a high percentage of oil removal in just 30 min of reaction time, in addition to improving the biodegradability of organic matters present in the wastewater. The biological treatment had a slower rate of removal than the photocataltic treatment; however the integration of both chemical and biological treatments resulted in high effluent mineralization. Additionally, the use of experimental design saved time by generating an optimization of the processes.

Acknowledgment

This study was supported by the Facultad de Ciencias of the Universidad Católica de la Santísima Concepción.

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