



## Remediation of oily wastewater from an interceptor tank using a novel photocatalytic drum reactor

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Received 25 November 2009; Accepted 7 May 2010

### ABSTRACT

A novel photocatalytic reactor has been developed to remediate oily wastewaters. In the first instance degradation rates of model organic compounds, methylene blue (MB) and 4-chlorophenol (4-CP) were determined. The experimental set-up investigated a 1:10 w/v catalyst to organic solution volume, 30 g catalyst, 300 mls MB (10 µM) or 4-CP (100 µM). The catalyst investigated was a pellet catalyst to improve separation of the remediated volume from the catalyst following treatment. MB concentration decreased by 93% after 15 mins irradiation whilst 4-CP concentration decreased by 94% following 90 mins irradiation. Oily waste water (OWW) from an interceptor tank typically containing diesel oils was obtained from Sureclean, an environmental clean-up company. The OWW was treated using the same conditions as MB and 4-CP, the model organic compounds. Levels of total organic carbon (TOC) and total petroleum hydrocarbon (TPH) were used to monitor the efficacy of the photocatalytic reactor. TOC reduced by 45% following two 90 mins treatment cycles. TPH reduced by 45% following 90 mins irradiation and by a further 25% during a second stage of treatment. This reactor can be used as a polishing technique assembled within a wastewater treatment plant. Allowing for more than one pass through the reactor improves its efficiency.

*Keywords:* 4-chlorophenol; Interceptor water remediation; Methylene blue; Photocatalytic reactor

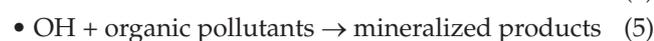
### 1. Introduction

Regulations that govern the allowable discharge of oil into municipal treatment plants and surface waters are becoming increasingly stringent [1]. Conventional approaches to treating oily wastewater have included gravity separation and skimming, dissolved air flotation, de-emulsification, coagulation and flocculation [2,3]. However many of these methods do not remediate the oily waste to a level where disposal to sea is appropriate.

When de-emulsification processes are applied the presence of the emulsifying agents facilitates the stabilisation of the oily emulsion therefore making remediation difficult [4,5]. Heterogeneous photocatalysis has been explored as a technology for the efficient treatment of industrial wastewater and contaminated ground and drinking water [6,7]. As a method of water purification, photocatalysis has considerable advantages over some existing technologies; it destroys pollutants rather than merely transferring them to another phase (e.g., activation carbon adsorption, gas sparging) and does so without the use of potentially hazardous oxidants (e.g., ozone, chlorination) [8]. When a semiconductor is

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illuminated with light of energy greater than its band-gap, electrons and holes are formed (Eq. 1). The band-gap energy is the energy difference between the valence band and the conduction band. The electron and holes formed are highly charged and initiate reduction and oxidation reactions, thereby mineralising the aqueous pollutants (Eqs. 2–4) [9–11]. The highly oxidizing positive hole has been considered to be the dominant oxidizing species contributing to the mineralization process resulting from the TiO<sub>2</sub> photocatalyst (Eq. 5).



Titanium dioxide (TiO<sub>2</sub>) is one of the most popular and widely used materials in photocatalysis due to its high photo stability and redox selectivity, non-toxicity and relatively inexpensive nature [12,13].

In this study, a new photoreactor based on a slurry-continuous flow reactor configuration is presented [14,15]. This configuration combines the high surface area contact of catalyst with pollutant of a slurry reactor with a high illumination of catalyst. Its unique array of serially constructed baffles on the inside wall of the reaction vessel. The baffles continuously remove catalyst from the aqueous solution allowing the catalyst to be exposed to UV illumination as the reaction vessel rotates perpendicular to the UV illumination source. The novel reactor configuration exhibits certain features which are important for the viability of the process in a large scale application, these include: the ability to operate the reactor in both batch and continuous mode. The use of Hombikat pellet catalyst removes the filtration problems associated with batch reactors; the reactor is constructed from perspex which has a high light penetration which leads to improved energy utilization. The reactor configuration also eliminates the need for oxygenation other than oxygen uptake from air through openings on both sides of the reaction vessels. The degradation of MB, 4-CP and OWW is reported under 2 sets of conditions (i) UV illumination alone and (ii) catalyst + UV illumination.

## 2. Materials and methods

### 2.1. Materials

Methylene blue, ~85%, (remaining 15% primarily) salt, and 4-chlorophenol were purchased from Aldrich and used in aqueous solution (Milli Q water).

OWW sample was sourced from an interceptor at Sureclean Ltd and was used as received. Titanium dioxide (TiO<sub>2</sub>) in pellet form was purchased from Sachtleben Chemie, Duisburg, Germany (Hombikat KO1) and used as purchased; the composition was reported to contain 80% anatase and 20% rutile. Specific surface area (BET) 95 m<sup>2</sup>g<sup>-1</sup>, primary particle size ~15 nm, mean pore diameter (N<sub>2</sub>) ~150 Å, pH ~5.5.

### 2.2. Photocatalytic reactor

The photocatalytic reactor consisted of (i) three serially connected rotating cylindrical vessels (570 mm length and 94 mm i.d.) with weir-like paddles constructed along the longitudinal length of the vessels and (ii) an external illumination source. Rotation of the cylindrical vessels was provided by three 12 V electrical motors and illumination was provided by 36 W Philips PL-L sunlamp UV tubes supplied by RS Components Ltd, Northants, UK. The tubes were mounted in pairs, adjacent to each other on a reflective mirror, and enclosed in a wooden box to provide control over exposure to ambient light. The lamps were cooled by air flowing freely within the openings between the reactor vessels and the UV tubes. Figs. 1(a) and 1(b) show the patented photocatalytic drum reactor configuration [14]. Sampling was achieved via the open air vents at the fluid inlet side of the reactor drum.

### 2.3. Photocatalytic experiments

Stock solutions of MB (10 μM) and 4-CP(100 μM) were prepared. MB (10 μM, 300 ml) was added into the reaction vessel containing the pre-weighed catalyst (10–40 g). Samples were drawn after 7, 15, 30, 45, 60 and 75 mins, centrifuged with Henderson T121 Centrifuge for 15 mins at 6000 rpm to eliminate any suspended TiO<sub>2</sub> particles produced during the experiment. The procedure was repeated for 4-CP. The change in absorbance of MB and 4-CP was monitored at different time intervals using UV-Vis Spectroscopy (Perkin Elmer Lambda 950). Maximum absorbances of 666 nm and 217 nm were used to calculate the concentration of MB and 4-CP respectively. Two other conditions were also investigated, the first was UV illumination alone and the second was with catalyst present and without any illumination using the same time intervals. The series of experiments were repeated for the remediation of OWW using the optimum catalyst concentration and the samples monitored using GCMS (Hewlett Packard 5890 with 5971A mass spectrometer) mobile phase: ZB-5 5% phenyl polysiloxane capillary column. Total petroleum hydrocarbon (TPH) content of OWW samples was assessed following the EPA standard method [16–19].

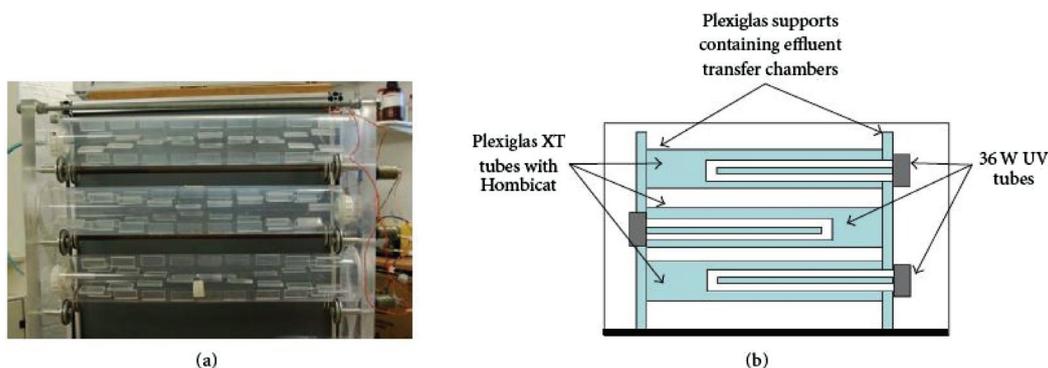


Fig. 1. Schematics of the photoreactor configuration.

Organic carbon was analysed using Shimadzu TOC-V series with AS1 automatic sampler analyser via the TOC = TC – IC method where sodium carbonate, sodium bicarbonate and potassium hydrogen phthalate were used as standards.

### 3. Results and discussion

Remediation of MB and 4-CP using photocatalysis has been widely reported and has become a standard model for the assessment of novel catalysts and novel photocatalytic reactors [20–26]. In this work a novel photocatalytic reactor [14] was assessed for the remediation of MB (10  $\mu\text{M}$ ) in the presence of  $\text{TiO}_2$  catalyst (10, 20, 30 and 40 g). Fig. 2 illustrates the remediation of MB in the presence and absence of varying weights of the pellet  $\text{TiO}_2$  catalyst. A comparison of the degradation efficiencies shows that 67, 73, 86 and 82% of the MB in the samples was removed after 7 mins of treatment with 10, 20, 30 and 40 g of catalyst. In contrast, 42% of the MB in the samples was degraded with UV irradiation alone, indicating that the catalyst increased the rate of MB

degradation. The MB solution was completely remediated after 60 mins of treatment in all experiments.

The advantage of using the pellet catalyst over the commonly investigated  $\text{TiO}_2$  powder Degussa P25 [27,28] is the ease of separation following remediation. The settling velocity of aggregated  $\text{TiO}_2$  with an average diameter of 0.3  $\mu\text{m}$  is very slow and would require a long retention time in a clarifier. As the dosage of  $\text{TiO}_2$  is increased in order to increase the photocatalytic rate, the high turbidity created by the high  $\text{TiO}_2$  concentration can actually decrease the depth of UV penetration. This shadowing effect can drastically lower the rate of photocatalytic reaction on a unit  $\text{TiO}_2$  weight basis. An obvious solution to this problem would be to immobilise the catalyst on a solid carrier [29,30], or use the pellet catalyst.

The optimum results achieved for the remediation of MB were recorded when 30 g  $\text{TiO}_2$  catalyst was employed. This catalyst weight was used for the remaining experiments. Fig. 3 illustrates the remediation of 4-CP (100  $\mu\text{M}$ ) following 60 mins irradiation in the presence and absence of  $\text{TiO}_2$  catalyst (30 g). 20% of 4-CP was remediated under photolysis alone. In the presence of the pellet

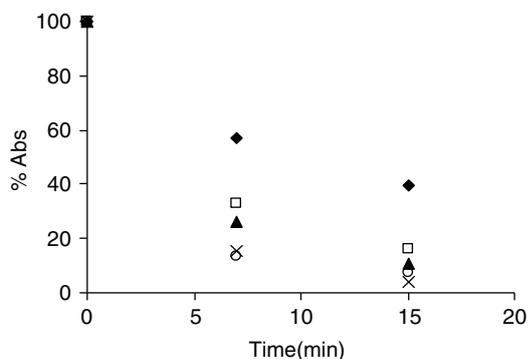


Fig. 2. Degradation of MB (10  $\mu\text{M}$ ) using in the presence and absence of catalyst loadings [10 g( $\square$ ), 20 g( $\blacktriangle$ ), 30 g( $\bullet$ ), 40 g( $\times$ )] and under UV irradiation ( $\blacklozenge$ ).

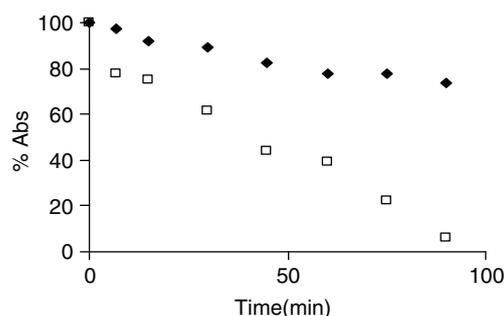


Fig. 3. Degradation of 4-CP (100  $\mu\text{M}$ ) using in the presence ( $\square$ ) and absence ( $\blacksquare$ ) of catalyst loadings (30 g) and under UV irradiation.

TiO<sub>2</sub> catalyst almost complete remediation of 4-CP was recorded following 90 mins irradiation, 94%, Fig. 3. Cao et al. reported the remediation of 4-chlorophenol using a F and La doped TiO<sub>2</sub> powder. 20% degradation of 4-CP was recorded with the undoped TiO<sub>2</sub> powder, increasing to 90% with the doped powder after 4 h irradiation under visible light [31]. This catalyst is more active than the pellet catalyst reported here however there would be problems associated with separation following remediation and therefore problems with scale-up. TiO<sub>2</sub> adsorbed on activated carbon results in a reduction in 3-CP concentration of 40% following 5 h irradiation [32]. Following the experiment the TiO<sub>2</sub> loaded activated carbon would need to be separated, a task that can be time consuming and not efficient.

The pellet catalyst has a reduced surface area compared to the TiO<sub>2</sub> powder but it compares favourably with immobilised TiO<sub>2</sub> for the remediation of 4-CP. A study by Orendorz et al. demonstrated the reduction of 4-CP by 50% adsorbed on a titania thin film and exposed to UV [33].

Visual analysis of the waste water samples before and after treatment shows noticeable differences between the treated and untreated waste water samples. OWW samples which appeared dark grey before treatment had a faint brown appearance after 180 mins of treatment with the drum photocatalytic reactor. Major components identified in the untreated interceptor 6 samples through a NIST library search were as follows decane at 15.56, dodecane at 17.52 and tetradecane at 19.32, all common components of OWW. Fig. 4 illustrates the decrease in abundance of decane, dodecane and tetradecane following 180 mins remediation in the photocatalytic reactor. This indicated that the photocatalytic

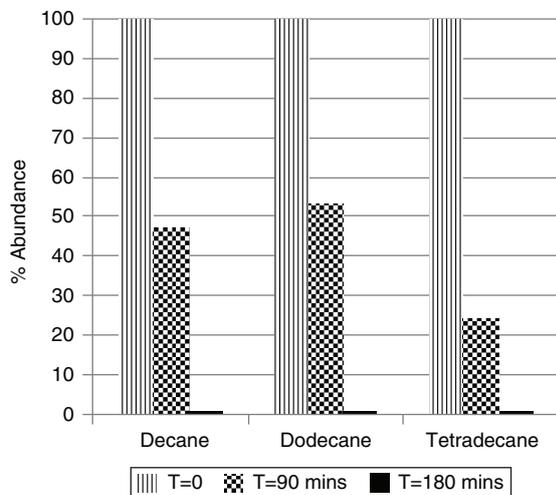


Fig. 4. Decrease in abundance of decane, dodecane and tetradecane following UV irradiation in the presence of 30 g TiO<sub>2</sub> OWW was sampled from Interceptor 6.

treatment was effective in removing volatile components of the OWW.

Fig. 5 illustrates the reduction in total petroleum hydrocarbon (TPH) in the OWW sample following photocatalytic remediation. The TPH was reduced to 441 ppm (15%) following UV irradiation alone for 180 mins whilst the number was reduced to 295 ppm (43%) following photocatalysis for 90 mins and to 156 ppm (70%) following a further 90 mins irradiation in the presence of the same catalyst sample.

Fig. 6 illustrates the reduction in TOC of the OWW sample following two treatment stages. OWW (1) illustrates the TOC value determined for OWW prior to treatment at 2263 ppm. Following irradiation in the presence of TiO<sub>2</sub> catalyst for 90 mins the TOC was reduced by 18% to 1892 ppm. This sample was removed from the reactor and a fresh sample of catalyst (30 g) was added and the sample was treated for a further 90 mins, OWW(2), Fig. 6. The TOC was reduced by a further 35% to 1230 ppm.

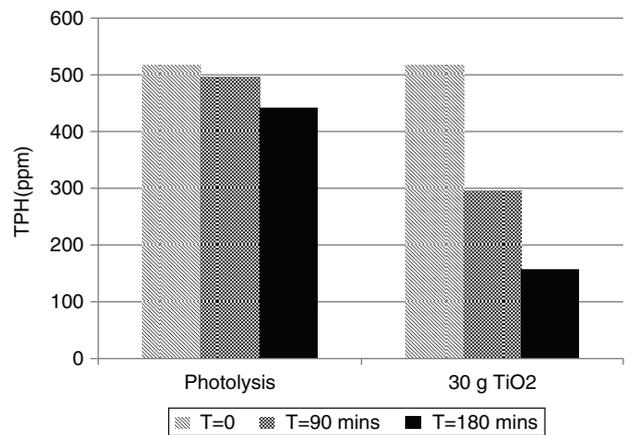


Fig. 5. Reduction of TPH following 180 mins irradiation in the presence and absence of TiO<sub>2</sub> catalyst (30 g).

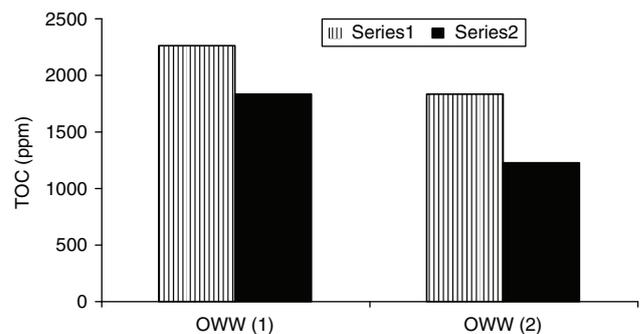


Fig. 6. Reduction in TOC following a 2-stage photocatalytic treatment of 2 90 minute irradiation periods in the presence of TiO<sub>2</sub> catalyst (30 g).

Rajakovic et al. reported the removal of oil from real waste water samples using wool based sorption materials, this method is non-destructive, the oil soaked sorbent material would then need to be treated [3].

#### 4. Conclusion

A novel photocatalytic reactor was assessed using MB and 4-CP as model compounds. In the presence of 30 g TiO<sub>2</sub> catalyst the reactor was capable of completely remediating the model waste streams. An oily waste water sample from an interceptor which stores diesel oil wastes was remediated. GCMS, TPH and TOC results illustrated the effectiveness of the novel photocatalytic reactor. This reactor could be applied within a waste water treatment system and used as a polishing technique.

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