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Development of a slurry continuous flow reactor for photocatalytic treatment of industrial waste water

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ABSTRACT

The water treatment capability of a novel photocatalytic slurry reactor was investigated using methylene blue (MB) as a model pollutant in an aqueous suspension. A pellet TiO_2 catalyst was employed and this freed the system from the need of filtration of catalyst following photocatalysis. This configuration combines the high surface area contact of catalyst with pollutant of the slurry reactor and also offers a high illumination of catalyst by its unique array of weir-like baffles. In this work, the batch adsorption of MB from aqueous solution (10 μM) onto the TiO_2 catalyst was studied, adsorption isotherms and kinetics were determined from the experimental data. Complete degradation of MB was achieved within 60 min illumination with various loadings of catalyst (30–200 g L^{-1}). A modest catalyst loading (30 g L^{-1}) achieved 98% degradation within 60 min of irradiation. Experimental results indicate that this novel reactor configuration has a high effective mass transfer rate and UV light penetration characteristics.

1. Introduction

Textile dyes and other commercial colourants have become the focus of environmental remediation efforts because their natural biodegradability is made increasingly difficult owing to the improved properties of the dyestuffs. Many dyes are highly water soluble in order to meet the colour requirement of deep dyeing [1–3].

The most commonly practised technology for the removal of dyestuffs from aqueous solution is chemical coagulation followed by sedimentation. This process generates large amounts of sludge which then needs disposal, essentially transferring the dye pollutant potential to another phase [3]. Heterogeneous photocatalysis has been widely explored as a promising technology for the efficient treatment of industrial wastewater and contaminated ground and drinking water [4,5]. 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) [6]. When a semiconductor is illuminated with light of energy greater than its bandgap, electrons and holes are formed. The bandgap 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 [7–9]. Titanium dioxide (TiO_2) 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 [10,11].

Developing a practical large scale photocatalytic reactor for water treatment has not yet been generally accepted in practice because there are many operational parameters which must be considered in particular: (i) the water treatment capability of the reactor is determined by the amount of catalyst that can be activated therefore a challenge posed for a large scale reactor is the efficient exposure of the catalyst to irradiation, (ii) another challenge is to ensure that the illuminated catalyst area in contact with the water is high, and (iii) mixing and mass transfer limitations of a large scale reactor also have to be overcome and in any design for industrial application, a high waste water throughput through the reactor should be attainable [12–14].

In this study, a new photoreactor based on a slurry continuous flow reactor configuration is presented [15,16]. This configuration combines the high surface area contact of catalyst with pollutant of a slurry reactor with a high illumination of catalyst. It has a unique array of serially constructed baffles on the inside wall of the reactor 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

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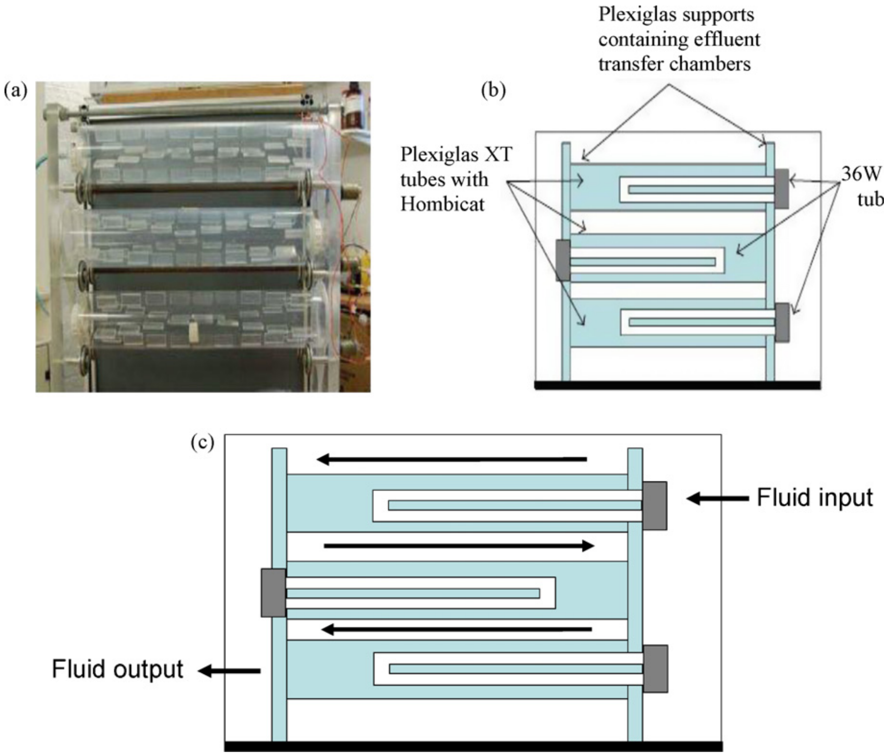

Fig. 1. Schematics of the photoreactor configuration.

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 is reported under 3 sets of conditions (i) UV illumination alone, (ii) catalyst + UV illumination and (iii) catalyst without UV illumination.

2. Materials and methods

2.1. Materials

Methylene blue, ~85%, (remaining 15% primarily) salt, was purchased from Aldrich and used in aqueous solution (Milli Q water). Titanium dioxide (TiO_2) 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 $m^2\,g^{-1}$, primary particle size ~15 nm, mean pore diameter (N_2) ~150 Å, pH ~5.5. Degussa P25 TiO_2 was used as received.

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. Fig. 1(a)–(c) shows the patented photocatalytic drum reactor configuration [15]. Sampling was achieved via the open air vents at the fluid inlet side of the reactor drum.

2.3. Photocatalytic experiments

A stock solution of MB (10 μM) was prepared and used for all experiments. The TiO_2 pellet catalyst was weighed and placed in the reaction vessel. To start the experiment, the feed solution was pumped (Auto Clude Peristaltic pump) from the reservoir to the reaction vessel containing the catalyst. MB (10 μM, 1 L) was added into the reaction vessel containing the pre-weighed catalyst. The motor was switched on and the aqueous suspension continuously agitated for 60 min in the dark. Samples were drawn at 5 min intervals, centrifuged with Henderson T121 Centrifuge for 15 min at 6000 rpm to eliminate any suspended TiO_2 particles. The change in absorbance of MB was monitored at different time intervals using UV–vis spectroscopy (Perkin Elmer Lambda 950). Absorption spectra of samples were recorded between 200 and 750 nm and a maximum absorbance at 666 nm was used to calculate the concentration of MB. To examine the effect of UV irradiation on the process the catalyst was immersed in distilled water for 60 min to allow adsorption equilibration to be reached. Then the lamps were switched on and the reactor rotated for 60 min. UV illumination alone was also investigated. Samples were taken at 5 min intervals and treated as described previously.

3. Results and discussion

3.1. Adsorption equilibrium

Adsorption of organic pollutants is generally considered to be an important parameter in determining the degradation rates of photocatalytic oxidation [17]. Adsorption of MB on the surface of TiO_2 strongly affects the degradation process [18]. Several mechanisms have been proposed to account for the initial steps of the photodegradation of organics with TiO_2 as a photocatalyst. One

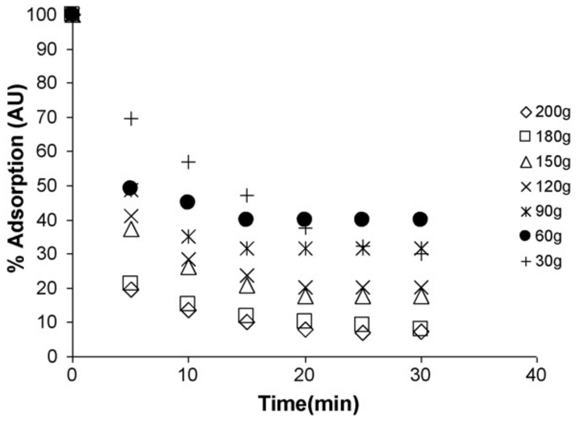

Fig. 2. Adsorption of MB (10 μM) on TiO_2 pellet catalyst at various catalyst loadings 30 g (+), 60 g (●), 90 g (*), 120 g (×), 150 g (△), 180 g (□), and 200 g (◇).

mechanism suggested that the oxidation of organic compounds occurs following adsorption of the organic compounds on the photocatalyst surface and then reacted with excited superficial e^-/h^+ pairs or OH^* to form the final products [19].

Fig. 2 illustrates the amount of MB adsorbed with contact time. The results show a gradual increase in the amount of MB adsorbed as the catalyst loading was increased. An apparent optimum loading of 180 g L^{-1} was observed, where a further increase in catalyst loading to 200 g L^{-1} did not result in any appreciable increase in the amount of MB adsorbed on the catalyst. The increased loading did not affect the adsorption of MB as saturation must have been achieved with a loading of 180 g L^{-1} of catalyst. Increased number of TiO_2 sites available with the 200 g L^{-1} loading does not increase the reaction rate. Lakshmi et al. reported 70% degradation of MB in 34 min using a tube reactor, 125 W medium pressure Hg lamp and 0.05 g Degussa P25 catalyst. Comparing this with our results demonstrates that the optimum catalyst loading and degradation time varies with photoreactor type and the catalyst investigated. Degussa P25 would have a greater surface area so an improved degradation rate would be expected. However, it is a difficult powder to separate from the remediated solution [20].

3.2. Photocatalytic experiments

Preliminary experiments were carried out to show the photocatalytic degradation of MB (Fig. 3). The rate of photodegradation was studied by monitoring the change in the maximum absorption in UV–vis spectra at 666 nm of the residual MB solution over irradiation time. Temporal changes in the concentration of MB were monitored by examining the changes in maximal absorption at 666 nm [20]. Absorbance of MB occurs typically at 668 and 609 nm [21]. The amount of residual MB decreased, while a blue shift of the maximum peak around 650–665 nm was observed, as the photocatalytic reaction proceeded, and this peak almost disappeared completely after 60 min of irradiation time (Fig. 3). It was reported that the blue shift was caused by photooxidative N-demethylation of MB resulting from the production of intermediate species [22]. Prior to the experiment the catalyst had been immersed in distilled water for 60 min. This was to ensure that the decrease in MB concentration observed resulted from photocatalysis and not adsorption of MB on to the catalyst surface.

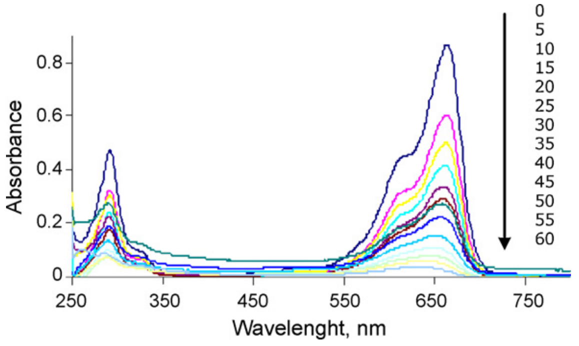

Fig. 3. Temporal absorption spectral pattern of MB during the photodegradation process in the presence of TiO_2 catalyst and under UV irradiation.

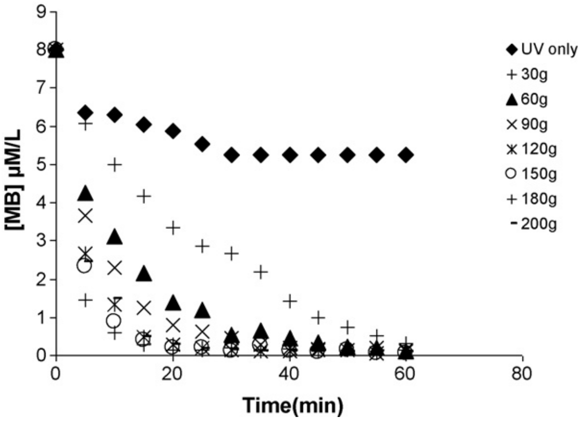

Fig. 4. Degradation of MB under UV irradiation in the presence of TiO_2 catalyst at various loadings 30 g (+), 60 g (▲), 90 g (×), 120 g (*), 150 g (◯), 180 g (+), and 200 g (–).

UV illumination alone causes a 20% decrease in MB absorbance following 60 min irradiation (Fig. 4). The catalyst loadings investigated ranged from 30 to 200 g L^{-1}. During the first 5 min irradiation the decrease in MB concentration observed without catalyst is similar to that observed when 30 g catalyst was present. The reactor whilst rotating results in a thin film of MB coating the reactor surface. This thin film exposed to irradiation is degraded and then returns to the reaction liquid where it remixes with the stock solution. This action causes the decrease in MB concentration observed in Fig. 4 without the addition of catalyst. The limit is reached after 30 min irradiation when the presence of catalyst enhances the degradation of MB.

Catalyst loadings greater than 90 g L^{-1} resulted in the complete degradation of MB within 30 min. The performance of loadings of 30 g/60 g/90 g was extremely effective with greater than 90% decrease of MB absorbance observed following 60 min irradiation (Fig. 4).

The apparent first order kinetic model derived from Langmuir–Hinselwood kinetics was used in this study [23,24]. For the degradation of MB in the presence of 30, 60 or 90 g catalyst plotting $\ln[MB]/[MB]_0$ as a function of reaction time yielded straight lines demonstrating that MB degradation follows apparent first order kinetics at these catalyst loadings. This confirms that photocatalysis was responsible for the MB degradation observed [8]. The photocatalytic degradation rate at each catalyst loading was 0.0525, 0.0813 and 0.111 min^{-1} for 30, 60 and 90 g loadings of catalyst, respectively. Fig. 5 illustrates the rate of reaction versus catalyst loadings at each catalyst weight investigated. A linear increase in rate was observed with increasing catalyst loading for each weight investigated until we reached 200 g. The rate for the 200 g loading was slower than 180 g confirming that saturation of the catalyst by MB must occur with a 180 g loading. Sivalingam et al. reported saturation limits of MB on their powder TiO_2 catalyst of 1 kg m^{-3}. They suggested that the substrate molecules were not sufficient for adsorption by the increased number of TiO_2 sites available above this concentration [25].

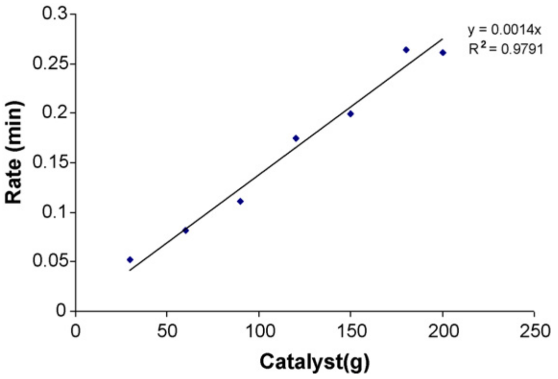

Fig. 5. Plot of rate of reaction versus catalyst loading for catalyst loadings of 30 g up to 200 g.

Another factor to consider in the development of a photocatalytic reactor for large scale wastewater remediation is economics. Continuing the experiments with a lower loading of catalyst (30 g) was viable as it had demonstrated a remediation of 98% in the initial study. Results of the degradation of MB in the presence and absence of TiO_2 are illustrated in Fig. 6. Irradiation of MB without any catalyst present resulted in a decrease in absorbance of MB of 20%.

The disappearance of MB colour observed in the degradation reactions in the presence of catalyst but without irradiation was due to the adsorption of MB molecules onto the catalyst pores rather than photocatalyzed degradation. This conclusion was supported by observing that the final solution from the photocatalyzed degradation experiments was more colourless than that of the non-irradiated set indicating that the presence of TiO_2 played an important role in the photodegradation of MB [26].

When the solution was exposed to UV irradiation in the presence of catalyst a gradual decrease in concentration of MB was observed. The control experiment (blank) showed that MB was not degraded in the absence of TiO_2 under the same irradiation conditions. Complete mineralisation occurs following 60 min irradiation in the presence of the pellet catalyst.

Fig. 6 also illustrates the degradation of MB in the presence of 0.1 g L^{-1} of Degussa P25 catalyst. Following 20 min irradiation of MB, 90% remediation of MB was observed. This result demonstrates the inherent advantage of the reactor design. The patented baffles allow an increased surface area contact between catalyst and pollutant as well as high illumination of the catalyst. There have been many reports of reactors utilising Degussa P25 with various lamps for the remediation for MB ranging from 100% degradation of 20 μM solution irradiated for 270 min with a 500 W Xe lamp in the presence of 0.2 g L^{-1} catalyst [27]. Zhang et al. remediated a 0.1 mM MB solution following 120 min irradiation from a 75 W Hg lamp [22]. The same group also reported the remediation of 25 μM MB solution using a parabolic round concentrator reactor and solar illumination. This required 30 min to completely degrade MB [28].

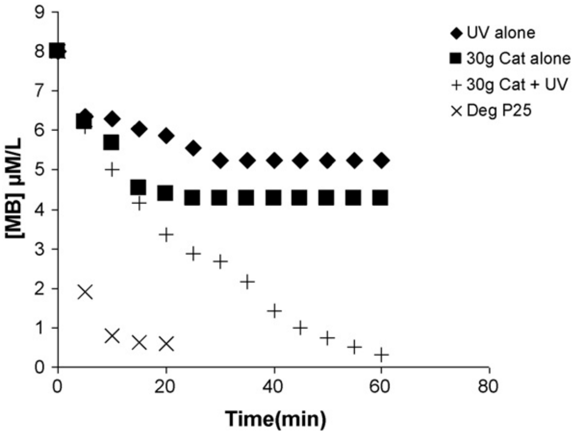

Fig. 6. Degradation of MB under UV irradiation alone, in the presence of 30 g TiO_2 catalyst, UV irradiation and 30 g TiO_2 catalyst and 0.1 g L^{-1} Deg P25 and UV irradiation. UV alone (♦), 30 g Cat alone (*), 30 g Cat and UV irradiation (+), and Degussa P25 and UV irradiation (×).

Comparing this to Degussa P25 the remediation using the pellet catalyst is slower than that recorded when Degussa P25 was investigated; obviously there is less surface area with the pellet compared with Degussa P25 powder. The advantage of using the pellet catalyst is ease of separation following remediation. The settling velocity of aggregated TiO_2 with an average diameter of 0.3 μM is very slow and would require a long retention time in a clarifier. As the dosage of TiO_2 is increased in order to increase the photocatalytic rate, the high turbidity created by the high 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 TiO_2 weight basis. An obvious solution to this problem would be to immobilise the catalyst on a solid carrier [29,30]. Immobilising Degussa P25 to a solid carrier reduces the surface area available for target molecule adsorption. It has also been shown to have decreased activity following repeated trials [31]. Utilising a pellet catalyst can overcome this problem offering an easily separable catalyst which could also be reused or recycled for further photochemical reactions.

4. Conclusion

The photocatalytic degradation of methylene blue in aqueous solution using a commercial pellet TiO_2 catalyst in a novel photocatalytic reactor was achieved. The adsorption characteristics of the commercial Hombikat-KCO pellet TiO_2 catalyst were studied and the maximum catalyst loading for adsorption of MB to be 180 g under natural conditions. A linear rate of reaction versus catalyst loading was observed with loadings up to 180 g.

A lower catalyst loading of 30 g achieved a 98% degradation of MB. The results indicate that in a slurry photocatalytic reactor system, catalyst dosage is an important parameter in the degradation capability of the photoreactor since it directly impacts on the adsorption rate and the amount of catalyst adequately illuminated for the generation of the radicals responsible for the degradation of pollutant. However, there are problems associated with the pellet catalyst where attrition of the catalyst leads to small TiO_2 particles being left in the remediated liquid. The stability of the pellet catalyst for commercial applications needs to be investigated.

Further work will investigate the effect of varying pH, presence of additives and the reactors capability to remediate interceptor fluid from an oil and gas waste stream.

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