Chapter 11
Catalytic Water Treatment

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Abstract With the increasing lack of access to safe drinking water and the lack of proper sanitation services largely due to the presence of toxic Azo dyes in wastewater, generated from the textile industry, increasing research has been done to investigate better methods to treat wastewater. Though conventional methods are already present, such as filtration, photodegradation of organic pollutants has recently been the most widely investigated to solve this problem. Studies have shown titanium dioxide catalyst (TiO_2) is one of the most efficient methods in degrading Azo dyes. This is investigated through photocatalytic reactions of TiO_2 plates with Congo red solution. The effects of various operational parameters of TiO_2 plates, such as the different calcination temperatures and the concentration of Congo red solution used, are first determined to identify the final optimum reaction conditions needed to determine the optimum shape of the stainless steel reflector (flat, semicircle, right angle, parabolic). By comparing the results obtained for the percentage removal of Congo red dye, the most effective removal is when the TiO_2 plates are at a calcination temperature of 400 °C for 2 h, and the most effective shape for the stainless steel reflector shape is the parabolic one. Moreover, the ability of TiO_2 plates to be dye-sensitised into solar cells was also investigated using I_3/I^- electrolyte, and the voltage of the solar cell was measured. This ability of TiO_2 plates to be able to harvest solar energy into electrical energy is beneficial especially in the less developed and poorer countries.

11.1 Introduction

According to the World Health Organisation (WHO), in 2017, 2.2 billion people around the world do not have safely managed drinking water services, while 4.2 billion people do not have safely managed sanitation services [1].

The textile industry is one of the world's leading sources of water consumption and pollution. Processes involved in the production of clothing, including dyeing and

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rinsing, release around 150 billion gallons of wastewater annually. This wastewater usually contains a large amount of Azo dyes with around 280,000 tons of dyes discharged in textile industrial effluent every year.

These disposal of toxic Azo dyes can cause extreme damage to the surrounding aquatic environment and the organisms living near the polluted water, due to the relatively high biochemical oxygen demand and chemical oxygen demand. These dyes are also carcinogenic for humans and difficult to degrade via natural means [2].

Although conventional methods such as chemical precipitation, filtration, electrodeposition, ion-exchange adsorption and membrane systems are already present to treat wastewater, these methods may not be very effective as it is often slow or non-destructive to certain persistent organic pollutants. Furthermore, these methods only serve to convert soluble pollutants into their solid phase, which would then require additional resources to remove [3, 4].

Currently, the use of titanium oxide photocatalysts is one of the most efficient methods of degrading Azo dyes. However, the use of the TiO_2 photocatalyst needs UV irradiation in order to degrade the dyes. This process is very expensive and inaccessible to those living in developing countries living near textile factories, where many lack access to clean drinking water. Thus, the use of photocatalyst is needed the most [5–8].

However, the metal sheets can be of different shapes, such as semicircle, flat or right angle. It is thus necessary to investigate the most efficient reflective shape for the best photocatalytic reaction of the TiO_2 plates. Past research has shown that the parabolic shape allows for the incident parallel rays to always converge at a single focal point no matter where on the surface of the mirror they actually strike, highlighting that the parabolic shape could be the most efficient shape [9]. As parabolic metal sheets are currently not present, the effectiveness of the parabolic shape of the metal sheet to act as a reflector will be investigated.

Additionally, in most of the developing countries, electricity is not easily accessible, while naturally sourced dyes may be easier to come by. One of the most commonly used and accessible fruits that are used in the making of the dye-synthesised solar cell is raspberry, which contains anthocyanin dye. Extensive research has been done on the efficacy of the TiO_2 solar cell to harvest light energy and its conversion to electrical energy. Due to the large band gap, suitable band edge levels for charge injection and extraction, long lifespan of excited electrons, exceptional resistance to photocorrosion, non-toxicity and low cost have made TiO_2 a popular material for solar energy applications. Hence, we plan to investigate the efficacy of the differently shaped plates on the generation of electricity via the dye-synthesised TiO_2 solar cell [10, 11].

11.1.1 Hypothesis

We hypothesise that the use of a parabolic surface will yield the most effective removal of CR dye as well as generate the highest current among all of the shapes.

11.2 Methodology

11.2.1 Preparation of TiO_2 Catalyst

The TiO_2 photocatalyst was prepared as follows: TiO_2 powder was grounded with acetic acid into a smooth paste using a mortar and pestle. A thin layer of the paste was then applied onto the conductive side of the fluorine-doped tin oxide (**FTO**) coated **glass** plates using a scalpel. The plates were then placed into an oven at 100 °C for 30 min to dry out the paste. The plates were then placed in the furnace at varying temperatures (200–600 °C) for 2 h to measure the effect on the temperature on the efficiency of dye removal.

11.2.2 Metal Sheet Preparation

Metal plates measuring 10 cm × 10 cm were hammered into four different shapes: straight, 90°, semicircle and a parabola.

11.2.3 Photocatalytic Experiments

11.2.3.1 Temperature

TiO_2-coated FTO glass plates were then placed in the furnace at different temperatures and were placed in a petri dish and filled with 40 ml of 20 mg/dl dye in the machine for 2 h, before they were taken out and the concentration was measured using a UV–vis spectrometer.

For the rest of the experiments, TiO_2-coated FTO plates were placed in the furnace for 2 $_h$ at 400 °C. A Hitachi TM3000 SEM machine was then used to scan the surface of the TiO_2 plates.

11.2.3.2 pH

To measure the optimum pH for solution of CR dye to use, three plates were placed in a petri dish and filled with 40 ml of 20 mg/dl dye of varying pH levels in a [UV] machine for 2 h, before they were taken out and the concentration was measured using a UV–vis spectrometer.

11.2.3.3 Shape of the Metal Sheets

In the UV machine, five dishes with the TiO_2 photocatalysts with 40 ml of 20 mg/dl CR dye were covered with the sheets of different shapes, one dish covered by one plate each, with one dish not covered with any plates. After 2 h, the concentration was measured using a UV–vis spectrometer.

11.2.4 TiO_2 Solar Cell

For the preparation of the raspberry dye, fresh raspberry was blended and filtered to obtain the dye. The TiO_2 plate was then soaked in a raspberry dye solution for 10 $_{min}$. It was then rinsed with ethanol to get rid of the excess dye. Next, another TiO_2-coated FTO plate, conducting side down, was passed through a candle flame to coat the conducting side with carbon. The I_3/I^- electrolyte solution was prepared using 0.5 M KI solution and 0.05 M I_2 in methanol. The electrolyte solution was sandwiched between a carbon-coated plate and a TiO_2-coated plate and bound together using binders. They were then placed on top of the different metal sheets, and the highest voltage recorded was taken using a multimeter. The experimentation was done in **Gelman** HLF **Class 100** Series Horizontal **Laminar Flow** workstation.

11.3 Results and Discussion

11.3.1 Concentration of Congo Red Solution

The rate of photocatalytic reaction is strongly influenced by concentration of the photocatalyst. Heterogeneous photocatalytic reactions are known to show proportional increase in photodegradation with catalyst loading. Generally, in any given photocatalytic application, the optimum catalyst concentration must be determined, in order to avoid excess catalyst and ensure total absorption of efficient photons. This is because an unfavourable light scattering and reduction of light penetration into the solution is observed with excess photocatalyst loading. The concentration of CR solution used in the experiment is 20 mg/dl.

11.3.2 Calcination Temperature of TiO_2 Plates

The increase in temperature enhances recombination of charge carriers and desorption process of adsorbed reactant species, resulting in decrease of photocatalytic

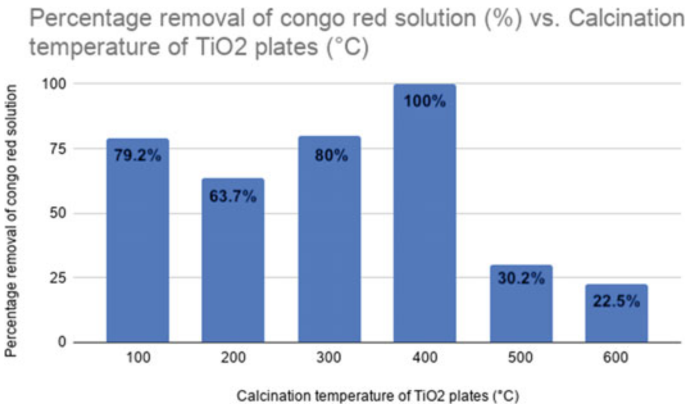

Fig. 11.1 Percentage removal of Congo red solution against calcination temperature of TiO_2 plates graph

activity. This is in conformity with Arrhenius equation, for which the apparent first-order rate constant Kapp should increase linearly with exponential $(-1/T)$. As shown in Fig. 11.1, the percentage removal of CR solution generally increases from 100 to 400 °C as products are able to desorb faster. Adsorption dominates here where desorption can be treated as the rate-limiting step. The optimum calcination temperature of TiO_2 plates is 400 C, with the 100% removal of the CR solution. Above 400 C, the TiO_2 plates become flaky and detached, and its photocatalytic activity is less effective. However, at high temperatures 500 and 600 °C, the reaction rate decreases with increasing temperature, because adsorption is decreasing with temperature in this range.

11.3.3 Analysis of the Optimum Shape of Stainless Steel Reflector

Figure 11.2 analyses the effectiveness of the different shapes of stainless steel reflector to increase light absorption. The most effective shape is the parabolic reflector as the percentage removal of the CR is the highest compared to the other shapes, at 68.8%. This is because the geometry of a parabola is effective in focusing light waves on a single location. The parabolic shape is such that incident parallel rays will converge at a single focal point no matter where on the surface of the mirror they actually strike. It can also be seen that with the stainless steel reflector, the percentage removal of CR doubles from 36.2 to 68.8%, highlighting how having a stainless steel reflector allows for a more efficient photocatalytic reaction.

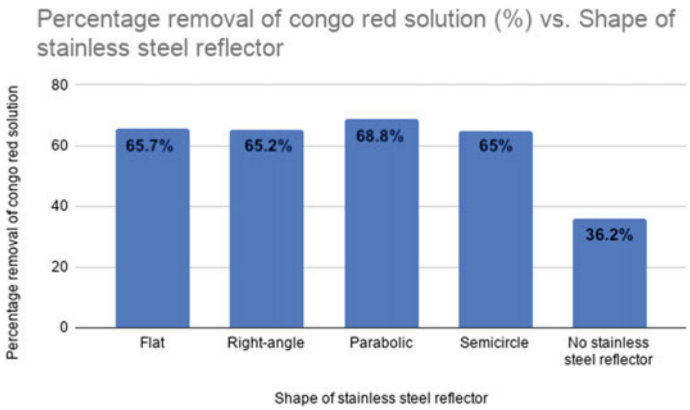

Fig. 11.2 Percentage removal of Congo red solution against the shape of stainless steel reflector graph

11.3.4 Titanium Dioxide Dye-Sensitised Solar Cell

The titanium dioxide (TiO_2) plates can act as a solar cell after being treated with raspberry dye. This takes place due to the condensation of alcoholic-bound protons with the hydroxyl groups that is present on the surface of the nano-structured TiO_2 plates. The plates generate electrons, allowing for electron transport, producing solar power. As seen from Fig. 11.3, this further highlights how the parabolic shape of the stainless steel reflector is most optimum for light absorption as the solar power generated by the dye-sensitised TiO_2 is the highest at 215.5 mV.

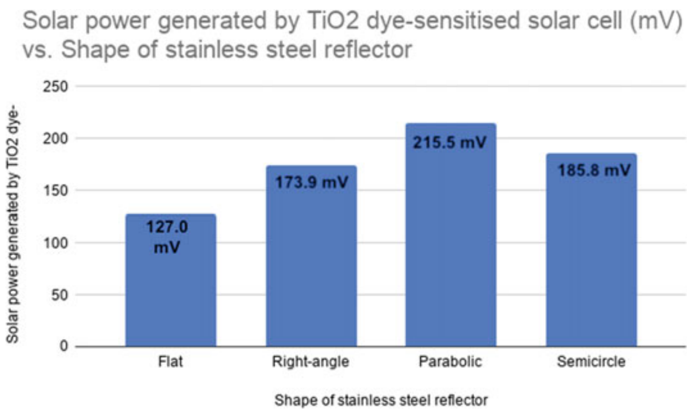

Fig. 11.3 Graph of solar power generated by TiO_2 dye-sensitised solar cell against the shape of stainless steel reflector used

11.4 Conclusion and Future Recommendations

This report addresses the non-strictly controlled discharge of industrial effluents, which has given rise to the current water contamination crisis. The photocatalytic degradation of these organic pollutants using titanium dioxide is the most widely studied method of overcoming the problem of water contamination by organic pollutants. Heterogeneous photocatalytic degradation using TiO_2 photocatalyst remains a viable alternative for the degradation of persistent organic contaminants in both air and water. Moreover, TiO_2 can also be dye-sensitised into a solar cell, harvesting light energy and converting it into electrical energy.

11.4.1 Future Works

The effectiveness of the TiO_2 photocatalyst can be investigated with more types of commonly used Azo dyes, like Chlorazol Blue B and Trypan blue. The metal sheets can also be bent into more shapes and angles, like 60°. The effectiveness of the TiO_2 substrate under constant flow of the dye solution can also be studied to provide information on the kinetics under actual application conditions. A pilot test can then be carried out. Moreover, the TiO_2-coated FTO plates can be placed in the furnace at more temperatures ranging from 400 to 500 °C.

Appendix 1. Calibration Curve

The absorbance of CR dyes of known concentrations (5–30 mg/dl) was measured using a UV–vis spectrometer to obtain the calibration curve.

Figure 11.4 allows for the understanding of the relationship between arbitrary units and concentration of the Congo red solution to aid in finding the percentage removal of the Congo red solution through the photocatalytic reaction of TiO_2.

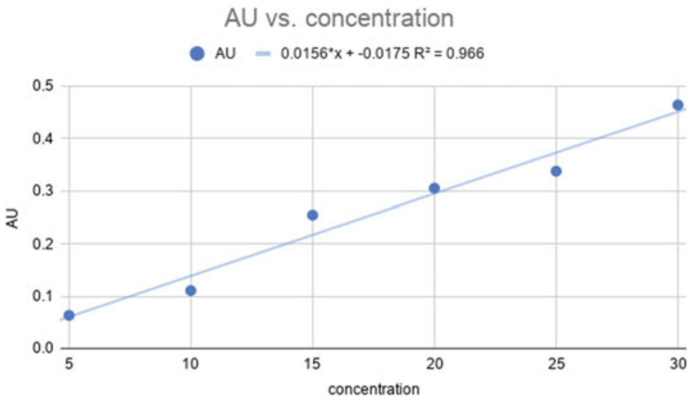

Fig. 11.4 Graph of arbitrary units (AU) against concentration

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