Solar photodegradation of methyl orange in the presence of cations (Pb^{2+} and Fe^{2+}) and anions (Cl^- and SO_4^{2-})

John Akach, Athiambi Davhana, Melody Masilela and Aoyi Ochieng

Abstract— The discharge of dyes from textile industries into water bodies is harmful to aquatic life due to the dye color which prevents light from penetrating the water. As a result, it is necessary to decolorize textile water before it is discharged into receiving water bodies. Current decolorization methods such a membrane processes and adsorption are costly due the need to replace the treatment media. Recently, solar photocatalysis has been developed as an alternative and low cost method of treating dyes. Photocatalysis has been observed to be very robust for the degradation of organic chemicals; however, photocatalysis reaction could be inhibited by inorganic chemicals. This is important since textile wastewater usually has dissolved ions. In this work, the effect of cations (Pb^{2+} and Fe^{2+}) and anions (Cl^- and SO_4^{2-}) on the photocatalysis of methyl orange (MO) was investigated. Nano TiO_2 catalysts were employed for MO photocatalysis in glass fluidized bed reactors under solar illumination. The effect of catalyst loading and concentration of Pb^{2+}, Fe^{2+}, Cl^- and SO_4^{2-} ions between 0.03 and 0.09 mM were investigated. It was found that the optimum catalyst loading was 200 mg/L. The presence of Pb^{2+} ions below a concentration 0.03 mM resulted in a reduction in the removal of MO. However, an increase in MO removal was observed in the presence of Fe^{2+}, Cl^- and SO_4^{2-} ions at all concentrations as well as in the presence of Pb^{2+} ions above 0.03 mM. This work showed that the enhancement or inhibition of the photocatalysis reaction depends on the type and concentration of the ion present in solution. As a result, ions which enhance photocatalysis should not be eliminated before photocatalysis while inhibiting ions should be removed from the wastewater before photocatalysis treatment.

Keywords— ions, methyl orange, solar photocatalysis, textile wastewater

I. Introduction

THE growth of textile and dyeing industry has resulted in an increase in the discharge of highly coloured wastewater into the environment. The strong colour of dye wastewater even at very low concentrations results in non-aesthetic pollution [1]. Colour also prevents light from penetrating into the water bodies thus interfering with the growth of aquatic plants which feed fish and other aquatic animals. Furthermore, some dyes are toxic and carcinogenic and can directly poison fish and human beings who use the water in the receiving water body. As a result, there is a need to decolourize dye wastewater prior to its discharge.

In this respect, various methods such as adsorption [2] membrane separation and the advanced oxidation processes such as photo-fenton, ozonation and photocatalysis have been developed. Some of these methods, such as adsorption merely transfer the dye molecules from one phase to another which creates secondary problems of disposal [1]. Membrane separation is costly in terms of the separating medium and high electricity requirements. Therefore, advanced oxidation processes such as photocatalysis have been preferred due to their high activity, low cost and ability to destroy pollutants instead of merely transferring them to another phase [1].

In the photocatalysis reaction, highly reactive holes and electrons are generated on the surface of a semiconductor catalyst, usually TiO_2, when irradiated by light of a sufficient quantity. The holes react with water to form hydroxyl radicals which then attack active sites in a dye molecule, such as the azo bond, which breaks and decolourizes the dye molecule [3]. Electrons are trapped by dissolved oxygen to prevent electron-hole recombination. Traditional photocatalysis has been carried out using mercury ultraviolet lamps as the light source. However, due to the high cost of running such lamps, sunlight has been investigated as an alternative energy source for photocatalysis due to its low cost [4].

Textile wastewater normally has ions which are used as fixing agents during the dyeing process. The presence of ions in wastewater is especially important for photocatalysis. Several researchers have found that metal and non-metal ions can increase or decrease the rate of photocatalysis [1]. In order to properly design a photocatalysis treatment system for textile wastewater, the effect of ions on the rate of photocatalysis needs to be investigated. In this work, solar photocatalysis of methyl orange was investigated using the commercial nano-sized catalyst P25 TiO_2. The effect of catalyst loading, cations and anions on the rate of methyl orange photocatalysis was evaluated. The aim of the work was to investigate the effect of Fe^{2+}, Pb^{2+}, Cl^- and SO_4^{2-} ions on the solar photocatalysis of methyl orange.

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II. Methodology

A. Experimental set up

Solar photocatalysis experiments were carried out in a fluidized bed reactor with a diameter of 32 mm and a working volume of 400 mL made of borosilicate glass. The reactor was set up on a roof top with no obstructions to sunlight. Catalyst particles in the reactor were fluidized by air from a compressor set at a flow rate of 40 L/h. The reactor was operated in batch mode for the liquid and catalyst with air being used for fluidization and as a source of oxygen electron acceptor.

B. Photocatalysis experiments

Solar Photocatalysis experiments were carried out in the reactor in order to determine the effect of catalyst loading and different ions on the rate of methyl orange photocatalysis. First, the mixture of 0.03 mM of methyl orange (Merck) and an ion solution of a specified concentration was mixed with the commercial nano-sized Aeroxide P25 TiO_2 catalyst (Evonik) of a specified loading. The mixture of wastewater and catalyst was then added into the reactor followed by air fluidization. During the photocatalysis reaction, sampling was carried out every 10 minutes. The samples were filtered by a 0.45 µm GHP syringe filter (Pall) and then the concentration of methyl orange was analysed using a UV-vis spectrophotometer (PG instruments, T60) at a λ_{max} of 465 nm. Solar experiments were carried out between 12.00 and 1.00 pm on sunny days. The salts for preparing the ions were obtained from Merck and used without further purification. Lead, Fe^{2+}, Cl^- and SO_4^{2-} ions were obtained from $Pb(NO_3)_2$, $FeCl_2$, NaCl and Na_2SO_4 salts, respectively.

III. Results and Discussion

A. Effect of catalyst loading

The effect of catalyst loading was investigated in the range of 50 – 400 mg/L. The results (Figure 1) show an increase in the photocatalysis rate constant with an increase in the catalyst loading. For example, an increase in the catalyst loading from 50 to 200 mg/L resulted in an increase in the rate constant from 0.015 to 0.0238 min^{-1}. However, a further increase in the catalyst loading to 400 mg/L resulted in a marginal increase in the rate constant to 0.0256 min^{-1}. This trend can be attributed to the fact that an increase in the catalyst loading results in an increase in the number of active sites leading to an increase in the rate of reaction [1]. However, an increase in the catalyst loading beyond the optimum loading results in catalyst self-shading; a situation in which some catalysts are not illuminated and do not participate in the photocatalysis reaction [1]. From the results, 200 mg/L was selected as the optimum catalyst loading and used for further studies.

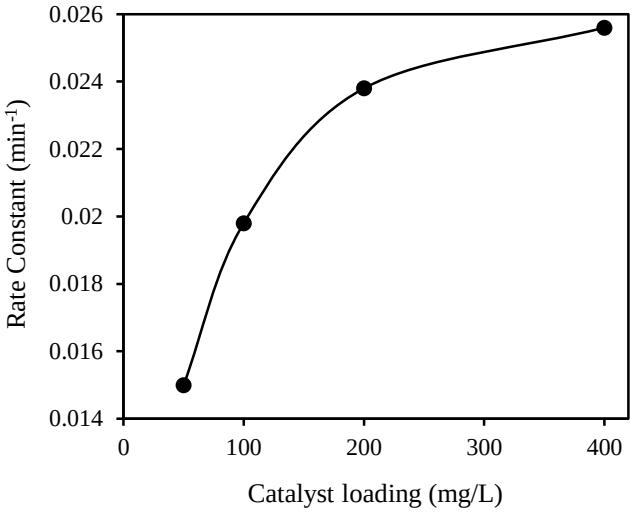

Fig. 1: Effect of catalyst loading on the photocatalysis rate constant. Methyl orange concentration = 0.03 mM

B. Effect of cations

The effect of Fe^{2+} and Pb^{2+} ions at different concentrations on the rate of photocatalysis was investigated. The results (Figure 2a – b) show an increase in the photocatalysis of methyl orange with an increase in the concentration of Fe^{2+} and Pb^{2+}.

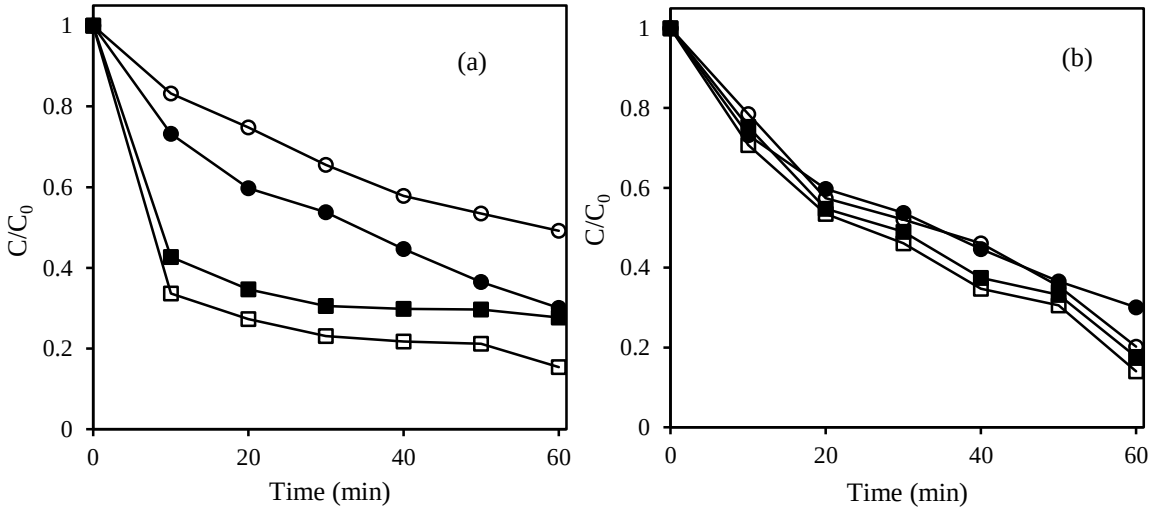

Fig. 2: Effect of different concentrations of (a) Pb^{2+} and (b) Fe^{2+} on methyl orange photocatalysis. 0 mM (●), 0.03 mM (○), 0.06 mM (■), 0.09 mM (□). Catalyst loading = 200 mg/L

However, Pb^{2+} inhibition was observed at a concentration of 0.03 mM. Cations have generally been found to inhibit the rate of photocatalysis [1]. However, Baran and co-workers [5], working with $FeCl_3$ found that Fe^{3+} has a catalytic effect on the photocatalysis of anionic dyes and an inhibitory effect on cationic dyes. This was attributed to the reaction between Fe^{3+} and anionic dyes resulting in the formation of insoluble complexes which resulted in fast decolourization. However, at low concentrations of Fe^{3+}, an inhibition in the removal of anionic dyes was observed.

The observations by Baran and co-workers [5] have very striking parallels with the results in this work for methyl orange photocatalysis in the presence of Pb^{2+}. The photocatalysis of the anionic methyl orange dye was inhibited at low concentrations of Pb^{2+}. However, in the presence of high concentrations of Pb^{2+}, methyl orange photocatalysis was found to be very fast. This suggests that the photocatalysis of methyl orange in the presence of Pb^{2+} could be attributed to the reaction between the anions react with hydroxyl radicals thus competing with the target substrate resulting in a reduced rate of photocatalysis [7]. However, at neutral pH, TiO_2 exist as $Ti\text{-}O^-$ species which repel anions resulting in a reduced adsorption and competitive reactions with hydroxyl radicals. Thus, at neutral pH, as was the case in this work, anions have been found to have almost no effect on the rate of photocatalysis. However, [7] have found that the presence of sulphate ions can result an increase in the rate of photocatalysis. This was attributed to the reaction between sulphate and hydroxyl radicals resulting in the formation of sulphate radicals:

$$SO_4^{2-} + {}^{\bullet}OH \rightarrow {}^{\bullet}SO_4^{2-} + H_2O \quad (1)$$

The generated sulphate radicals are very strong oxidizing agents and may increase the rate of photocatalysis. A similar mechanism can be attributed to the increase in the photocatalysis of methyl orange in the presence of chloride ions.

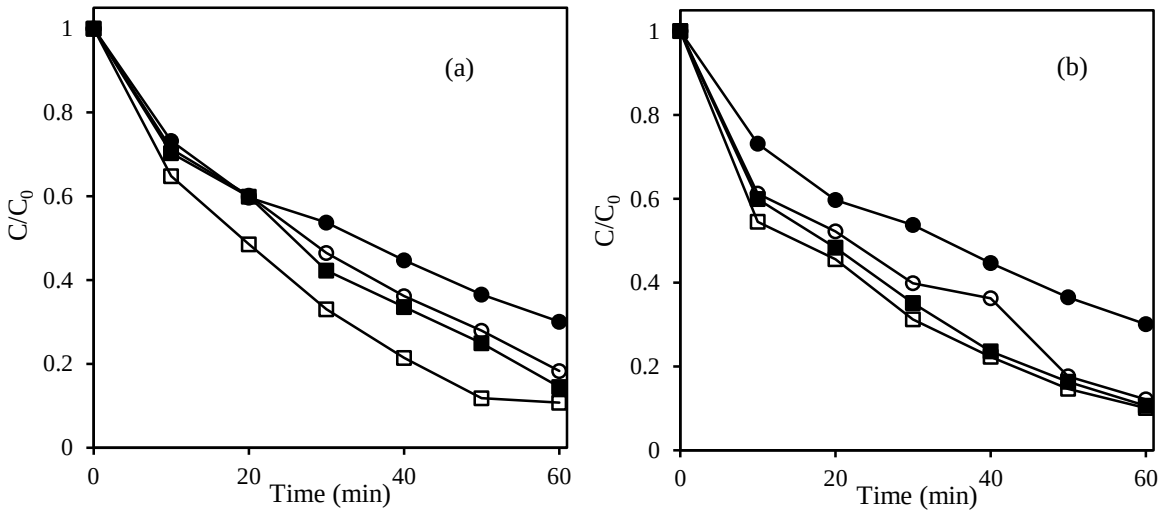

Fig. 3: Effect of different concentrations of (a) Cl^- and (b) SO_4^{2-} on methyl orange photocatalysis. 0 mM (●), 0.03 mM (○), 0.06 mM (■), 0.09 mM (□). Catalyst loading = 200 mg/L

Pb^{2+} and methyl orange.

The presence of Fe^{2+} ions in solution has been associated with an increase in the rate of photocatalysis. During dark adsorption, Fe^{2+} ions are adsorbed on the surface of the catalyst where the ions acts as an electron scavengers thus reducing the electron-hole recombination rate [6]. This process results in an increase in the number of generated holes and hydroxyl radicals leading to an increase in the photocatalysis reaction rate. This explains why the presence of Fe^{2+} ions results in an increase in the removal of methyl orange by photocatalysis.

C. Effect of anions

The effect of different concentrations of Cl^- and SO_4^{2-} ions on the rate of photocatalysis was investigated. The results (Figure 3a – b) show an increase in the photocatalysis of methyl orange with an increase in the concentration of Cl^- and SO_4^{2+} ions. In photocatalysis studies, anions have been observed to inhibit the reaction in acidic pH as they are adsorbed by TiO_2 which exist in the form of $Ti\text{-}OH_2^+$ species. After adsorption,

IV. Conclusion

In this work, the effect of catalyst loading, cation concentration and anion concentration on the rate of methyl orange concentration was investigated. An increase in the catalyst loading resulted in an increase in the photocatalysis rate constant up to an optimum catalyst loading of 200 mg/L. The presence of Cl^-, SO_4^{2+}, Fe^{2+} and high concentrations of Pb^{2+} ions in the wastewater resulted in an increase in methyl orange removal by photocatalysis. Low concentrations of Pb^{2+} ions were found to inhibit the photocatalysis of methyl orange. This study showed that the influence of ions on photocatalysis depends on the type and concentration of the ion. Thus, in the design of the treatment process, the influence of ions needs to be considered to ensure optimal operation of photocatalysis.

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