Effect of Oxidants on the Photocatalytic Degradation of Methylene Blue and Congo Red under Sunlight

E. Fosso-Kankeu, Frans Waanders and L. Taljaard

Abstract— Photocatalytic degradation of dyes is a promising method. The addition of a strong oxidant is likely to increase the photocatalytic effects of catalysts. The radiation was simulated under sunlight in a light proof chamber that was held at constant temperature of 25°C. The photocatalyst used in this study was the commercial zinc oxide (ZnO) powder which can be excited under sunlight. The experiments were conducted with two different dyes namely Congo red, a diazo dye and methylene blue, a cationic dye. The oxidants chosen were liquid hydrogen peroxide (H_2O_2), peroxydisulfate ($S_2O_8^{2-}$) which dissociates from the salt, potassium persulfate ($Na_2S_2O_8$) and Potassium peroxymonosulfate ($KHSO_5$), also referred to as Oxone. The Oxone is supplied as a triple salt with the following formula $2KHSO_5 \cdot KHSO_4 \cdot K_2SO_4$.

The zinc oxide was found to degrade the methylene blue much better than congo red. The addition of most oxidants greatly increased the degradation effect of the photocatalyst. The performance of the photocatalyst was negatively impacted if the concentration of oxidants was too high.

From the mentioned oxidants, $S_2O_8^{2-}$ performed the best followed by $KHSO_5$. The peroxide performed the worst due to over saturation of OH^{-1} ions. Because of the ionic nature of the dyes, ZnO adsorbed much more congo red in comparison to methylene blue. The experiments supported the fact that photocatalytic degradation of dyes under sunlight and with the addition of an oxidant, is a very effective process for the removal of dyes from contaminated water.

Index Terms- Photocatalyst, Oxidants, Sunlight, ZnO, H_2O_2, $S_2O_8^{2-}$ and $KHSO_5$

I. INTRODUCTION

Water also plays a very important role for the physiology of human being as well as for the industrial sector. Most water that runs through an industrial process gets contaminated with chemicals and metals and has to go through expensive treatment processes. Amongst these, contaminant dyes are the most revealing. Improving the effectiveness of these methods to minimize the discharge of contaminants, will increase profits and also benefit the environment.

It is estimated that over 700 000 tons of synthetic dyes are annually produced worldwide [1]. According to Ogugbue & Sawidis [2], the textile industry consumes most of the dyes. Approximately 200 000 tons, almost 30%, of dyes are lost due to the ineffective dying process and most of the lost dyes are disposed as waste water. The dying of textile also consumes a lot of clean water and the ratio of dye to water is around 1:30. It is clear that the dyeing industry needs an effective and cost saving way to treat their waste water. The most conventional cleaning methods produce even more harmful compounds in water, thus research for more effective and cost saving cleaning methods are needed.

There is a wide variety of ways to remove dyes from water. Methods used in the industry include: coagulation and flocculation, bio-sorption, photo-decomposition, ultra-filtration, oxidizing agents, membrane and electrochemical. The advantages and disadvantages of each technique have been widely studied. A very promising solution to the problem is to degrade dyes with the use of a photo catalyst. Sunlight will be used to drive the reaction therefore making it very energy efficient. The addition of an oxidant will improve the efficacy of the photocatalytic degradation. Thus it is important to understand the effect that various oxidants will have on the degradation process [3].

A. Materials

The photocatalysts used for the experiments were commercial Zink oxide (ZnO) powder, supplied by ACE. The concentrations used were 0.5 g/L, 1 g/L and 2g/L. The experiments were conducted with two different dyes; Congo red, a diazo dye and methylene blue, a cationic dye. The oxidants chosen were liquid hydrogen peroxide (H_2O_2, 12%), supplied by Dischem, peroxydisulfate ($S_2O_8^{2-}$) which dissociates from the salt, potassium persulfate ($Na_2S_2O_8$) and Potassium peroxymonosulfate ($KHSO_5$), also referred to as Oxone. The Oxone was supplied as a triple salt with the following formula $2KHSO_5 \cdot KHSO_4 \cdot K_2SO_4$. Both salts were supplied by Merck

B. Photocatalytic chamber

The photocatalytic chamber that was used for the degradations of dyes is completely light proof. It also consists of a heating element that keeps the chamber at room temperature i.e. 25°C. The light source consists of three UV lights sources and one LED light source in order to simulate sunlight. The chamber also consists of a magnetic stirrer as well as a 250 ml-Erlenmeyer flask that was used for the experiment.

Elvis Fosso-Kankeu is with the School of Chemical and Minerals Engineering of the North West University, Potchefstroom-South Africa

Frans Waanders is with the School of Chemical and Minerals Engineering of the North West University, Potchefstroom-South Africa

Louricus Taljaard is with the School of Chemical and Minerals Engineering of the North West University, Potchefstroom-South Africa

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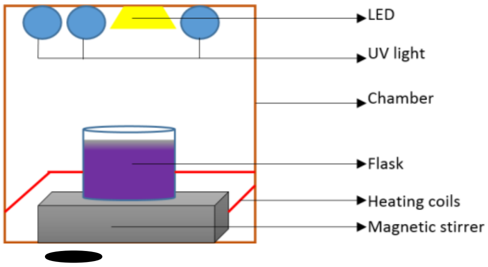

Fig. 1 Photoctalytic Chamber

C. Characterization of photocatalyst

The morphology of the photocatalyst was determined by SEM photographs, model VEGA 3 XMU from TECSAN. The SEM was equipped with a 10 micron lens. The FTIR analysis was done to determine the infrared spectrum of adsorption of the photocatalyst over a spectral range of 4000-400 cm^{-1}. The analysis was done using a Shimadzu IRAffinity-1S with a resolution of 4 cm^{-1}. XRD analysis was also done on the zinc oxide powder to check the phase formation and purity. An XRD pattern was recorded using an X-ray diffractometer, Philips model X'Pert pro MPD, with a power rating of 1.6 kW and capable of reaching 40 kV.

D. Adsorption

Adsorption occurred and had to be taken into account [4]. This was accomplished by placing the photocatalyst in a 200 mL dye solution. The solution was then placed in the photocatalytic chamber for 30 min to account for adsorption. Samples were drawn at 30 min and centrifuged for 10 min at 4000 rpm. The made of the centrifuge used was Hettich model, Rotofix 32 A. The concentration was then determined by using a spectrophotometer (SHIMADZU model, UVmini-1240).

E. Degradation

The amount of degradation was determined by exposing the solution to simulated sunlight, with a strength of 92.4% compared to regular sunlight. The solution was kept in the dark for 30 min. Samples were then taken at 15 min, 30 min and 60 min intervals. The samples were centrifuged at 4000 rpm for 10 min to separate all the solids from the liquid. The final concentration was then determined by using a spectrophotometer (SHIMADZU model, UVmini-1240). The concentrations were used to derive the kinetics and the percentage of dye removed.

F. Isotherm and kinetic models

The adsorption of various dyes at equilibrium can be fitted by both the Langmuir and Freundlich isotherms [5]. The Langmuir equation can be linearized as follows [5]:

$$\frac{C_e}{q_e} = \frac{1}{Q_0 b} + C_e/Q_0 \tag{1}$$

Where q_e is the amount of dye adsorbed per unit weight of the catalyst at equilibrium in mg/g. Q_0 is the amount of dye adsorbed corresponding to monolayer coverage in mg/g .b is the Langmuir adsorption constant. C_e is the concentration of the dye at equilibrium in mg/L

The Freundlich isotherm can be linearized to obtain values for K_F and n as followed [5]:

$$\ln q_e = \ln K_F + \left(\frac{1}{n}\right) \ln C_e \tag{2}$$

Where q_e is the amount of dye adsorbed per unit weight of the catalyst at equilibrium in mg/g. K_F is the Freundlich isotherm constant in (mg/g). C_e is the concentration of the dye at equilibrium in mg/L. Where 1/n is an indication of the favourability of adsorption

The degradation rate is determined by plotting the concentration of dye in mg/L vs. time. The graphs will show the degradation rate, effect of catalyst loading and the effect that the various oxidants will have on the degradation rate.

II. RESULTS AND DISCUSSION

A. Characterization of photocatalyst

To obtain a better understanding of the photocatalyst the following tests were performed:

1. SEM photography to determine the morphology and structure of the photo catalyst
2. FTIR analysis to determine the adsorption affinities of the photo catalysts
3. XRD analysis was done to determine the composition of the photocatalyst that was used.

1) SEM photography

The shape of the zinc oxide was analysed through SEM photography shown below:

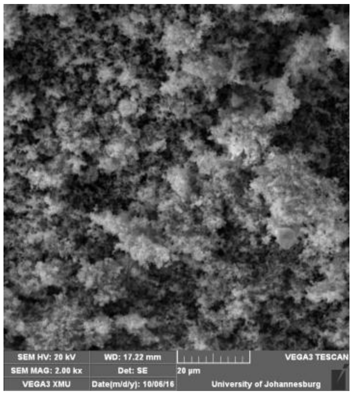

Fig. 2 SEM photography of commercial Zno

The commercial zinc oxide particles are very small and mostly appearing as crystal as shown in Figure 2.

2) FTIR analysis

The FTIR analysis was done to determine the infrared spectrum of adsorption of the photocatalyst over a spectral range of 4000-400 cm^{-1}.

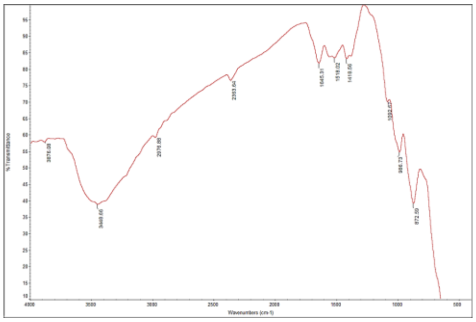

Fig. 3 FTIR infrared spectrum analysis of ZnO particles

The FTIR analysis of the ZnO is depicted by Figure 3. The spectrum shows absorbance peaks at the following wavelengths 3876.06, 3448.66, 2976.88, 2363.64, 1645.31, 1518.02, 1418.56, 1092.67, 986.73 and 872.59 cm^{-1}. The peaks located at 3448.66 and 2976.88 cm^{-1} correspond to the O-H mode and C-H mode respectively. The peak at 1645.31 indicates the characteristics of the C=O stretching [6].

3) XRD analysis

XRD analysis was done on the zinc oxide powder to check phase formation and purity

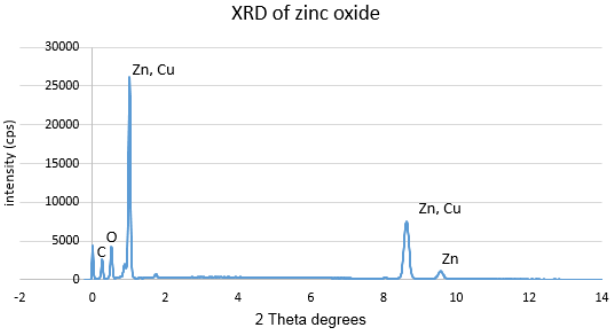

Fig. 4 XRD of xinc oxide

The XRD analysis in Figure 4 shows three main components Zn, Cu and O. The copper might be an isotherm of zinc due to the electron configuration of both metals being very similar.

B. Adsorption behavior of photocatalyst

The adsorption behaviour of the Zinc oxide for both dyes where determined by using the Freundlich and Langmuir isotherm models. The isotherm models did not fit the adsorption equilibrium data for the removal of methylene and therefore could not be used to determine the adsorption capacity.

TABLE I
LANGMUIR AND FREUNDLICH ISOTHERM MODELS

Langmuir			
Concerntration	**Parameter**	**Methylene blue**	**Congo red**
0.5 g/L Zinc Oxide	**R^2** **Qo** **b**	0.0249 -1.178 -0.015	0.1863 -35.876 0.026
1 g/L Zinc Oxide	**R^2** **Qo** **b**	0.2214 0.459 -0.001	0.0372 130.416 0.124
2 g/L Zinc Oxide	**R^2** **Qo** **b**	0.0736 1.134 0.028	0.9903 35.746 0.682

Freundlich			
Concerntration	**Parameter**	**Methylene blue**	**Congo red**
0.5 g/L Zinc Oxide	**R^2** **n** **kf**	NA NA NA	0.9213 0.818 0.445
1 g/L Zinc Oxide	**R^2** **n** **kf**	NA NA NA	0.7178 1.304 1.256
2 g/L Zinc Oxide	**R^2** **n** **kf**	NA NA NA	0.9630 2.585 2.423

The adsorbed of congo red by ZnO showed a good fit with the Freundlich isotherm model compared to the Langmuir model as seen in Table I. It therefore implies that adsorption of congo red onto ZnO mostly occurred on an heterogeneous surface involving several layers. The Freudlich isotherm plots between log (qe) and log (Ce) can be seen in Fig. 5 below for congo red.

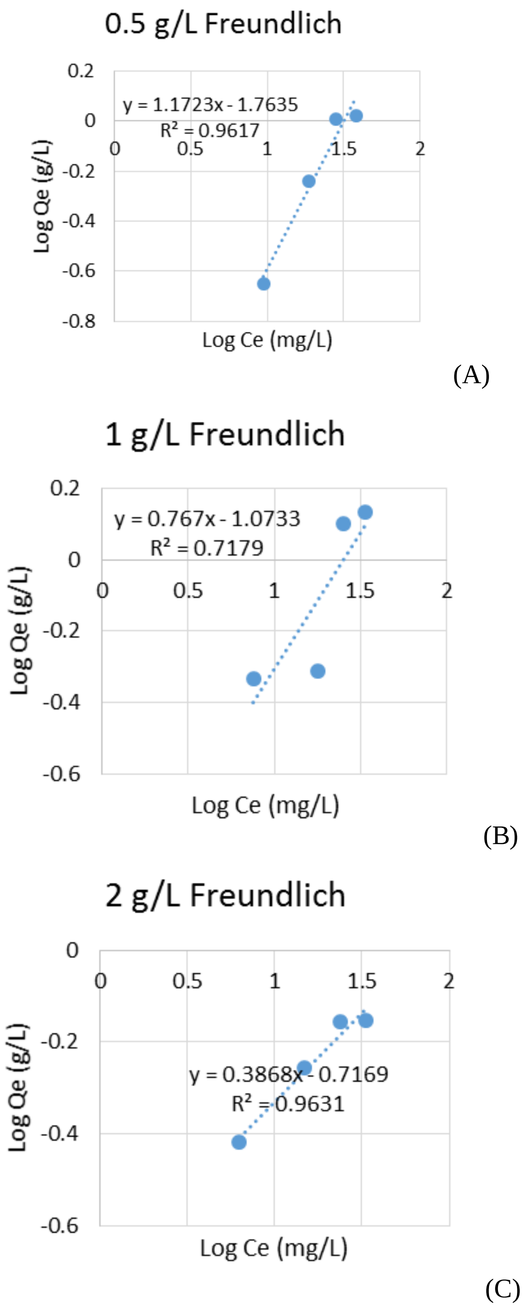

Fig. 5 The various Freundlich isotherm plots for congo red (A) Freundlich isotherm plot of 0.5 g/L ZnO (B) Freundlich isotherm plot of 1 g/L ZnO (C) Freundlich isotherm plot of 2 g/L ZnO

As seen in Figures 5A, B and C above the Freundlich models fits all the data very well with all gradients being positive. Figure 3 (C) and Table 1 indicate that both isotherm models fit almost perfectly the adsorption equilibrium data for the removal of congo red by ZnO at concentration of 2 g/L.

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C. Degradation effect of photocatalyst

The photocatalytic degradation was determined by first allowing the photocatalyst to adsorb and reach equilibrium. The photocatalytic chamber that was used for the degradations of dyes is completely light proof. It also consists of a heating element that will keep the chamber at room temperature. Samples were extracted at set intervals after adsorption equilibrium has been reached. The oxidant was added and the degradation rate was monitored. The effects of the oxidants were easily observed by plotting the dye concentration against time and comparisons were made to zinc oxide without the addition of any oxidant. The concentrations that were used in the plots below are as followed: congo red and methylene blue both at 30 mg/L.

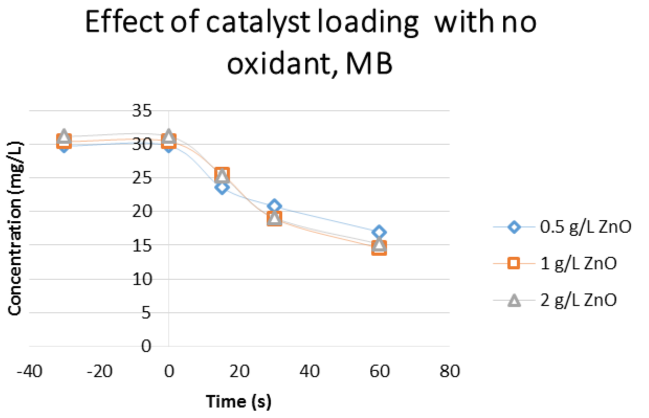

Fig. 6 the effect of catalyst loading with no oxidant using methylene blue as dye

The effect of initial catalyst load shown in Figure 6 clearly indicates that the amount of catalyst had little effect on the degradation of methylene blue as 0.5 g/L of catalyst achieve almost the same performance as 1 g/L and 2 g/L which exhibited similar performance.

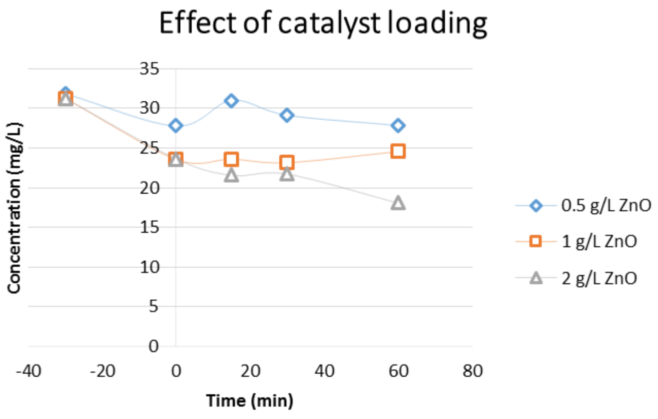

Fig. 7 Effect of catalyst loading with no oxidant using congo red as dye

The amount of catalyst added had a clear impact on the degradation rate of congo red as seen in Figure 5. When comparing Figure 5 and Figure 4 it is clear that methylene blue is degraded much more effectively than congo red which is likely due to the electrostatic interaction between methylene blue a cationic dye and ZnO therefore resulting in better degradation [7].

D. Effect of oxidants

The addition of a strong oxidant improved the photocatalytic degradation of the dyes in the following ways: increasing the concentration of the hydroxyl radical $^{\bullet}$OH, thus increasing the decolourisation of the dyes. The oxidant accepts the conduction band electron and thereby removing the electron-hole recombination. Finally it accelerates the decolourisation efficiency by generating other oxidizing compounds and radicals.

Peroxydisulfate can generate two sulphide radical anions ($2SO_4^-$). This can be achieved thermally or photolytically. The radicals then react with water to produce $^{\bullet}$OH radicals. Potassium peroxymonosulfate also referred to as Oxone will dissociate when mixed with water and produce $^{\bullet}$OH radicals. [8]. The effect of oxidants on the photocatalytic degradation of dyes is shown below in Figure 8 where oxidants were added at a concentration of 1 mM while the catalyst concentration was kept constant at 1 g/L

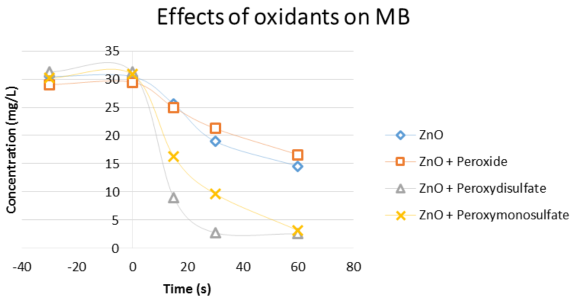

Fig. 8 The effects of various oxidants on methylene blue

Figure 8 shows that the oxidants had a significant effect on the degradation rate as peroxydisulfate performed by far the best with a steep degree of degradation compared to peroxymonosulfate. The Peroxide performed the worst and it is clear that it inhibits the photocatalytic degradation capabilities of the dyes.

The performance of the catalyst is depended on the amount of oxidants that are added to the solution; when the oxidant is present at much higher doses, the efficiency will slowly decrease and this is applicable to all oxidants as shown in Figure 8 where peroxide inhibited the reaction.

When H_2O_2 is abundant in a solution it could consume the $^{\bullet}$OH radicals and valence bond holes as depicted below:

$$^{\bullet}OH + H_2O_2 \rightarrow HO_2^{\bullet} + H_2O \qquad (3)$$

$$^{\bullet}OH + HO_2^{\bullet} \rightarrow O_2 + H_2O \qquad (4)$$

$$Catalyst(h_{vb}^{+}) + H_2O_2 \rightarrow catalyst + O_2 + 2H^{+} \qquad (5)$$

$$HO^{\bullet} + HO^{\bullet} \rightarrow H_2O_2 \qquad (6)$$

Figure 9 below shows the effect that various oxidants had on the photocatalytic degradation of congo red by ZnO. The oxidants had little to no effect on the degradation of congo reddue to it natural loading.

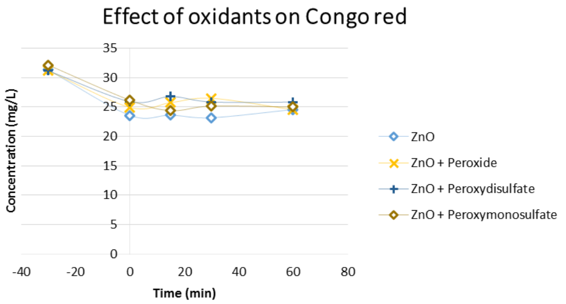

Fig. 9 The effect of various oxidants on congo red

III. CONCLUSION

In this study the effect that various oxidants had on zinc oxide catalyst was investigated. The ZnO was excited under artificial sunlight. Most of the oxidants performed as expected and improved the photocatalytic degradation of the dyes. Peroxydisulfate performed the best followed by peroxymonosulfate. The hydrogen peroxide inhibited the degradation process as the amount added was relatively high. This resulted in a high concentration of •OH radicals which will negatively impact the degradation. The best results were obtained with the cationic dye, methylene blue. The methylene blue did not adsorb well, while the congo red, a cationic dye adsorbed very well. For more accurate readings, samples should be centrifuged at higher rpms and more studies should be done on the effect that a mixtures of oxidants will have on the degradation rate. The addition of a minute amount of oxidant is an inexpensive way to greatly improve the degradation rate of a photocatalyst

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The corresponding author is currently an Associate Professor in the School of Chemical and Minerals Engineering at the North-West University (Potchefstroom). He is an NRF rated researcher who has published journal articles, book chapters and book.

Prof Elvis Fosso-Kankeu has been the recipient of several merit awards.