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TEMPERATURE, SALINITY AND PH DEPENDENCE OF ZINC OXIDE PHOTOCATALYTIC PROPERTIES FOR DYE REMOVAL APPLICATION

Wan Rafizah Wan Abdullah[1], Nur Mimi Nazira Mohd Nazri[2], Nur Ain Ismail[3], Farahana Atikah Dzulkarnain[4] and Mohd Sabri Mohd Ghazali[5]
[1,2, 3, 4]School of Ocean Engineering, Universiti Malaysia Terengganu, 21030 Kuala Terengganu, Terengganu, Malaysia
[5]School of Fundamental Science, Universiti Malaysia Terengganu, 21030 Kuala Terengganu, Terengganu, Malaysia
**corresponding author: [1]wanrafizah@umt.edu.my; [2] nazira93@gmail.com; [3]ainmael93@gmail.com; [4]farahana.eddy@gmail.com; [5]mohdsabri@umt.edu.my*

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ABSTRACT

ZnO based photocatalysis process is considered as promising cost-effective and environmental friendly technology to decompose recalcitrant organic contaminants in water by converting them into CO_2 and H_2O. Existing photocatalysis of ZnO commonly involve the near-room-temperature photoreaction under illumination of the UV light or sunlight. In this study, the influence of operational conditions such as temperature, salinity and pH on photocatalytic activity of Zn were thoroughly investigated. Methylene blue ($C_{16}H_{18}N_3SCl$), (MB) dye was selected as the model contaminant. 10 mg/L of MB dye was photodegraded under UV-light irradiation in the present of 1 g/L of ZnO for 60 minutes. The reaction was conducted under different sets of operational conditions such as temperature (30 – 45 ^oC), salinity (25-100 g/L NaCl) and pH (5-9). The optimum operational condition for the photodecomposition of MB using ZnO catalyst were found to be at high temperature (45 ^oC), low pH (pH 5) and high salinity (100 g/L NaCl).

Keywords: *ZnO; photocatalyst; salinity; temperature; pH; methylene blue.*

1. INTRODUCTION

ZnO based photocatalysis process is considered as cost-effective and environmental friendly technology to decompose recalcitrant organic contaminants in water. The efficiency of this process strongly depends on the generation of reactive free radical species particularly hydroxyl radicals (•OH) in the presence of photocatalyst (ZnO). Once the surface of photocatalyst is illuminated by photons with an energy equal to or higher than its band gap energy, electron-hole pairs are generated due to excitation of electron (e^-) from the valence band to the conduction band. The oxidizing •OH radicals are rapidly generated as a reaction product of adsorbed water molecules with the hole (h+) on the surface of catalyst. Further action by these radical species decomposes dye or organic molecules into intermediate compounds which subsequently converted it into CO_2 and H_2O. Current research trend shows that this treatment approach has been extensively explored for decomposing various groups of synthetic dye solutions.

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Despite extensive research works on utilization of ZnO photocatalysis for mineralization of organic water contaminants, previous studies commonly considers the near-room-temperature photoreaction in which the degradation of pollutants/dyes is achieved under ambient operating condition (Baiju et al., 2005; Ahmad et al., 2010; Wan et al., 2009; Zong et al., 2014). On contrary, the high-temperature photocatalytic oxidation of pollutants using ZnO remains unexplored.

Photocatalysis is not only a photo-activated process but also involves a thermally activated reaction. Therefore, the efficiency of a photocatalytic reaction could be potentially improved by altering the reaction temperature. Westrich et al., (2011) reported that the photo-generated charge carriers are able to get involved in thermo-catalytic chemical reactions, in that way improving the catalytic rates. Based previous research works on TiO_2 photocatalyst, some observations strengthened that elevation of temperature resulted in the dynamic change of reaction rate (Kometani et al., 2008; Hu et al., 2010; Lee et al., 2013; Yamamoto et al., 2013). Hu et al., (2010) observed that the photoreactivity of TiO_2 to decompose methyl orange dye increased 5 times when the temperature was elevated from 38 to 100 ^oC. Above 100 ^oC, excessive heating has led to a decrement in photocatalytic rate as dye molecules adsorbed on the catalyst surface and limits further photoreaction process.

In this study, the influence of temperature, salinity and pH on photocatalytic properties of ZnO is discussed. The interactive effects of temperature and other factors such as pH and salinity were also investigated. These two factors are also known for their influential effects on various aqueous phase mediated photocatalytic system (Gaya et al., 2009; Surolia et al., 2007; Farzana et al., 2014; Kaur & Singhal, 2015).

2. EXPERIMENTAL

2.1 Materials

Commercial grade ZnO with 99 wt% purity with particle size of less than 1 micron obtained from Sigma Co. was used as the photocatalyst. Methylene blue (MB) dye obtained in the form of reagent grade methylene blue trihydrate, $C_{16}H_{18}N_3SCl.3H_2O$ was selected as the model dye. The salinity of the solution was adjusted using 25 - 100 g/L sodium chloride (NaCl) whereas 1 M of sodium hydroxide (NaOH) and 0.5 M sulfuric acid (H_2SO_4) were used to adjust the pH of solution. Photocatalytic reaction was performed in a batch photoreactor with the capacity of 1.5 L. A 10 – watt UV – C lamp (λ= 254 mm) was used to provide the source of light. Figure 1 indicates the illustration of the photoreactor set-up.

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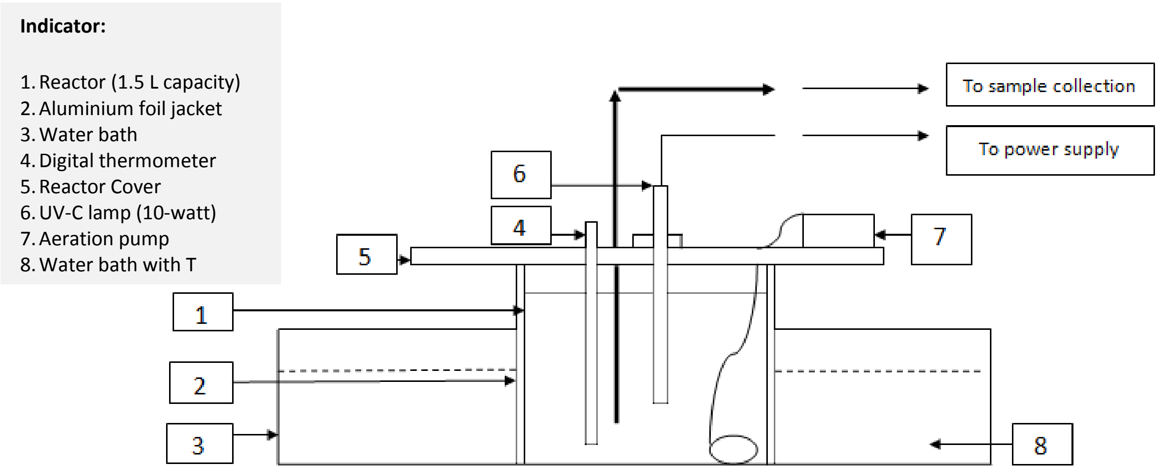

Figure 1: Photoreactor set-up

2.2 Methods

MB solution with initial concentration of 10 mg/L was photodegraded under different sets of temperature, salinity and pH. The concentration of ZnO photocatalyst was set constant at 1 g/L. The mixture was vigorously stirred to prevent sedimentation of ZnO. An aeration pump was used to supply the required oxygen for photocatalytic reaction at the flow rate of 1.6 L/min. The solution was kept in the dark for 60 minutes before being illuminated with luminous light from vertical UV lamp for maximum of 60 minutes. Every 30 minutes, 15 ml of sample was collected, centrifuged twice to remove suspended ZnO and the remaining MB concentration was analysed using UV–Visible spectrophotometer. The efficiency of photocatalytic degradation, R (%) was evaluated based on the Equation (1).

$$R(\%) = \frac{A_0 - A_t}{A_0} \times 100 \qquad (1)$$

where A_0 is the initial MB absorbance intensity of the 664 nm peak at time, t=0 and A_t is the MB absorbance intensity of the 664 nm peak at any time, t. The spent ZnO catalyst was also recovered, rinsed with deionized water and characterized using XRD.

2.3 Experimental Design

Simultaneous effect of multiple factors on response and the levels where these factors must be kept to optimize the operational conditions can be determined using statistical design of experiment technique. In this work, temperature, pH and salinity were identified as potential factors that influencing the efficiency of photodegradation of dye using ZnO. Therefore, experimental design was performed using 2^3 Full Factorial Model with three replicates. A total of 24 runs of experiments were required. Table 1 summarizes the minimum and maximum level of each chosen factor.

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Table 1: Coded level and actual value for studied factors

Factors	**Code**	**Levels**	
		Low (-1)	**High (+1)**
Temperature (^oC)	X_A	30	45
pH	X_B	5	9
Salinity (g/L NaCl)	X_C	25	100

The codified mathematical model expression for the factorial model is represented in Equation (2).

$$R\,(\%) = ß_0 + ß_A X_A + ß_B X_B + ß_C X_C + ß_{AB} X_A X_B + ß_{AC} X_A X_C + ß_{BC} X_B X_C + ß_{ABC} X_A X_B X_C \quad (2)$$

where R is the predicted response, $ß_0$ is the model of intercept, $ß_A$, $ß_B$ and $ß_C$ are the linear coefficients, $ß_{AB}$, $ß_{AC}$ and $ß_{BC}$ are the cross product coefficient and X_A, X_B and X_C are the independent variables influencing the response.

3. RESULTS AND DISCUSSION

3.1 Full Factorial Model

Table 2 summarizes the photocatalytic efficiency, R value for ZnO obtained for each designed experiment. Based on regression analysis performed on the experimental data, the correlation between R and three selected factors (in coded units) can be expressed in Equation (3). All terms in the equation are significant with the P value of <0.05. The R^2 and R^2 adj values for the model equation are 0.9868 and 0.9810, respectively.

$$R(\%) = 86.458 + 6.958X_A - 5.208X_B + 3.292X_C + 2.625X_AX_B - 2.542X_AX_C + 6.292X_BX_C - 5.875X_AX_BX_C \quad (3)$$

Temperature, pH and salinity factors including their interaction have significant influence on the R value. Based on the statistical analysis in Table 3 and 4, the value of coefficient signify that both temperature and salinity factors positively impact R, whereas pH has a negative effect on R. Interestingly, temperature factor has the largest coefficient value and considered as the most dominant main effect. This is consistent with Barakat et al., (2013) which proposed that elevation of temperature may increase the photocatalytic performance by either modifying the activation energy of the photoreaction or increasing the kinetic energy of dye molecules near the active site on photocatalyst surface.

Salinity and pH have relatively smaller role. Chloride ion (Cl^-) is known for its inhibition effect towards numerous photocatalytic systems mainly using TiO_2 by serving as •OH radical scavenger (Zhang et al., 2005; Zhu et al., 2007; Barakat et al., 2013). However, it was observed that ZnO photocatalysis in this work, exhibited opposite trend. Increment in photocatalytic efficiency in high salinity condition can be associated to transformation of chloride ions into free chlorine radicals which assisted with the degradation of dye (Wang et

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al., 2004). Solution pH value on the other hand controls the electrostatic interaction between pollutant and catalyst surface (Petit et al., 2007). In this case, MB removal process in the presence of ZnO favors low pH setting.

Table 2: Design and experimental results of 2^3 full factorial design

Run	**Coded Experiments Matrix**			**Response**
	X_A	**X_B**	**X_C**	**Photocalatytic efficiency, R (%)**
1	-1	1	-1	54
2	-1	1	1	88
3	-1	-1	1	81
4	-1	-1	-1	93
5	1	1	1	91
6	1	1	-1	93
7	1	-1	1	98
8	1	-1	-1	98
9	-1	1	1	91
10	1	1	-1	88
11	-1	1	-1	52
12	-1	-1	1	92
13	1	-1	1	96
14	1	1	1	93
15	-1	-1	1	82
16	1	-1	-1	96
17	-1	-1	1	80
18	1	1	-1	88
19	-1	1	-1	55
20	-1	-1	-1	96
21	-1	1	1	90
22	1	-1	-1	93
23	1	-1	1	95
24	1	1	1	92

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Table 3: Design and experimental results of 2^3 full factorial design

	Symbol	Coeff.	Estimated Effect	Std. Error	P value
Constant	β_0	86.458		0.3819	<0.05
Main Effects	β_A	6.958	13.917	0.3819	
	β_B	-5.208	-10.417	0.3819	
	β_C	3.292	6.583	0.3819	
Two-way Interaction	β_{AB}	2.625	5.250	0.3819	
	β_{AC}	-2.542	-5.03	0.3819	
	β_{BC}	6.292	12.583	0.3819	
Three-way interaction	β_{ABC}	-5.875	-11.750	0.3819	

Table 4: Analysis of variance for R (%) in coded units

Source		**DF**	**Seq SS**	**F**
Main effects	Temperature	1	1162.04	332 .01
	pH	1	651.04	186.01
	Salinity	1	260.04	74.30
Two-way interactions	Temperature*pH	1	165.37	47.25
	Temperature*Salinity	1	155.04	44.30
	pH*Salinity	1	950.04	271.44
Three-way interactions	Temperature*pH*Salinity	1	828.37	236.68

Interacting effects between temperature, pH and salinity have strong influence on the overall performance of ZnO in aqueous solution. Figure 2 to 4 indicate a series of contour plots generated from the full factorial model equation.

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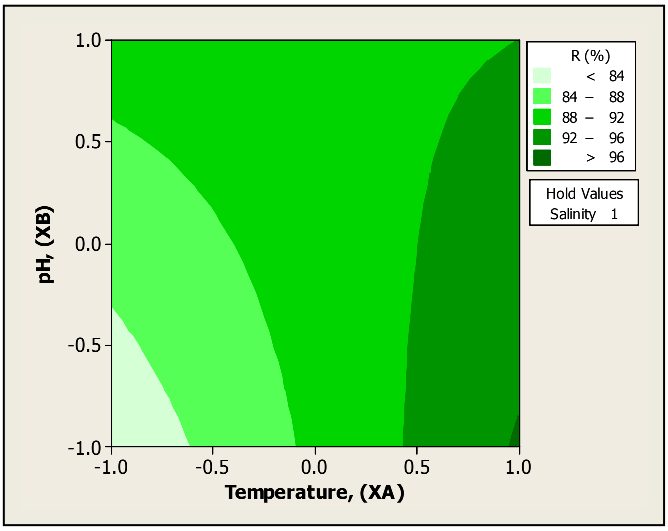

Figure 2: Degradation profile of MB dye as a function of pH (X_B) and temperature (X_A)

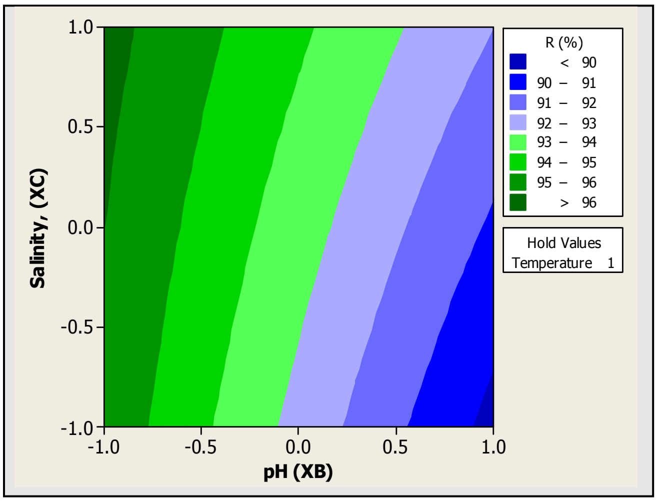

Figure 3: Degradation profile of MB dye as a function of salinity (X_C) and pH (X_B)

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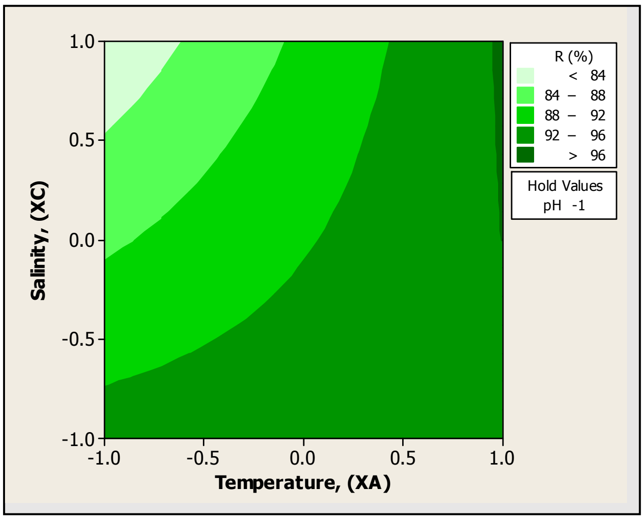

Figure 4: Degradation profile of MB dye as a function of temperature (X_A) and salinity (X_C)

Based on the surface curve in contour plot, pH-salinity have the most prominent interacting effects. A curvier contour lines reflecting a stronger relationship between the interacting factors. pH-salinity interaction has prominent effect in adjusting the stability of dye molecules in solution (Zhu et al., 2005). However, Figure 4 highlights that the maximum R value (>96%) can be achieved at the optimum operational conditions where temperature is high (~45 ^{o}C), salinity is high (100 g/L) and pH is low (pH 5). Experimental data also supports that the R value obtained in these combination of conditions was in the range of 96 – 98 %. For this reason, the photocatalytic efficiency of ZnO to remove dye in aqueous medium is dependence on temperature, pH and salinity.

4. CONCLUSION

The findings of this study highlighted that the photocatalytic efficiency of ZnO photocatalyst particularly towards removal of dye are strongly dependent on the temperature, pH and salinity. Within the studied range, these factors have individual and interacting effects on the overall R value. Temperature and salinity have positive influence on R while pH shows adverse effect on the R value.

To obtain the ZnO photocatalytic efficiency of more than 96 %, the photoreaction process should be performed at the optimum conditions where temperature is high (~45 ^{o}C), salinity is high (~100 g/L) and pH is low (pH 5).

In conclusion, the performance of ZnO to remove dye or other water contaminants can be maximized by elevation of temperature. However, the operating pH and salinity should be controlled as different types of dyes or contaminants may have behave differently in diverse pH-salinity combinations.

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