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Effect of Transitional Metal Ions on Photodegradation of Remazol Black B (RBB) in the Aqueous Suspension of ZnO under Solar Light Irradiation

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ABSTRACT

The photocatalytic decolorizing of Remazol Black B (RBB) has been performed in the presence of ZnO suspension and the momentum of the reaction was eagle-eyed spectrophotometrically. The impact of various operating parameters such as amount of photocatalyst, the effect of addition of transition metal ions (Fe^{3+}, Co^{2+}, Pb^{2+} and Ni^{2+} ions from $Fe(NO_3)_3.9H_2O$, $Co(NO_3)_2.6H_2O$, $Pb(NO_3)_2$ and $Ni(NO_3)_2.6H_2O$ salt precursors, respectively), concentration variations of Co^{2+} and Fe^{3+} ions, has been enquired. It was observed that trace quantities of Co^{2+} and Fe^{3+} ions boost the reaction rate to some extent. The augmentation in the photocatalytic activity might be due to halt the recombination of electron-hole pairs by trapping photogenerated electrons because of incorporation of these metal ions on the semiconductor surface. On the other hand, the addition of Pb^{2+} and Ni^{2+} ions in aqueous medium impede photodegradation efficiency by blocking the active sites.

1. Introduction

The discharge of industrial wastewater in a natural environment is very enigmatic to aquatic life and perilous to human [1]. The physico-chemical methods are not annihilative and since they only relocate the non-biodegradable matter into sludge giving rise to new type of pollution which needs further treatment [2]. The azo linkage is transformed to aromatic amines under anaerobic conditions that can be baneful and potentially carcinogenic [3]. A number of physical and chemical processes have been reported for the removal of dye compounds such as adsorption on activated carbon [4], biodegradation, ozonation [5] and advanced oxidation processes (AOPs) such as Fenton and photo-fenton catalytic reactions [6, 7], H_2O_2/UV processes [8] and semiconductor photocatalysis [9]. Among the AOPs, heterogeneous photocatalytic oxidation using ZnO as photocatalyst has been extensively studied. ZnO is very effective due to chemically stable and having moderate band gap energy. Doping of non-metallic elements (e.g. C, N, S), noble metal [10], rare earth metal [11], transitional metal ions [12-14] can be suppressed the recombination of photogenerated electron-hole pairs and thus augments photocatalytic efficiency. Moreover, the transition metal ion doping in the semiconductor revamps the local electronic structure and induces the visible light absorption usually by acquainting localized electronic states within the band gap and it also begets different surface structure that can intrinsically mutate the surface transfer of charge carriers and appreciates the photocatalytic activity [15]. Additionally, solar light was chosen as irradiation source rather than UV light for the purpose of utilizing natural resource in the industrial wastewater treatment with low cost and facile process. So in the present research work, addition of some transition metal ions into aqueous suspended ZnO during photo degradation of RBB under solar light irradiation was in prime focus.

2. Experimental Methods

2.1 Reagents

Remazol Black B (RBB), commercial ZnO, $Fe(NO_3)_3{\cdot}9H_2O$, $Co(NO_3)_2{\cdot}6H_2O$, $Pb(NO_3)_2$, $Ni(NO_3)_2.6H_2O$ were purchased from Fluka, Switzerland. All chemicals were of reagent grade and used without further purification. Deionized water was used for the whole process. Stock solution of RBB was prepared by dissolving the appropriate amount of solid substance in water. 0.3471 g RBB was taken in a 500 mL volumetric flask and then deionized water was added up to the mark to prepare $7{\times}10^{-4}$ mol/L solution of Remazol Black B. Further dilution was made whenever necessary.

2.2 Photodegradation of RBB

A fixed quantity of ZnO was taken in a 100 mL beaker and acertain amount of ultrapure water was added to it and kept overnight for soaking. All solar photocatalytic experiments were run under same conditions. The solar light was irradiated in the open air. After a definite time interval, a certain portion of the irradiated solution was taken out and centrifuged to obtain clear solution for observing absorbance. The absorbance of the clear solution was measured at the λ_{max} = 594.50 nm using UV-visible spectrophotometer (UV-1650 PC, Shimadzu, Japan). Solar light intensity was measured by pyranometer and the average light intensity over the experimental courses was calculated. The average intensity was 700-720 Wm^{-2} (source: Renewable Energy Research Centre, University of Dhaka) and was nearly constant during the experiments.

3. Results and Discussion

3.1 Adsorption of RBB on ZnO

In order to investigate the adsorption behavior of RBB on ZnO, adsorption experiments were carried out with $7{\times}10^{-5}$ M RBB solution at pH 5.83 and 30 °C temperature. The result of adsorption is shown in Fig. 1.

Fig. 2 shows the SEM image of ZnO and Fig. 3 is the XRD pattern of it. Fig. 2 reveals the formation of nearly hexagonal shape and Fig. 3 confirms the crystalline structure of ZnO as hexagonal wurtzite. Of the three forms of ZnO, the wurtzite structure is most stable and thus most common at ambient conditions. The presence of some large particles should be attributed to the aggregation or overlapping of smaller particles. It is found that the adsorption of RBB onto 1.20 g of ZnO is almost negligible. This observation can be explained by the SEM image and XRD pattern of ZnO. These clearly indicate that the ZnO is crystalline in nature which has a little tendency.

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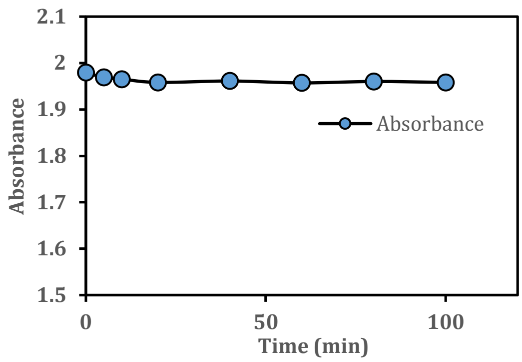

Fig. 1 Absorbance vs time curve for the investigation of adsorption property of hexagonal wurtzite structure of ZnO $[RBB]_o = 7\times10^{-5}$ mol/L, ZnO = 1.20 g

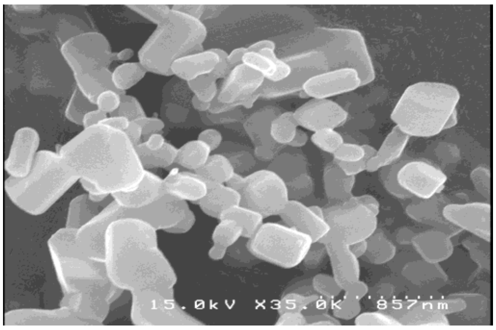

Fig. 2 SEM image of ZnO

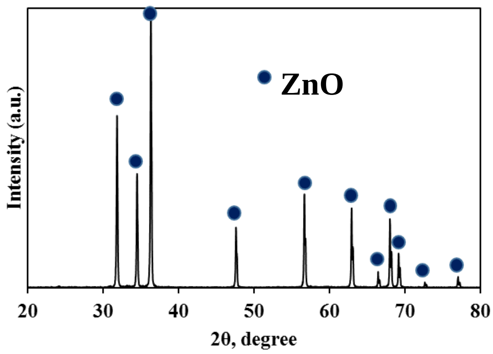

Fig. 3 XRD pattern of ZnO

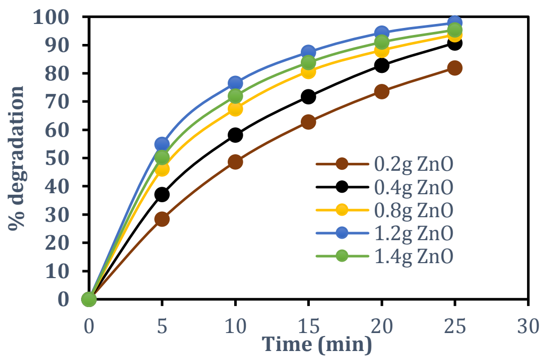

Fig. 4 % degradation vs time curve for the photodegradation of RBB in presence of different amounts of ZnO, $[RBB]_o = 7\times10^{-5}$ mol/L

3.2 Effect of ZnO Loading on Photodegradation

With increasing the amount of ZnO, % degradation of RBB increases first and reaches maximum at 1.20 g of ZnO and then decreases again (Fig. 4). The initial rate in the photodegradation process is also maximum for 1.20 g of ZnO (Fig. 5). This may be due to the fact that initially the increase in the amount of catalyst, the number of active site increases that in turn inflates the number of •OH and O_2•−radicals [16, 17]. But beyond the optimum amount of catalyst loading, particle-particle interaction becomes more significant [18]. These reduce the site density for surface holes and electrons, hence decrease the reaction rate. Moreover, effective light intensity may drop as solution opacity increases and consequently the concentration of photogenerated holes and electrons decreases [19]. This deleterious effect may be further compounded by light shadowing and scattering due to the presence of aggregated particles [16, 20]. As a result, solar light cannot penetrate properly into the highly loaded suspension and thus rate of photodegradation decreases.

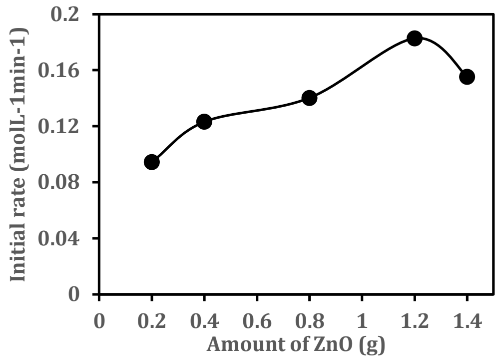

Fig. 5 Initial rate vs different amount of photocatalyst for the photodegradation of RBB, $[RBB]_o = 7\times10^{-5}$ mol/L

3.3 Effect of Transition Metal Ions on Photocatalytic Bleaching of RBB by ZnO

The effect of addition of transition metal ions ($M^{n+} = Co^{2+}$, Fe^{3+}, Pb^{2+} and Ni^{2+}) has been investigated under solar light (Fig. 6). The result shows that trace quantities of Co^{2+} and Fe^{3+} ions enhance the rate of photocatalytic bleaching of RBB to some extent. The increase of photocatalytic efficiency by these two metal ions may be due to the introduction of new trapping sites by incorporating of these ions [21]. On irradiation, migrating electrons from the valence band of ZnO are trapped by Co^{2+} and Fe^{3+} because of having partially filled d-orbital and thus electron–hole recombination is suppressed [16, 22-24]. The hole is then free to diffuse to the semiconductor surface where oxidation of organic species can occur. On the other hand, the Pb^{2+} and Ni^{2+} ions inhibit the photocatalytic bleaching of RBB under solar light irradiation. This retardation effect may be due to the blocking of active sites and reduces the surface area of ZnO by the deposition of these metal ions on the ZnO surface which decreases the degradation rate.

The mechanism for metal ion modified photodegradation can be represented as follows: Metal ions modified photodegradation:

$^1Dye + h\nu \longrightarrow {}^1Dye_1$ (singlet excited state)
$^1Dye_1 \longrightarrow {}^3Dye_1$ (triplet excited state)
$ZnO \longrightarrow ZnO^*\ (h^+_{vb} + e^-_{cb})$
$M^{n+} + e^-_{cb} \longrightarrow M^{(n-1)+}$
$M^{(n-1)+} + O_2 \longrightarrow M^{n+} + O_2^{\bullet-}$
$ZnO^*\ (h^+_{vb}) + OH^- \longrightarrow ZnO + {}^\bullet OH$
$^3Dye_1 + {}^\bullet OH/\ O_2^{\bullet-} \longrightarrow$ Degradation of the dye.

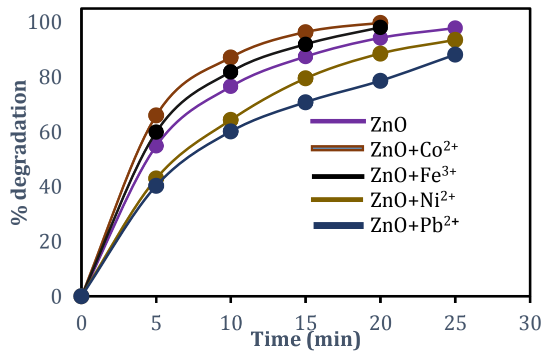

Fig. 6 % degradation vs time curve for the photodegradation of RBB in presence of different transition metal ions, $[RBB]_o = 7\times10^{-5}$ mol/L, ZnO = 1.20 g

3.4 Effect of Concentration Variation of Co^{2+} and Fe^{3+} Ions

Since Co^{2+} and Fe^{3+} ions increase the photodegradation under solar light, the experiments were carried out with different concentrations of these ions. The effect of Co^{2+} ions on photocatalytic degradation of the dye was investigated by varying its concentration from 2×10^{-4} mol/L to 3×10^{-3} mol/L under solar light irradiation and the result is shown in Fig. 7.

In this case, the degradation rate of RBB increases up to a maximum at 4×10^{-4} mol/L and then decreases again. For Fe^{3+} ion, the vertex point of degradation of RBB is for 5×10^{-4} mol/L Fe^{3+} solution (Fig. 8) and degradation rate decreases with further increasing of Fe^{3+} ion into the solution.

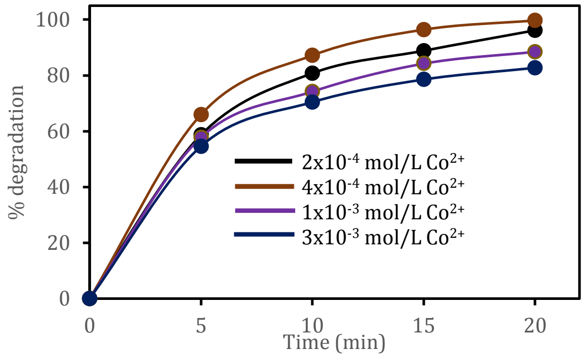

Fig. 7 % degradation vs time curve for the photodegradation of RBB with the presence of different concentrations of Co^{2+} ions, $[RBB]_o = 7\times10^{-5}$ mol/L, ZnO = 1.20 g

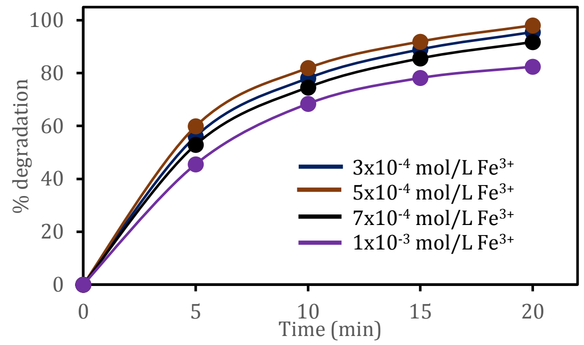

Fig. 8 % degradation vs time curve for the photodegradation of RBB with the presence of different concentrations of Fe^{3+} ions, $[RBB]_o = 7\times10^{-5}$ mol/L, ZnO = 1.20 g

First, increasing the photodegradation rate is due to scavenging of photogenerated electrons by metal ions (Eq. (4)) which give the holes more opportunities for the Eq. (2) and Eq. (3) causing the rapid formation of •OH radicals. Therefore, the percent degradation of RBB is expected to raise [25]. But beyond the optimum level of doping concentration, the decrease in photocatalytic activity may result from decreasing surface area and blocking the active sites of ZnO by deposition of extra metal ions on the semiconductor photocatalyst surface. Moreover, after optimum loading of these metal ions, photodegradation efficiency may turn down by narrowing space charge region and the penetration depth of radiation into photocatalyst may exceed the space charge layer, so that the recombination of the photogenerated electron-hole pairs turns to be easier.

$ZnO + h\nu = ZnO\,(h^+ + e^-)$ (1)
$h^+ + H_2O = \bullet OH + H^+$ (2)
$h^+ + OH^- = \bullet OH$ (3)
$M^{n+} + e^- = M^{(n-1)+}$ (4)

3.5 Kinetics of Photocatalytic Degradation of RBB

Influence of the initial amount of photocatalyst on the rate of photocatalytic degradation of most organic compounds has been described by pseudo-first order kinetics as suggested by Langmuir-Hinshelwood model,

$$R = dC/dt = k_r KC/(1+KC) \quad (5)$$

where R is rate of the reaction, k_r is the reaction rate constant, K is the adsorption coefficient of the reaction, C is the reactant concentration at any time t, dC is the small change of reactant concentration within a little change of time interval (dt). Integration of Eq. (5), yields the following Eq. (6):

$$-\ln(C/C_0) + K'(C_0 - C) = k_r{*}K{*}t \quad (6)$$

where K′ is a constant, t is the reaction time and when the initial concentration C_0 is small, Eq. (6) changes into Eq. (7), which expresses a pseudo-first order reaction kinetic regime.

$$-\ln(C/C_0) = k_r{*}K{*}t = kt \quad (7)$$

where k is the pseudo-first order reaction rate constant, $k = k_r{*}K$. Fig. 9 and correlation coefficient (R^2) value (Table 1) of each line authenticates that the photocatalytic decolorization of the RBB follows pseudo-first order kinetic pathways because $-\ln(C/C_0)$ vs time plot give straight lines and passing through origin [26-28].

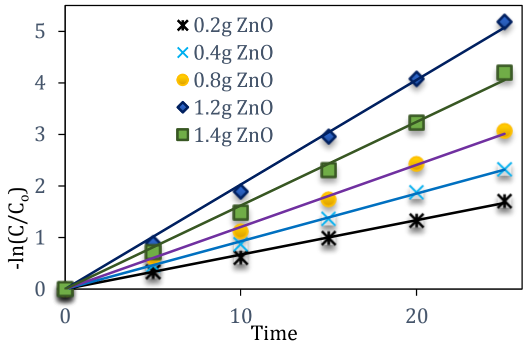

Fig. 9 A plot of $-\ln(C/C_0)$ vs time for different amount of ZnO photocatalysts considering the reaction follows pseudo-first order kinetics, $[RBB]_o = 7\times10^{-5}$ mol/L

Initial decolourization rate constants were determined from the slope of these straight lines. We know rate constant is a measure of the rate of reaction and the greater the value of the rate constant, the faster is the reaction. It can be seen from the data of Table 1 that value of rate constant is maximum for 1.2 g of ZnO which indicates faster degradation of RBB per unit time than any other amount of photocatalyst loading.

Table 1 Data of pseudo-first order rate constants (k) and correlation coefficient (R^2) for the degradation of Remazol Black B under solar light irradiation

Amount of ZnO (g)	Rate constant k (min^{-1})	R^2
0.2	0.0147	0.9947
0.4	0.0188	0.9975
0.8	0.0229	0.9978
1.2	0.0301	0.9988
1.4	0.0282	0.9976

4. Conclusion

Photodegradation has been carried out by varying the amount of ZnO, addition of transition metal ions under solar light. With increasing amount of ZnO, percent degradation increases up to a concentration of 1.2 g and further increase in the amount of ZnO, the % degradation decreases. The addition of Co^{2+} and Fe^{3+} ions into the suspension was found to increase the photodegradation efficiency, up to a certain level concentration of these ions, due to retarding recombination of electron-hole pairs, and then decreased with further increases of these metal ions concentration. The decrease of photodegradation efficiency by Pb^{2+} and Ni^{2+} ions might be due to blocking the active sites of photocatalyst. The whole photodegradation process was found to follow pseudo-first order kinetic pathway.

Acknowledgments

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