Effect of Inorganic Anions on Photodegradation of Remazol Black B (RBB) in the Aqueous Suspension of ZnO under Solar Light Irradiation

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1. Introduction

Dyes are found as dry powders, granules, pastes, liquids, pellets etc., and used as colorants for plastics, inks, ceramics, paints, wax biomedicine, cosmetics, food, paper and pulp etc., touching our life in everywhere. It caters to specialty industries often come with specialized properties such as it conducts electricity, resistances to heat, weather conditions, ultraviolet light etc. But these industries produce large volume of dye effluents, in different steps in the dyeing and finishing processes, which are non-biodegradable and toxic [1, 2]. These dye effluents are often rich in color, containing reactive dyes and chemicals and create several environmental problems by discharging into the aqueous phase. Various physical and chemical processes such as reverse osmosis, adsorption, precipitation, ultrafiltration, flocculation and air stripping can be used for removal of color from dye effluents [3, 4]. These techniques, however, are non-destructive because they only transfer pollutants into sludge, which needs further treatment.

Recent interest in advanced oxidation processes (AOPs) has considerably increased for the complete degradation of dyes. These processes are based on the generation of hydroxyl radicals that react with a broad range of organic contaminants rapidly and non-selectively [5]. AOPs include photocatalytic systems such as combination of light and semiconductors, and oxidants with semiconductor. Heterogeneous photocatalytic has emerged as a significant destructive technology leading to the total mineralization of most of the organic contaminants including organic dyes [6, 7].

Zinc oxide (ZnO) is characterized by non-toxicity, cheap production cost, moderate band gap energy (3.37 eV) and chemical stability, therefore it represents one of the most important oxides that used in various fields of photochemistry, for instance, in photo electrolysis of water, environmental remediation and dye-sensitized solar cells [8, 9]. In some cases, a combination of various treatment processes is needed to improve the overall efficiency of the industrial effluent treatment. Solar light was chosen as light source for green environment, utilizing natural resource, economically reasonable and facile degradation process. Moreover, to degrade industrial hazardous effluents by UV is costly and very risky to human health and environment [10]. So in the present research study, mineralization of reactive dyes by naturally abundant solar light in presence of ZnO with optimizing operational parameters was in foremost focus.

2. Experimental Methods

2.1 Reagents

Remazol Black B (RBB) (Sigma Aldrich), commercial ZnO (Fluka, Switzerland), Na2SO3, Na2CO3, NaCl, and K[Fe(CO3)3]-3H2O were purchased from merck, 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 500.0 mL volumetric flask and then deionized water was added up to the mark to prepare 7×10−4 mol/L solution of RBB. Further dilution was made whenever necessary.

2.2 Photodegradation of RBB

A definite amount of ZnO was taken in a 100 mL baster. 25 mL of deionized water was added to it and kept overnight for soaking the sample properly. Then previously prepared dye solution was added to the suspension to prepare desired dye concentration for total 100 mL volume of the suspension. A magnetic stirrer was also added to the suspension to rotate the solution. All photocatalytic experiments were carried out in open air on sunny days between 11 am to 1 pm after definite time interval, a certain portion of the irradiated solution was taken out and centrifuged to obtain clear solution for monitoring absorbance. Solar light intensity was measured for every minute by pyranometer and the average light intensity over the duration of each experiment was calculated. The average solar light intensity was 700-720 Wm−2 (source: Renewable Energy Research Centre, University of Dhaka) and was nearly constant during the experiments.

2.3 Determination of αmax and Molar Absorption Coefficient (εmax) of RBB

The absorbance maximum (αmax) of aqueous solution RBB was determined spectrophotometrically from its absorption spectrum. The spectrum of RBB in aqueous solution (Fig. 1) has several peaks. Among these, the peak at 594±50 nm is the most intense and this peak was used to monitor the change of the concentration of RBB in most of the subsequent

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experiments. However, the calibration curves were constructed at 594.50 nm, 391.50 nm and 310.00 nm by maintaining the following conditions:

Reference : Water
Temperature : 30 °C
pH : 5.83
The molar extinction coefficient of RBB solution (Fig. 2) were found to be ε = 30120 Lmol⁻¹cm⁻¹ at λmax = 594.50 nm, ε₁ = 9375 Lmol⁻¹cm⁻¹ at λ₁ = 391.50 nm and ε₂ = 21040 Lmol⁻¹cm⁻¹ at λ₂ = 310.00 nm at room temperature.

3. Results and Discussion

3.1 Effect of Irradiation Time on Photodegradation

The photodegradation of Remazol Black B was tested under solar light irradiation in presence of ZnO suspension with average light intensity of 700-720 Wm⁻² during the experimental courses. The relationship between the photodegradation efficiency of RBB and illumination time is shown in Fig. 3. It is observed from Fig. 4 that the photodegradation efficiency of RBB increases from 54.85% to 97.88% while increasing illumination time from 5 to 25 minute. In general, the photocatalytic degradation involves several steps such as adsorption-desorption, electron-hole pair production and redox chemical reaction. When photocatalyst (PC) is irradiated by photons with energy of equal or more than band gap energy of PC then the electrons (e⁻) excited from valence band (VB) to conduction band (CB) with simultaneous creation of holes (h⁺) in the VB

\[ PC + h\nu \rightarrow e_{cb} + h_{vb} \]

where hν is the energy essential to transfer the electron from valence band to conduction band. The electrons generated through irradiation could be readily trapped by O₂ adsorbed on the photocatalyst surface or the dissolved O₂ to give superoxide radicals (O₂⁻).

\[ e_{cb} + O_2 \rightarrow O_2^- \]

\[ 2O_2^- + 2H_2O \rightarrow 2OH + 2OH^- + O_2 \]

Simultaneously, the photo induced holes could be trapped by surface hydroxyl groups (or H₂O) on the photocatalyst surface to give hydroxyl radicals (OH):

\[ h_{vb} + OH^- \rightarrow OH \]
\[ h_{vb} + H_2O \rightarrow OH + H^+ \]

Finally, the organic molecules will be oxidized to yield intermediate degraded products, CO₂ and H₂O as follows:

\[ \text{-OH/ O}_2^- + \text{organic molecules } \rightarrow \text{Mineralized intermediate products } + \text{CO}_2 + \text{H}_2\text{O} \]

So the more packets of photon irradiation in the suspension, the more creation of -OH and O₂⁻ radicals in the reaction medium [11-13]. As a result, augmentation RBB degradation is expected with the increase photolysis time if other parameters remain constant.

3.3 Effect of Initial Dye Concentration on Photodegradation

The photocatalytic degradation was investigated by varying initial concentration of RBB over the range of 3×10⁻⁵ to 11×10⁻⁵ mol/L (Fig. 6). With increasing the initial concentration of dye, % degradation of RBB decreases gradually under solar light. It can be shown from Fig. 7 that about 99.27% of 3×10⁻⁵ mol/L RBB solution has been degraded within 10 minutes of solar light irradiation whereas 76.19% degradation was observed for 11×10⁻⁵ mol/L RBB solution in 25 minutes keeping other parameters constant. It is also evident from Fig. 7 that % degradation efficiency is inversely affected by the concentration of dye and Fig. 8 reveals that initial rate of photo mineralization decreases with increasing initial concentrations of RBB. These all phenomena can be explained as the dye concentration is increased, the equilibrium adsorption of dye on the
catalyst surface active sites increases, hence competitive adsorption of OH on the same sites decreases, meaning a lower formation rate of -OH/O₂⁺ radicals, which are the principal oxidants for acquiring high degradation efficiency [14, 15, 18]. On the other hand, considering the Beer-Lambert law, as the initial dye concentration increases, the path length of photons entering the solution decreases resulting in lower photon absorption by photocatalyst particles and consequently a lower photodegradation rate [19, 20]. The present observations are in agreement with results obtained by other groups of researchers [21, 22].

On the other hand, enhancement of photodegradation was occurred in the presence of Fe³⁺(C₆O₄)⁻² ion due to intramolecular electron transfer from the ligand to Fe(III) ion by absorbing photon of light or accepting photogenerated electrons in conduction band of semiconductor with formation of a primary radical complex [(C₆O₄)Fe²⁺(C₆O₄)⁻²] and it dissociates reversibly into oxalate ion and a secondary radical complex, [(C₆O₄)Fe²⁺(C₆O₄)⁻²]. The latter reacts with the initial complex and dissociates to Fe⁶⁺(C₆O₄)⁺ and oxalate radical (C₆O₄⁻). Then the oxalate radical reacts as follows and produce reactive oxidant which is the major species for photodegradation.

\[ \text{C}_6\text{O}_4^- + \text{OH} \rightarrow \text{OH} + \text{C}_6\text{O}_4^2^- \]  

Fig. 6 Absorbance vs time curve for the photodegradation of RBB in presence of different concentration of RBB at pH 5.83, ZnO = 1.20 g/100 mL, Light intensity = 700-720 Wm⁻²

Fig. 7 % degradation vs time curve for the photodegradation of RBB in presence of different concentration of RBB, ZnO = 1.20 g/100 mL, Light intensity = 700-720 Wm⁻²

Fig. 8 Initial rate vs [RBB] for the photodegradation of RBB in presence of ZnO, Light intensity = 700-720 Wm⁻²; ZnO = 1.20 g/100 mL.

3.4 Effect of Inorganic Anions on Photocatalytic Bleaching of RBB by ZnO

The effect of addition of inorganic anions on photo degradation by ZnO was investigated under solar light irradiation (Fig. 9). It has been reported that the inorganic anions may influence photodegradation in several ways [23, 24]. On one hand, anions can compete with target pollutant for adsorption on the surface of catalyst, or react with photogenerated holes and OH and form less reactive ionic radicals, which may decrease the pollutant degradation efficiency [23]. On the other hand, the anions may form an electrostatic field in the vicinity of the catalyst so as to promote the adsorption of the target pollutant and separation of electrons and holes [24, 25]. The effect of presence of chloride, sulfate, nitrate, carbonate and ferrousate anions was investigated using corresponding Na⁺ as cation except for ferrousate where K⁺ was cation on RBB (7×10⁻⁵ mol/L) degradation catalyzed by ZnO (1.2 g/100 mL) at solar light intensity between 700-720 Wm⁻². It is seen from Fig. 9 that all anions except Fe⁶⁺(C₆O₄)⁻² were found to inhibit photocatalysis with the order of NO₃⁻ > Cl⁻ > CO₃²⁻ > SO₄²⁻. This can be explained on the basis of reaction of RBB and OH with scavengers as well as inhibitors and thus the inhibition effect of these ions is due to the reaction of these ions with holes and OH (according to reaction (1) - (5)).

\[ \text{SO}_4^{2-} + \text{h}^+ \rightarrow \text{SO}_4^- \]  
\[ \text{SO}_4^{2-} + \text{OH} \rightarrow \text{SO}_4^- + \text{H}^+ \]  

3.5 Effect of Concentration Variation of [Fe(C₆O₄)²⁻] ions

Since [Fe(C₆O₄)²⁻] ion increases the photodegradation under solar light, the experiments were carried out with different concentrations of this ion. The effect of [Fe(C₆O₄)²⁻] ions on photocatalytic degradation of RBB was investigated by varying its concentration from 7×10⁻⁶ to 5×10⁻⁵ mol/L under solar light irradiation and the result is shown in Fig. 10. In this case, the degradation rate of RBB increases up to a maximum at 1×10⁻⁵ mol/L, and then decreases again. Initially, increasing the photodegradation rate may be due to scavenging of photogenerated electrons by ferrousate (reaction (10)) which gives the holes more opportunities for the reactions (8) and (9) causing the rapid formation of -OH radicals. Therefore, the percent degradation of RBB is expected to rise. But beyond optimum level of the [Fe(C₆O₄)²⁻] ion, decrease in photocatalytic activity may results from decreasing surface area and blocking the active sites of ZnO by deposition of newly formed long-lived intermediate ions on the semiconductor photocatalyst surface [18].

Fig. 9 Effect of inorganic anions on the photodegradation of RBB by ZnO under solar light, [RBB] = 7×10⁻⁶ mol/L, ZnO = 1.20 g/100 mL, Light intensity = 700-720 Wm⁻²

Fig. 10 Effect of concentration variation of [Fe(C₆O₄)²⁻] ion on the photodegradation of RBB by ZnO under solar light, [RBB] = 7×10⁻⁶ mol/L, ZnO = 1.20 g/100 mL, Light intensity = 700-720 Wm⁻²

3.6 Kinetics Analysis of Photocatalytic Degradation of RBB

The photocatalytic degradation of most organic compounds follows pseudo-first order kinetics according to the Langmuir-Hinshelwood model. The final modified pseudo-first order kinetic models of photodegradation can be expressed by following equation.

\[ \ln \left( \frac{C}{C_0} \right) = k t \]  

where, \( C_r \) is the initial concentration (mol/L) of compound, \( C_t \) is the concentration (mol/L) at time \( t \) is the irradiation time and \( k \) is the reaction rate (min\(^{-1}\)). According to the equation (11) plot of \( \ln(C_r/C_t) \) against \( t \) will give a straight line for first order reactions and the rate constant can be obtained from the slope of the line.

4. Conclusion

Photodegradation has been carried out by varying concentration of Remazol Black B, addition of inorganic anions, metal complex ion as oxidant under solar light irradiation. With increasing the concentration of dye, photodegradation rate decreases. The addition of anionic salt into the suspension was found to decrease the photodegradation efficiency might be due to blocking the active sites of photocatalyst. On the other hand, degradation rate was increased by adding ferric oxide complex due to intramolecular electron transfer from the ligand to Fe(III) ion with formation of a primary radical complex \([(C_3O_8)Fe(C_3O_8)]^– \) and oxolate radical. The whole photodegradation process was found to follow pseudo-first order kinetic model.

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