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Photodegradation Study of Toluidine Blue Dye in Aqueous Solution using Magnesium Oxide as a Photocatalyst

Haydar A. Mohammad Salim[1], Sabir Ayob Mohammad Salih[1]

[1]Dept. of Chemistry, Faculty of Science, University of Zakho, Kurdistan Region-Iraq

Correspondence: Haydar A. Mohammad Salim, Dept. of Chemistry, Faculty of Science, University of Zakho, Kurdistan Region-Iraq. E-mail: Haydar.kovly@gmail.com

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Abstract

The photocatalytic degradation of Toluidine Blue dye (TB) in aqueous solution was investigated under UV light in the presence of magnesium oxide (MgO) as a photocatalyst at different operating parameters. The operating conditions were photocatalyst dose, initial dye concentration and the pH of the solution. Increasing of photocatalyst dose from 10 to 70 mg enhanced the degradation rate of TB dye. However, the increasing of TB dye concentration from 2 to 8 mg/L negatively affected the degradation rate. It was found that the percent of dye removal reached the maximum value at high acidic medium. In dark condition, 15 % of dye was adsorbed by MgO. Furthermore, the kinetics involved in the degradation of TB dye was examined and the degradation was found to follow pseudo first order kinetic model.

Keywords: Photocatalyst, MgO, Toluidine Blue, Kinetic, Dye, AOPs

1. Introduction

Textile industries consume large amount of water and produce large volume of dye effluents, in deferent steps in the dyeing and finishing processes, which are non-biodegradable and toxic (Reife & Freeman, 1996). These dye effluents are often rich in colour, 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 colour from dye effluents (Georgiou, Melidis, Aivasidis, & Gimouhopoulos, 2002; Ledakowicz, Solecka, & Zylla, 2001; Peralta-Zamora et al., 1999; Robinson, McMullan, Marchant, & Nigam, 2001). These techniques, however, are non-destructive because they only transfer pollutants into sludge, which needs further treatment (Arslan, Balcioglu, Tuhkanen, & Bahnemann, 2000; Chaudhuri & Sur, 2000; Stock, Peller, Vinodgopal, & Kamat, 2000).

Recent interest in advanced oxidation processes (AOPs) has considerably increased for the complete degradation of dyes. These processes are based on generation of hydroxyl radicals that react with a broad range of organic contaminants rapidly and non-selectively (Das, Kamat, Padmaja, Au, & Madison, 1999; Yang, Wyatt Ii, & Bahorsky, 1998). 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 (Galindo, Jacques, & Kalt, 2001; Khodja, Sehili, Pilichowski, & Boule, 2001; Kusvuran, Samil, Atanur, & Erbatur, 2005; Neppolian, Choi, Sakthivel, Arabindoo, & Murugesan, 2002).

Titanium dioxide (TiO_2) is characterized by non-toxicity, cheap production cost and chemical stability, therefore it represents one of the most important oxides that used in various fields of photochemistry, for instance, in photoelectrolysis of water, environmental remediation, and dye-sensitized solar cells (Anpo, 2004; Cappelletti et al., 2009; Chen & Mao, 2007; Gratzel, 2001). Furthermore, the Fenton process is being increasingly used in the treatment of textile industries (Bautista, Mohedano, Gilarranz, Casas, & Rodriguez, 2007; Lofrano, Meriç, Belgiorno, Nikolaou, & Napoli, 2007; Meriç, Lofrano, & Belgiorno, 2005). Among AOPs, homogeneous photocatalysis using UV with hydrogen peroxide, H_2O_2, have received a great attention in degrading or reducing organic pollutant by generation of two molecules of hydroxyl radicals (Al-Ekabi, Safarzadeh-Amiri, Sifton, & Story, 1991; Chu, Lau, & Fung, 2006; Saien, Ojaghloo, Soleymani, & Rasoulifard, 2011). In some cases, a combination of various treatment processes is needed to improve the overall efficiency of the water treatment systems and to optimize economic requirements (Oller, Malato, & Sánchez-Pérez, 2011; Parrino, Camera-Roda,

Loddo, Palmisano, & Augugliaro, 2014; Rueda-Márquez, Pintado-Herrera, Martín-Díaz, Acevedo-Merino, & Manzano, 2015).

Although TiO_2 and ZnO well known metal oxides for AOPs and have higher band gap than MgO, however; MgO is less expensive and commercially available (Khan, Adil, & Al-Mayouf, 2015; Raza, Haque, Muneer, & Bahnemann).The aim of this study was to present the photocatalytic degradation of Toluidine Blue (TB) dye in aqueous solution using MgO as a photocatalyst under various operating conditions. The operating conditions were MgO quantity, TB concentration and pH of the solution. The adsorption and kinetic study of TB on MgO surface were also studied.

2. Method

2.1 Materials

Toluidine blue (TB) dye was purchased from Labpak Chemicals Ltd, UK, and used as received to prepare solutions that used in this research. Table 1 shows the characteristics of TB dye. A stock solution of TB (1000 mg/L) was prepared using deionized water and other concentrations (2, 4, 6 and 8 mg/L) were prepared by dilution the stock solution of TB. The stock solution of TB (1000 mg/L) was covered and stored in a dark place. Magnesium oxide (MgO) was purchased from ROTH, Germany, and used as received without any modification and used as photocatalyst in this study. Sodium carbonate and ethanol were purchased from Fisher-Scientific, UK. Nitric acid (HNO_3) and sodium hydroxide (NaOH) were purchased from Fisher-Scientific, UK. Various molarities of HNO_3 and NaOH were used to adjust the pH value of solutions between 2 and 12 using pH meter. The pH of the solution was determined using pH meter (EUTECH, Malaysia). UV lamp with 254 nm (12 watt) was purchased from SEMTEC, China. Visible spectrophotometer (Jenway, 6700) was used to analyse the collected samples.

Table 1. Characteristics of TB dye

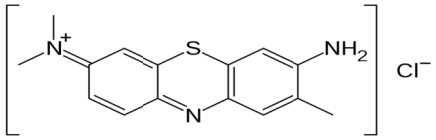
C.I. index	C.I. Basic Blue 17 (C.I. 52040)
Chemical Name	3-Amino-7-(dimethylamino)-2- methylphenothiazin-5-ium chloride
Chemical Formula	C15-H16-N3-S-Cl
Molecular Mass	270.374 g/mol
Molecular structure	
Colour	Blue
λ_{max}	625 nm
pKa	2.4, 11.6

Figure 1. Photocatalytic Reactor Design

2.2 Experimental Procedure

A closed reactor with a volume of 600 mL was used in this research as shown in Figure 1. At a specific concentration of TB solution, 500 mL of solution was charged into a reactor. MgO with a specific amount (10, 30, 50 and 70 mg) was added to TB solution as a photocatalyst. The volume of the reactor was 600 mL. It is

made from PYREX glass and fitted with a sample port. The reactor was equipped with a plunging tube in which a SEMTEC 12 watt lamp was placed horizontally. A glass syringe with 5 mL volume was used, at a specific schedule, to collect samples. The pH values, from 2 to 12, of these solutions were adjusted using different molarities of NaOH and HNO_3.

3. Results and Discussion

3.1 Effect of Photocatalyst Dose

The catalyst dose, in photocatalytic process, is an important parameter since increasing in the amount of photocatlyst increased the active sites number on the photocatalyst causing generation more $OH^{\bullet}$ radicals (Nishio, Tokumura, Znad, & Kawase, 2006). The degradation of TB was studied in the semi-batch reactor. A 500 mL volume of TB solution with the concentration of 4 mg/L were charged in the reactor with different amount of MgO (10, 30, 50 and 70 mg). As shown in Figure 2, the concentration of TB reduced with time. It also shows that the increasing of MgO amount increases the removal efficiency. This is due to the formation of highest amount of hydroxyl radical when more amount of MgO was used. The degradation of TB reaches maximum value when 50 mg of MgO was used in 70 min of reaction time. A further increase in the catalyst dose does not affect the removal efficiency of TB dye. This is due to the blocking of UV light penetration with increasing photocatalyst amount (Saquib, Abu Tariq, Haque, & Muneer, 2008).

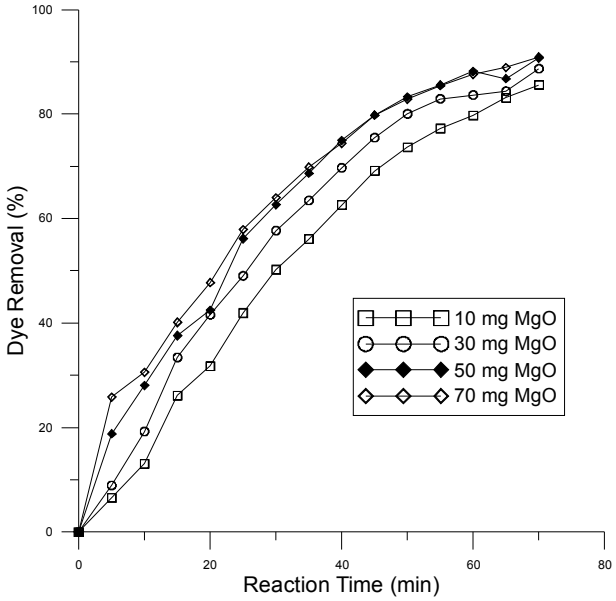


Figure 2. Effect of Photocatalyst Dose ($[TB]_o$= 4 mg/L, Volume = 500 mL, pH = 4)

3.2 Effect of Initial TB Concentration

The influence of the initial concentration of TB dye on its photocatalytic degradation rate was studied for (2, 4, 6 and 8 mg/L) using 50 mg of MgO. The results show that increasing the initial concentration of TB reduced the degradation rate (see Figure 3). As shown in Figure 3, when TB concentration increased from 10 to 70 mg/L, the removal percentage of TB at 70 min of reaction time decreased from 95 % to 81 %, respectively. The results presented in this study are in agreement with the previous study for other dyes such as Reactive Orange 5, methylene blue and Mercurochrome dyes when MgO used as a photocatalyst (Bandara & Ranasinghe, 2007; Kamel, Mashaly, & Abdelghaffar, 2013; Xiang, Xie, Li, & Li, 2013). The deeper colour of TB solution, at high concentration, would not be high transparent to UV light as in low concentration of dye and a significant amount of UV light would be absorbed by the TB molecules causing less light to reach MgO particle. Hence, the formation of $OH^{\bullet}$ radicals reduced. The rate constant, k', was found to decrease linearly with increased initial TB concentration. The photodegradation of TB dye on the surface of MgO catalyst follows pseudo first order kinetic law and, expressed as follows:

$$\ln (C/C_o) = -k' t \quad (1)$$

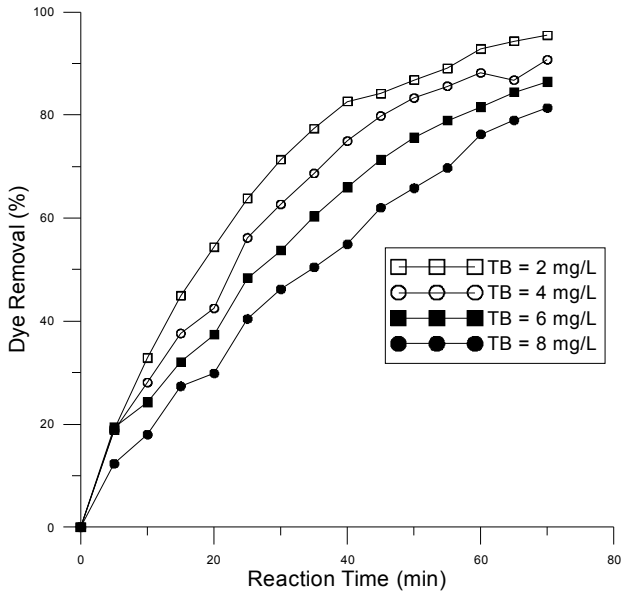


Figure 3. Effect of initial TB concentration (MgO= 50 mg/L, Volume = 500 mL, pH = 4)

Where C_o and C are the dye concentration at t=0 and t=t, respectively, k' is the rate constant. The plot of the experimental data (ln C/C_o against t) yielding to a straight line, as shown in Figure 4, with relatively high regression coefficients (R^2). The kinetic parameters of photocatalytic degradation of TB by MgO in aqueous solution at various initial TB concentrations were recorded in Table 2.

Table 2. Kinetic parameters of photocatalytic degradation of TB as a function of initial TB concentration

TB concentration (mg/L)	k'	R^2	Dye Removal %
2	0.0437	0.9951	95.5
4	0.0343	0.9901	90.7
6	0.0285	0.9953	86.4
8	0.0238	0.9868	81.4

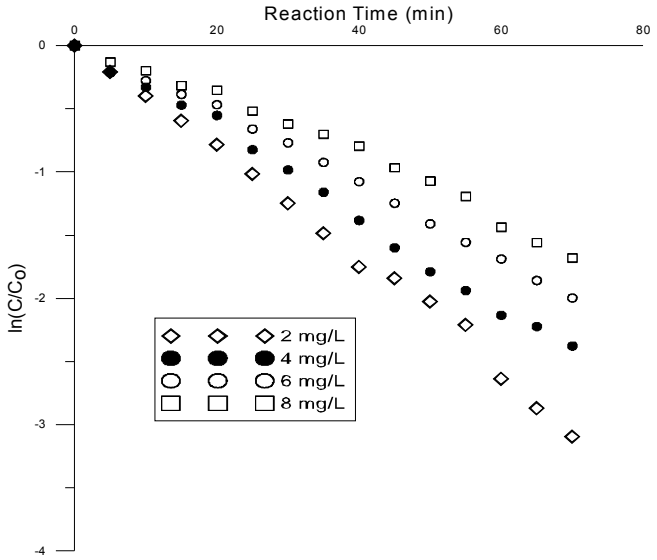


Figure 4. Pseudo first order kinetics of photocatalytic degradation of TB as a function of initial TB concentration (MgO= 50 mg/L, Volume = 500 mL, pH = 4).

3.3 Effect of pH

A series of experiments were performed at various pH values to test the pH effect on photocatalytic degradation of TB dye. Figure 5 illustrated the removal percent of TB in aqueous solution at different pH solutions. As shown from the figure, the initial pH of solution plays an important role in controlling the removal of TB dye using MgO. The pH effect was studied in the range 2-12. Since TB has two pKa values (2.4 and 11.6) (Sabnis, 2010),

see Figure 5, the degradation rate increases in high acidic and high basic medium. The photodegradation was significantly enhanced at low pH values, while at high pH values insignificantly enhanced. The removal percent reached maximum value in high acidic medium with a value of 92%; however, removal percent reached minimum value at pH 8 with a value of approximately 60 %.

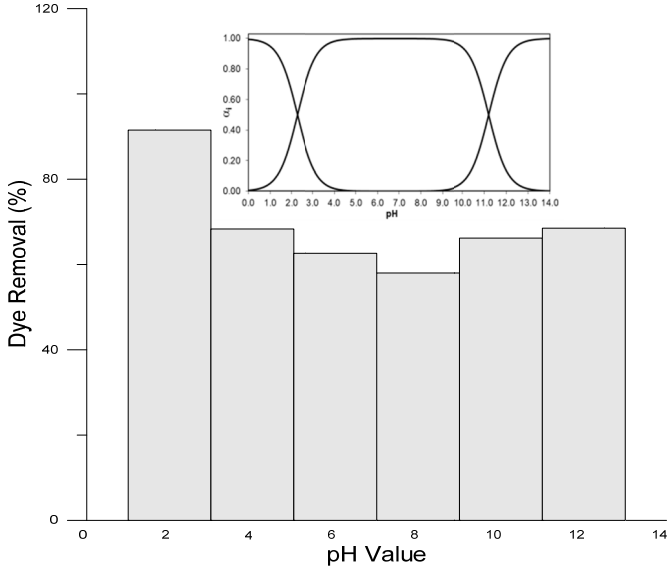


Figure 5. Effect of pH ($[TB]_o$= 4 mg/L, MgO= 50 mg/L, Volume = 500 mL)

3.4 Adsorption of TB on MgO Surface

The TB adsorption on MgO was obtained at 20 ^oC, pH 4 and constant shaker under dark conditions. The experiment was performed with 200 mL of TB dye with 4 mg/L and 50 mg of MgO. As Shown in Figure 6, around 14 % of TB dye was removed from MgO surface at 80 min of adsorption time.

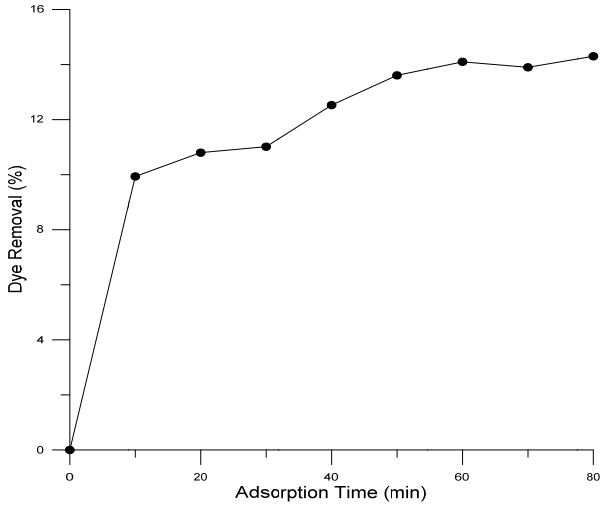


Figure 6. Adsorption of TB on MgO surface (MgO= 50 mg/L, Volume = 500 mL, pH = 4)

4. Conclusion

Toluidine Blue dye was degraded in aqueous solution under UV light in the presence of MgO as a photocatalyst. The degradation of TB was conducted at different operating parameters including TB concentration, MgO dose and pH of the solution. The most effective improvements on the degradation of TB were recorded with initial TB concentration of 2 mg/L. It was also found that the increasing of MgO quantity enhanced the reaction rate of TB removal. The removal efficiency of TB was favorable in the high acidic medium and reached the maximum value. The degradation of TB at different initial dye concentration follows the pseudo first order kinetics.

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