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A comparison study of two different types of clay for heterogeneous photo degradation of dye

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ABSTRACT

Acid alizarin black (AAB) dye (C.I. 21725) was degraded in aqueous solution using UV light in the presence of two types of clay (C1 and C2) as a catalyst at different operating conditions. The operating conditions were concentration of catalyst dosage (10, 30 and 50 mg), initial concentration of AAB dye (10, 20 and 30 mg/L), pH (2, 4, 6, 9 and 11) and intensity of UV light (6 and 12 watt). It was found that the increasing of catalyst concentration enhanced the dye decolourisation. C1 and C2 exerted positive effects on the AAB removal whilst the initial concentration of AAB negatively affected its removal. It was also found that the removal efficiency of AAB significantly depend on pH value. In high and low pH values removal percent increase, while a reversed trend was observed at with the pH value close to neutral. The result shown that removal percent of dye increased when 12 watt lamp used instead 6 watt lamp. C1 and C2 clay were analysed by X-Ray fluorescence to determine the metal oxides in clays.

1. Introduction

The effluent from many industries such as textile, dyeing, paper, carpet manufacturing and pulp contains various types of dyes with large molecular weight. These industries discharge a huge quantity of dyes into the water, which cause pollution of water and serious environmental problems (Aksu 2005; Mohan, Balasubramanian et al. 2007). Therefore, many modern techniques of treatment (i.e. adsorption, oxidation and flocculation-precipitation) have been used over the last few decades to treat and purify water. Among oxidation methods, photolysis and ozonation techniques, for example, have been used successfully to degradate and reduce a range of biological and organic pollutants (Rice and Hoff 1981; Rice and Hoff 1981; Rice and Browning 1981; Beltran 2004; Barakat, Tseng et al. 2005). Stronger oxidant, however, are produced (i.e. radicals) when these techniques are combined with some additives such as hydrogen peroxide and catalysts, and these processes together with additives are called Advanced Oxidation Processes (AOPs) (Glaze, Kang et al. 1987). Typically, AOPs are based on redox reactions as a result of losing and gaining electrons by organic molecules and radicals, respectively (Rice and Netzer 1982; Rice and Netzer 1983). Among AOPs, in recent years, heterogeneous photocatalysis methods have received a great attention in degrading or reducing organic pollutant (Al-Ekabi, Safarzadeh-Amiri et al. 1991; Prihod'ko and Soboleva 2013).

Metal oxides, as a photocatalysts, are promising materials for oxidation of organic pollutants by applying UV light. TiO_2 has been widely used in the photocatalytic degradation of many organic pollutants and it is regarded as the most efficient and environmentally benign catalyst for photodegradation (Matthews 1987; Pelizzetti, Maurino et al. 1989; Yamagata, Loo et al. 1989). Platinised WO_3 has been used as an environmental photocatalyst. Many studies have shown this materials to be an effective visible live potocatalyst for photodegradation of organic pollutants (Anandan, Sivasankar et al. 2014). ZnO, as compared to TiO_2, is more efficient in the degradation of some organic compounds (Han, Liu et al. 2012; Srivastava 2015). However, using ZnO as photocatalyst was limited due to its photoinstability in aqueous solution (Zhong, Li et al. 2012).

Clay is a fine-grained natural rock or soil material that combines one or more clay minerals with traces of metal oxides and organic matter. Most common heterogeneous photocatalyts are transition metal oxides and semiconductors, which have unique characteristics. In the present work, two different types of clay different places in Kurdistan Region, Duhok Governorate, have been used as a photocatalyst for degradation of Acid Alizarin Black (AAB) in aqueous solution. Various operating

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parameters were studied in this research including initial AAB concentration, amount of clay and pH.

2. Materials and Methods

2.1. Materials

Acid alizarin black (AAB) was purchased from Hopkin and Williams LTD, UK and used as received. A stock solution of AAB (1000 mg/L) was prepared on a daily basis in distilled water and other concentrations (10, 20 and 30 mg/L) were prepared by dilution the stock solution of AAB. The prepared stock solution was covered by aluminum foil and kept in dark. UV lamps with 254 nm (6 and 12 watt) were purchased from SEMTEC, China. Three clays in different places in Duhok governorate, Iraq, were collected and used as a catalyst in this study.

2.2. Experimental procedures

A closed semi-batch reactor, as shown in Fig. 1, was used in this study. A 500 mL, at a specific concentration, of the AAB solution was charged into the reactor, this solution prepared from the stock solution by dilution. Clays at a specific amount (0.01, 0.03 and 0.05 mg) was added to the AAB solution. 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 lamps were placed horizontally. A glass syringe with 5 mL volume was used, at a specific schedule, to collect samples. The pH values (2, 4, 6, 9, and 11) of these solutions were adjusted using 0.1M of NaOH and 0.1M of HNO3. The pH of the solution was determined using pH meter (EUTECH, Malaysia). Visible spectrophotometer (Jenway, 6700) was used to analyse the collected samples.

2.3. Clays Analysis

X-ray fluorescence Spectroscopy was used for three types of clay to determine the percent of metal oxides in the structure of clay. The results for three types of clay by X-Ray fluorescence are shown in Table 1. The used clays (C1 and C2) are grinded and then sieved by scientific sieve type (mesh number 200) to produce the same particle size.

Table 1: Metal Oxide in Local Clay (C1 and C2) According to X – Ray Fluorescence Spectroscopy

Metal Oxides	C1 (%W)	C2 (%W)
SiO_2	38.30	41.50
Al_2O_3	7.42	7.29
Fe_2O_3	8.98	9.20
CaO	6.57	10.38
MgO	11.27	9.82
K_2O	0.42	0.65
Na_2O	0.26	0.47
Total	73.22	79.31

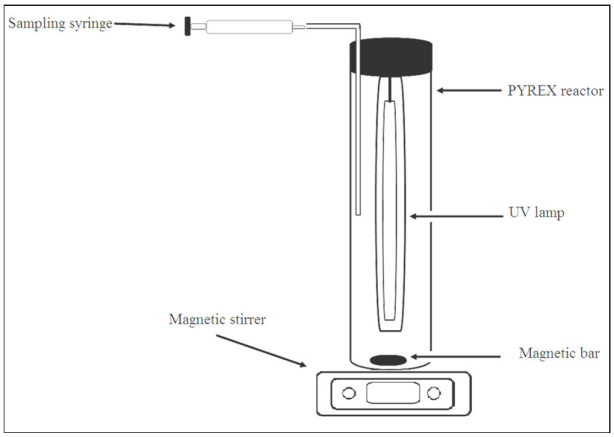

Fig. 1: Photocatalytic reactor

3. Results and Discussion

3.1. Effect of dye concentration

The effect of dye concentration on removal percent of AAB is shown in Fig. 2. The experimental results of AAB removal were obtained at various concentrations (10, 20 and 30 mg/L). It was indicated that the removal percent of dye from solution decreased with increase in initial concentration of dye. It was also found that the removal percent increased when C2 used instead of C1 this is due to the formation of OH radical when C2 used because C2 contain more metal oxide than C1.

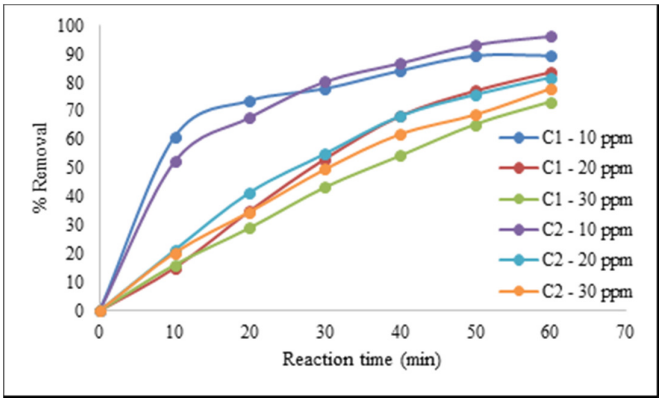

Fig. 2: Effect of AAB concentration on removal percent

3.2. Effect of pH

The effect of pH on removal percent of AAB is shown in Fig. 3. As shown, the initial pH of solution plays an important role in controlling the removal of dye using C1 and C2. The pH effect on the degradation of AAB was studied in the pH range 2-11. The photodegradation was significantly enhanced at low and high pH values and almost 100 % of AAB removed in these two pH values. The effect of pH on photodegradation was versatile relying on the metal oxides percent in C1 and C2 (see Table 1).

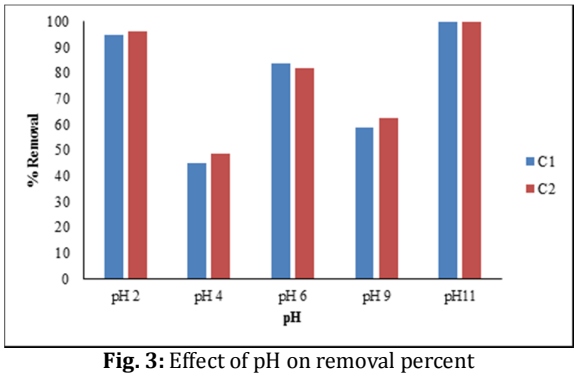

Fig. 3: Effect of pH on removal percent

3.3. Effect of catalyst dosage

The effect of catalyst dose on the degradation of AAB was investigated by employing doses of C1 and C2 varying from 10 to 50 mg/L. The removal percent of dye increased rapidly with increase of C1 and C2 quantity as shown in Fig. 4.

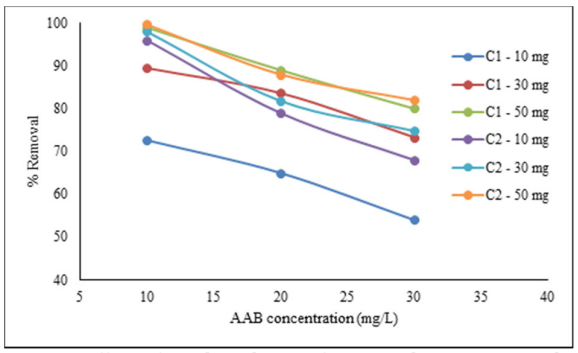

Fig. 4: Effect of catalyst dosage for C1 and C2 on removal percent of AAB

3.4. Effect of UV light intensity

In the photochemical reaction, the initiation rate for photocatalysis electron-hole formation is strongly relying on the intensity of light (Cassano and Alfano 2000). The effect of UV lamp intensity was studied in this study as shown in Fig. 5. The UV lamps used were 6 and 12 watt. It has been reported that increasing light intensity during photocatalytic degradation reaction, the rate of photodegradation also increased (Torimoto, Aburakawa et al. 2004; Ahmed, Rasul et al. 2010; Jia, Wang et al. 2010). The results in this study clearly indicate the 12 watt UV lamp causes higher degradation rate for AAB as compared to 6 watt UV lamp, because higher intensity light is suitable for the excitation of many electrons from the valence band of the metal oxide (Bibak and Aliabadi 2014).

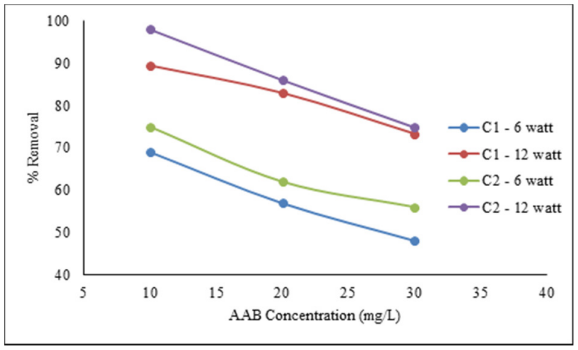

Fig. 5: Effect of UV light intensity on removal percent of AAB

3.5. Adsorption of Dye on catalyst

The adsorption of AAB was obtained at 20 oC, pH 6 and constant shaker under dark conditions. The experiments were performed with 200 mL dye solution and 0.03 g of both C1 and C2. It was found that the removal percent of AAB increase when C2 used instead C1 as shown in Fig. 6.

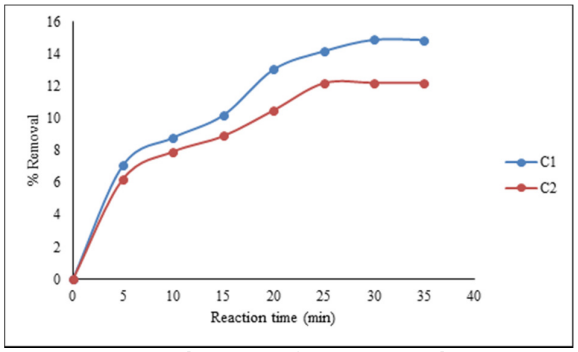

Fig. 6: Adsorption of AAB on C1 and C2

3.6. Kinetic Study

The rate constant, k', was found to decrease linearly with increased initial AAB concentration. When AAB concentration increased from 10 to 30 mg/L, the decolourisation percentage of AAB decreased, as mentioned previously. The dye loss, according to the following equation, was observed as a function of time and data were fitted to a pseudo first order rate model (Esplugas, Giménez et al. 2002; Bali, Çatalkaya et al. 2004):

$$\ln\left(\frac{C}{C_o}\right) = -k't$$

The plot of ln (C/C_o) versus time gives a straight line with **k'** = - slope (**k'**, as seen from figure, depends on the clays concentration), so the reaction follows a pseudo-first order scheme. Table *2* and Table *3* show the effect of dye concentration and amount of clays on rate constant.

4. Conclusion

Photocatalytic degradation, in the presence of C1 and C2 catalyst, of AAB under different operating conditions was studied in this research. The operating conditions were initial dye concentration, amount of catalyst dosage, pH and lamp intensity. The most effective improvements on the degradation of AAB were recorded with initial AAB concentration of 10 mg/L.

Table 2: Effect of AAB concentration on a pseudo-first order kinetic for the degradation of AAB

a-C1			b-C2		
[AAB](mg/L)	K(min^{-1})	R^2	[AAB](mg/L)	K(min^{-1})	R^2
10	0.044	0.89	10	0.0539	0.99
20	0.0287	0.98	20	0.034	0.998
30	0.0208	0.987	30	0.024	0.994

Table 3: Effect of clays amount on a pseudo-first order kinetic for the degradation of AAB

a-C1			b-C2		
C1(mg)	K(min^{-1})	R^2	C1(mg)	K(min^{-1})	R^2
10	0.0234	0.95	10	0.047	0.98
30	0.0443	0.89	30	0.053	0.99
50	0.0742	0.97	50	0.058	0.96

It was also found that the increasing of C1 and C2 quantity enhance the reaction rate of AAB decolourisation. The removal efficiency of AAB was favorable in the acidic and basic medium more than the neutral medium. The removal percentage reached the maximum value at pH close to 2 an 11.

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