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COLOR AND COD REMOVAL OF AZURE A DYE BY UV-ClO_2 PHOTOCHEMICAL OXIDATION

H. A. HABEEB ALSHAMSI[*] and H. A. KHAYOON AL SHDOOD

Chemistry Department, College of Education, University of Al-Qadisiya, P.O. Box 88,
DIWANIYA, REPUBLIC OF IRAQ

ABSTRACT

This research investigates the efficiency of UV-ClO_2 assisted decolorization of azure A dye. The aim of the research is to find the optimum conditions of treatment to reach best mineralization. The study included the investigating effects of dye concentration, temperature, rate flow of gas and light intensity. The maximum removal of color was obtained at temperature of 318 K and within 60 min of irradiation. The results showed that rate of decolorization increases as initial dye concentration and temperature was increased.

The activation energy for decoulorization of aqueous solution of dye was found 19.470 kJ $Mole^{-1}$. It was found that with the increase of both air flow rate velocity and incident light intensity, the ratio of removal increases for dye. The decolorizaition reaction was found to follow pseudo first order kinetic with respect to the dye concentration. Chemical oxygen demand (COD) was simulation investigated in all above studied parameters.

Keywords: Decolorization, Textile dyes, Photooxidation, ClO_2/UV, COD.

INTRODUCTION

Textile industry is one of leading industry for most countries, also is one of the most complicated industries and chemical intensive industries worldwide[1]. The textile wastewater is characterized by high content of dyestuff, salts, high COD deriving from additives, suspended solid due to the fact that 21-377 $m^3 \times tons^{-1}$ of textile fabric in textile factories[2,3]. To protect the aquatic environment, many methods such as adsorption, advance chemical oxidation, nano filtration and chemical coagulation followed by sedimentation were used to remove dyes from waste water[4]. Specifically, advance oxidation processes (AOP's) involving generation of hydroxyl radical introduced to treat textile dyes effluents[5,6]. Advance oxidation processes are better treatment options than the conventional treatment methods

[*]Author for correspondence; E-mail: hassan.habeeb@qu.edu.iq

commonly adopted in wastewater treatment plants[7]. Ultraviolet irradiation following chlorine dioxide (UV/ClO_2) is the one of the most importance methods for water pollution treatment[8-10]. Chlorine dioxide is commonly used as a oxidant and primary disinfectant during treatment of drinking water[11,12]. Chlorine dioxide is less reactive than chlorine, but it has fewer side reactions[13]. The literatures indicates that ClO_2 oxidized the pollutants better than H_2O_2 under irradiation with UV light, as a result of standard oxidation potential of the ClO_2 is larger than that of H_2O_2 (-0.95 volts and –1.78 volts, respectively)[10,14] and hence providing more oxidative strength .The present study was carried out to investigate the removal of azure A dye (Fig. 1) from aqueous solution by using (UV/ClO_2) technique and various reaction conditions involved initial dye concentration, temperature, light intensity and gas flow rate.

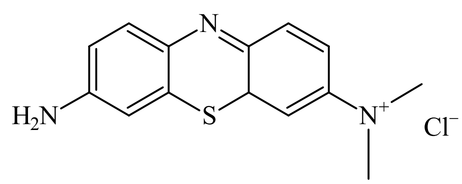

Fig. 1: Structural formula of azure A dye

EXPERIMENTAL

Materials

Sulphuric acid (98%) and sodium chlorite were supplied from B.D.H. Azure A dye was purchased from Omega. All the other solutions were prepared with double distilled water.

Instruments

UV-Visible 1650 spectrophotometer (Shimadzu, Japan) was used to recording the absorption spectra of aqueous solutions of dye. The temperature was adjusted using regulator water bath WB (Optima). The equipment of chlorine dioxide preparation is locally collected. COD was measured by using Lovibond, Vario LR and a thermometer TR 300 (Merck, Jermany).

Photoreactor setup

Schematic diagram for the photoreactor setup shown in Fig. 2[15,16], was fitted with a fixed low-pressure mercury lamp (4, 6, 8 and 12 W) with a highest intensity of the emitted light at 254 nm. The UV lamp was putted in the side of reactor and the quartz sleeve was enclosed. The photoreactor was fitted with a regulator water bath to maintain the temperature and a circulation pump to continuous feed and collection of dye solution in a 1L flask. A syringe was fitted with photoreactor to withdrawn of dye solution samples at meaning time.

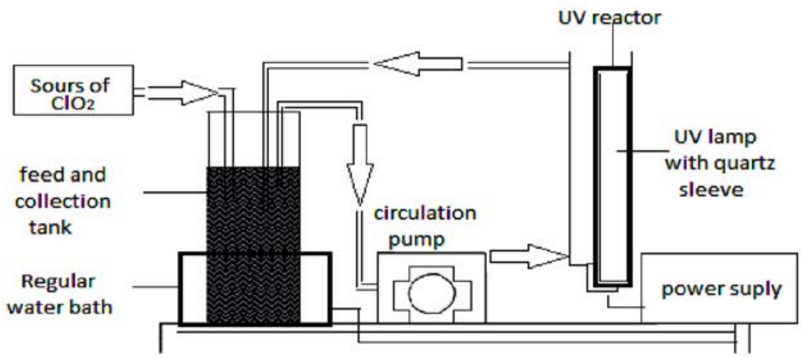

Fig. 2: Photoreactor setup

Preparation of chlorine dioxide

A pure solution of chlorine dioxide was prepared by slowly adding of diluted sulfuric acid to a sodium chlorite solution. Removing any contaminants such as chlorine by sodium chlorite scrubber, and passing the gas into distilled water by a steady steam of air. The experimental setup to generate the chlorine dioxide is described Fig. 3[17].

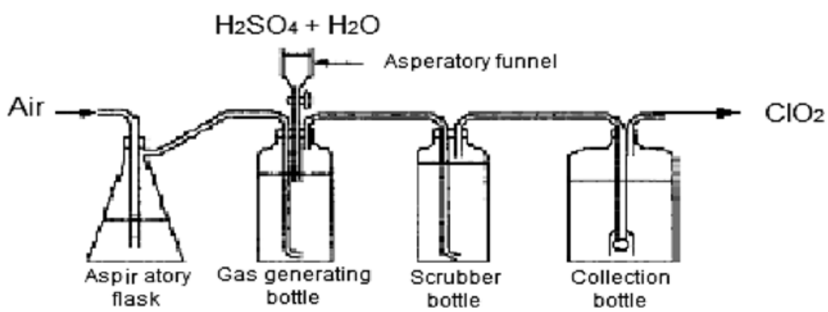

Fig. 3: Chlorine dioxide generation and absorption system

Procedure

The irradiation time for all experiments were fixed at 60 min. Due to the primary experiments indicated that the most dye molecules are degraded and the dye solution become colorless at the time similar to the period. Control experimental were carried out under UV irradiation with ClO_2 in the solutions. In all experiments, the lamp was warmed for 10 min. prior to initiation of reaction. Determination of dye concentration was carried out by using the calibration curve shown in Fig. 4. The absorbance of dye was measure at maximum absorption λ = 632 nm (Fig. 5). In all experiments, ClO_2 was passed prior to exposure of the solutions to UV.

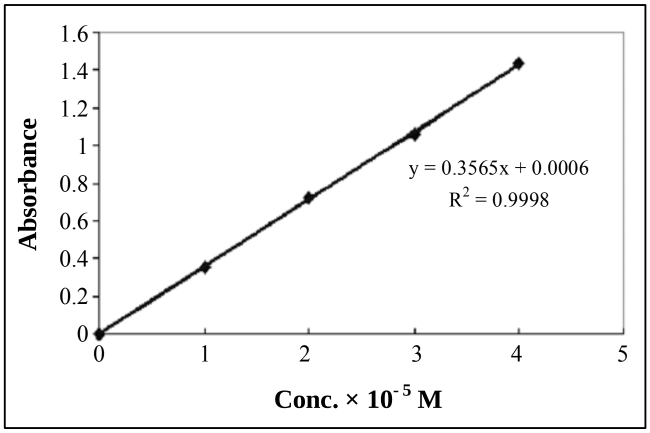

Fig. 4: Calibration curve for azure A at T = 298 K

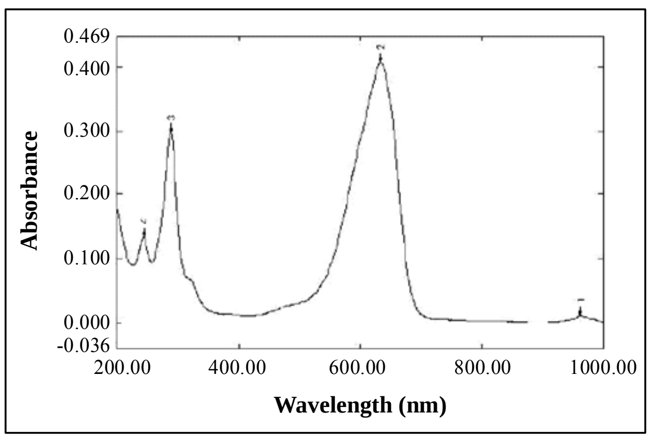

Fig. 5: UV-Visible spectrum of aqueous solution of Azure A (1 x 10^{-5} M, T = 298 K)

RESULTS AND DISCUSSION

Influence of initial dye concentration

The study effect of initial dye concentration on color removal shows that by varying the IDC from 1 x 10^{-5} – 5 x 10^{-5} M the removal efficiency significantly drops. This may be due to reduce of penetration of photons, which enter into the dye solution that cause lowering of formation of hydroxyl free radicals. The behavior of concentration impact may be sometimes depends on the structure of dye[18]. The results are shown in Fig. 6. Also the overall spectrum of dye decreases as the irradiation time increases (Fig. 7).

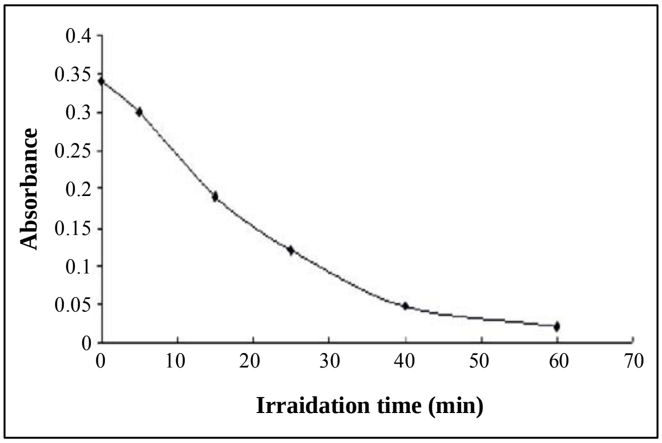

Fig. 6: Absorption of azure A as a function of irradiation time at T = 298 K, I_o = 173.711 mW/cm^2 and f = 160 L/h

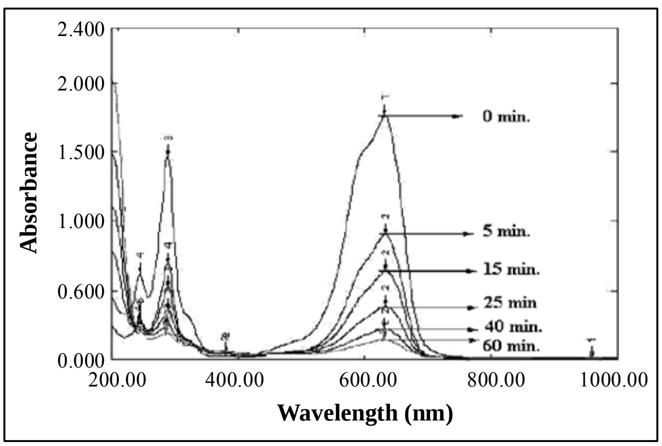

Fig. 7: The UV-visible spectra of dye solution 1 x 10^{-5} M as a function of irradiation time at T = 298 K, I_o = 173.711 mW/cm^2 and f = 160 L/h

The relation between C_t/C_o and irradiation time are shown in Fig. 8. It is clear that the higher dye concentration increase the absorption of UV, lead to decreasing the availability of UV and lower the formation of hydroxyl radicals in the solution.

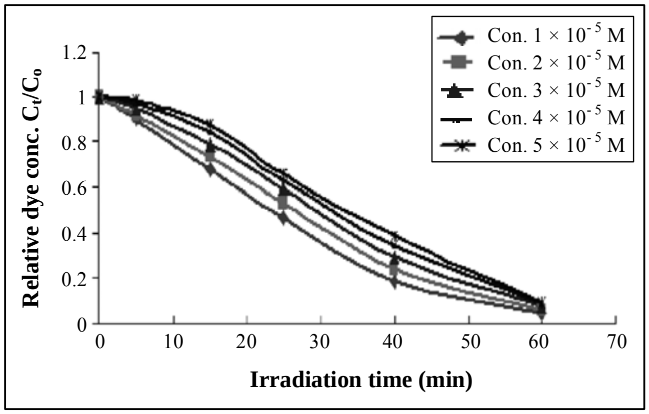

Fig. 8: Relative dye concentration versus irradiation different initial dye concentration, T = 298 K, I = 173.711 mW/cm^2 and f = 160 L/h

The results shown in Fig. 9 prove that the photooxidation reaction of azure A dye is of first order with respect to dye concentration according to the following equation[19]:

$$\log k = \log R - n \log C \qquad \ldots(1)$$

Where : C: concentration of dye, n: order reaction, R: reaction rate, k: reaction rate constant.

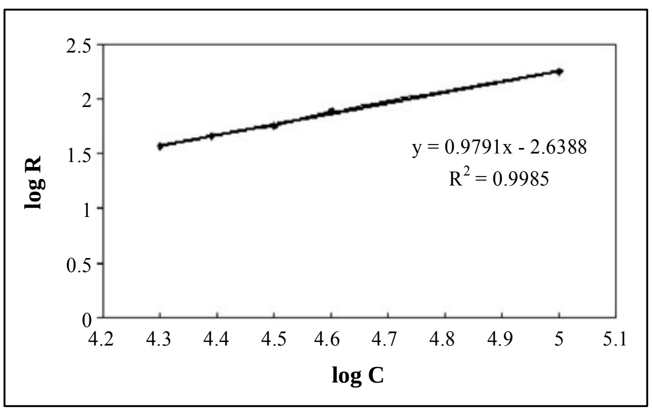

Fig. 9: Relationship between log R and log C of oxidation of Azure A dye (1 x 10^{-5} M, T = 298 K, I$_o$ =173.711 mW/cm^2 and f = 160 L/h)

Temperature influence

Temperature also has a notable effect on the efficiency of color and COD removal. Also, Temperature is an important kinetic factor on enhancing the color and COD removal from polluted water. Experiments were performed in the range 298-38 K. It has been found that increasing of temperature leads to increase in the decolorization rate under UV-ClO_2 system as shown in Figs. 10 and 11.

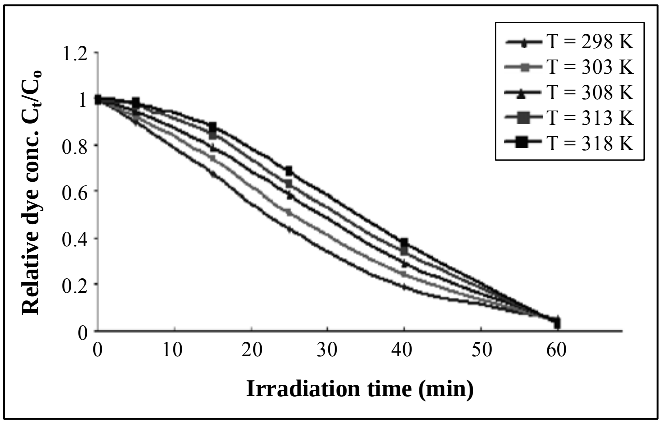

Fig. 10: Effect of different temperature on the relative dye concentration [A.A] = 1 x 10^{-5}M, I_o = 173.711 mW/cm^2 and f = 160 L/h

The Arrhenius equation is used to describe the relationship between rate constant and temperature and draw this relationship as show in Fig. 11.

$$k = A\, e^{(-Ea/RT)} \qquad \text{…(2)}$$

Where: k: rate constant, A: frequency factor, E_a: activation energy, R: ideal gas constant. Activation energy calculated in plot was equal 19.470 kJ $mole^{-1}$.

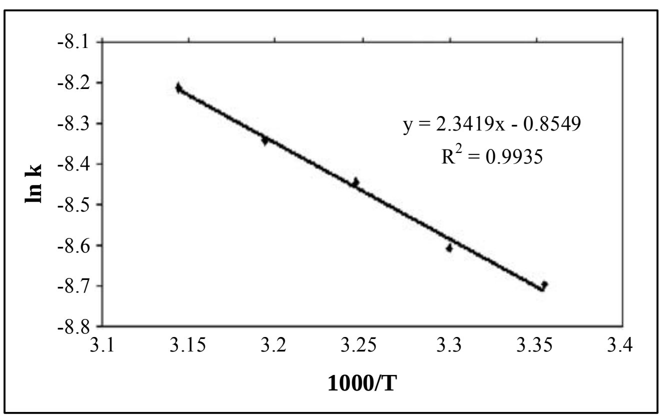

Fig. 11: Arrhenius plot of color removal of dye (1 x 10^{-5} M, I_o = 173.711 mW/cm^2 and f = 160 L/h)

Influence of gas flow rate

Fig. 12 shows the relationship between C_t/C_o and irradiation. The effect of gas flow rate was evaluated at f = 40, 80, 120 and 16 L/h. The results proved that high color removal was 93.8% at high gas flow rate and low value 90.2% was obtained in low gas flow rate as illustrated in Fig. 13.

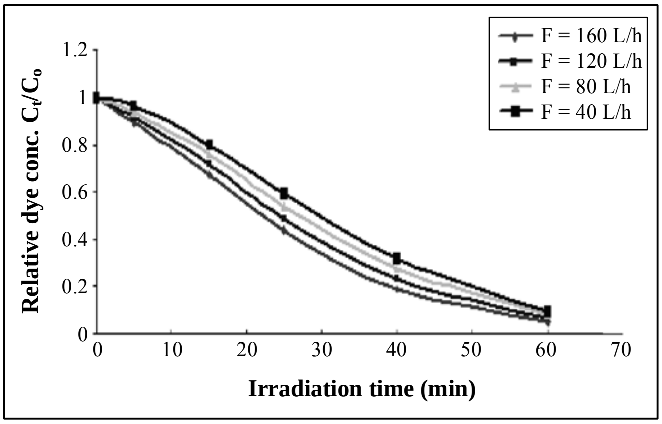

Fig. 12: Effect of gas flow rate value on color removal from azure A dye as function of irradiation time, [A.A] = 1 x 10^{-5} M, T = 298 K and I_o = 173.711 mW/cm^2

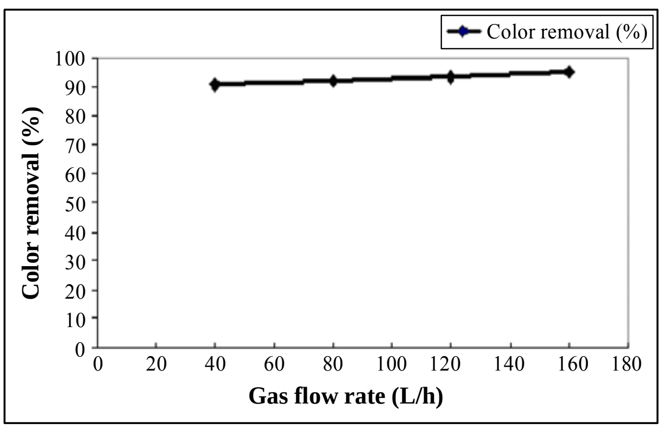

Fig. 13: Effect of the gas flow rate on the color removal from azure A dye [A.A] = 1 x 10^{-5} M, T = 298 K and I_o = 173.711 mW/cm^2

Light intensity influence (I_o)

The impact of the change in the incidence light intensity on the decolorization rate was studied by changing the lamp. The effect of light intensity was investigated at I_o = 173.711, 141.542, 131.781 and 113.739 mW cm^2 by changing lamp power. Fig. 14 shows the relation ship between C_t/C_o and irradiation time. Fig. 15 illustrates high color removal was 93.8% was obtained at higher light intensity. Many workers[20-24] proved that the rate of removal of organic pollutants increase gradually with increase of light intensity, because the number of photons entering the dye solution increases and hence increasing the rate of degradation. So the speed of removing the color depends on the number of photons collide with the dye molecules and its ability to break down the bonds in the dye molecule.

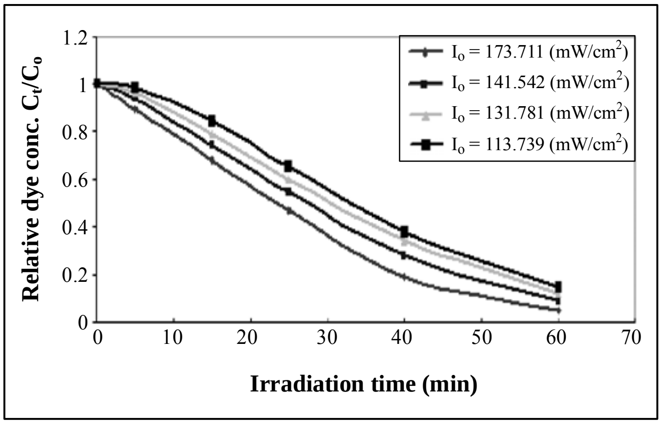

Fig. 14: Effect of different light intensity value on color removal from azure A dye as function of irradiation time, [A.A] = 1 x 10^{-5} M, T = 298 K and f = 160 L/h

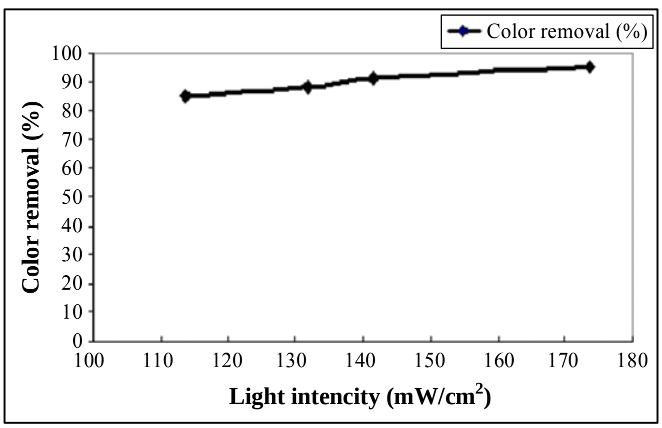

Fig. 15: Effect of the light intensity on the color removal from azure A dye [A.A] = 1 x 10^{-5} M, T = 298 K and f = 160 L/h

CONCLUSION

Chlorine dioxide treatment with UV irradiation is an effective treatments for color and COD removal for organic pollutants. The decolorization is directly influenced by various parameters, particularly the temperature, dye concentration, gas flow rate, light intensity as well as irradiation time. Faster decolorisation, rate and higher color removal efficiency was observed at high temperature, high light intensity, long irradiation time and low dye concentration.

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