Int. J. Chem. Sci.: 13(2), 2015, 1039-1050
ISSN 0972-768X
www.sadgurupublications.com

PHOTO-OZONOLYSIS OF AZURE B, C AND METHYLENE BLUE DYES : OPTIMIZATION AND KINETIC STUDY

HASSAN A. HABEEB ALSHAMSI[*] and IBRAHIM G. SAHIB

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

ABSTRACT

In this study, photo-ozonolysis has been used as advanced oxidation process for removal of color of dyes. The effect of concentration of dye, temperature, pH, flow rate of gas and light intensity has been studied. A complete removal has been achieved in a somewhat short period alternatively (60 min). The maximum removal of color adopted of high pH and temperature. The results have been shown that the rate of removal decreases with the increase of initial dye concentration, also it is found that the ratio of removal increases with increase of temperature. Moreover, one can notice from the results that with the increase of air flow rate and incident light intensity, the ratio of removal increases for all days used. The chemical oxygen demand (COD) was also studied in different conditions. The ratio of COD removal associates positively with the ratio of color removal for all dyes. The decolonization reaction was found to follow first order kinetics with respect to the dye concentration.

Key words: Ozone, Kinetic study, Photo-ozonolysis, COD, Azure dyes, Methylene blue (MB).

INTRODUCTION

Textile industries consume enormous amounts of water, which equal (21-377 $m^3 \times tons^{-1}$ of textile). As a result, huge amounts of wastewater are generated after the processes of dyeing and finishing[1]. The wastewater contains toxic materials such as the dyes, which preserve their colours and their structural formula when exposed to sunlight in addition to their high resistance to biological decomposition, which renders it into a source of environmental pollution, Hence, it is necessary to originate methods for treating of pollution that depend upon efficiency and low economical cost[2]. The decolorization of wastewater greatly attracted researchers because of the great amount of colored industrial water and the toxicidity of dyes and without proper treatment those dyes remains in the environment for long time[3]. The wastewater is characterized by the high acidity and temperature and contains soluble materials and other properties that are generated because of dying process[4]. Hence,

[*]Author for correspondence; E-mail: hasanchem70@gmail.com; Ph.: +96 425032840

this properties and toxicity for wastewater renders treating process by routine chemical method and biological techniques difficult[5,6]. Photo-oxidation technique is one of the important techniques that is used in many fields which was high efficiency in the removal of the toxic effects of the environmental pollutants[7]. The hydroxyl radical species posses a higher oxidation potential (2.80 V) as compared to other common oxidants like ozone (2.07 V) that used with UV/visible radiation to accelerate the rate of degradation of the pollutants[8].

The present study was carried out to investigate the removal of azure B, C and MB dyes from aqueous solution by using UV/O_3 technique and various reaction conditions which involve initial dye concentration, temperature, initial pH, light intensity and gas flow rate.

EXPERIMENTAL

Materials

Sodium hydroxide and hydrochloric acid were supplied from Sigma. Azure B, C while MB dyes (product of USA. MSDS) was purchased from Omega. All chemicals were used without further purification. Solutions were prepared with double distilled water.

Instruments

UV-Visible 1650 spectrophotometer (Shimadzu, Japan) was used to record the absorption spectra of aqueous solutions of dye. The pH was adjusted by using microprocessor pH meter 211 (Hanna, Romania) instruments. The temperature was adjusted by using regulator water bath WB (Optima). COD was measured using (Lovibond, Vario LR) and a Thermoreactor TR 300 (Merck, Germany). The ozone is generated by ozone generator (MQ-12038, China) by corona discharge method[9].

Photoreactor setup

The photoreactor is shown in Fig. 1, which was fitted with a fixed low-pressure mercury lamp with the high light intensity emitted at 253.7 nm. The UV lamp was put beside 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 1 L tank. A syringe was fitted with photoreactor to withdrawn of dye solution samples at meaning time.

Experimental procedure

The operating irradiation time for all experiments were fixed at 60 min, due to the primary experiments indicated that the most of dye molecules are degraded and the dye solution become colorless at the time near to this period. The pH was adjusted to the desired value using 0.1 N of sodium hydroxide and hydrochloric acid. COD was measured according to the colorimetric methods[10]. In all experiments the lamp was warming on for 10 min prior to initiation of reaction.

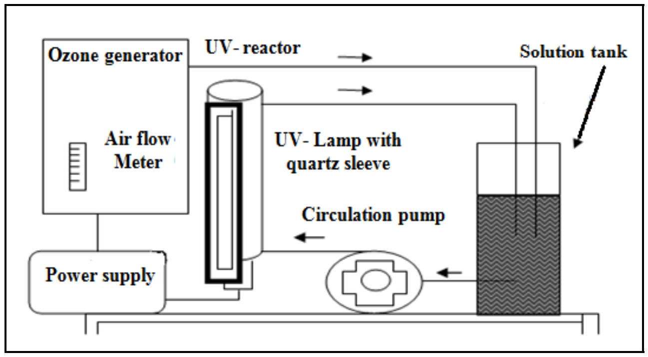
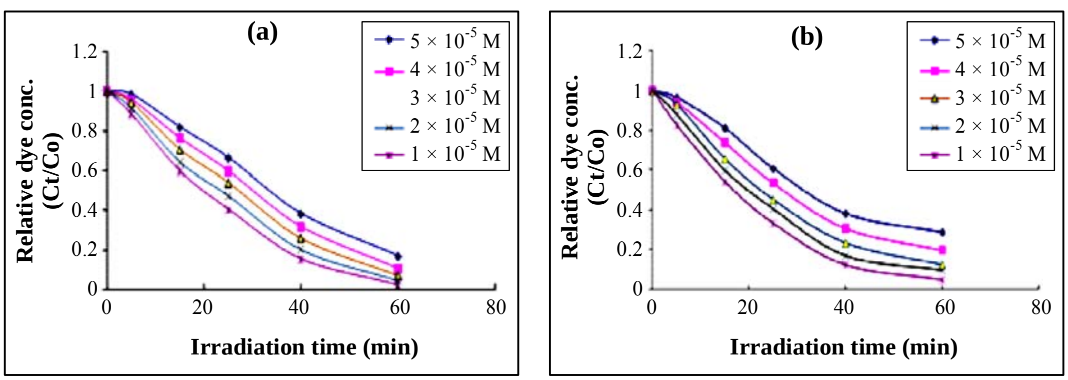


Fig. 1: Photoreactor setup

RESULTS AND DISCUSSION

Effect of initial dye concentration

Various dye concentrations in the range 1 x 10^{-5} – 5 x 10^{-5} M were exposed to UV/O_3. It has been found that increasing in the initial concentration of dye leads to decrease the color removal and COD due to decreased penetration of entering photons into the solution and lowering the formation of hydroxyl free radicals[11]. The results proved that the highest percentage with COD was at the concentration 1 x 10^{-5} M while lowest one was at 5 x 10^{-5} M. The results are shown in Figs. 2 and 3.



Cont…

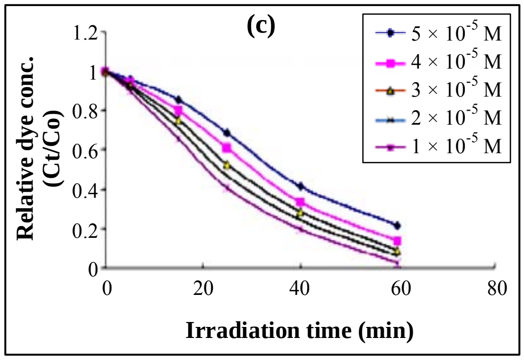


Fig. 2: Effect of dye concentration on the color and COD removal of (a) azure B, (b) azure C and (c) MB dyes at pH 6, T = 298 K, I_o = 173.711 mW/cm^2

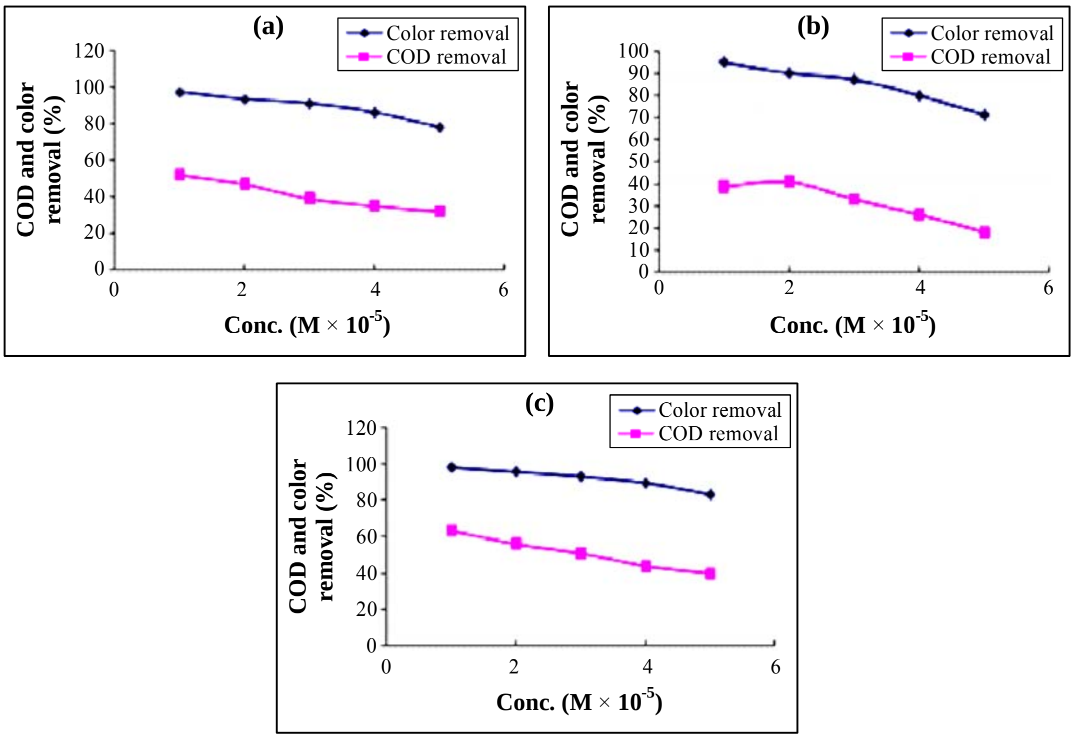


Fig. 3: Effect of different initial dye concentration on the colour removal of (a) azure B, (b) azure C and (c) MB dyes by using UV method at pH 6, T = 298 K, I = 173.711 mW/cm^2

It is clear that the higher dye concentration increases the absorption of UV radiation by dye molecules, and lead to decrease the availability of UV to enhance the O_3 decomposition, which causes the lowering of hydroxyl radicals in the solution.

The results shown in Fig. 4 prove that the photooxidation reactions of azure B, C and MB dyes are of first order with respect to dye concentration according to the following equation[12]:

$$\text{Log R} = \log k + n \log C \qquad \ldots(1)$$

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

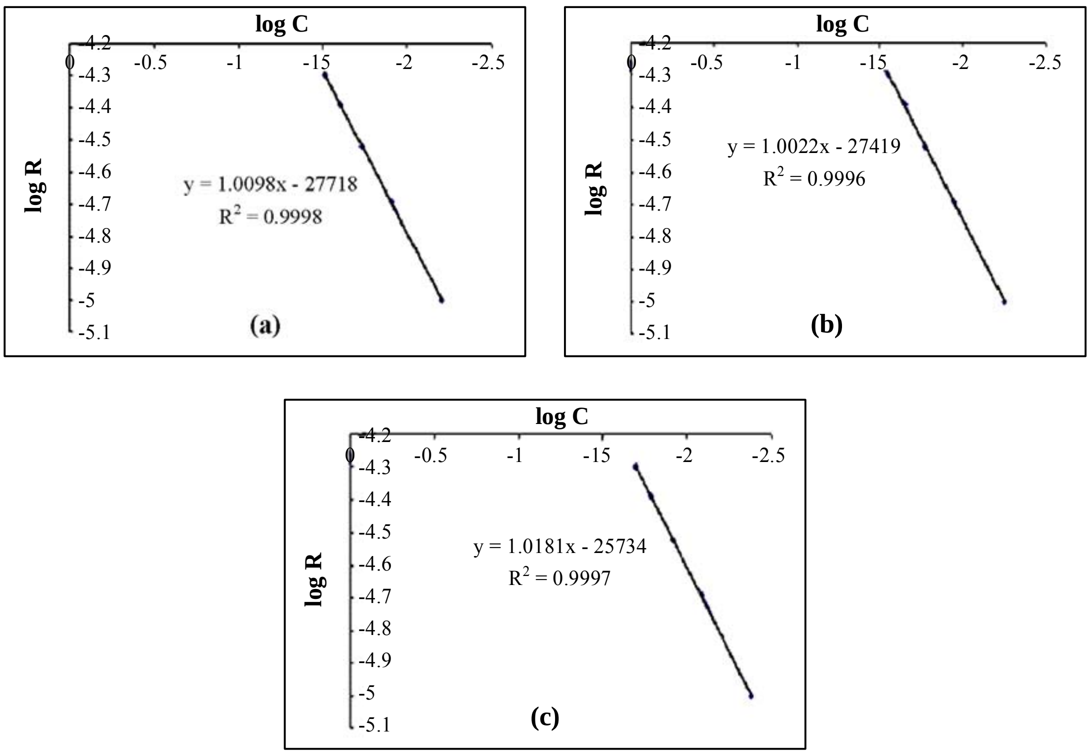


Fig. 4: Relationship between Log R and Log C for oxidation of (a) azure B, (b) azure C and (c) MB dyes by using UV method at pH 6, T = 298 K, I = 173.711 mW/cm^2

Effect of temperature

Temperature is an important kinetic factor on enhancing the color and COD removal. The dye removal rate by using the UV/O_3, increased with the increasing temperature of the system as shown in Figs. 5 and 6. In this work, we found out that with the increase in the temperature, the value of COD removal increases as a result of oxygen reduction required for oxidation, as the oxygen decreases, COD also increases[13].

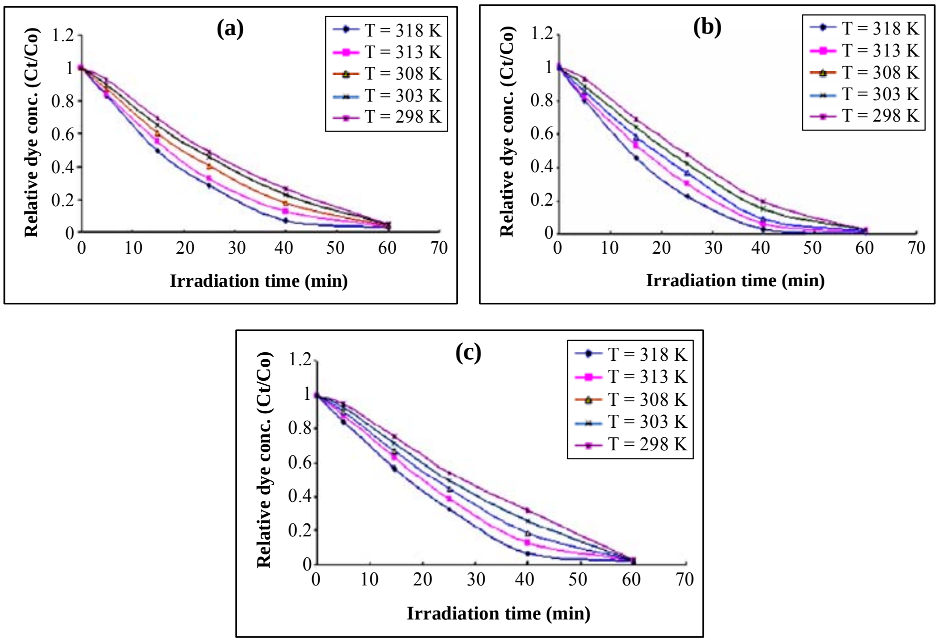


Fig. 5: Effect of different temperature on the colour removal of (a) azure B, (b) azure C and (c) MB dyes using UV/O_3. [AB] = 1 x 10^{-5} M, pH 6, I_o = 173.711 mW/cm^2

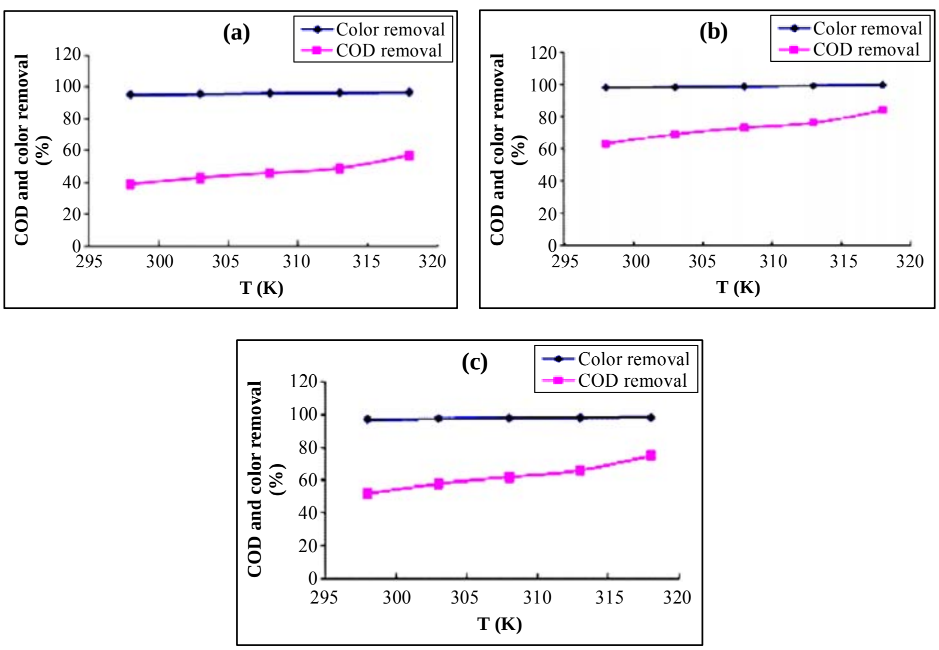


Fig. 6: Effect of the temperature degree on colour removal and COD of the (a) azure B, (b) azure C and (c) MB dyes [B, C and MB] = 1 x 10^{-5} M at pH 6, I_o = 173.711 mW/cm^2

The Arrhenius equation is used to describe the relationship between rate constant and temperature and draw this relationship according to:

$$k = A\ e(-E_a/RT) \qquad \ldots(2)$$

where: k: rate constant, A : frequency factor, E_a : activation energy, R : ideal gas constant. Calculated activation energy from Fig. 7 for azure B, C and MB was equal 12.55, 13.14 and 7.43 kJ/mole, respectively.

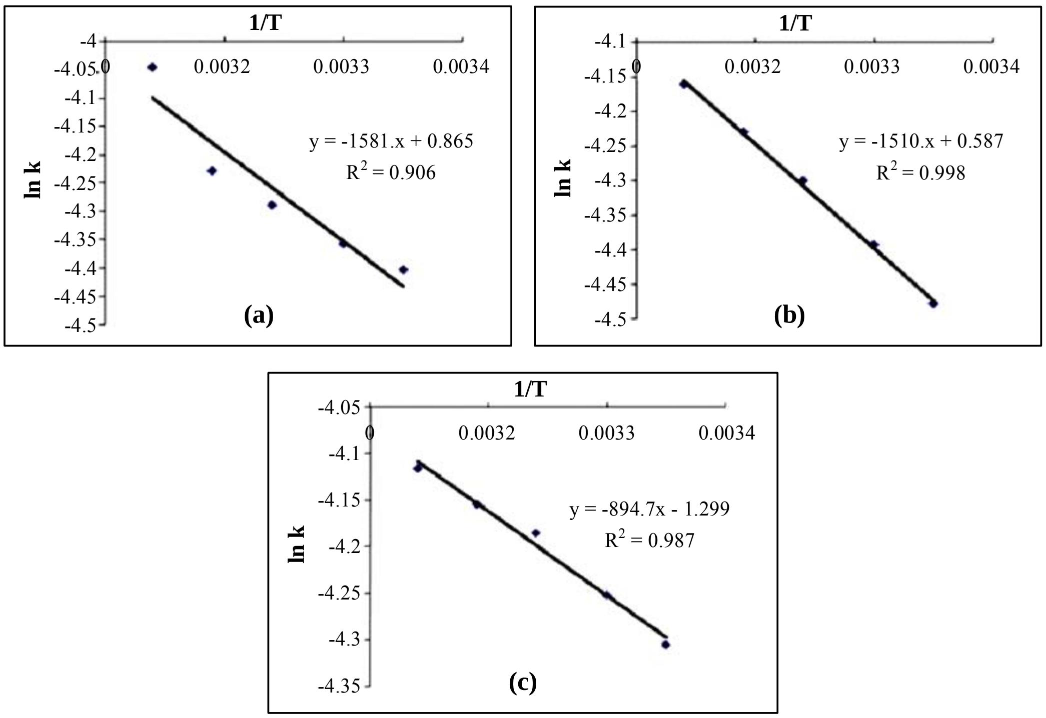


Fig. 7: Arrhenius plot of colour removal of (a) azure B, (b) azure C and (c) MB dyes [B, C and MB] =1 x 10^{-5} M at pH 6, I_o = 173.711 mW/cm^2

Effect of initial pH

The results showed a clear effect of initial pH in photooxidation reaction of azure B, C and MB dyes. The high color removal was obtained under a basic media because the formation of hydroxyl radicals from ozone decomposition and duration of ozone molecules stable in low pH values[14]. The higher ratio color removal of azure B, C and MB dyes were obtained at pH 8. From Fig. 8, it has been found that the relative dye concentration C_t/C_o was decreased as the pH value increased.

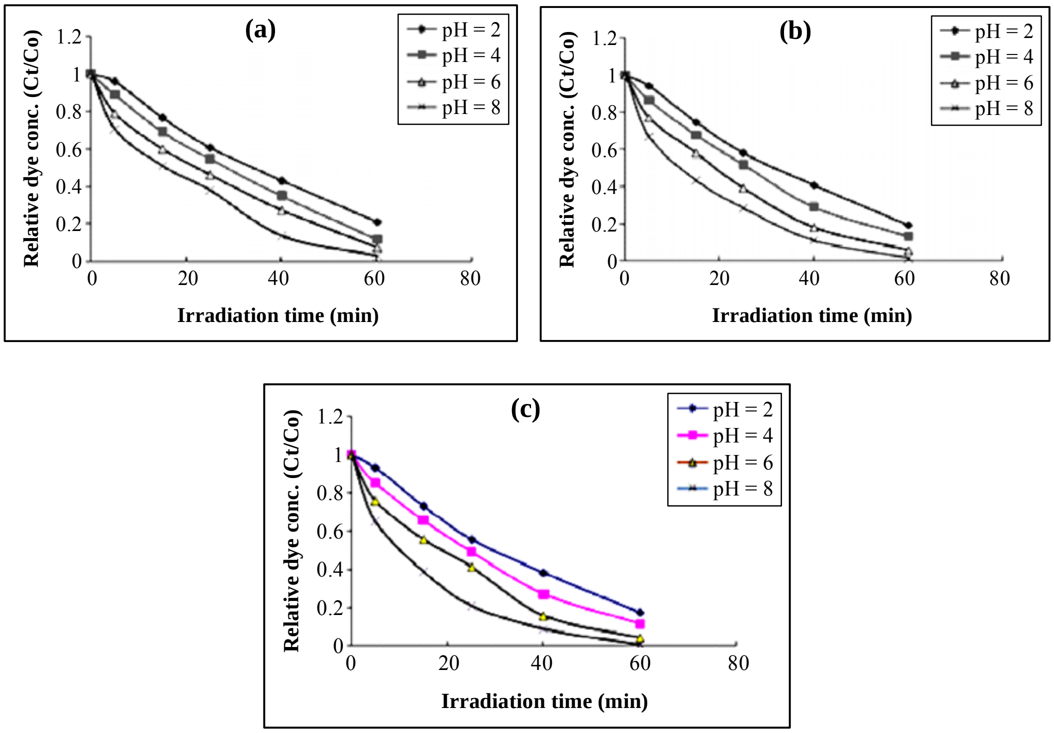
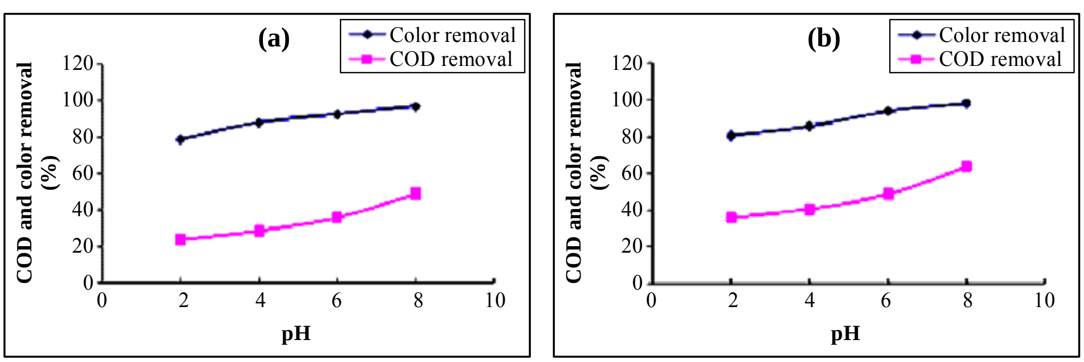


Fig. 8: Effect of different pH value on colour removal from (a) azure B, (b) azure C and (c) MB dyes as function of irradiation time, [B, C and MB] = 1 x 10^{-5} M, T = 298 K, I_o = 173.711 mW/cm^2

On the other hand, the ratio of COD removal for azure B, C and MB dyes was increased with increase in pH values because of incomplete oxidation of organic materials[15]. Fig. 9 shows the effect of initial pH on COD and color removal.



Cont…

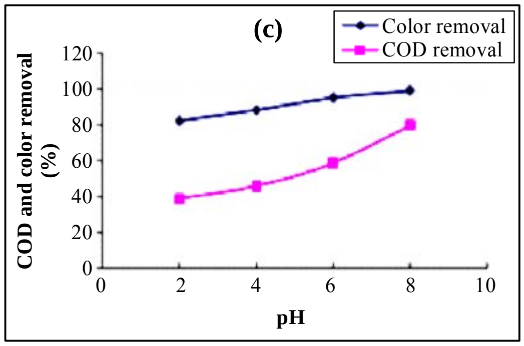


Fig. 9: Effect of the initial pH on the COD and color removal from (a) azure B, (b) azure C and (c) MB dyes, [B, C and MB] = 1 x 10^{-5} M , T = 298 K, I_o = 173.711 mW/cm^2

Effect gas flow rate

When the rate of gas flow (air) was increased, it led to increase ozone generation[16]. Figs. 10 and 11 proved the high and COD color removal of azure B, C, MB, which was achieved at high gas flow rate.

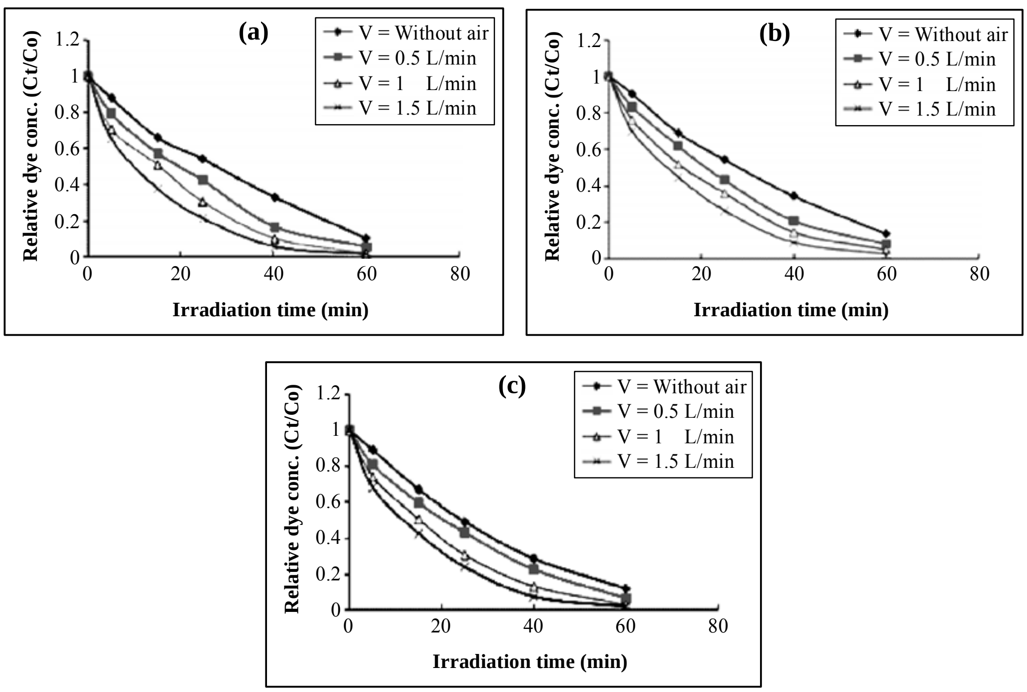


Fig. 10: Effect of gas flow rate value on colour removal from (a) azure B, (b) azure C and (c) MB dyes as function of irradiation time, [B, C and MB] = 1 x 10^{-5} M, T = 298 K, pH 6 and I_o = 173.711 mW/cm^2

The effect of gas flow rate on the color and COD removal of dyes is shown in Fig. 11.

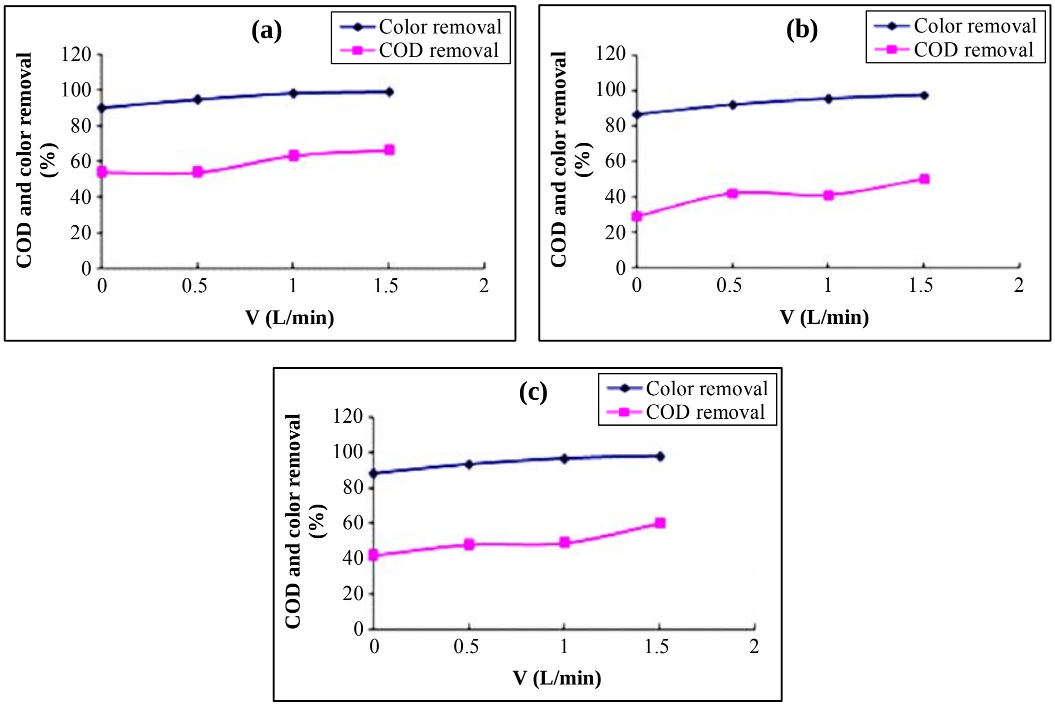
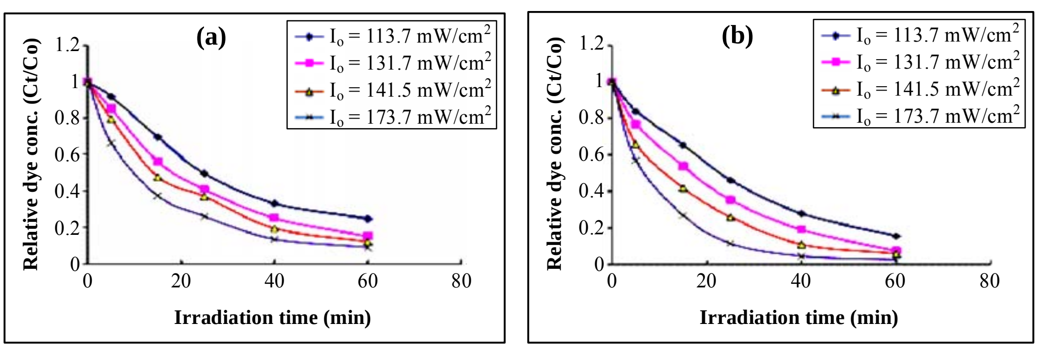


Fig. 11: Effect of the gas flow rate on the COD and colour removal from (a) azure B, (b) azure C and (c) MB dyes [B, C and MB] = 1 x 10^{-5} M, T = 298 K, pH 6 and I_o = 173.711 mW/cm^2

Effect of light intensity

The effect of light intensity was invistigated at I_o = 173.711, 141.512, 131.781 and 113.739 mW/cm^2 by changing lamp power. From Fig. 12, the results proves that the high



Cont…

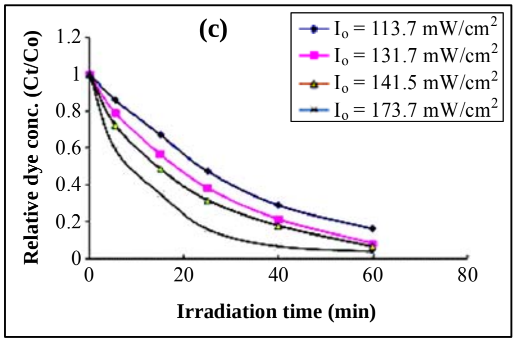


Fig. 12: Effect of different light intensity value on colour removal from (a) azure B, (b) azure C and (c) MB dyes as function of irradiation time, [B, C and MB] = 1 x 10^{-5} M, T = 298 K, pH 6

color removal at high light intensity and low value was obtained in low light intensity[17], which attribute to availability of high energy photons.

The effect of different light intensity on the colour and COD removal of azure B,C and MB dyes by using the UV/O_3 method was studied and shown in Fig. 13.

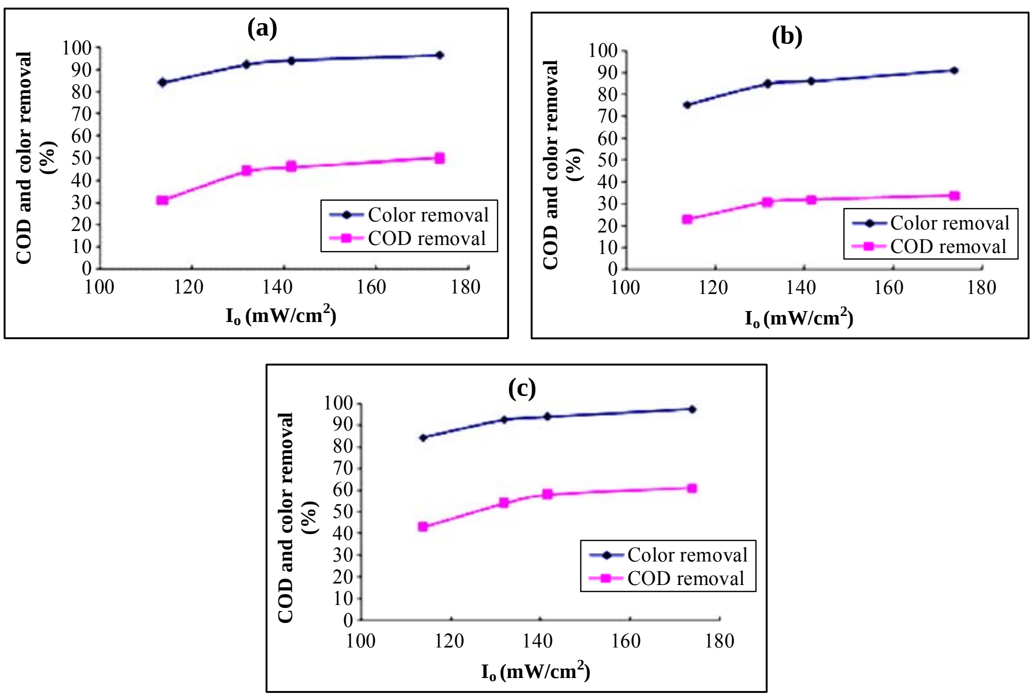


Fig. 13: Effect of the light intensity on the COD and colour removal from (a) azure B, (b) azure C and (c) MB dyes [B, C and MB] = 1 x 10^{-5} M, T = 298 K, pH 6

CONCLUSION

The degradation was strongly influenced by various parameters, particularly the pH, temperature, dye concentration, gas flow rate, light intensity as well as irradiation time. Faster degradation kinetics, higher colour and COD removal efficiency was observed at higher temperature. The photooxidation of azure B by using the UV/O_3 is more effective in basic medium at pH = 8.

REFERENCES

1. S. S. Kalra, S. Mohan, A. Sinha and G. Singh, Adv. Int. Conference on Environ. Sci. Development, **4**, 271 (2011).
2. N. U. Asamudo, A. S. Doba and O. U. Ezeronye, J. Biotechnol., **4(13)**, 1548 (2005).
3. M. R. Karim, S. A. Ahmad and M. Shahidullah, J. Health, Populat, Nut. Early Child Res., Q, **26**, 237 (2006).
4. C. Namasivayam and S. Sumithra, J. Environ. Manage., **74(3)**, 207 (2005).
5. O. Yavuz and A. H. Aydin, Polish J. Environ. Studies, **15(1)**, 155 (2006).
6. I. Arslan-Alaton, B. H. Gursoy and J. E. Schmidt, Dyes and Pigments, **78(2)**, 117 (2008).
7. A. J. Attia, S. H. Kadhim and F. H. Hussein, E-J. Chem., **5(2)**, 219 (2008).
8. R. Vinu and G. Madras, J. Indian Inst. Sci., **90(2)**, 189 (2010).
9. K. Rakness, New Book about Ozonation Process Design, Operation and Optimization (2005).
10. A. R.Tehrani-Bagha and F. L. Amini, Color Sci. Tech., **4**, 151 (2010).
11. A. Rezaee, M. T. Ghanaian, S. J. Hashemian, G. Moussavi, A. Khavanin and G. Ghanizadeh, J. App. Sci., **8**, 1108 (2008).
12. R. K. Ramasamy and N. A. Rahman, Color. Technol., **117**, 95 (2001).
13. D. Chen and A. Ray, Wat. Res., **32(11)**, 3223 (1998).
14. E. Oguz, B. Keskinler, C. Celik and Z. Celik, J. Hazard. Mater, **131(1-3)**, 66 (2006).
15. M. F. Sevimli and C. Kinaci, Water Sci. Technol., **45**, 279 (2002).
16. A. H. Konsowa, Desalination, **158**, 233 (2003).
17. D. Sharma, A. Bansal, R. Ameta and H. S. Sharma, Int. J. Chem. Tech. Res., **3(2)**, 1008 (2011).

Accepted : 18.04.2015