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Comparison among O_3, PAC adsorption, O_3/HCO_3^-, O_3/H_2O_2 and O_3/PAC processes for the removal of Bomaplex Red CR-L dye from aqueous solution

Ensar Oguz [a,*], Bülent Keskinler [b]

[a] Atatürk University, Environmental Problems Research Center, 25240 Erzurum, Turkey
[b] Gebze Institute of Technology, Environmental Engineering Department, 41400 Çayırova, Kocaeli, Turkey

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Abstract

Various processes including O_3, powder activated carbon (PAC) adsorption, O_3/HCO_3^-, O_3/H_2O_2 and O_3/PAC were used in order to remove dye and chemical oxygen demand (COD) from synthetic wastewater containing Bomaplex Red CR-L dye in a semi-batch reactor. These processes rapidly removed the dye and COD from dye solution. The dye removal efficiency was over 99% for a reaction period of 30 min for all the processes. It was observed that PAC adsorption and O_3/PAC processes were considerably more effective than ozonation process for the removal of COD from dye solution. The COD removal efficiency of O_3/PAC was higher than PAC adsorption process. O_3/PAC process was considerably effective to remove COD from dye solutions despite using less amount of PAC (approximately four times less than one used for PAC adsorption) for the same amount of COD removal with a higher efficiency. O_3/HCO_3^- process positively affected the COD removal efficiency, whereas O_3/H_2O_2 process negatively affected the COD removal efficiency as compared to the ozonation process alone. In addition, the yield and mechanisms of dye removal were also explained on the basis of the results of Fourier transform infrared spectroscopy (FTIR). It was concluded that the O_3/PAC process is a highly efficient process to remove dye and COD from synthetic textile wastewaters as compared to the other processes.

Keywords: Ozonation; Dye; Hydrogen peroxide; COD; PAC

1. Introduction

One of the main problems in the treatment of textile dyeing wastewaters is the removal of color [1]. In the late 195Os, the trickling filter and activated sludge processes were started to be used for the removal of the color in textile wastewater [2]. However, the color of wastewater from new products of nowadays is much more difficult to remove by physical techniques such as adsorption and chemical coagulation, especially for highly soluble dyes. Apart from the physical methods of decolorization, chemical oxidation using oxidants such as ozone, chlorine or hypochlorite, hydrogen peroxide and potassium permanganate can be used to degrade the dye substances; then the breakdown products can be removed by conventional biological treatment processes [2].

The use of ozone in textile effluent treatment appears to be a very attractive alternative with considerable application potential. Ozone is a powerful oxidizing agent ($E^o = 2.08$ V), when compared with other well-known oxidizing agents such as H_2O_2 ($E^o = 1.78$ V), and can react with several classes of compounds through direct or indirect reactions. Ozone is capable of causing the degradation of dyes. Chromophore groups, generally organic compounds with conjugated double bonds can be broken by ozone (directly or indirectly) into smaller forms, decreasing the color of the effluent [3–6].

Chemical oxygen demand (COD) and biological oxygen demand (BOD) of aqueous dyes decrease after ozonation

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[*] Corresponding author. Tel.: +90 442 231 4601.
E-mail address: eoguz@atauni.edu.tr (E. Oguz).

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[7]. It was reported that COD decreased only in the case of pure dye solution, but for a real industrial wastewater, both COD and total organic carbon (TOC) content remained unchanged [8]. Ozone is also very effective for removing color caused by water-soluble dyes, particularly fiber acid and reactive dyes [1,9].

However, ozonation alone was proven to be rather inefficient for the reduction in COD or TOC, usually not exceeding 50% and 40%, respectively, independent from the initial dye concentration [10].

The aim of this study is to research the synergic effect of O_3 on conventional PAC adsorption for removing dye from wastewater. In this work, the removal of Bomaplex Red CR-L dye and COD from wastewater was studied using various processes such as O_3, PAC adsorption, O_3/HCO_3^-, O_3/H_2O_2 and O_3/PAC. The results of these processes were compared in order to determine the highest efficiency.

2. Materials and methods

2.1. Preparation of Bomaplex Red CR-L dye solutions

Bomaplex Red CR-L dye (1000 mg) was dissolved in 1 l of distilled water and used as stock solution which had a pH value of 9.3. The concentration of Bomaplex Red CR-L dye in the stock solution was measured, and this solution was used for further experimental solution preparation.

2.2. Preparation of H_2O_2 and HCO_3^- solutions

The solutions of 7, 14 and 21 mM hydrogen peroxide and 6.5, 13 and 26 mM HCO_3^- were prepared from hydrogen peroxide (50% solution, 1.2 g/ml) and $NaHCO_3$ (Merck), respectively.

2.3. Analytical methods

The measurement of COD was based on the "closed reflux, colorimetric method" described in section 508 B.4. of Ref. [11]. The digestion solution was first prepared by adding 10.216 g of $K_2Cr_2O_7$ (Merck), which was previously dried for 2 h at 103 °C, 167 ml of concentrated H_2SO_4 (Merck) and 33.3 g of $HgSO_4$ (Merck) into 500 ml of distilled water. The mixture was then left to cool to room temperature before diluting to 1000 ml. Samples (1 ml) were put in tubes and 0.6 ml of digestion solution was added. Then 1.4 ml of sulphuric acid reagent was carefully poured into each tube so that an acid layer was formed under the sample/digestion solution layer. The tubes were inverted three times to mix properly. The mixtures were placed in an oven preheated to 150 °C for 2 h. After cooling the samples were analysed using a UV spectrophotometer (UV Spectrophotometer, Shimadzu 160A) at a wavelength of 600 nm. Potassium hydrogen phthalate (KHP) (Merck) was used to prepare standard solutions in the range 20–900 mg/l. KHP has a theoretical COD of 1.176 mg O_2/mg.

It was defined that the Bomaplex Red CR-L dye gave a peak at 505 nm as it can be seen from Fig. 1. Dye removal capacity was determined by the absorbance measurements at this maximum visible absorbance wavelength of 505 nm.

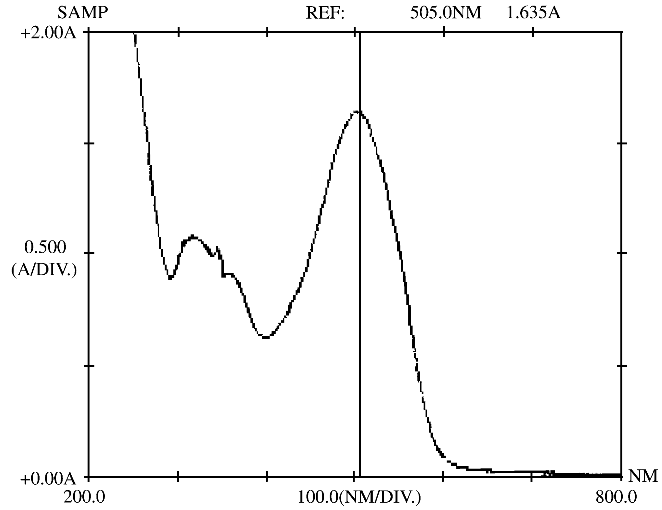

Fig. 1. The spectrum curve of the Bomaplex Red CR-L dye at 505 nm.

A commercial activated carbon from Merck was used as the adsorbent throughout this study. The surface area of the PAC particles was measured by BET method at 77 K using a Quantachrome QS-17 model apparatus [12]. The surface area of the PAC particles was defined as 465 m^2/g.

Fourier transform infrared (FTIR) spectra were recorded with a Perkin–Elmer 1720 spectrometer (16 scans; resolution, 2 cm^{-1}) over KBr pellet. Pullulan sample (2 mg) was first manually well blended with 100 mg of KBr powder. This mixture was then desiccated overnight at 50 °C under reduced pressure prior to FTIR measurement. The objective of FTIR analysis in this study is the observation whether dye intermediates adsorbed on the PAC modify the peaks of functional groups on the PAC.

2.4. Adsorption studies

The adsorption studies were carried out at Bomaplex Red CR-L concentration of 1000 mg/l. A given amount of powder activated carbon was placed in 250-ml volumetric flasks and mixed with 250 ml of stock solution. The experiments were carried out at 18 °C and at a pH of 9.3. Concentrated HCl and NaOH solutions were used to adjust pH. The mixture was filtered before each measurement.

2.5. Ozonation studies

The experimental set-up shown in Fig. 2 includes an air dryer, compressor, ozone generator and semi-batch reactor having 1 l of volume. The air dryer consisted of a column that was filled with a high adsorptive anhydrous $CaCl_2$. Ozone was generated using an ozonizer Model OG-24. The ozone–oxygen mixture was then fed into the contact place through a porous plate gas sparger placed into the semi-batch reactor's base.

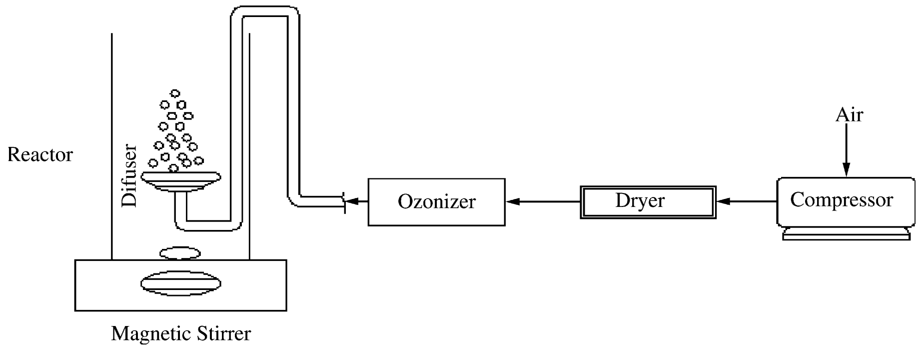

Fig. 2. Diagram of ozonation system.

The ozonation reactor consisted of a glass column of 7-cm diameter, 40-cm height with a water-cooling jacket keeping the reactor at constant temperature. A dye solution of 250 ml was used for each batch ozonation. A magnetic stirrer was used together with the gas diffuser for sufficient circulation of the dye solution. The Bomaplex Red CR-L dye used in this study was supplied from a textile mill in Turkey (dye textile industry company project, GaziAntep). The chemical structure of the water-soluble dye is given in Fig. 3.

Ozone was generated from air, and was supplied into the system through an Opal OG-24 model ozonizer at the rates of 5, 10 and 15 l/min. Ozonation was performed in a cylindrical semi-batch glass reactor (volume: 1 l). The Bomaplex Red CR-L dye was ozonated for 30 min in the semi-batch reactor. The ozone–air mixture percentage (0.7, 1.1 and 1.4 O_3%) was continuously sparged through a diffuser.

3. Results

The effect of adsorbate concentration in the range of 500–1000 mg/l on the removal of Bomaplex Red CR-L dye from aqueous solutions is shown in Fig. 4. The equilibrium concentration of the dye increased with increasing adsorbate concentration since the surface area per unit adsorbent decreases. The dye removal efficiency after an adsorption process of 30-min is approximately 99% at the initial dye concentration of 1000 mg/l.

Fig. 5 shows the change in the initial dye and COD concentrations (from 400 to 1000 mg/l, from 285 to 695 mg/l O_2) with time during ozonation. The rate of the dye removal is high at the beginning and then decreases with time. The efficiency of dye removal after 30-min ozonation scarcely increases with increasing initial dye concentration in the wastewater. The dye removal efficiency at the end of the 30-min ozonation is above 99%. The COD removal efficiency is approximately 54% and does not change with increasing initial COD concentration. Fig. 5 shows that ozone cleaved the conjugated double bonds of dye chromophores, leading to dye and COD removal.

Fig. 6 shows the change in the dye and COD removal efficiencies during ozonation by O_3/PAC process. PAC and O_3 in the O_3/PAC processes were used as synchronize. The rate of dye removal is high at the beginning and then decreases with increasing contact time. For an ozonation of 30 min, the dye removal efficiency was over 99%. As it is seen in

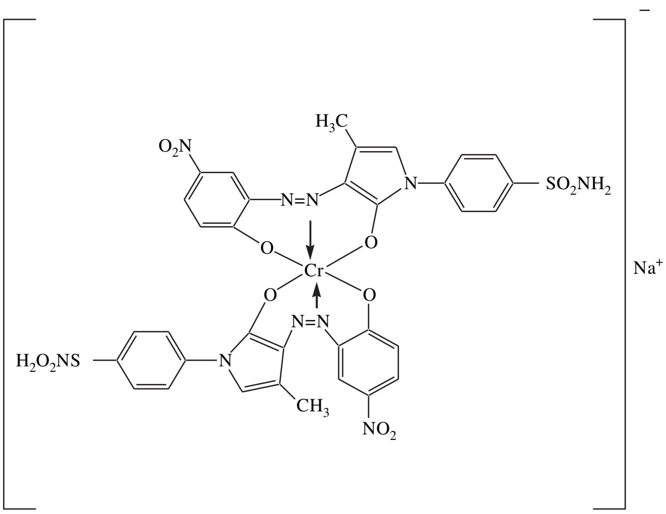

Fig. 3. The general chemical structure of the Bomaplex Red CR-L group of dyes.

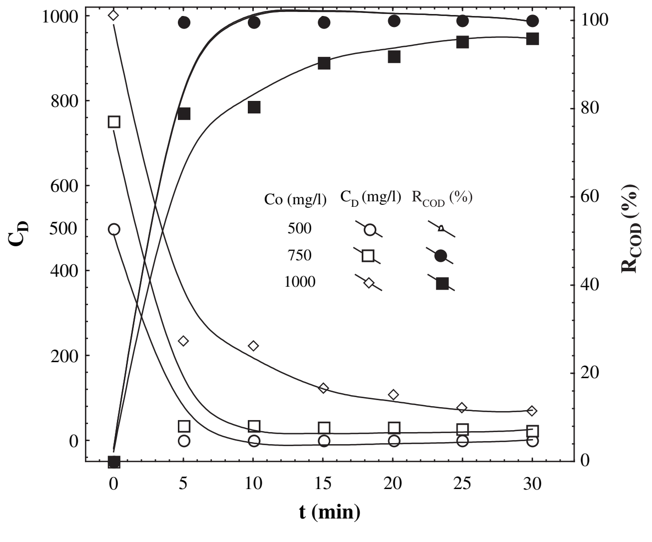

Fig. 4. Effect of adsorbate concentration on the removal of dye and COD by PAC process (C_D: concentration of dye, R_{COD} (%): removal of COD efficiency, PAC dose: 16 g/l, agitation rate: 5 rps, T: 18 °C, pH: 9.3).

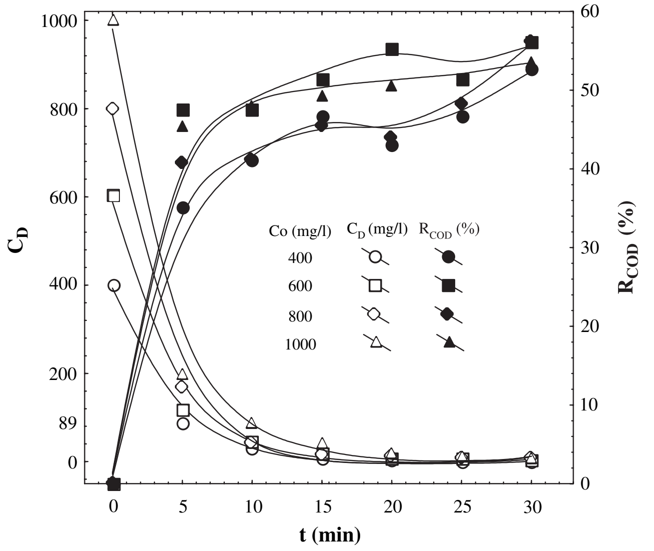

Fig. 5. Effect of contaminant concentration on the removal of dye and COD by ozonation process (C_D: concentration of dye, R_{COD} (%): removal of COD efficiency, pH: 9.3, T: 18 °C, ozone–air flow rate: 5 l/min, ozone generation percentage: 1.4 O_3 (%)).

Fig. 6, PAC dosage used in the O_3/PAC process was found to be lower than the one used in the PAC adsorption process. The ratio of PAC amount used in the O_3/PAC process to PAC adsorption process was approximately 0.375. After a reaction time of 30 min by O_3/PAC process, the maximum efficiencies of dye and COD removal were above 99 and 84%, respectively. Following the ozonation of solution, it was thought that dye molecules were degraded into smaller and more polar structures. O_3/PAC process was found to be an effective process to remove dye and COD removal as compared to ozonation alone, O_3/H_2O_2 and O_3/HCO_3^- processes.

Fig. 7 shows FTIR spectra of ozonated powder activated carbon with different functional groups. The functional groups on the PAC contain specific values of absorbance at different wavenumbers. Bomaplex Red CR-L dye intermediates adsorbed on the ozonated PAC after O_3/PAC process considerably shifted FTIR spectra of ozonated PAC from 500 to 4000 wavenumbers, as it is seen from Fig. 8. It shows that the dye intermediates adsorbed on the ozonated PAC modified the peaks of functional groups on the ozonated PAC.

According to the FTIR spectra, there is an electrostatic (columbic) attraction between the degradative dye intermediates and PAC particles. As it is seen in Fig. 8, the interaction between intermediates and PAC particles fairly increased with the formation of the more polar structures during ozonation.

Fig. 9 shows the change in the dye and COD removal efficiencies by O_3/HCO_3^- process during ozonation. As it can be seen from Fig. 9, at the end of 30 min, O_3/HCO_3^- process removed a little more COD than that of ozonation process alone. HCO_3^- ions in the O_3/HCO_3^- process were used to scavenge $OH^\bullet$ radicals that occurred during ozonation. It is likely that bicarbonate is the principal consumer of the hydroxyl radicals, particularly when relatively high concentrations of bicarbonate are present in water. The scavenging effect of bicarbonate also lies in the fact that it reacts with hydroxyl radicals, to generate bicarbonate radicals ($HCO_3^{\bullet -}$). These act as a very selective additional oxidation species and which have a much lower

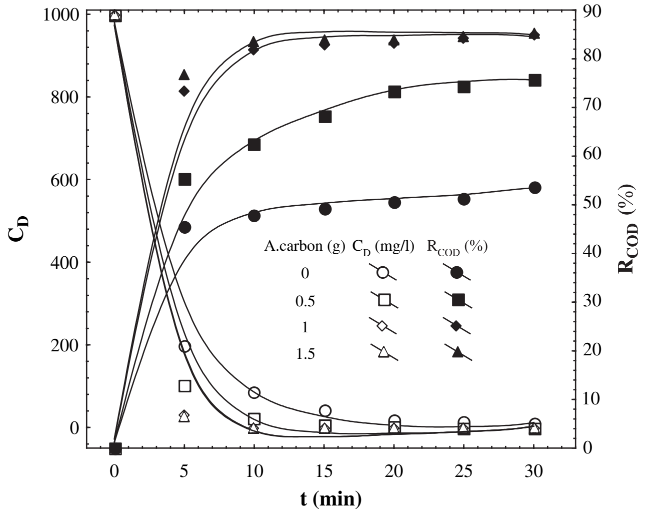

Fig. 6. Effect of contaminant concentration on the removal of dye and COD by O_3/PAC process (C_D: concentration of dye, R_{COD} (%): removal of COD efficiency, Co: 1000 mg/l, pH: 9.3, T: 18 °C, ozone–air flow rate: 5 l/min, ozone generation percentage: 1.4 O_3 (%)).

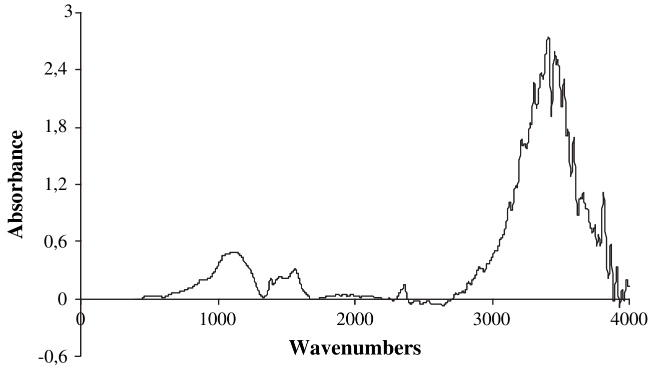

Fig. 7. FTIR spectra of ozonated powder activated carbon (Bomaplex Red CR-L concentration: 0 mg/l, PAC dosage 1 g/250 ml, ozone flow rate 15 l/min, reaction time: 30 min and T: 18 °C).

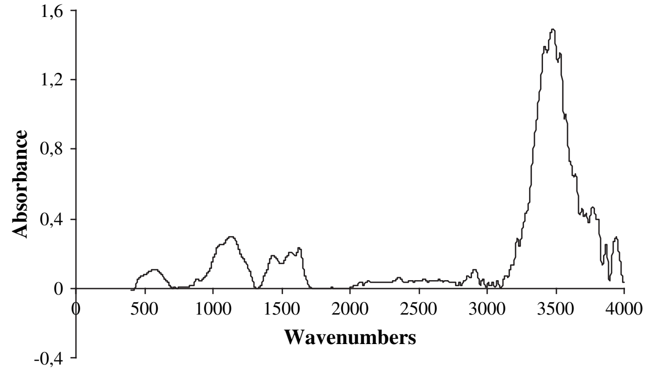

Fig. 8. FTIR spectra of ozonated PAC containing adsorbed dye intermediates (Bomaplex Red CR-L concentration: 1000 mg/l, PAC dosage 1 g/250 ml, ozone flow rate 15 l/min, reaction time and T: 18 °C).

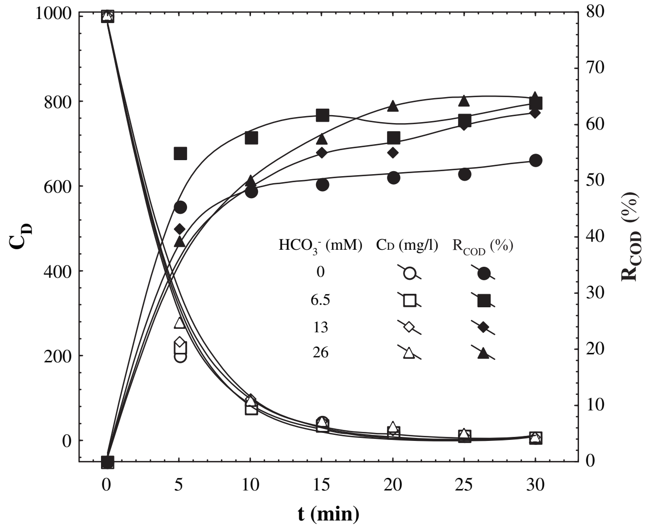

Fig. 9. Effect of contaminant concentration on the removal of dye and COD by O_3/HCO_3^- process (C_D: concentration of dye, R_{COD} (%): removal of COD efficiency, Co: 1000 mg/l, pH: 9.3, *T*: 18 °C, ozone–air flow rate: 5 l/min, ozone generation percentage: 1.4 O_3 (%)).

reaction rate constant than hydroxyl radicals for the oxidation of organic micropollutants [13]. It was reported that bicarbonate ions scavenge hydroxyl radicals to produce intermediates not releasing a radical-type chain carrier, thereby quenching the radical-type chain reaction [13].

However, under neutral pH conditions, the inorganic carbon exists mainly in the form of bicarbonate, which is present in surface and ground waters at concentrations typically in the range of 50–200 mg/l. Higher concentrations may be encountered in high alkalinity waters. Bicarbonate ions take part in reactions with hydroxyl radicals in competition with refractory organic pollutants which has a relatively lower rate constant. For example, for bicarbonate ion the rate constant is $8.5 \times 10^6\ M^{-1}\ s^{-1}$ [14].

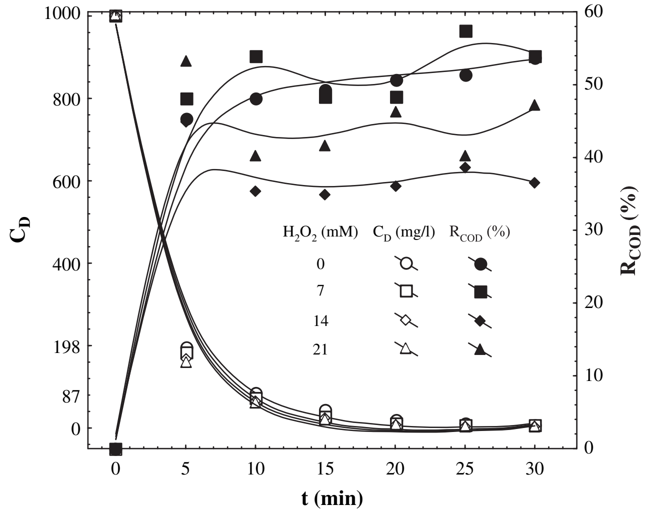

Fig. 10. Effect of contaminant concentration on the removal of dye and COD by O_3/H_2O_2 process (C_D: concentration of dye, R_{COD} (%): removal of COD efficiency, Co: 1000 mg/l, pH: 9.3, *T*: 18 °C, ozone–air flow rate: 5 l/min, ozone generation percentage: 1.4 O_3 (%)).

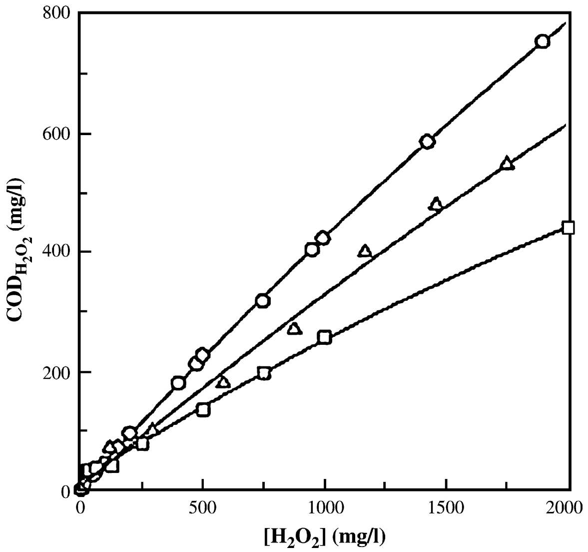

Fig. 11. Plot of the $COD_{H_2O_2}$ value vs the concentration of hydrogen peroxide in water solution: (○) experimental; (Δ) data of Ref. [16]; (□) data of Ref. [6].

Fig. 10 shows the effect of contaminant concentration on the removal of dye and COD by O_3/H_2O_2 process. Since the oxidation potential of hydroxyl radicals is much higher than that of the ozone molecule, direct oxidation is slower than radical oxidation. The increase in $OH^\bullet$ radicals in the solution showed a positive enhancement in the Bomaplex Red CR-L dye removal as examined in Fig. 10. But, H_2O_2 used in the O_3/H_2O_2 process negatively affected the removal of COD from synthetic wastewater. It was thought that $OH^\bullet$ radicals in the O_3/H_2O_2 process transformed dye molecules into much more intermediates, these intermediates caused to increase COD values.

The stability of hydrogen peroxide solutions depends on many factors, including concentration, temperature, pH, concentration of stabilizer, and the presence of contaminants such as chromium, copper, iron, zinc, and has a maximum at pH 2.5–4.5 [15].

The experimental COD values of the samples having different concentrations of hydrogen peroxide have been quoted from the study of Refs. [6] and [16] (Fig. 11). As it can be seen in Fig. 11, which shows the comparison between the experimental values and those of Refs. [6] and [16], the results are very different from one another.

Kuo showed that the increase in the COD value with increasing dosage of hydrogen peroxide is caused by the remaining hydrogen peroxide influents. Kuester and Mize have studied the interference of hydrogen peroxide on the COD test. They proposed Eq. (1) for calculating the COD value. The correlation coefficient (*R*) is used to represent the degree of fit with $R^2 = 1$ corresponding to a perfect fit [17] in the regression analysis.

$$COD_{H_2O_2}(mg/l) = 0.4706[H_2O_2] - 4.06 \times 10^{-5}[H_2O_2]^2 \qquad (1)$$

A theoretical COD value of 1000 mg/l hydrogen peroxide according to the reaction given in Eq. (1) is 470.6 mg/l [17].

Thus the ratio of the COD value to the concentration of hydrogen peroxide is 0.4706. The H_2O_2 concentrations used in this study were defined as 7, 14 and 21 mM, respectively. In this study, to define values of COD arising from H_2O_2 was used Eq. (1), and the values of interference were subtracted from total COD values. In this way, the real COD values were modified.

4. Conclusion

In this study, the dye and COD removal from synthetic textile wastewaters in a semi-batch reactor were conducted by using processes such as O_3, PAC adsorption, O_3/HCO_3^-, O_3/H_2O_2 and O_3/PAC, and compared with ozonation process alone. Ozonation was a much more effective process to remove dye from textile wastewater, but not sufficient to remove COD when used alone. The much more effective processes to remove dye and COD were PAC adsorption and O_3/PAC. However, O_3/PAC process was found to be more adequate than ozonation alone with respect to the used PAC dosage. The ratio of PAC used between the O_3/PAC process and PAC adsorption process was obtained as 0.375. PAC used in the O_3/PAC process displayed both characteristic of adsorbent and catalyst. At result of a reaction time of 30 min, the efficiencies of dye and COD removal from Bomaplex Red CR-L synthetic textile wastewater by O_3/PAC process were over 99 and 84%, respectively. As a consequence of this study, it was concluded that O_3/PAC process, which has a synergic effect, was a much more effective method to remove dye and COD from textile wastewaters.

References

[1] Snider H, Porter JJ. Ozone treatment of dye waste. J Water Pollut Control Fed 1974;46:886–94.

[2] Konsowa AH. Desalination 2003;158:233–40.

[3] Kunz A, Mansilla H, Baeza J, Freer J, Duran N. Chemical treatment (ozone) of dyes present in textile effluents: toxicity of intermediate formed in the process. In: Proceeding of the fifth Brazilian symposium on the chemistry of lignins and other wood components (Curitiba, Brazil), vol. VI; 1997. p. 92–8.

[4] Kanzelmeyer J, Adams CD. Water Environ Res 1996;68:222–8.

[5] Koyuncu I, Afsar HJ. Environ Sci Health 1996;31:1035–41.

[6] Talinli I, Anderson GK. Water Res 1992;26:107–10.

[7] Hassan MdM, Hawkyard CJ. Catal Commun 2002;3:281–6.

[8] Arslan I. J Hazard Mater 2001;85:229–41.

[9] Peralta-Zamora P, Kunz A, Gomes de Moraes S, Pelegrini R, Moleiro PC, Reyes J, Duran N. Chemosphere 1988;38:835–52.

[10] Arslan I, Balcioglu IA. Desalination 2000;130:61–71.

[11] APHA, AWWA, WPCF. Standard methods for the examination of water and wastewater. 16th ed. Washington, DC: APHA, AWWA, WPCF; 1985.

[12] Brunauer S, Emmett P, Teller E. Adsorption of gases in multimolecular layers. J Am Chem Soc 1938;60:309–19.

[13] Hoigne J. Chemistry of aqueous ozone and transformation of pollutants by ozonation and advanced oxidation processes, The handbook of environmental chemistry, 5 (part C). Berlin, Heidelberg, Germany: Springer; 1998.

[14] Acero JL, Gunten V. Influence of carbonate on advanced oxidation process for drinking water treatment. In: Proceedings of ozonation and AOPs in water treatment: applications and research (France, Poitiers); 1998. p. 131–9.

[15] Grayson M. Kirk-Othmer encyclopedia of chemical technology. 3rd ed., vol. 13. Wiley-Interscience; 1981. p. 12–29.

[16] Kuo WK. Water Res 1992;26:881–6.

[17] Kuester JL, Mize JH. Optimization techniques with Fortran. New York: McGraw-Hill; 1973. p. 205–10.