Asian Journal of Chemistry Vol. 22, No. 5 (2010), 3885-3894

Comparison of Ozonation and Catalytic Ozonation Processes for the Decolourization of Reactive Red 195 Azo Dye in Aqueous Solution

SERMIN GUL*, GONCA BAHAR and OZLEM OZCAN YILDIRIM
Department of Chemistry, Faculty of Science & Letters,
Cukurova University, Adana-01330, Turkey
Fax: (90)(322)3386070; Tel: (90)(322)3386590; E-mail: csg@cu.edu.tr

Reactive red 195 (RR195) triazine containing azo dye was treated by ozone (O_3) and ozone combined with granular activated carbon (O_3/GAC) processes. Effects of pH and amount of catalyst on treatment efficiency were examined. At ambient temperature and pH 11, the decolourization efficiency of ozone oxidation was 99.61 % within 0.5 h. However under the same conditions, the decolourization efficiency of GAC catalytic ozonation process reached to 99.71 %. The effect of *t*-butanol (TBA) of 1 mM as radical scavenger on the O_3 and O_3/GAC processes suggests that the decolourization reaction in O_3/GAC process proceeds by mainly radical type mechanism whereas O_3 process proceeds by molecular ozone. FTIR was used for characterization of untreated dye and degradation products obtained after catalytic ozonation. The microstructures of the activated carbons obtained before and after ozonation process were examined by scanning electron microscope.

Key Words: Ozonation, Granular activated carbon, CI Reactive red 195, Catalytic ozonation, Decolourization, Dearomatization.

INTRODUCTION

Dyes are released into the environment mainly from textile and dyestuff industries, most of which are azo dyes[1]. Azo dyes are abundant class of synthetic, coloured and organic compounds, which are characterized by the presence of one or more azo group (-N=N-)[2]. Among azo dyes, those with triazine group are particularly important due to resistance of light induced fading[3]. It has been documented that some azo dyes are toxic and even mutagenic to living organisms in aquatic environments[4]. Azo dyes released without proper treatment represent about 15 % of the total world production, that is, 150 tons/day[5]. The stability of triazine containing azo dye molecular structures makes them resistant to biological and even chemical degradation[6]. Due to their toxicity and recalcitrance, these dyes can be hazardous to the environment though present at low concentrations.

Traditional physical techniques (adsorption on activated carbon, ultra filtration, reverse osmosis, coagulation, ion exchange, *etc.*) can be used efficiently for the removal of pollutants[7]. Nevertheless, they are non-destructive. Due to large degree of aromatics present in dye molecules and their stability, conventional biological treatment methods are ineffective for decolourization and degradation. Chlorination and ozonation can also be used for the removal of certain dyes, but they have high operation costs.

During the last two decades, advanced oxidation processes (AOPs) have been proposed as an alternative way of treating dyestuffs[8,9]. Homogeneous systems without irradiation (O_3/H_2O_2, O_3/OH^-), homogeneous systems with irradiation (O_3/UV, O_3/H_2O_2/UV), heterogeneous systems with irradiation (TiO_2/O_2/UV, TiO_2/O_3/UV) are the main advanced oxidation processes[10-12]. Advanced oxidation processes were based on generation of very reactive hydroxyl radicals ($OH^•$) that oxidize a broad range of pollutants non-selectively and quickly.

Both ozonation and adsorption on granular activated carbon (GAC) have proved to be efficient in removing colour and some of the organic matter from highly coloured effluents[13]. The effect of GAC on the ozone reaction must have a promoting action by hydroxyl radical generation[13-17].

Reactive red 195 (RR195), an azo dye commonly used in textile industry for dyeing and printing of celluloses, was chosen as a model compound for present study. Recently ultrasonic energy technique has only been reported to destroy RR195 due to wash fastness[18]. However, few studies on triazine dye degradation have been reported in the literature[3,4,19]. Despite growing interest of the researchers, catalytic ozonation needs more attention. The objective of this study is to compare the performance of ozonation and catalytic ozonation processes in the degradation of RR195 azo dye in aqueous solution. Optimization of the reaction pH and the amount of catalyst were realized in accordance with the absorbance values of treated aqueous solutions (absorbance at 532 nm), the absorbance of benzene ring and the absorbance of naphthalene ring (absorbencies at 220 and 292 nm), respectively.

EXPERIMENTAL

C.I. Reactive red 195 (RR195) azo dye was obtained from Eksoy Kimya Ltd., Adana, Turkey and used without further purification. The purity of C.I. reactive red is 150 %. The dye has both vinyl sulphone (VS) group and monochloro triazine (MCT) group. The chemical structure of the dye is given in Fig. 1. The coal-based granular activated carbon (GAC) was purchased from Fluka. In inhibition experiments, t-butanol (TBA) obtained from Merck was employed as the radical scavenger.

The solution of RR195 was prepared by dissolving 100 mg/L in deionized water. The pH of dye solutions were adjusted to 3, 7 and 11 and each was subjected to ozonation for 0.5 h to demonstrate the effect of pH on treatment efficiency. Following ozone treatment, the aqueous solutions were filtered through 0.20 μm Millipore syringe filter to remove GAC prior to analytic investigations (TOC and UV/vis absorbance).

Scanning electron micrographs of carbon samples were recorded by the Jeol-JSM 5500 model scanning electron microscope (SEM).

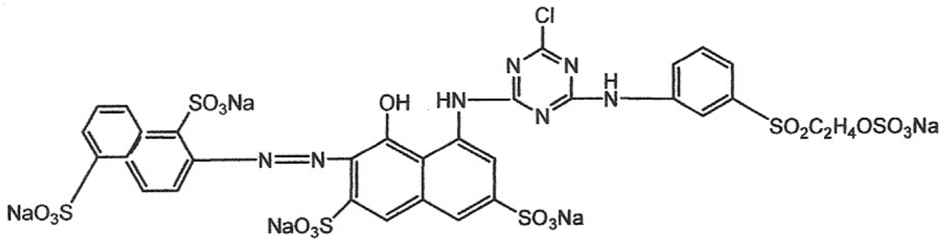


Fig. 1. Molecular structure of reactive red 195

Analytical procedure: Ozonation reaction was carried out in a 1 L stirred semi-batch lab scale glass reactor by passing ozone gas through the aqueous solution with a dose of 28 mg O_3/min. The reactor was filled with 1 L of dye solution and 0.5, 1.0, 5.0 and 10 g of GAC were added. A magnetic stirrer was used to mix the reactor contents. Ozone was produced from pure oxygen in a Hermann firm ozone generator with a gas flow of 0.8 L/min. Two wash bottles filled with 2 % potassium iodide solution buffered with phosphate were connected in series in the exit of the reactor to quench the unreacted ozone gas passing through the reactor. Most of the test runs usually lasted within 0.5 h. Samples (*ca.* 5 mL) were withdrawn at regular times for analysis.

The colour removal of the dye solution was determined with the absorbance value of the remaining dye by monitoring UV-vis spectrum using Shimadzu UV-2101 PC double beam spectrophotometer. The absorption band at 532 nm was chosen to measure the colour parameter (A_{532}) associated with a long conjugated π system[20], whereas the absorption bands at 292 and 220 nm (expressed in terms of A_{292} and A_{220}) were indicative of benzene ring and naphthalene ring, respectively.

Fourier transform infrared (FTIR) absorbance spectra of RR195 samples were taken between 4400-450 cm^{-1}, at a resolution of 4 cm^{-1} using Perkin-Elmer RX I FTIR spectrometer equipped with IR detector. The initial and treated dye solutions were freeze dried and then mixed with KBr powder to get spectra.

Scanning electron microscope (SEM) was carried out on GAC samples which were taken before and after ozonation with 4000x magnification. Samples were analyzed on the double carbon plates.

RESULTS AND DISCUSSION

Effect of the initial pH value: pH is an important parameter influencing performance of the ozonation, the pH of dye solution was adjusted to 3, 7 and 11 and each solution subjected to ozonation for 0.5 h to demonstrate the effect of pH on treatment efficiency. Decolourization (degradation of diazo linkage between aromatic structures, decrease in A_{532}) and dearomatization (decrease in A_{220} and A_{292}) took place more effectively in alkaline solution compared to neutral and acidic media (Fig. 2).

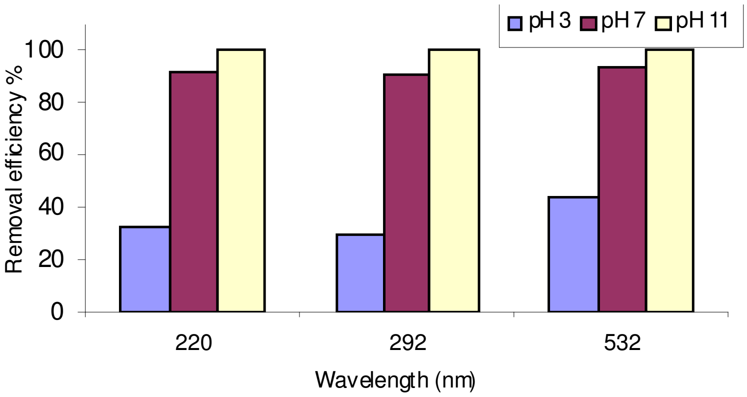


Fig. 2. Effect of pH on the decolourization and dearomatization efficiency of RR195 by ozone. $C_{0(O_3)}$: 28 mg/L, $C_{0(dye)}$: 100 mg/L, ozonation time: 0.5 h

Effect of the amount of catalyst: The effect of the amount of GAC on colour reduction was shown in Fig. 3. The results demonstrated that the addition of GAC to an optimum amount of 1.0 g/L has beneficial improvement of on colour removal in RR195 solution. Thus, an optimum amount of GAC will be beneficial for catalyzing the oxidation of refractory organics *via* creation of oxidative radical specie, however if the amount exceeds a certain quantity, then its role is reverted.

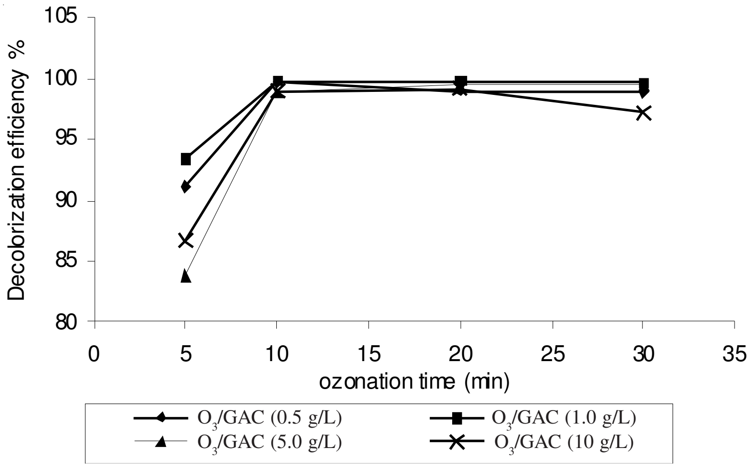


Fig. 3. Effect of GAC amount on decolourization of RR195. $C_{0(O_3)}$: 28 mg/L, $C_{0(dye)}$: 100 mg/L, ozonation time: 0.5 h

Comparison of O_3 and O_3/GAC for decolourization of RR195: The comparison of ozone oxidation and ozone/GAC oxidation for the degradation of RR 195 is illustrated in Figs. 4 and 5. Fig. 4 displays the UV/vis spectral changes of RR195 at pH 11 in O_3 and O_3/GAC processes. Before treatment, the UV/vis spectra of RR195 have three main absorption bands-two in the UV region (A_{292} and A_{220}) and one in the visible region (A_{532}). A_{292} is due to two adjacent rings, whereas A_{220} is associated with benzene ring. A_{532} is due to the long conjugated π-system of aromatic ring connected to an azo group[20]. After 0.5 h of reaction, the intensity of A_{220} declines extremely from 3.43 to 1.15 in O_3 alone and from 3.43 to 0.58 in O_3/GAC. A_{532} is totally and 98.5 % of A_{292} chromatographic peak is disappeared after 0.5 h ozonation.

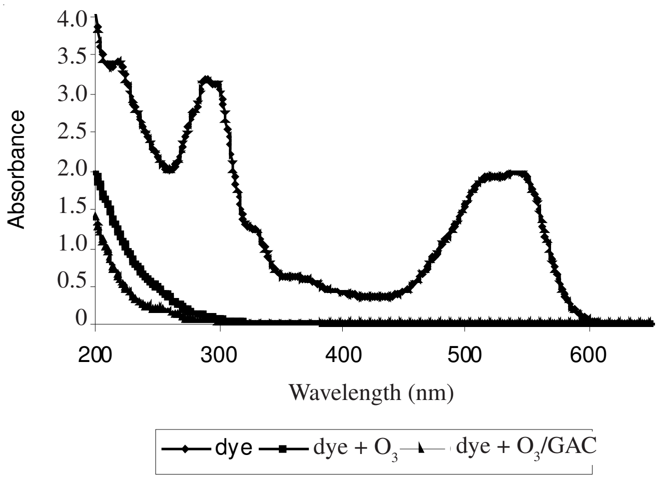


Fig. 4. UV/vis spectral changes of RR195 by O_3 and O_3/GAC processes at pH 11. $C_{0(O_3)}$: 28 mg/L, $C_{0(dye)}$: 100 mg/L, ozonation time: 30 min

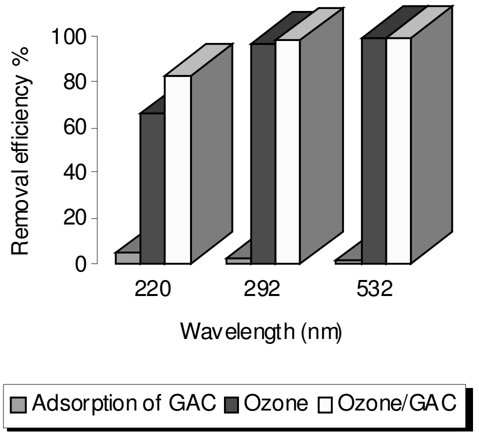


Fig. 5. Comparison of ozone/GAC oxidation, ozone oxidation and the adsorption of GAC for the decolourization and dearomatization of RR 195

The comparison of ozone/GAC oxidation, ozone oxidation alone and the adsorption of GAC for the decolourization and dearomatization of RR 195 are illustrated in Fig. 5. At ambient temperature and pH 11, the decolourization efficiency of ozone oxidation within 0.5 h was 99.61 % while under the same conditions, the decolourization efficiency of O_3/GAC process reached up to 99.71 %. 1.0 g/L GAC was only 1.12 % decolourization efficiency when the contact time of RR195 was 30 min and the concentration of RR195 was 100 mg/L. The particular removal efficiency (83 %) of A_{220} is attributed to the substituted benzene ring being less amenable to hydroxyl radical.

The experimental results indicated that N=N chromophore group are more easily destroyed than aromatic structures by hydroxyl radicals and destruction of azo group led to the decolourization of dye solution. The elimination of adjacent ring structure needs a longer time. Lucas and Peres obtained a similar result for reactive black 5 in a photo-Fenton system[21].

Degradation mechanism of O_3 and O_3/GAC processes: It is expected that O_3 and O_3/GAC processes might follow a radical mechanism. *tert*-Butanol (TBA) which is a well known radical scavenger was added to dye solution to ascertain the mechanism of two processes. If the both processes were to proceed by the hydroxyl radical reaction mechanism, then the presence of *tert*-butanol would rapidly consume hydroxyl radicals and hence reduce decolourization. As shown in Fig. 6, ozone oxidation for RR195 was not affected in the presence of 1 mM *tert*-butanol and 0.5 h ozonation time pH being kept at 11.

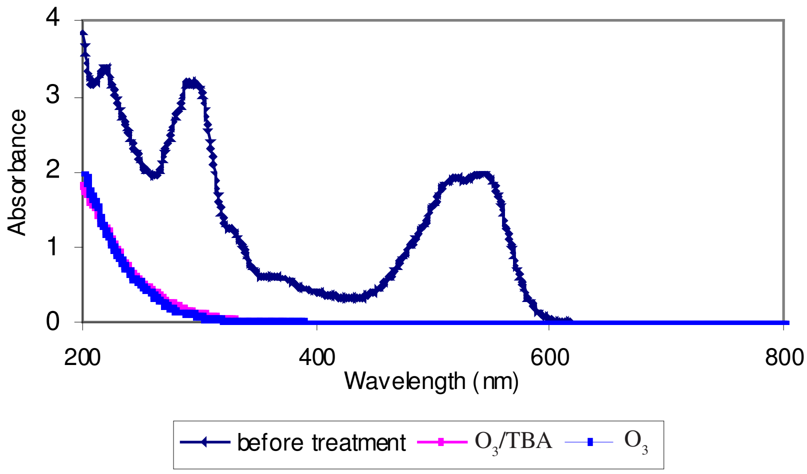


Fig. 6. Effect of TBA on O_3 process. $C_{0(O_3)}$: 28 mg/L, $C_{0(dye)}$: 100 mg/L, ozonation time: 30 min

For O_3/GAC process, a substantial (about 48 fold) retardation was observed using the same conditions of ozonation (Fig. 7). Consequently it is possible to say that hydroxyl radicals are to be the dominant oxidant species in the O_3/GAC process, whereas molecular ozone is dominant in the case of ozonation alone. Ma *et al.*[22] presented a similar result for degradation of nitrobenzene by catalytic ozonation.

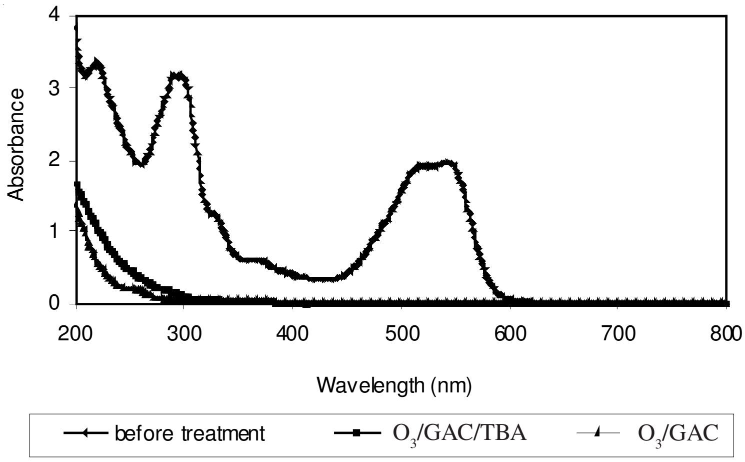


Fig. 7. Effect of TBA on O_3/GAC process. $C_{0(O_3)}$: 28 mg/L, $C_{0(dye)}$: 100 mg/L, ozonation time: 30 min

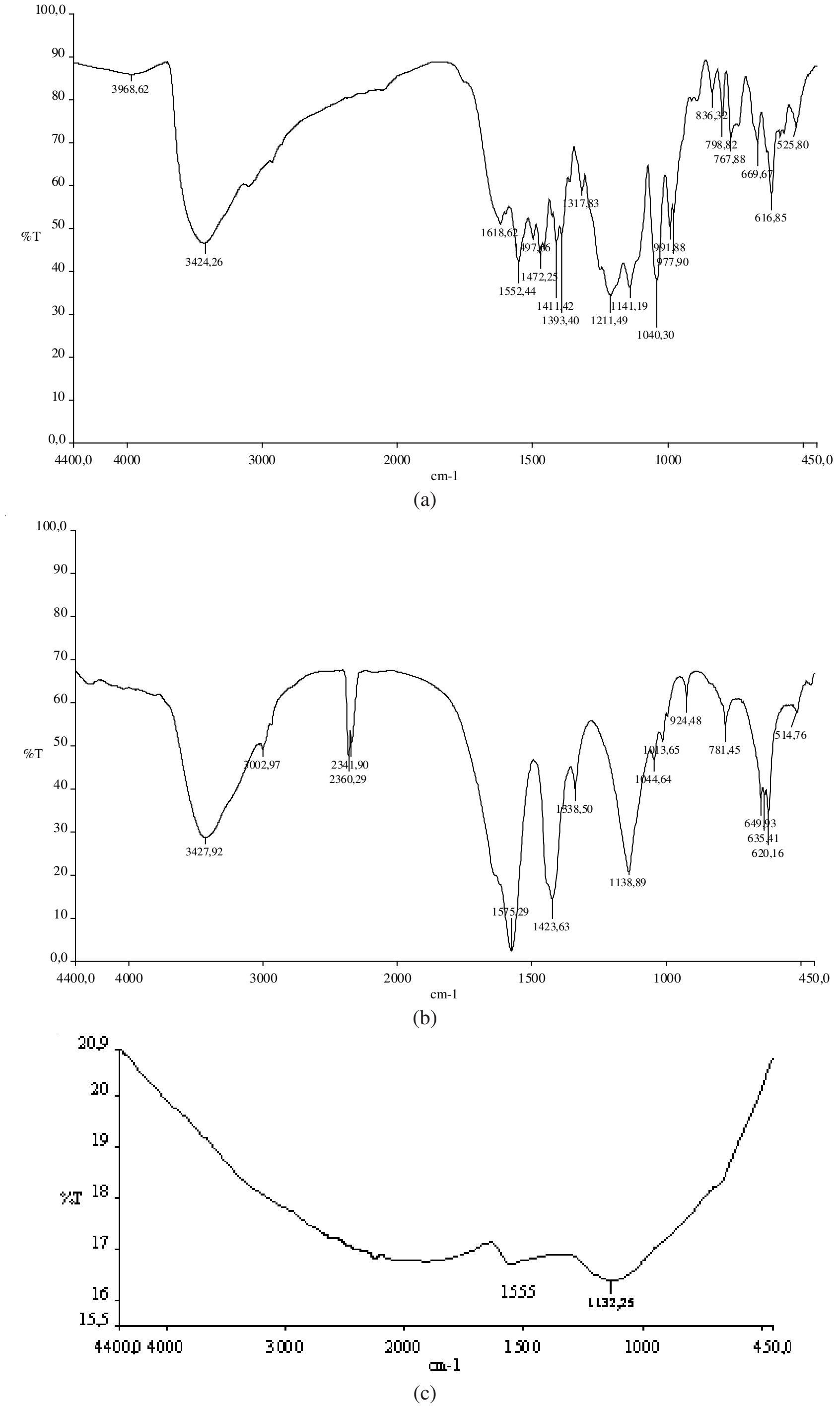
FTIR spectra of the RR195: The FTIR spectra obtained from RR195 before and after ozone/GAC treatments with reaction durations of 10 and 30 min are shown in Fig. 8. Several bands can be distinguished in the region of 4400-450 cm^{-1}, as follows [Fig. 8(a)][23].

The peak located at 3424 and 1339 cm^{-1} can be assigned to N-H vibration of primar amine and aromatic amine, respectively. The bands at 1552 and 1472 cm^{-1} are attributed to the -N=N- band vibrations or to aromatic ring vibrations sensitive to the interaction with the azo bond or to the bending vibration mode δ(N-H) of the hydrazone form of the azo dye as stated Stylidi *et al.*[2]. The bands at 1141 and 1040 cm^{-1} are linked to the coupling between the benzene mode and $\nu_s(SO_3)$. Finally, triazine absorption is observed in the broad region between 800 and 700 cm^{-1}.

The spectrum of RR195 treated with ozone/GAC with reaction time of 10 min is illustrated in Fig. 8(b). The band at 1618 cm^{-1}, associated with the -C=C- bond of conjugated diens disappeared after ozonation. A slight shift of the bands and increased intensities are observed in the region of 1550-450 cm^{-1} with respect to the Fig. 8(a), showing degradation products associated with the chromophoric part of the dye. The slight shifted bands at 924 and 780 cm^{-1} representing mono nuclear aromatic and triazine, respectively are still present after 10 min ozonation.

The spectrum of RR195 treated with ozone/GAC with reaction duration of 0.5 h is displayed in Fig. 8(c). After 0.5 h catalytic ozonation almost all peaks disappeared except the weak peaks at 1565 and 1130 cm^{-1} representing aromatic skeletal vibrations. This result is evidence to persistence of the band associated to the aromatic ring to catalytic ozonation.

SEM characterization: SEM micrograph of studied granular activated carbon (before ozonation) is shown in Fig. 9. SEM micrographs of GACs which are used as catalysts in ozonation procedure are shown in the figure as well.

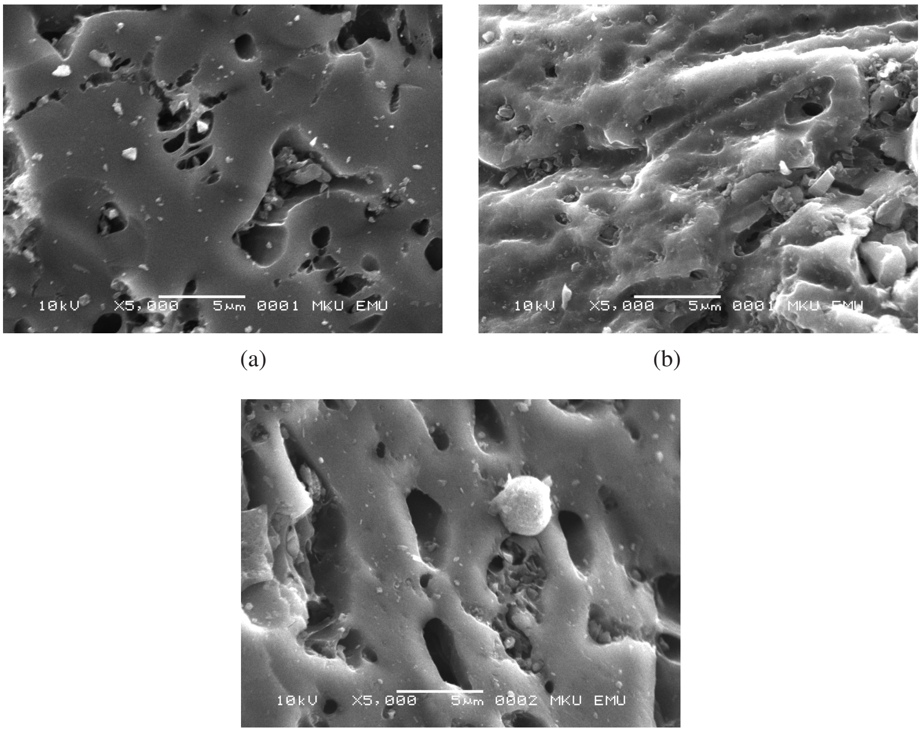


(a)

(b)

(c)

Fig. 8. FTIR spectra obtained for (a) RR195 before treatment, (b) RR195 after 10 min ozone/GAC treatment, (c) RR195 after 30 min ozone /GAC treatment



(a) (b)

(c)

Fig. 9. SEMs of (a) initial GAC (before ozonation); (b) 0.5 g/L GAC (after ozonation); (c) 1.0 g/L GAC (after ozonation); Ozonation time: 20 min

SEM results showed that carbon texture and development of porosity was strongly affected by the amount of catalyst. Initial (before ozonation) GAC had not a homogeneous structure with a predominance of macropores with an average 5 µm diameter. Ozonated 0.5 g/L GAC sample gave rougher texture with heterogeneous surface and greater variety of randomly distributed pore size. A comparison between 0.5 and 1.0 g/L GAC samples (after ozonation) showed major differences in their external surface characteristics. More porosity, more homogeneity and some salt particles on the surface of 1 g/L GAC (after ozonation) sample were observed. It can be concluded that surface texture highly dependent on the amount of the catalyst duration of ozonation. Increased amount of catalyst caused more polar surface. The addition of GAC to an optimum amount of 1.0 g/L has beneficial improvement on colour removal in RR195 solution because of increased homogeneity and porosity of catalyst which was caused effective surface area and hydroxyl radical production.

Conclusion

The results of this study showed that decolourization and dearomatization of aqueous solutions contaminated by the reactive dye (RR195) can be achieved by treating the solutions with ozone only. On the other hand, the presence of an optimum amount of granulated activated carbon catalyzes the cleavage of aromatic rings due to the formation of active hydroxyl radicals, thus enhancing both decolourization and dearomatization of the dye contaminated aqueous solutions. This work indicated that the GAC catalyzed ozonation process can complete the decolourization for RR195.

ACKNOWLEDGEMENT

The authors would like to thank Academic Research Projects unit of Çukurova University for supporting this research under Contract No. FEF2006YL57.

REFERENCES

1. H. Chun and W. Yizhong, *Chemosphere*, **39**, 2107 (1999).
2. M. Stylidi, D.I. Kondarides and X.E. Verykios, *Appl. Catal. B: Environ*., **40**, 271 (2003).
3. C. Hu, J.C. Yu, Z. Hao and P.K. Wong, *Appl. Catal. B: Environ*., **42**, 47 (2003).
4. C.M. So, M.Y. Cheng, J.C. Yu and P.K. Wong, *Chemosphere*, **46**, 905 (2002).
5. J. Bandara, J.A. Mielczarski and J. Kiwi, *Langmuir*, **15**, 7670 (1999).
6. S. Dai, W. Song, T. Li and Y. Zhuang, *Adv. Environ. Sci*., **4**, 1 (1996).
7. I.K. Konstantinou and T.A. Albanis, *Appl. Catal. B: Environ*., **49**, 1 (2004).
8. E. Kusvuran, O. Gulnaz, S. Irmak, O.M. Atanur, H.I. Yavuz and O. Erbatur, *J. Hazard. Mater*., **109B**, 85 (2004).
9. E. Kusvuran, S. Irmak, H.I. Yavuz, A. Samil and O. Erbatur, *J. Hazard. Mater*.,**119**, 109 (2005)
10. H. Lachheb, E. Puzenat, A. Houas, M. Ksibi, E. Elaloui, C. Guillard and J.M. Hermann, *Appl. Catal. B: Environ*., **39**, 75 (2002).
11. B. Kasprzyk-Hordern, M. Ziolek and J. Nawrock, *Appl. Catal. B: Environ*., **46**, 639 (2003).
12. E. Yildiz, H. Vapur, S. Gul, O. Ozcan and O. Bayat, *Trans Inst. Min. Metall. C*, **114**, 115 (2005).
13. P.C.C. Faria, J.J.M. Orfao and M.F.R. Pereira, *Water Res*., **39**, 1461 (2005).
14. B. Legube and N.K.V. Leitner, *Catal. Today*, **53**, 1 (1999).
15. U. Jans and J. Hoigne, *Ozone Sci. Eng*., **20**, 67 (1998).
16. B.S. Oh, S.J. Song, E.T. Lee, H.J. Oh and J.W. Kang, *Water Sci. Tech*., **49**, 45 (2004).
17. S. Gul, O. Ozcan and O. Erbatur, *Dyes Pig*., **75**, 426 (2007).
18. M. Akalin, N. Merdan, D. Kocak and I. Usta, *Ultrasonics*, **42**, 161 (2004).
19. C. Hu, Y. Wang and H. Tang, *Appl. Catal. B: Environ*., **35**, 95 (2001).
20. E. Pretsch, P. Buhlmann and C. Affolter, Berlin: Springer (1991).
21. M.S. Lucas and J.A. Peres, *Dyes Pig*., **71**, 236 (2006).

22 J. Ma, S. Ming-Hao, C. Zhong-Lin and W. Li-Ning, *Ozone Sci. Eng.*, **26**, 3 (2004).

23 R.M.C. Silverstein, G.C. Bassler and G.C. Morrill, New York, Wiley (1991).

(*Received*: 20 August 2009; *Accepted*: 22 January 2010) AJC-8349