

Investigation on the Removal of COD from Colored Aqueous Solutions with O_3 , H_2O_2 , HCO_3^- , and PAC

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In this study, chemical oxygen demand (COD) was removed using different processes containing O_3 , H_2O_2 , HCO_3^- , and powder activated carbon (PAC) from the synthetic dye solutions. The effects of the experimental parameters such as temperature, ozone dose, dye concentration, pH, and time on the removal of COD were investigated. The Taguchi method was applied to determine the optimum conditions. An orthogonal array L_{18} ($2^1 \times 3^7$) experimental design plan was selected to define the optimum conditions. In addition, the mechanism of the COD removal was explained on the basis of the results of Fourier transform infrared (FTIR) spectroscopy. To gain information about COD removal mechanism at various pHs, electrophoretic mobilities of particles were measured. The chosen experimental parameters and their ranges are: HCO_3^- (0–39 mM); temperature (18–70 °C); ozone dose (164–492 mg/min); dye concentration (200–600 ppm); PAC (0–1.5 g); H_2O_2 (0–0.056 mM); pH (3–12); and time (10–30 min). Under these optimum conditions, it was found that the COD removal efficiency from the synthetic dye solutions was 98%.

Keywords Ozone, Bicarbonate Ion, COD Removal, Hydrogen Peroxide, Powdered Activated Carbon (PAC)

INTRODUCTION

Considerable amounts of high quality water are needed for dyeing and finishing operations in the textile industry. Color and recalcitrant compounds are among the vital environmental concerns in effluent treatment. Wastewater from these industries represents a variety of pollutants such as high strength load and high in color depending on the stage of the process and the nature of discharge. The high pollution load is generated from spent dyeing baths, first and second rinses

carried out after dyeing processes. These effluents consist of unbound colorants or reaction products, which remain in the substrate and are washed out in subsequent rinses, dye impurities, auxiliaries, and surfactants. These compounds exhibit slow degradation kinetics for conventional biological processes and the resulting effluent is high in color and violates the discharge limits imposed by legislation (Hao et al. 2000; Krull et al. 1998; Pierce 1994; Tabrizi et al. 2011).

COD and biological oxygen demand (BOD) of aqueous dyes decreases after ozonation (Hassan and Hawkward 2002). It was reported that COD decreased only in the case of pure dye solution, although for real industrial wastewater, both COD and TOC content remained unchanged (Arslan 2001). Ozone is also very effective in removing color caused by water-soluble dyes, particularly fiber acid and reactive dyes (Konsowa et al. 2010; Snider and Porter 1974). 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 (Arslan and Balcioglu 2000).

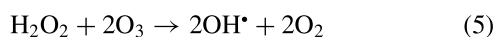
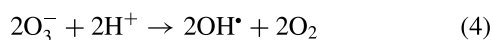
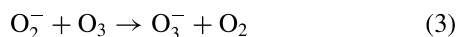
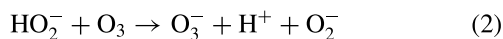
The use of ozone in textile effluent treatment appears to be a very attractive alternative because of its application potential. Ozone is a powerful oxidizing agent (E° 2.08 V), when compared with other well-known oxidizing agents such as H_2O_2 (E° 1.78 V), and can react with several classes of compounds through direct or indirect reactions. Ozone is capable of degrading dyes. Chromophore groups, generally organic compounds with conjugated double bonds can be broken by ozone (directly or indirectly) into smaller forms in order to decrease the color of the effluent (Beltran 2004; Beltran et al. 2001; Carriere et al. 1993; Koyuncu and Afsar 1996; Rice 1997).

Hydrogen peroxide may react directly or after it is first ionized or dissociated into free radicals. In spite of the powerful oxidizing ability of hydrogen peroxide, it acts as a reductant when reacting with stronger oxidizing agents. The

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reaction mechanism is very complex and may be affected by the reaction conditions. The decomposition of ozone by hydroperoxide generating hydroxyl radicals (Staehelin and Hoigné 1982) is given in detail as follows:



Since the oxidation potential of hydroxyl radicals is much higher than that of the ozone molecule, direct oxidation by O_3 is slower than radical oxidation (OH^\bullet).

HCO_3^- ions in the $\text{O}_3/\text{HCO}_3^-$ process were used to scavenge occurring OH^\bullet radicals during ozonation. It is likely that bicarbonate is the principal consumer of the hydroxyl radicals, particularly as 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 ($\text{HCO}_3^{\bullet-}$). These act as a very selective additional oxidation species and which have a much lower reaction rate constant than hydroxyl radicals for the oxidation of organic micropollutants (Hoigné 1998).

Ozonation can modify the surface property of an activated carbon such as specific surface area, pore volume and functional group. Treatment of activated carbon with ozone increases the surface area and the concentration of surface functional group, which in turn can enhance the adsorption capacity (Chiang et al. 2002; Deitz and Bitner 1972a,b).

There is a wide range of applications of the Taguchi method, from chemistry to engineering and from microbiology to the construction business (Abali et al. 1997; Donmez et al. 1998; Khoei et al. 2002; Tortum et al. 2005; Yesilyurt et al. 2005). The advantage of the Taguchi method on the conventional experimental design methods, in addition to keeping the experimental cost to a minimum, is that it minimizes the variation in product response while keeping the mean response on target. Its other advantage is that the optimum working conditions determined from the laboratory work can also be reproduced in the real production environment (Logothetis 1992; Ross 1987; Roy 1990). The various studies relative to Bomaplex Red CR-L textile dye were published prior to this study (Oguz et al. 2005; Oguz and Keskinler 2005, 2007, 2008).

This investigation was aimed to determine the optimum process conditions for the removal of COD from synthetic dye solutions using integrated processes containing O_3 , H_2O_2 , HCO_3^- , and PAC. Integrated processes were realized at the different experimental conditions such as temperature, ozone

dose, dye concentration, pH, and treatment time. In this article, eight controllable factors were identified for the removal of COD. The eight parameters were set (one parameter was set at two levels and seven parameters were set at three levels) to observe the main effects. At the result of an oxidation time of 10 min, the COD removal efficiency by the combined processes was found to be 98%.

MATERIALS AND METHODS

Preparation of the Dye Solutions

The Bomaplex Red CR-L dye was acquired from a textile mill located in Turkey. The chemical structure of the water-soluble dye was given in Figure 1. Bomaplex Red CR-L dye (1000 mg) was dissolved in 1 L of distilled water and used as a 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. The initial dye concentrations used in optimization study were 200, 400, and 600 ppm, respectively.

Preparation of the HCO_3^- Solutions

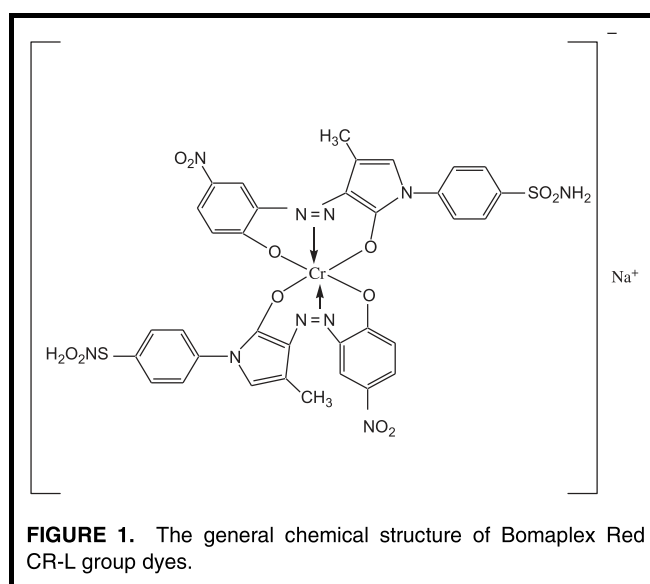
The solutions of 0 and 39 mM HCO_3^- were prepared from NaHCO_3 (Merck).

Preparation of the H_2O_2 Solutions

The solutions of 0.028 and 0.056 mM hydrogen peroxide were prepared from hydrogen peroxide (50% solution, 1.2 g/mL, from Merck).

Powder Activated Carbon (PAC)

In the O_3/PAC process, a commercial PAC from Merck was used as the adsorbent throughout this study. The surface area of the PAC was measured by BET method at 77 K using



a Quantachrome QS-17 model apparatus. The surface area of the PAC was defined as 455 m²/g (Brunauer et al. 1938). The PAC samples of 0.5, 1, and 1.5 g per solution of 250 mL were taken to obtain the optimum conditions.

Ozonation Studies

The ozone was generated from air using an Opal OG-24 model ozone generator, Turkey. This generator operates based on a corona discharge producing ozone from air or pure oxygen. Air was fed to the ozone generator with a regulated pressure in the cylinder of 1.13 kg/cm², before entering the ozone generator cell. The maximum operating voltage was 220 V, as indicated on the voltmeter. The equipment was cooled through the continuous circulation of tap water. The application doses of ozonation for the reactor are 164, 328, and 492 mg/min for the ozone-air flow rates of 5, 10, and 15 L/min, respectively. The maximum ozone production potential of the ozone generator was volumetrically 1.8% as a function of electric voltage. Ozonation was performed in a cylindrical semibatch glass reactor with a volume of 1 L. Ozone-air mixture was continuously sparged through a diffuser. Synthetic dye solutions were ozonated for 30 min.

Analysis of FTIR

FTIR spectra were recorded with a Perkin-Elmer 1720 spectrometer (16 scans, resolution of 2 cm⁻¹) over a KBr pellet. A sample of 2 mg was first manually 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 or not the ozonized dye intermediates adsorbed on the PAC modify the peaks of functional groups on the PAC.

Analysis of Zeta Potential

The zeta potential values of the PAC and contaminated PAC particles were determined using a micro-electrophoresis cell (Zeta meter 3.0+). The adsorbents were previously conditioned as follows; 100 mg of the adsorbent was added to an Erlenmeyer flask containing 100 mL of distilled water, the pH of the solution was adjusted at definite initial values and the flasks were placed in a temperature controlled shaker at 291 K for 30 min. Then the flasks were removed and the dispersion was transferred to the micro-electrophoresis cell (Zeta meter 3.0+). Then, the zeta-potential was measured. The zeta potentials of the PAC particles were defined as a function of suspension pH.

Analytical Method

The measurement of COD was based on the “closed reflux, colorimetric method” described in Ref (Standard Methods 1985). The digestion solution was first prepared by adding 10.216 g of K₂Cr₂O₇ (Merck), which was previously dried for 2 h at 103 °C, 167 mL of concentrated H₂SO₄ (Merck)

and 33.3 g of HgSO₄ (Merck) into 500 mL of distilled water. The mixture was then left to cool to room temperature before diluting to 1000 mL.

Samples were put in tubes and 0.6 mL of digestion solution was added. Next, 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 the content. The mixtures were placed in an oven preheated to 150 °C for 2 h. After cooling, the samples were analyzed using a UV spectrophotometer (UV Spectrophotometer, Shimadzu 160A, Japan) 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 O₂/mg.

Experimental System

The experimental setup consists of an air dryer and compressor, ozone generator and semi-batch reactor. The air dryer consisted of a column that was filled with a high adsorptive anhydrous CaCl₂. Ozone was generated using an ozone generator Model OG-24; water was used as the cooling medium. The ozone-air mixture was then fed into the contact place through a porous plate gas sparger located at the semi-batch reactor's base. All experiments were carried out in a 1000 mL cylindrical semibatch reactor. The reactor had a glass column of 7 cm diameter, 40 cm height, and a water cooling jacket to keep the reactor contents at constant temperature. COD solution of 250 mL was used during each batch of ozonation.

Taguchi Method

The Taguchi method is a systematic application of design and analysis of experiments for the purpose of designing and improving product quality. There are some differences in this method from other statistical experimental design methods. The main difference is that the parameters affecting an experiment can be investigated as controlling and not controlling (noise factor). The use of the parameter design in the Taguchi method to optimize a process with multiple performance characteristics includes the following steps (Celik and Burnak 1998; Phadge 1989): (a) to identify the performance characteristics and select the process parameters to be evaluated; (b) to determine the number of parameter levels for the process and possible interaction between the process parameters; (c) to select the appropriate orthogonal array (OA) and assignment of process parameters to the orthogonal array; (d) to conduct the experiments based on the arrangement of the orthogonal array; (e) calculate the performance statistics; (f) to analyze the experimental result using the performance statistics and ANOVA; (g) to select the optimal levels of process parameters; and (h) to verify the optimal process parameters through the confirmation experiment.

This investigation was aimed to determine optimum process conditions for the removal of COD from synthetic dye solutions. The experimental parameters effect on the removal

TABLE 1. Experimental Parameters and Their Levels

Parameters	Parameters levels		
	1	2	3
A HCO_3^- (mM)	0	39	—
B Temperature ($^{\circ}\text{C}$)	18	40	70
C Ozone dose (mg/min)	164	328	492
D Dye concentration (ppm)	200	400	600
E PAC dosage (g)	0	1	1.5
F H_2O_2 (mM)	0	0.028	0.056
G pH	3	9,3	12
H Treatment time (min)	10	20	30

of COD and their levels were determined in the light of preliminary tests and given in Table 1.

The orthogonal array experimental design method was chosen to determine experimental plan, $L_{18} (2^1 \times 3^7)$ as seen in Table 2, because it is the most suitable for the conditions being investigated; one parameter with two levels and seven parameters with three levels. The interactive effects of parameters other than the interaction between HCO_3^- and temperature were not taken into account in the theoretical analysis because some preliminary tests show that they could be neglected. The validity of this assumption was checked by confirmation experiments conducted in the optimum conditions.

In order to observe the effects of noise sources on the COD removal, each experiment was repeated three times under the same conditions at different times. The performance statistics were chosen as the optimization criteria. There are three categories of performance statistics; the larger-the better, the smaller-the better and the nominal-the better. In this study, the performance statistics of the smaller-the better was used to define the optimum conditions (Phadke 1989; Pignatiello 1988). The smaller-the better performance statistics were given by Equation [6];

$$SN_s = -10 \log \left(\frac{1}{n} \sum_{i=1}^n Y_i^2 \right) \quad [6]$$

where SN_s is performance statistics, n the number of repetition done for an experimental combination, and Y_i the performance value of the i th experiment. In the Taguchi method, the experiment corresponding to optimum working conditions might not have been done during the whole period of the experimental stage. In such cases, the performance value corresponding to the optimum working conditions can be predicted by utilizing the balanced characteristic of OA. For this, the additive model in Equation [7] may be used.

$$Y_i = \mu + X_i + e_i \quad [7]$$

Where μ is the overall mean of performance value, X_i the fixed effect of the parameter level combination used in the

TABLE 2. Chosen $L_{18} (2^1 \times 3^7)$ Experimental Plan Table and the Results of Experiment

Experiment No.	Parameters and their levels								The results of experiment Y_i			$SN_s = -10 \log \left(\frac{1}{n} \sum_{i=1}^n Y_i^2 \right)$
	A	B	C	D	E	F	G	H	1	2	3	
1	1	1	1	1	1	1	1	1	40	32	25	−30.277
2	1	1	2	2	2	2	2	2	72	21	65	−35.155
3	1	1	3	3	3	3	3	3	72	19	82	−36.135
4	1	2	3	1	2	2	3	3	40	22	72	−33.859
5	1	2	1	2	3	3	1	1	68	222	161	−44.278
6	1	2	2	3	1	1	2	2	280	247	260	−48.386
7	1	3	3	2	1	3	2	3	398	256	455	−51.571
8	1	3	1	3	2	1	3	1	0	0	0	3070.000
9	1	3	2	1	3	2	1	2	0	0	0	3070.000
10	2	1	1	3	3	2	2	1	133	60	130	−40.764
11	2	1	2	1	1	3	3	2	76	0	32	−33.570
13	2	1	3	2	2	1	1	3	0	0	0	3070.000
13	2	2	2	2	3	1	3	2	30	31	70	−33.582
14	2	2	3	3	1	2	1	3	398	360	437	−52.040
15	2	2	1	1	2	3	2	1	40	11	0	−27.650
16	2	3	2	3	2	3	1	2	72	36	81	−36.398
17	2	3	3	1	3	1	2	3	39	46	40	−32.418
18	2	3	1	2	1	2	3	1	166	108	131	−42.549

i th experiment and e_i the random error in the i th experiment. Because Equation [7] is a point estimation, which is calculated using experimental data in order to determine whether or not the results of the confirmation experiments are meaningful, the confidence interval must be evaluated. The confidence interval at the chosen error level may be calculated by Equation [8];

$$Y_i \mp \sqrt{F_{\alpha;1,DF_{MSe}} * MS_e \left(\frac{1+m}{N} + \frac{1}{n_i} \right)} \quad [8]$$

where F is the value of the F -table, α the error level, DF_{MSe} the degrees of freedom of mean square error, m the degree of freedom used in the prediction of Y_i , N the number of total experiments, and n_i the number of repetitions in the confirmation experiment.

The order of the experiments was obtained by inserting parameters into columns of OA, L_{18} ($2^1 * 3^7$), chosen as the experimental plan given in Table 2. The order of experiments was made random in order to avoid noise sources which had not been considered initially and could occur during an experiment and negatively affect the results.

A confirmation experiment is a powerful tool for detecting the presence of interactions among the control parameters. If the predicted response under the optimum conditions does not match the observed response, it implies that the interactions are important. If the predicted response matches the observed response, it implies that the interactions are probably not important and the additive model is a good approximation.

RESULTS AND DISCUSSION

The collected data was analyzed with a PC for evaluation of the effect of each parameter on the optimization criteria. To see the effective parameters and their confidence levels on the COD removal process, an analysis of variance was performed. A statistical analysis of variance (ANOVA) was performed to see which process parameters are statistically significant. The F -test is a tool to determine which process parameters have a significant effect on COD removal value. The F -value for each process parameter is simply a ratio of the mean of the squared deviations to the mean of the squared error.

The removal of COD from the synthetic dye solutions was investigated at different experimental conditions. To determine the optimum conditions for the COD in the ozonized dye solutions, the effects of HCO_3^- ions, temperature, ozone dose, dye concentrations, PAC, H_2O_2 , pH, and treatment time were investigated, respectively. The reaction conditions in which the effects of parameters were investigated and the experimental results are given in Table 2. The degrees of the influences of parameters on the performance statistics are given in the graphs in Figures 2–7.

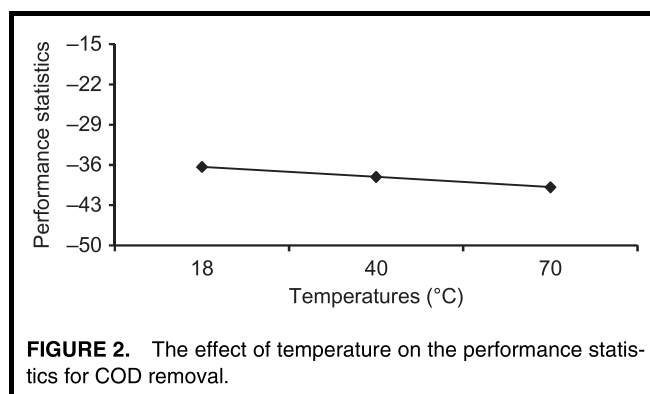
The numerical value of the maximum point in each graph marks the best value of particular parameter. The HCO_3^- ions that have a scavenger effect on the OH^\bullet radicals positively affected the COD efficiency. The performance statistics value is in proportion with the COD removal efficiency. With the increasing HCO_3^- ions level, the performance statistics value of COD removal efficiency increased. The fact that the HCO_3^- ions are present in the COD removal processes is important because of their scavenger effect.

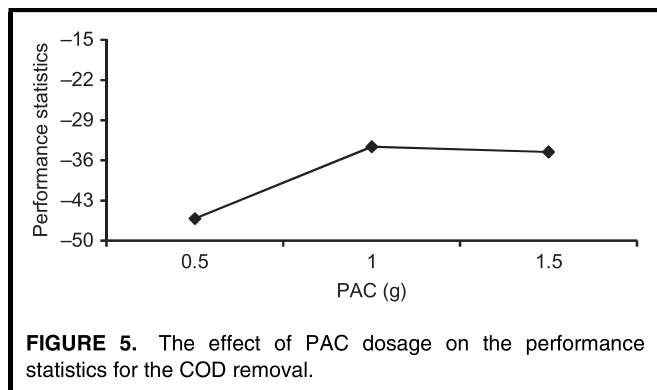
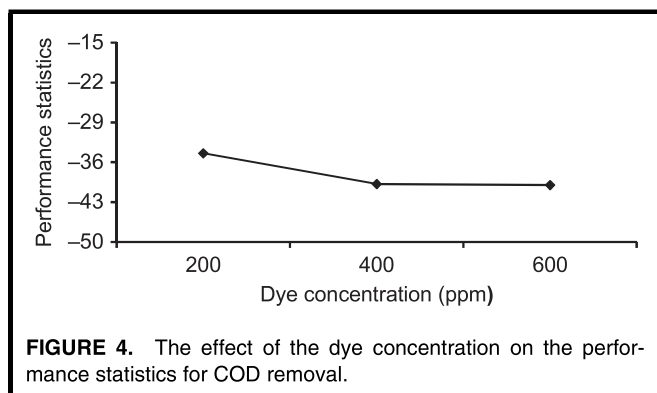
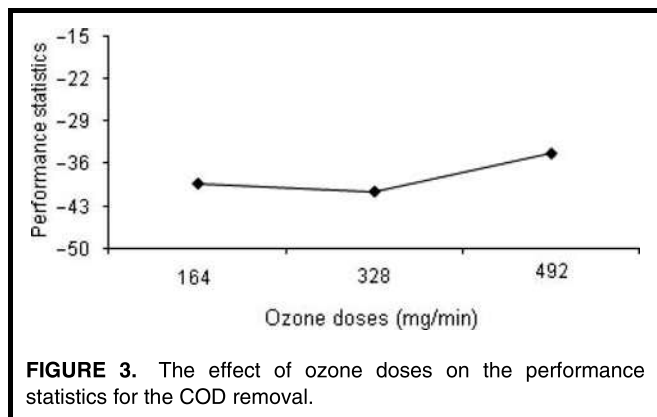
HCO_3^- ions in the $\text{O}_3/\text{HCO}_3^-$ process were used to scavenge the OH^\bullet radicals occurring during ozonation. It is likely that bicarbonate is the principal consumer of the hydroxyl radicals, particularly as relatively high concentrations of bicarbonate are present in water. The scavenging 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 have a much lower reaction rate constant than hydroxyl radicals for the oxidation of organic micro pollutants. It has been reported that bicarbonate ions scavenge hydroxyl radicals to produce intermediates which do not release a radical-type chain carrier, thereby quenching the radical-type chain reaction (Hoigné 1998).

Figure 2 shows that the removal of COD has increased with decreasing temperature ranges. Ozone solubility in solution decrease with the increasing solution temperature. Because of that, the COD removal performance statistics increased with decrease of temperature levels. The temperature of 18 °C was defined as the best level for the COD removal process. The change of performance statistics values with increasing the temperature can be seen in Figure 2.

As can be seen in Figure 3, the COD removal performance statistic values for the ozone doses of 164 and 328 mg O_3/min were almost fixed, although they increased with the increase of the ozone doses from 328 to 492 mg O_3/min . From Figure 3, the most effective level of ozone dose in the COD removal was defined as 492 mg O_3/min .

Figure 4 shows the change of the initial dye concentrations respectively (from 200 to 600 ppm) according to the performance statistics values. The performance statistics value was high at the level of 200 ppm, and it then decreased with the increase of the dye concentration.





As can be seen in Figure 5, the COD removal performance statistics value increased with the increase of the PAC dosage level from 0 to 1 g, although it decreased from 1 to 1.5 g. In the present integrated process, it was thought that PAC particles could play an important role as adsorbent for intermediates of ozonized dye molecules. The PAC used to remove COD from synthetic dye solutions has a positive effect on the treatment of the ozonized synthetic dye solutions. For the PAC, the performance statistics value was maximal at the level of 1 g, which was defined as the optimum level. As is known, the ozone dissolved in the solution is consumed by PAC dosage. Two mechanisms are involved in the oxidation of carbon black by ozone: (i) direct oxidation of elemental carbon to CO_2 and (ii) oxidation of elemental carbon to intermediates that are soluble

in alkaline solutions are subsequently oxidized to CO_2 (Deitz and Bitner 1972a,b).

Because of these mechanisms, it was thought that the PAC particles at the level of 1.5 g, which were too abundant in the solution partly prevented ozone molecules from reacting with the dye molecules. The excessive PAC particles reduced the dissolved ozone concentration, the formation of more polar groups (which are able to be adsorbed easily on the surface of the PAC particles because of polarization) and the synergic effect among the dye, ozone and PAC in the solution. Because of these reasons, the PAC level of 1 g was determined as the optimum level as seen from Figure 5.

Kuo studied the interference of hydrogen peroxide on the COD test. They proposed Equation [9] for calculating the COD value. The correlation coefficient (R) is used to represent the degree of fit with R^2 1 in the regression analysis (Kuo 1992).

$$\text{COD}_{\text{H}_2\text{O}_2} (\text{mg/L}) = 0.4706 [\text{H}_2\text{O}_2] - 4.06 \times 10^{-5} [\text{H}_2\text{O}_2]^2 \quad [9]$$

A theoretical COD value of 1000 mg/L hydrogen peroxide according to the reaction given in Equation [9] is 470.6 mg/L. Therefore, 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 0.028 and 0.056 mM, respectively. In this article, Equation [9] was used to define values of COD that arose from H_2O_2 , and the values of interference were subtracted from the total COD values. In this way, the real COD values were obtained.

Hydrogen peroxide may react either directly or after it is first ionized or dissociated into free radicals. The reaction mechanism of hydrogen peroxide is very complex and may be affected by the reaction conditions and the type of the catalyst. The stability of hydrogen peroxide solutions depends on many factors, including concentration, temperature, pH, the concentration of stabilizer, and the presence of contaminants. In general, ozone oxidation pathways include direct oxidation by ozone or radical oxidation by OH^\bullet radical. The radical oxidation is less selective and predominates under basic conditions, while direct oxidation is more selective and predominates under acidic conditions.

The COD removal performance statistics values partly increased at the level of 0 mM, although it seldom decreased at the level of 0.028 and 0.056 mM. It was thought that the COD removal at the level of 0 mM occurred due to ozonation mechanism and H^+ ions and these two factors partly increased the performance statistics value when compared with OH^\bullet radicals, even if it was low. The COD removal at levels of 0.028 and 0.056 mM was realized by ozonation and (OH^\bullet) radical mechanisms. It was thought that OH^\bullet radicals in the $\text{O}_3/\text{H}_2\text{O}_2$ process transformed the dye molecules into much more intermediates; these intermediates partly caused the increase in the COD values. In other words, the performance statistics values for H_2O_2 were almost identical to each other.

The structure of Bomaplex Red CR-L dye of 1000 ppm in the both acidic and basic conditions was explained as a function of pH values without the ozonation. The structure of the dye changed at acidic pH values (pH 1–4) because of the decrease of the initial dye and COD concentrations with the decrease of the pH values as seen from Figure 6. It was thought that H^+ ions at the lower pH values reacted with the double bonds on the structure of the dye and the dye and COD concentrations decreased with the decrease of pH value.

Figure 7 shows the change of the treatment times respectively (from 10 to 30 min) according to performance statistics values. The performance statistics value was high at the level of 10 min. This treatment time was sufficient to remove COD from synthetic dye solutions, as seen in Figure 7. The performance statistics value at the time of 10 min received a maximum value which was an important parameter economically.

The selection of the optimum reaction conditions for the removal of COD from synthetic dye solutions was done according to the conditions in which the removal of maximum COD with minimum cost was an important criterion. The optimum process conditions for the removal of COD were

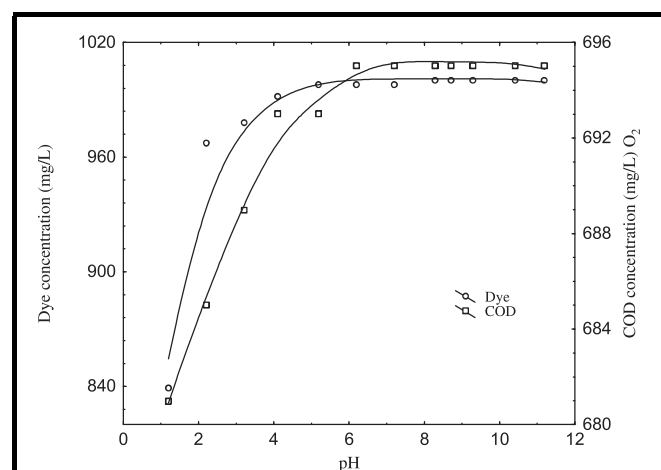


FIGURE 6. Effect of pH on the initial dye and COD concentration of the solution without ozonation (C_0 : 1000 ppm, T : 18 °C, agitation rate: 5 rps).

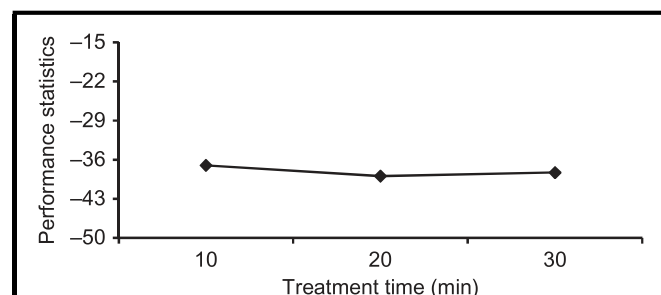


FIGURE 7. The effect of treatment time on the performance statistics for the COD removal.

TABLE 3. Observed Optimum Working Conditions and Predicted Values for the COD Removal

Parameters	Optimum working conditions	
	Value	Level
A HCO_3^- (mM)	39	2
B Temperature (°C)	18	1
C Ozon dose (mg/min)	492	3
D Dye concentration (ppm)	200	1
E PAC dosage (g)	1	2
F H_2O_2 (mM)	0	1
G pH	12	3
H Treatment time (min)	10	1
Predicted COD concentration (ppm) O_2	0	
Predicted confidence interval	0.00–30.56	
Observed COD concentration (ppm) O_2	2	

determined as HCO_3^- (39 mM); temperature (18 °C); ozone dose (492 mg/min); dye concentration (200 ppm); PAC (1 g); H_2O_2 (0 mM); pH (12); and time (10 min). The effectiveness of each parameter on optimization criteria and the selected optimum reaction conditions are shown in Table 3.

In order to test the predicted results, confirmation experiments were carried out twice in the same working conditions. The fact that the COD removal from confirmation experiments is within the calculated confidence intervals (see Table 3) shows that experimental results are within $\pm 5\%$ in error. This case states that there is a good agreement between the predicted values and experimental data, and the interactive effects of parameters other than HCO_3^- and temperature are indeed negligible. It may be concluded that the additive model is adequate for describing the removal of COD from synthetic dye solutions by the various operational parameters.

Studies of Zeta Potential and FTIR

From Figure 8, the zeta potential values of the PAC at pH (4, 10, and 12) in the distilled water were different from these of the contaminated PAC. The change of the zeta potential values of the PAC in the ozonized dye solution shows the removal of the ozonized dye molecules from the synthetic dye solutions. It was thought that the intermediates of ozonized dye molecules in the solution were electrostatically attracted by PAC and adsorbed on the surface of the PAC particles then the zeta potential values of the PAC particles changed. H^+ ions in the solution caused a positively increase of the zeta potential values of the PAC, while OH^- ions caused a negatively increase of the zeta potential values of the PAC particles. The change in the zeta potential values of the PAC particles was a sign of adsorption of the intermediates of ozonized dye molecules from aqueous solutions.

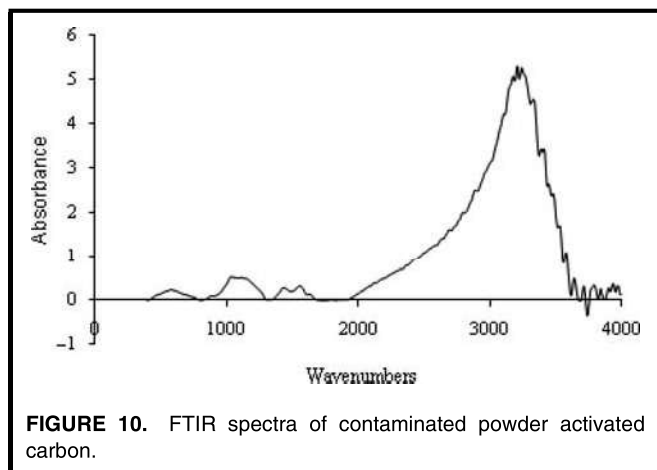
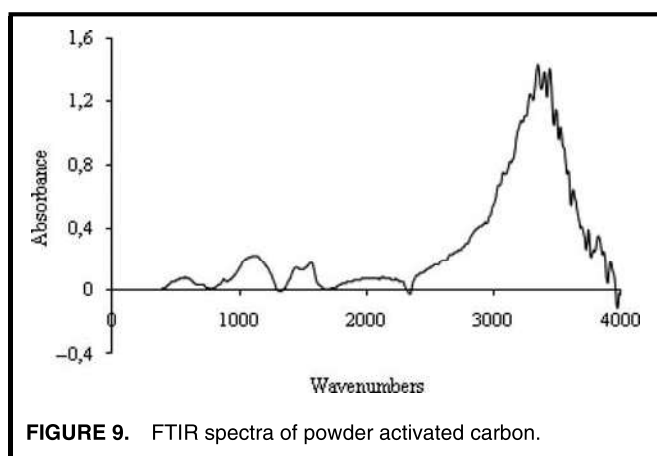
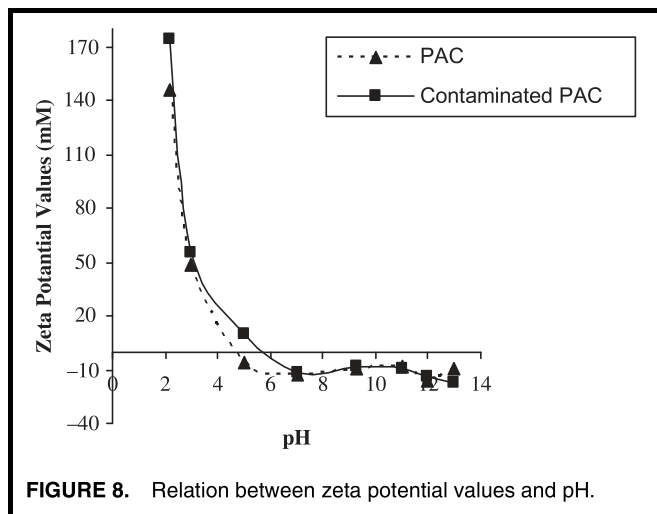


Figure 9 shows FTIR spectra of the powder activated carbon that has different functional groups. The functional groups onto the PAC have specific value of absorbance at different wavenumbers as seen in Figure 9.

According to the FTIR spectra in Figure 10, it was thought that there was an electrostatic (Columbic) attraction between

intermediates and the PAC particles. This interaction between ozonized dye molecules and the PAC particles modified the absorbance spectra of the PAC. Therefore, a considerable shifting of peaks was observed from 500 to 4000 wavenumbers as seen in Figure 10 and the absorption spectra of functional groups onto the PAC changed.

CONCLUSIONS

The major conclusions derived from the present study in which all of the parameters were used together in the semi-batch reactor are: According to performance statistics values, the most important parameter affecting the COD removal from the synthetic dye solutions was PAC. The COD removal performance statistics value increased with increasing PAC dosage and received maximum value at the level of 1 g. The increase of parameter levels such as PAC dosage, ozone dose, pH, and HCO_3^- positively affected the removal of the COD and performance statistics values. However, the increase of parameter levels such as H_2O_2 , reaction temperature, treatment time and dye concentration negatively affected on the performance statistics. As examined in Table 3, it is seen that the predicted and observed COD values are close to each other and between the predicted confidence intervals (0.00–30.56), so it was concluded that the Taguchi method applied for the removal of COD from synthetic dye solutions was the most successful.

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