

Removal of colour and COD from synthetic textile wastewaters using O_3 , PAC, H_2O_2 and HCO_3^-

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Received 24 December 2006; received in revised form 12 June 2007; accepted 13 June 2007

Available online 19 June 2007

Abstract

This study aimed to investigate removal of colour and chemical oxygen demand (COD) from synthetic textile wastewaters using O_3 , powder activated carbon (PAC), H_2O_2 and HCO_3^- in a semi-batch reactor. 1:2 metal complex dyestuffs containing two molecules of dyestuffs versus a chromium atom was used. Experiments were conducted under the various pHs (3–12), temperatures (18–70 °C), ozone doses (164–493 mg min⁻¹). The combined effect of substances used on the removal of colour and COD was investigated. The mechanisms of colour and COD removal on the PAC were explained on the basis of the results of Fourier transform infrared spectroscopy (FTIR). In addition, the zeta potential values of PAC, ozonated PAC and ozonated PAC contaminated with intermediates were determined. The zeta potential values and FTIR plots of PAC particulates showed that PAC acted as an adsorbent in the combined processes. It was thought that all of the substances used in the semi-batch reactor had the combined effect on the removal of colour and COD because of the short treatment time of 5 min and high efficiencies of the removal of colour and COD. The efficiencies of removal of colour and COD in combination were compared with adsorption and ozonation only. In this study, the efficiencies of colour and COD removal during a reaction time of 30 min were obtained as 99 and 95%, respectively. At the result of this study, it was concluded that O_3 , PAC and H_2O_2 were an important substances for the removal of colour and COD from synthetic textile wastewater when they were used in combination. © 2007 Published by Elsevier B.V.

Keywords: Ozonation; Oxidation; Combined processes; PAC; Textile wastewater

1. Introduction

Theoretically, ozone is able to oxidize inorganic and organic to their highest oxidation states, depending on the molecular selectivity and decay rates [1]. The decomposition rate of ozone is affected by pH and temperature. Ozone decomposition is also affected by the presence of inorganic/organic species in the reaction medium. Ozone reacts with organic compounds dissolved in water through either direct ozone attack or indirect free radical attack. The hydroxyl radicals are generated by ozone decomposition in aqueous solutions and especially catalyzed by hydroxide ions [2].

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 decomposition of ozone catalyzed by hydroperoxide (HO_2^-) generating hydroxyl radicals presents in details [3].

HCO_3^- ions in the O_3/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 ($HCO_3^{\bullet-}$). 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. 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 [4].

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 ppm. Higher concentrations may be encountered in

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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 $8.5 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$ [5].

The predominance of the oxidation reactions by molecular ozone at a lower pH has already been established, while beyond some critical pH level, hydroxyl radicals might become the predominant oxidizing species. The critical pH is expected to differ for different chemical composition in the aqueous phase [6]. During the ozonation process, dyes lose their colour by the oxidative cleavage of the chromophores. The cleavage of carbon–carbon double bonds and other functional groups, which have high electron densities, will shift the absorption spectra of the molecule out of the visible region [7].

Different types of dyes are used in many industries such as textile, paint, ink, plastics and cosmetics. A certain amount of them are lost in the process of their manufacturing and utilization and often cause environmental problems. Considerable amount of high quality water is needed for textile industry for dyeing and finishing operations [8–12]. Colour and recalcitrant compounds are among the vital environmental concerns in effluent treatment. Wastewaters from the textile industry are characterized by their intense colour, high organic pollution load and extreme variable and recalcitrant nature. 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 resulting effluent is still high in colour and violates the discharge limits imposed by legislation [8–12].

One of the main problems in the treatment of textile dyeing wastewater and dye manufacture wastewater is the removal of dye colour [13]. In the late 1950s, the trickling filter and activated sludge processes were shown to be capable of removing between 84 and 93% of the colour in textile effluents [14]. However, the colour of wastewater from today's new dyes is much more difficult to treat by physical techniques such as adsorption and chemical coagulation to achieve complete decolourization, especially for highly soluble dyes. Apart from the physical methods of decolourization, chemical oxidation using oxidants such as ozone, chlorine or hypochlorite, hydrogen peroxide and potassium permanganate can be used to destroy the dye to a colourless solution; the breakdown products can be removed by conventional biological treatment processes. The various studies concerned with 1:2 metal complex dyestuffs containing two molecules of dyestuffs versus a chromium atom were conducted and given in literature [15–18].

The main objective of this work was to investigate removal of colour and COD from 1:2 metal complex dyestuffs containing two molecules of dyestuffs versus a chromium atom using O_3 , powder activated carbon (PAC), H_2O_2 and HCO_3^- in combination in a semi-batch reactor and to compare the efficiencies of colour and COD removal with each others. Semi-batch ozonation experiments were realized under the different reac-

tion conditions using HCO_3^- , H_2O_2 , ozone doses and PAC at the different pHs (3–13) and temperatures (18–70 °C). The concentrations of the 1:2 metal complex dyestuffs were analyzed as a function of colour at specified time intervals. High colour removal efficiency increased with destruction of conjugated double bonds that can be broken by ozone (directly or indirectly). However, the reaction intermediates formed during ozonation were not examined. This work focuses on the removal of colour and COD from synthetic textile wastewater under the combined processes. At the result of an oxidation time of 30 min, the efficiencies of colour and COD removal were over 99 and 95%, respectively.

2. Material and method

In this study, the reason of that 1:2 metal complex dyestuffs containing two molecules of dyestuffs versus a chromium atom was selected as research base is that the treatment of wastewaters of 1:2 metal complex dyestuffs used in a textile mill located in Türkiye. Dyestuffs concentration was selected at high doses because of that the ozone concentrations produced in the ozone generator were too high to follow decolourization kinetic at low dye concentrations.

The dyestuffs used in the present work which is one of the group of metal complex dyestuffs is water soluble having the structure. 1:2 metal complex dyestuffs do not include ionizing substituents, but all of the dyestuffs are in anion. These substituents are in salt of Na^+ . The complex is broken under the values of lower pHs. The solubility of dyestuffs is proved by groups such as sulfonamides ($-\text{SO}_2-\text{NH}_2$), methyl sulfonamides ($-\text{SO}_2-\text{NH}-\text{CH}_3$) and methyl sulfonyl ($-\text{SO}_2-\text{CH}_3$) which are non-ionic groups.

1:2 metal complex dyestuffs containing two molecules of dyestuffs versus a chromium atom was ensured from a textile mill located in Türkiye. Solutions of dyestuffs were prepared with distilled water in concentrations of 1000 ppm. It was defined that 1:2 metal complex dyestuffs gave a peak at 505 nm using spectrophotometry (UV Spectrophotometer, Shimadzu 160A) as a function of colour. All the samples were analyzed at 505 nm [15–18].

The experimental set-up was given in previous studies [15–16,18] and consisted of an air dryer, compressor, ozone generator and semi-batch reactor. The air dryer consisted of a column which was filled with a high adsorptive anhydrous CaCl_2 . Ozone was generated using an ozonizator 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 1 L cylindrical semi-batch 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. Dyestuffs solution of 250 mL was used during each batch ozonation.

Ozone was generated from air, and ozone–air mixture was supplied into the system through an Opal OG-24 model ozonizator at doses of 164, 328 and 493 mg min^{-1} per initial COD

of solution. The dyestuffs were ozonated for 30 min in the semi-batch reactor. The ozone–air mixture percentages (0.7, 1.1 and 1.4% O₃) were continuously sparged through a diffuser [15,16,18].

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. PAC of 0.1–0.2 g was put into a sample cell. The area of pick was obtained after adsorption, desorption and calibration process. Bet surface area of PAC was calculated substituting the area of pick into Eq. (1) [19]. The surface area of the PAC, ozonated PAC and PAC contaminated with intermediates was defined as 455, 498 and 319 m²/g, respectively.

$$S = \left(1 - \frac{P}{P_0}\right) \left(\frac{A}{A_c}\right) \frac{V_c N A_{cs} P_a}{RTW} \quad (1)$$

P is the partial pressure of adsorbate, P_0 the saturated pressure of adsorbate, N the Avogadro's number: 6.02×10^{23} , R the gas constant ($82.1 \text{ cm}^3 \text{ atm K}^{-1} \text{ mol}^{-1}$), V_c the calibration volume, P_a the ambient pressure (atm), A the signal area, A_c the area of calibration, A_{cs} the cross-sectional area of adsorbate molecule (m²), T the temperature of calibration volume (ambient temperature) (K), W the sample weight, and S is the surface area per gram sample (m²/g).

The measurement of COD was based on the “closed reflux, colorimetric method” described in Section 508 B.4. of Ref. [20]. 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 (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 pre-heated to 150 °C for 2 h. After cooling the samples were analyzed 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 O₂/mg.

3. Results and discussion

In this study, the COD values derived from H₂O₂ during the ozonation studies were subtracted from total COD values. Eq. (2) was used to define the values of COD arised from H₂O₂ [21]. In this way, the real COD values were obtained.

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

The reason of that every experiment was conducted at different experimental conditions is that the best conditions relating to substances are investigated, and the efficiencies of optimum

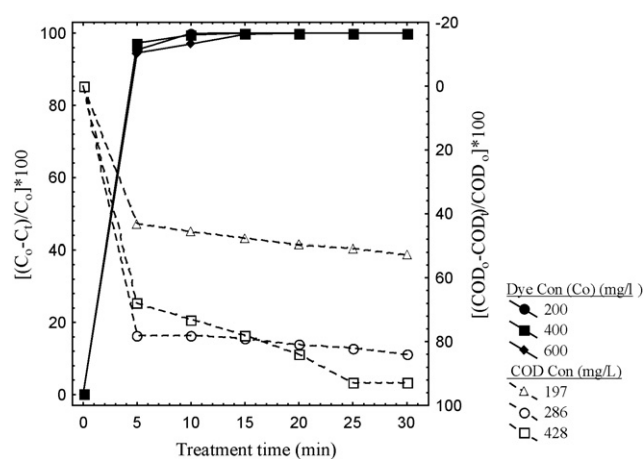


Fig. 1. The colour and COD removal efficiencies for ozonation, H₂O₂ and PAC. (●, △) [C₀: 200 ppm, COD₀: 197 ppm, HCO₃⁻: 0 mM, T: 18 °C, Q: 164 mg min⁻¹, pH 13, PAC: 0 ppm, H₂O₂: 0 mM]; (■, ○) [C₀: 400 ppm, COD₀: 286 ppm, HCO₃⁻: 0 mM, T: 18 °C, Q: 328 mg min⁻¹, pH 9.3, PAC: 4000 ppm, H₂O₂: 14 mM]; (◆, □) [C₀: 600 ppm, COD₀: 428 ppm, HCO₃⁻: 0 mM, T: 18 °C, Q: 493 mg min⁻¹, pH 3, PAC: 6000 ppm, H₂O₂: 28 mM].

colour and COD removal are obtained. At different empirical conditions, the effect of substances used in combination on the removal of colour and COD from synthetic textile wastewater were shown in Fig. 1. The efficiencies of colour removal have hardly changed with the increase of initial dyestuffs concentrations. Ozone doses used per initial COD for experiments of (●, △), (■, ○) and (◆, □) were 0.834, 1.140 and 1.151 mg O₃/(min mg COD), respectively. At the result of a reaction time of 30 min, at the various initial dye concentrations of 200, 400 and 600 ppm, the efficiencies of colour removal was averagely 99%. A reaction time of 5 min was enough to remove the colour of 99%. As seen from Fig. 1 at the result of a reaction time of 30 min and ozone dose of 164.4 mg min⁻¹, the efficiency of COD removal by ozonation alone was 50%, but the efficiencies of COD removal increased with the usage of the PAC, and for experiments of (●, △) and (◆, □), they were obtained as 85 and 95%, respectively. It was thought that electrostatic attraction forces between the intermediates of ozoned dye molecules and PAC particles were bigger than pushing forces and the more intermediates were adsorbed on the surface of the PAC.

The effect of substances used in combination on the removal of the colour from synthetic textile wastewater at the various empirical conditions in which every parameter was changed, respectively, was shown in Fig. 2. Ozone doses per initial COD used for experiments of (●, △), (■, ○) and (◆, □) were 0.834, 1.140 and 1.151 mg O₃/(min mg COD), respectively. At a reaction time of 5 min, the efficiencies of colour removal for experiments of (●, △), (■, ○) and (◆, □) were 100, 100 and 70%, respectively. Because of the combined effect, at a reaction time of 5 min, the colour and COD removal efficiencies in experiments of [(●, △), (■, ○)] in Fig. 2 increased with the usage of the PAC, but the removal of COD decreased in experiment of (◆, □) in Fig. 2 because of not usage of the PAC. At the studies of combination, because the dyestuffs is broken under the values of the low pHs, as if the effect of H₂O₂ on the removal of colour and COD is seen little as seen from Fig. 2, but the effect of OH⁻

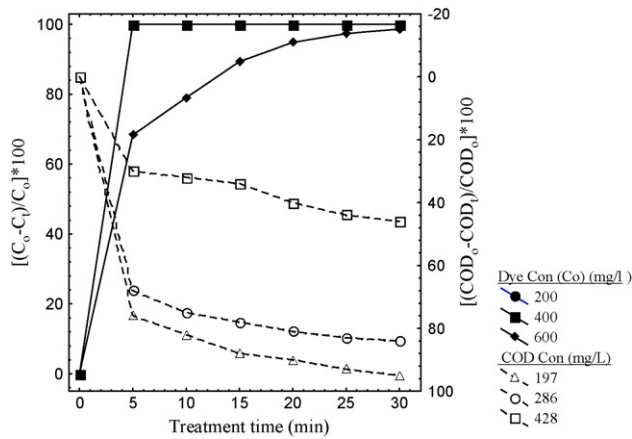


Fig. 2. The colour and COD removal efficiencies for ozonation, H_2O_2 and PAC. (●, △) [C_0 : 200 ppm, COD_0 : 197 ppm, HCO_3^- : 0 mM, T : 18 °C, Q : 164 mg min^{-1} , pH 13, PAC: 6000 ppm, H_2O_2 : 14 mM]; (■, ○) [C_0 : 400 ppm, COD_0 : 286 ppm, HCO_3^- : 0 mM, T : 40 °C, Q : 328 mg min^{-1} , pH 3, PAC: 4000 ppm, H_2O_2 : 28 mM]; (◆, □) [C_0 : 600 ppm, COD_0 : 428 ppm, HCO_3^- : 0 mM, T : 40 °C, Q : 493 mg min^{-1} , pH 9.3, PAC: 0 ppm, H_2O_2 : 0 mM].

radicals on the colour and COD removal from synthetic textile wastewater is most important. The reason of that the decrease of efficiencies of the colour and COD removal in Fig. 2 is that PAC and H_2O_2 were not used in experiment of (◆, □). At the result of a reaction time of 30 min, for the experiments of (◆, □), (■, ○) and (●, △), the COD removal efficiencies in Fig. 2 were 50, 85 and 95%, respectively.

The effect of adsorbent dosage on the efficiency of colour removal from the solution of 1000 ppm by adsorption alone was investigated and shown in Fig. 3. Adsorbent dosages were been varied from 1 to 4 g in the solutions of 250 mL. The colour content in the equilibrium decreased with the increase of adsorbent dosage. At the result of a reaction time of 30 min and the initial dyestuffs concentration of 1000 ppm, the PAC dosage used in the adsorption to obtain an efficiency of 99% was obtained as 4 g in the solution of 250 mL. The PAC dosage used in the adsorption to obtain an efficiency of 99% was four times more than that in

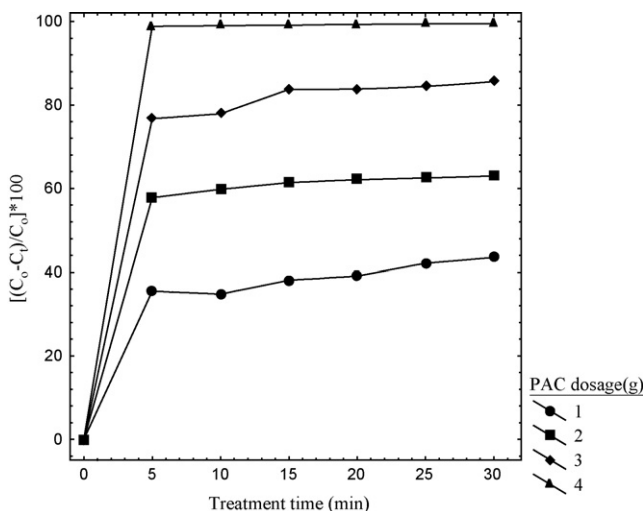


Fig. 3. The adsorption of dyestuffs on the PAC (C_0 : 1000 ppm, agitation rate: 150 rpm, T : 20 °C, pH 9.3).

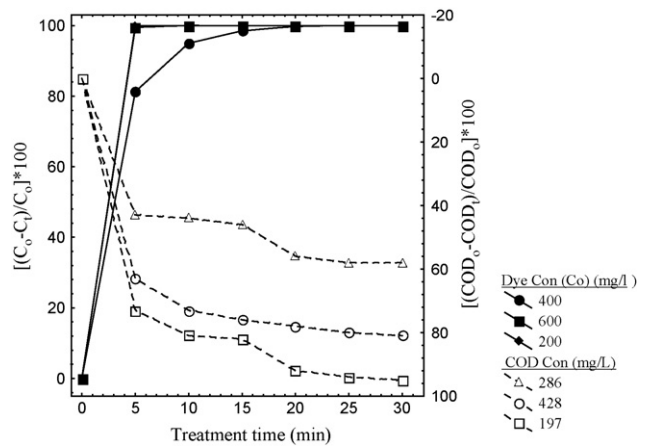


Fig. 4. The colour and COD removal efficiencies using the combined substances at various ozone, H_2O_2 and PAC doses. (●, △) [C_0 : 400 ppm, COD_0 : 286 ppm, HCO_3^- : 0 mM, T : 70 °C, Q : 164 mg min^{-1} , pH 9.3, PAC: 0 ppm, H_2O_2 : 28 mM]; (■, ○) [C_0 : 600 ppm, COD_0 : 428 ppm, HCO_3^- : 0 mM, T : 70 °C, Q : 328 mg min^{-1} , pH 13, PAC: 4000 ppm, H_2O_2 : 0 mM]; (◆, □) [C_0 : 200 ppm, COD_0 : 197 ppm, HCO_3^- : 0 mM, T : 70 °C, Q : 493 mg min^{-1} , pH 3, PAC: 6000 ppm, H_2O_2 : 14 mM].

the combined ozonation processes when the PAC dosage used in the adsorption processes was compared with the combined processes. Because of this ratio, the advantage of the combined processes on the adsorption alone is considerably important as compared with each other. At the combined processes, it was thought that the dyestuffs degraded by ozone and hydroxyl radicals converted into the more easily adsorbable intermediates which were more easily adsorbed on the sites of the PAC.

As seen Fig. 4, at the result of a reaction time of 5 min, for experiments of [(●), (■), (◆)], the colour removal efficiencies at the various initial dyestuffs concentrations of 400, 600 and 200 ppm were averagely 80, 99 and 99%, respectively. A reaction time of 5 min was enough to remove a colour of 99% when substances were used in combination. As seen Fig. 4, at the result of a reaction time of 5 min, the efficiencies of colour and COD removal by the experiments of [(■), (◆)] were bigger than that in the experiment of (●), the reason of them is that H_2O_2 and PAC are used in the experiments of [(■), (◆)], but the decrease in the efficiencies of removal of colour and COD by the experiment of (●) arise from the usage of H_2O_2 only. The efficiencies of colour and COD removal increased by the usage of the PAC with ozone and H_2O_2 as compared with the usage of ozone only. In Fig. 4, because of a combined effect among parameters such as O_3 , H_2O_2 and PAC, the efficiencies of the colour removal by experiments of [(■), (◆)] did not change with increasing of the initial dyestuffs concentration. As seen Fig. 4, the efficiency of COD removal from synthetic wastewater increased with the usage of the PAC and H_2O_2 and it was obtained as 96%. It is likely that the observed interaction among substances such as H_2O_2 , O_3 , pH and PAC affected on the efficiencies of colour and COD removal.

At the various empirical conditions, the advantage of combined processes on the ozonation alone was shown in Fig. 5 which shows the efficiencies of COD removal by the combined processes and ozonation only, respectively. The initial

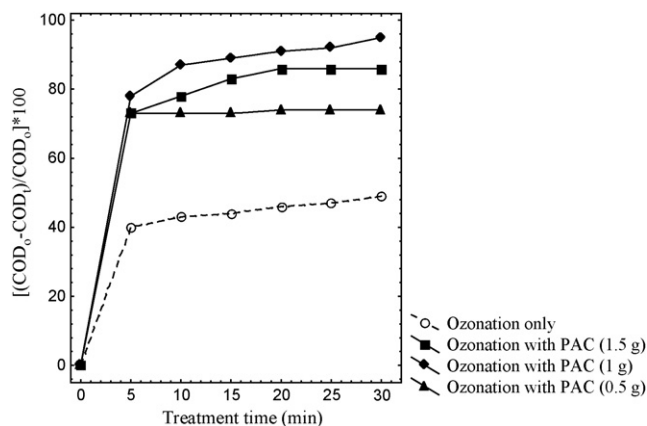


Fig. 5. The efficiencies of COD removal by ozonation only and ozonation with PAC (C_0 : 1000 ppm, COD_0 : 631 ppm, O_2 : 18°C , pH 9.7, O_3 : 5 L min^{-1}).

PAC dosages used in the combined processes changed from 0.5 to 1.5 g during ozonation. Ozone dose in the combined processes and ozonation only was 164 mg min^{-1} . The efficiencies of COD removal by the combined processes were highest as compared with ozonation only. The efficiency of COD removal increased with the increase of the PAC dosage from 0.5 to 1 g in the combined processes while it decreased with increase of PAC dosage from 1 to 1.5 g in the combined processes. It was thought that the increase of PAC dosage in the combined processes caused to be spent of ozone dissolved in the solution by the PAC particles, and in this way the efficiency of the COD removal decreased. At the result of a reaction time of 30 min, as seen Fig. 5, the efficiency of the COD removal by the combined process and ozonation only were 96 and 51%, respectively. Thus, the optimum PAC dose was decided to be 4 g/L and it was thought that the dyestuffs being degraded by ozonation in the solution converted into the most intermediates which were easily adsorbed on the PAC electrostatically. The plots concerned with the combined processes clearly indicate that the colour removal of 99% by ozonation alone required longer treatment time than that of the combined processes. Whereas the removal of colour and COD by combined processes was more short term and effective than that of ozonation and adsorption only.

At the various empirical conditions, the effect of the combined processes on the removal of colour from synthetic textile wastewater was also shown in Fig. 6. At a reaction time of 5 min, the efficiencies of colour and COD removal by the combined processes for empirical conditions of [(\blacklozenge , \square), (\bullet , Δ), (\blacksquare , \circ)] in Fig. 6 were (100, 96 and 64%) and (80, 88 and 52%), respectively. At the result of a reaction time of 5 min, for experimental condition of (\blacksquare) as seen Fig. 6, the efficiency of colour removal by combined ozonation process decreased with the increasing of HCO_3^- ions which scavenged OH^\bullet radicals and was approximately 64%. When the Fig. 6 was examined, the O_3 , H_2O_2 and PAC dosages used in the different empirical conditions were thought to be the more effective parameter for the removal of colour. As seen from Fig. 6, the removal of COD increased with the use of PAC in the combined processes. The PAC used in the combined processes positively affected on the removal of colour and COD from the synthetic textile wastewater.

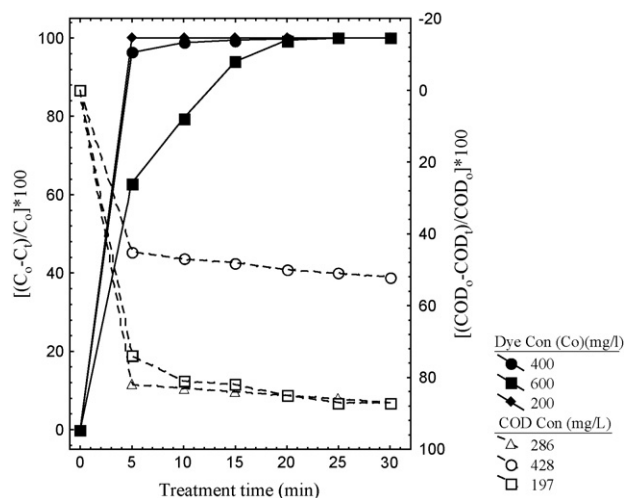


Fig. 6. The colour and COD removal efficiencies for ozonation, H_2O_2 and PAC. (\bullet , Δ) [C_0 : 400 ppm, COD_0 : 286 ppm, HCO_3^- : 28 mM, T : 18°C , Q : 164 mg min^{-1} , pH 9.3, PAC: 6000 ppm, H_2O_2 : 14 mM]; (\blacksquare , \circ) [C_0 : 600 ppm, COD_0 : 428 ppm, HCO_3^- : 28 mM, T : 18°C , Q : 324 mg min^{-1} , pH 13, PAC: 0 ppm, H_2O_2 : 28 mM]; (\blacklozenge , \square) [C_0 : 200 ppm, COD_0 : 197 ppm, HCO_3^- : 28 mM, T : 18°C , Q : 493 mg min^{-1} , pH 3, PAC: 4000 ppm, H_2O_2 : 0 mM].

Fig. 7 shows the efficiencies of colour and COD removal from synthetic solutions by ozonation only, ozonation with HCO_3^- and H_2O_2 processes, respectively. At the result of a reaction time of 5 min, the efficiencies of the colour removal by ozonation only, ozonation with HCO_3^- and H_2O_2 processes were obtained as 80, 78 and 84%, respectively. As seen from Fig. 7, the most effective process in the removal of colour was ozonation with H_2O_2 process in which hydroxyl radicals have a potential of 2.8 V increased the degradation of dyestuffs, the ozonation with HCO_3^- process decreased the removal of COD in which it was thought that HCO_3^- ions scavenged hydroxyl radicals and prevented formation the smaller intermediates, and in this way the efficiency of COD removal decreased. As seen from Fig. 7, in ozonation only at pH 9.7, it was thought that both ozoned and hydroxyl mechanisms were effective.

As seen Fig. 8, at the result of a reaction time of 5 min, for experiments of [(\bullet , Δ), (\blacksquare , \circ), (\blacklozenge , \square)], the colour and COD

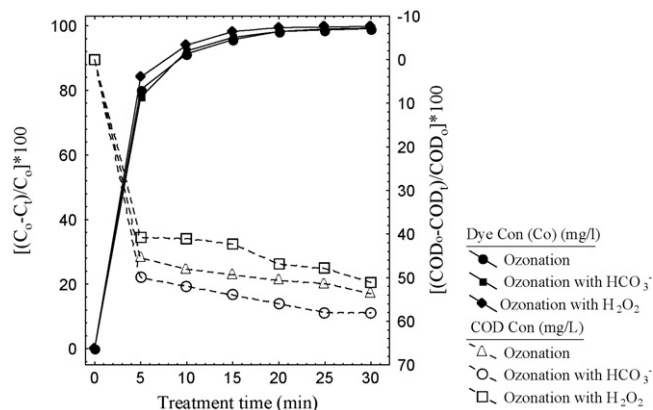


Fig. 7. The efficiencies of colour and COD removal by ozonation alone, ozonation Q_3 with HCO_3^- and ozonation with H_2O_2 (C_0 : 1000 ppm, COD_0 : 631 ppm, O_2 , H_2O_2 : 28 mM, HCO_3^- : 14 mM, ozone flow rate: 5 L min^{-1} , pH 9.3, T : 20°C).

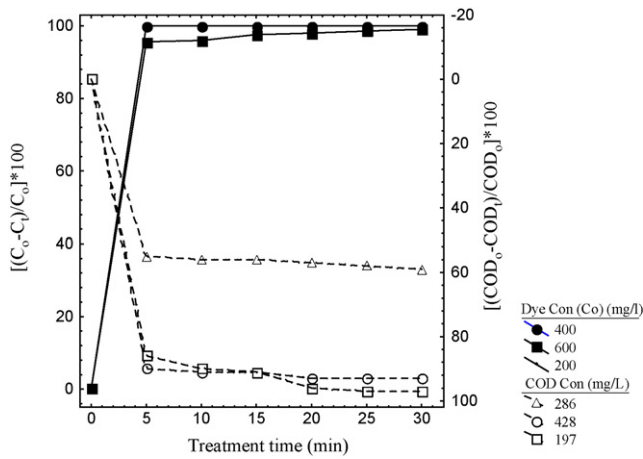
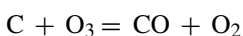
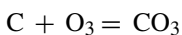


Fig. 8. The colour and COD removal efficiencies using the combined substances at various empirical conditions. (●, △) [C_0 : 400 ppm, COD_0 : 285 ppm, HCO_3^- : 28 mM, T : 40 °C, Q : 164 mg min⁻¹, pH 13, PAC: 0 ppm, H_2O_2 : 0 mM]; (■, ○) [C_0 : 600 ppm, COD_0 : 428 ppm, HCO_3^- : 28 mM, T : 40 °C, Q : 324 mg min⁻¹, pH 3, PAC: 6000 ppm, H_2O_2 : 14 mM]; (◆, □) [C_0 : 200 ppm, COD_0 : 197 ppm, HCO_3^- : 28 mM, T : 40 °C, Q : 498 mg min⁻¹, pH 3, PAC: 4000 ppm, H_2O_2 : 28 mM].

removal efficiencies at the various initial dyestuffs and COD contents of (400, 600 and 200 ppm) and (286, 428 and 197 ppm O_2) were averagely (99, 96 and 99%) and (56, 88 and 86%), respectively. A reaction time of 5 min was enough to remove a colour of 99% when substances were used in combination. As seen in Fig. 8, at the result of a reaction time of 5 min, the efficiencies of COD removal increased by the usage of PAC with ozone and H_2O_2 as compared with ozonation only. Because of a combined effect among substances such as O_3 , H_2O_2 and PAC, the efficiencies of the COD removal by experiments of [(■, ○), (◆, □)] in Fig. 8 scarcely changed with increasing of the initial COD content. As seen in Fig. 8, the efficiency of COD removal from synthetic wastewater increased with the usage of the PAC. It is likely that the interaction among substances such as H_2O_2 , O_3 , pH and PAC affected on the efficiencies of colour and COD removal.

Ozonation can modify the surface property of an activated carbon such as specific surface area, pore volume and functional group [22]. 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. 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 and are subsequently oxidized to CO_2 . Deitz and Bitner [23,24] showed that a large amount of ozone was adsorbed on the graphite surface, C, with the formation of ozonated surface complexes such as CO_3 and CO [22–24]:



In this study, the surface areas of the PAC, ozonated PAC and ozonated PAC particles contaminated with intermediates particles were defined as 455, 498 and 319 m²/g, respectively At

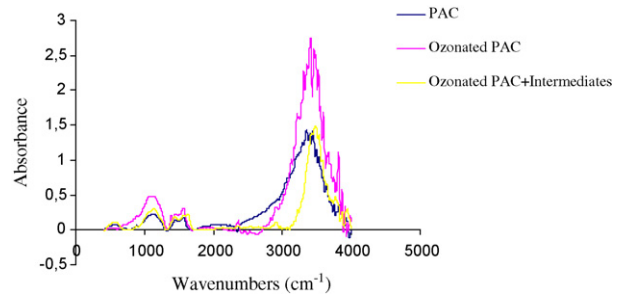


Fig. 9. FTIR spectra of the PAC, ozonated PAC and ozonated PAC contaminated with intermediates.

the result of ozonation, the surface area of the PAC particles increased from 455 to 498 m²/g.

In the combined study, at the result of adsorption of intermediates on the surface of ozonated PAC, the surface area of ozonated PAC decreased from 498 to 319 m²/g. This decreasing in the surface area of ozonated PAC particles shows the accumulation of the intermediates on the ozonated PAC.

Fig. 9 shows FTIR spectra of PAC, ozonated PAC and ozonated PAC contaminated with intermediates of different functional groups. After the PAC was ozonated, FTIR spectra of PAC shifted and the surface area of ozonated PAC increased. As seen from Fig. 9, the intermediates of dyestuffs adsorbed on the ozonated PAC after the combined process considerably shifted FTIR spectra of the ozonated PAC from 500 to 4000 wavenumbers (cm⁻¹). It shows that the intermediates of dyestuffs adsorbed on the ozonated PAC modified the peaks of functional groups on the ozonated PAC. According to the FTIR spectra, the PAC particles acted as adsorbent and there was an electrostatic (columbic) attraction between the intermediates and ozonated PAC particles. This interaction between intermediates and PAC particles fairly modified the FTIR spectra of ozonated PAC.

From Fig. 10, at pHs (2–13), the zeta potential values of the ozonated PAC in the distilled water were different from these of ozonated PAC contaminated with intermediates. The change of zeta potential values of the ozonated PAC in the ozonated dye solution shows the removal of the ozonated dye molecules from the synthetic textile wastewater. It was thought that the

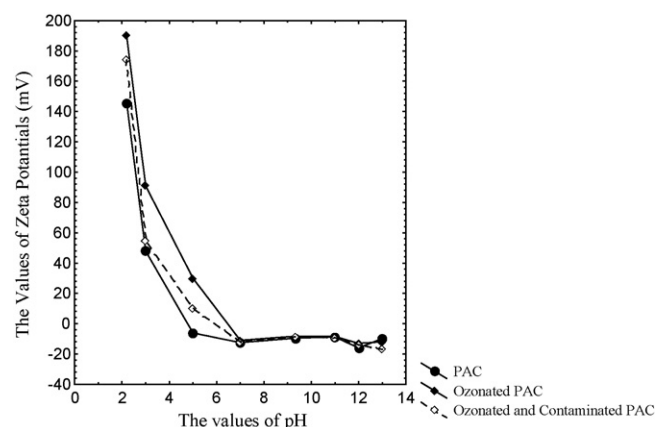


Fig. 10. Relation between zeta potentials and values of pH.

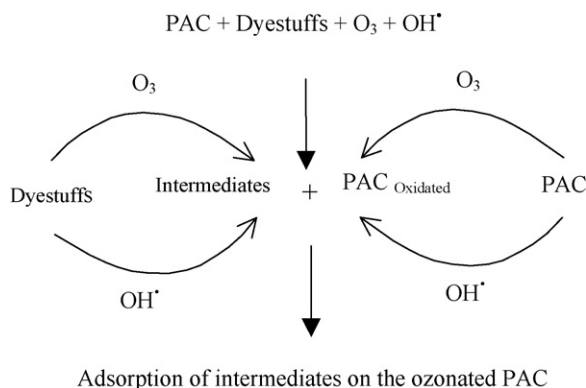
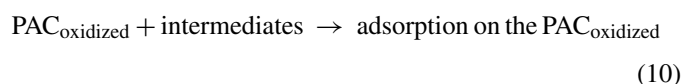
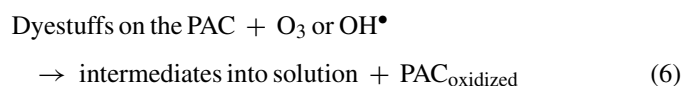
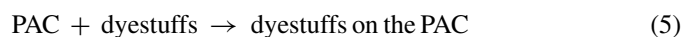


Fig. 11. The dye removal mechanism by the combined processes.

intermediates of ozonated dye molecules in the solution were electrostatically attracted by PAC and adsorbed on the surface of PAC particles then the zeta potential values of ozonated PAC particles changed. As seen Fig. 10, H^+ ions in the solution caused a decrease of the zeta potential values of the ozonated PAC (for example, after intermediates were adsorbed on the ozonated PAC, the zeta potential value of ozonated PAC at pH 2.2 decreased from 190 to 174 mV) while OH^- ions caused a negatively increase of the zeta potential values of the ozonated PAC particles (for example, after intermediates were adsorbed on the ozonated PAC, the zeta potential value of ozonated PAC at pH 13 increased negatively from -12 to -17 mV) as seen Fig. 10. The change in the zeta potential values of the ozonated PAC particles was a sign of adsorption of the intermediates of ozonated dye molecules from aqueous solutions.

In the present combined studies, it was thought that the PAC could play an important role as adsorbent in respect of the values of zeta potential and the figures of FTIR of PAC. In this study, according to data obtained from experiments and the results of FTIR of PAC, the generalized kinetic mechanisms for dyestuff, ozone, OH^\bullet and PAC are proposed in Fig. 11.



In the kinetic mechanism in Fig. 11, the pollutant (dyestuffs) and PAC in the liquid phase are directly oxidized by ozonation or indirectly hydroxyl radicals to form intermediates, CO_2

and the PAC_{oxidized} . Intermediates could be adsorbed onto the PAC_{oxidized} surfaces via the adsorption path. The COD concentration decreased with the removal of CO_2 from solution and adsorption of intermediates onto the PAC_{oxidized} surfaces. It was thought that the adsorption of intermediates on the PAC_{oxidized} surfaces was easier and had less treatment time than dye molecules only. It was thought that electrostatic attraction forces between ozonated PAC and intermediates were bigger than pushing forces.

4. Conclusion

This study revealed the prospect of the combined process for removal of colour and COD from synthetic textile wastewater. Substances such as O_3 , PAC and H_2O_2 , were an important role for the removal of colour and COD from the synthetic textile wastewater while HCO_3^- in the combined process decreased the removal of colour and COD. The colour removal efficiency increased with the increase of pH, PAC, H_2O_2 , but decreased with the increase of HCO_3^- ions. The colour removal efficiency was not affected by the ozonation doses. An increase in ozone dose from 164 to 498 $mg\ min^{-1}$ did not significantly affect the colour removal efficiency. The increase of temperature decreased the ozone concentration in the solution, but increased the adsorption of intermediate products on the PAC surfaces. The combined process was positively affected with the increase of pH, PAC and H_2O_2 dosage. The increase of PAC dose from 0.5 to 1 g in the combined process positively affected the treatment time and the colour removal efficiency. At the range of 5–15 min, in the combined processes, both adsorption and ozonation played an important role. After 15 min, ozonation became a dominating factor in the treatment process. At the result of this study, it was thought that the combined treatment is the more effective process than adsorption and ozonation alone.

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