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Catalytic ozonation with non-polar bonded alumina phases for treatment of aqueous dye solutions in a semi-batch reactor

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Abstract

Semi-batch experiments were conducted to investigate the effects of catalyst type, pH, initial dye concentration and production rate of ozone on the catalytic ozonation of the dyes, namely Acid Red-151 (AR-151) and Remazol Brilliant Blue R (RBBR). The used catalysts were alumina, 25% (w/w) perfluorooctyl alumina (PFOA), 50% (w/w) PFOA and 100% (w/w) PFOA. The results showed that the overall percent dye removal after 30 min of the reaction was not affected significantly by the catalyst type. However, highest COD reduction was achieved by ozonation with alumina for AR-151, and 100% PFOA for RBBR at pH 13. The behavior of COD reduction with the increasing amount of perfluorooctanoic (PFO) acid amount can be explained by the enhancement of catalytic activity of PFOA with alkyl chains. For both of the dyes, the highest dye and COD removals were reached at pH 13. The overall dye reduction after 30 min of ozonation was almost independent of the initial dye concentration at relatively low values while at the higher concentrations, it changed with the initial dye concentration for both of the dyes. Similarly, COD reduction changed on a limited scale with the increasing initial dye concentration from 100 mg/L to 200 mg/L; however, an increase of initial dye concentration to 400 mg/L decreased the COD reduction significantly. All the studied production rates of ozone were sufficient to provide almost 100% dye removal in 30 min, whereas the COD removal percentage was increased gradually by the increasing ozone input to the reactor. The reaction kinetics for the ozonation of each dye with and without catalyst was investigated and discussed in the paper.

Keywords: Acid Red-151; Remazol Brilliant Blue R; Perfluorooctyl alumina (PFOA); Heterogeneous catalysis; Catalytic ozonation; Ozone production rate

1. Introduction

In water treatment, ozonation is a widely used method to remove organics from wastewaters (WWs), especially the colored substances. Textile WWs containing a high concentration of dyes can be efficiently treated by ozone giving 90% or higher color removals. However, chemical oxygen demand (COD) removal cannot be achieved at high levels, it is limited to around 50% [1–3]. The reason of low COD removal is due to the incomplete mineralization of organics to carbon dioxide and water by sole ozonation, since some of the ozonation by-products show resistance to further oxidation.

In the recent years, new advanced oxidation techniques have been searched to overcome the limitations of sole ozonation and to use ozone more effectively. Among them, catalytic ozonation has become a promising method. Many studies have been made for the catalytic ozonation of organics in a homogeneous or heterogeneous phase with several different catalysts [4–10]. In the literature, alumina was shown to be an effective catalyst and support in the removal of organics by ozonation. Catalytic ozonation using metal ions (Fe_2O_3, TiO_2) impregnated on alumina (Al_2O_3) provided higher removals of both target organic and also DOC–TOC than those achieved by sole ozonation. Cooper and Burch [7] found oxalic acid degradation to be 85%, 88%, 87% in catalytic ozonation with Al_2O_3, Fe_2O_3/Al_2O_3, TiO_2/Al_2O_3, respectively. At the same conditions, the target acid removal was only 15% by ozone alone. Similarly, Ernst et al. [6] investigated the catalyst effect on the ozonation of oxalic, succinic and salicyclic acids by using Al_2O_3. In non-buffered conditions, the initial DOC was reduced by 90% in catalytic ozonation compared to 20% in ozonation alone.

Efficient two-phase ozonation has been provided by the immobilization of perfluorinated hydrocarbons on the surface of alumina so as to avoid the dissolution of perfluorinated molecules into the aqueous phase [11]. This innovative method involves the liquid–liquid extraction of organic substances from the aqueous phase into the organic phase and subsequent oxidation by molecular ozone dissolved in the organic phase

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Nomenclature

A_{BET}	BET area of the catalyst in Table 1 (m^2/g)
AR-151	Acid Red-151
$C_{d,i}$	initial dye concentration (mg/L)
$C_{O_3,s}$	equilibrium O_3 concentration in solution (mg/L)
COD	chemical oxygen demand (mg/L)
D_{pore}	pore diameter of the catalyst in Table 1 (Å)
DOC	dissolved organic carbon (mg/L)
m_{cat}	Catalyst dose (g)
m_{PFOA}	PFOA dose (g)
PFO acid	perfluorooctanoic acid
PFOA	perfluorooctyl alumina
pH_{PZC}	the pH of “point of zero charge” of the catalyst
PR_{O_3}	production rate of ozone (g/h)
PZC	point of zero charge
Q_G	gas volumetric flow rate (L/h)
RBBR	Remazol Brilliant Blue R
S_{BET}	catalyst surface area (m^2/g)
t	time (min)
T	temperature (°C)
TOC	total organic carbon (mg/L)
V_T	total pore volume in Table 1 (cm^3/g)

Greek letter

ρ_p	particle density (kg/m^3)

(non-polar perfluorinated hydrocarbon solvent saturated with ozone) [11]. It was found that ozone solubility in fluorinated hydrocarbon solvents was 10 times higher than that in water. Non-polar perfluorinated alkyl chains on the alumina surface were very active towards ozone and organics. Accordingly, ozone and organic matter reacted on the surface of hydrocarbon fixed alumina. The most preferred perfluorinated hydrocarbons were perfluorooctanoic (PFO) and perfluorooctadecanoic (PFOD) acids; especially the prepared perfluorooctyl alumina (PFOA) using PFO acid was observed to increase the stability of ozone in perfluorinated solvent [4].

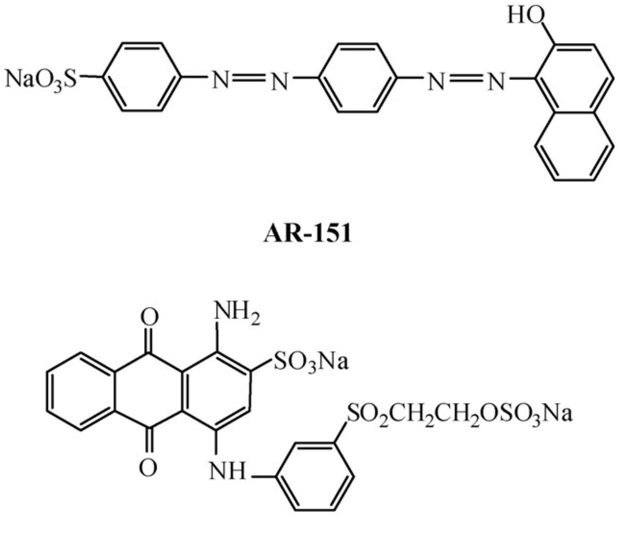
Kasprzyk-Hordern et al. [4,12] used PFOA in the ozonation of humic acid and natural organic matter (NOM). They found that ozonation with PFOA was more effective than ozonation alone for both of the organics. Also, TOC analysis showed that degradation of NOM in aqueous phase was mainly due to PFOA/O_3 system. The same researchers in another study [5] conducted ozonation for the removal of several ethers with PFOA. They observed no improvement of ether removal with alumina. In the case of PFOA, it was shown that the catalytic activity of PFOA depended on the alkyl chains on the alumina. The presence of more PFO acid on the surface created longer alkyl chains making PFOA more active. The hydrophobicity of the surface enhanced the adsorption capacity of PFOA.

The cost effectiveness of two-phase catalytic ozonation (PFOA/O_3 system) can be emphasized with the high adsorption capacity of bare alumina toward anionic perfluorinated surfactants from water [13]; thus, the bare alumina usage in the removal of perfluorinated surfactants from water can be considered as profitable because of the further possible application of the formed perfluorinated alumina as a catalyst in the ozonation process. Also FT-IR studies proved that ozone did not deactivate the catalyst [4]. Therefore, the aim of this study is to investigate the two-phase catalytic ozonation process using alumina and different types of PFOA as the catalysts in the degradation of Acid Red-151 and Remazol Brilliant Blue R, by determining dye and COD removals and the reaction kinetics at different operating conditions, the experimental parameters being pH, initial dye concentration ($C_{d,i}$), and production rate of ozone (PR_{O_3}).

2. Experimental

2.1. Materials

Acid Red-151 (AR-151) and Remazol Brilliant Blue R (RBBR) are the dyes used in the sole ozonation and catalytic ozonation experiments. AR-151 was purchased from Aldrich Chemical Company (Milwaukee, USA), whereas Acros Organics (New Jersey, USA) was the supplier of the RBBR. The structures of the dyes are shown in Fig. 1. AR-151 is an azo dye containing two azo groups with a maximum wavelength of 512 nm. RBBR has no azo group but one hydrocarbonated sulphonate group. It is an anthraquinone dye with a maximum wavelength of 591 nm. All other chemicals used were reagent grade and were supplied by Aldrich Chemical Company or Acros Organics.



AR-151

RBBR

Fig. 1. The structures of the dyes used in the experiments.

2.2. Preparation and characterization of the catalysts

For the experiments, alumina particles (Damla Kimya Ltd., Ankara) were used as a catalyst and also as a support for PFO acid. The screen analysis of these particles composed of active γ-alumina was carried out, thus the appropriate sized particles of

2 mm were selected. The types of PFOA catalyst were prepared by the impregnation of PFO acid (Aldrich Chemical Company, Milwaukee, USA) on 2 mm sized alumina particles. The type of PFOA called 100% PFOA was prepared, according to the procedure described in the literature [5,14] as follows: 10 g of alumina was reacted with 100 mL of 0.15 M PFO acid aqueous solution in a flask at 60 °C for 4 h. Then, 100 mL of 0.1 M sodium bicarbonate solution was prepared. After half an hour, catalyst was filtered under vacuum by washing with sodium bicarbonate solution and 200 mL of H_2O. Finally, the catalyst was dried at 60 °C in an incubator for about 2 h. Then, the other types of PFOA (25% (w/w) PFO on alumina and 50% (w/w) PFO on alumina) were also prepared by the reaction of different amounts of PFO acid with 10 g of alumina. For the preparation of 50% PFOA, 100 mL of 0.075 M PFO acid was used with 10 g of alumina. Similarly, 25% PFOA was prepared by the reaction of 100 mL of 0.0375 M PFO acid with 10 g of alumina. After the preparation of these catalysts, the catalytic ozonation experiments were conducted with bare alumina, 25% PFOA, 50% PFOA and 100% PFOA catalysts.

Alumina and PFOA samples were analyzed for the catalyst surface area and pore size distribution. The surface characterization analyses were made in the Central Laboratory of M.E.T.U. The surface area of the catalysts was determined by physical adsorption of nitrogen on the solid surface using the BET method. The pore volume and pore size distribution were determined by the nitrogen adsorption/desorption method. The nitrogen desorption isotherm was used for the calculation of pores and average pore size. The characterization data are presented in Table 1. It is observed that alumina has the highest surface area, and the surface area decreases with the increasing amount of PFO acid in alumina. Since AR-151 has an acidic character, the dye molecules can be adsorbed easily on the acidic alumina, whereas the adsorption on PFOA may be limited due to both its lower surface area and the hydrophobic surface characteristics.

Table 1
The characterizations of alumina and PFOA catalysts

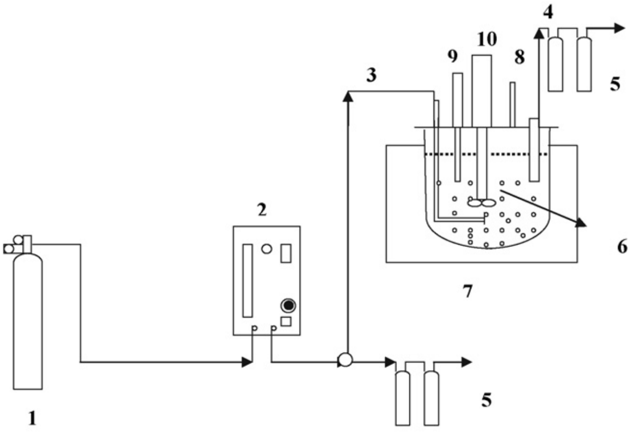
Type of the catalyst	A_{BET} (m^2/g)	D_{pore} (Å)	V_T (cm^3/g)
Alumina	276.6	50.51	0.35
25% PFOA	209.6	50.26	0.26
50% PFOA	195.8	51.42	0.25
100% PFOA	140.8	66.56	0.17

2.3. Semi-continuous experiments

The experimental set-up used consists of 1 L rounded bottom glass reactor with several input/output ports for ozone gas inlet, sampling, pH electrode and stirrer [15]. The experimental set-up is shown in Fig. 2. Ozone gas is produced from dry air by Fischer type OZ-502 generator. The gas flow rate is monitored by a flow meter on the generator and the temperature during the experiments is kept at 25.0 ± 0.5 °C using a water bath around the reactor. The gas diffuses into water through a glass sparger at the bottom of the reactor. Ozone traps containing 2% potassium iodide (KI) solution are used at the gas inlet to measure the ozone concentration in the off-gas and the inlet ozone concentration via a three-way valve. The reactor is operated in a semi-continuous mode by feeding ozone gas continuously into the reactor containing the dye solution at the desired initial concentration, at a chosen pH and at a temperature of 25 °C.

For an experimental run, a dye solution at the desired concentration was prepared by dissolving a proper amount of the dye in 50 mL of distilled water and mixing for 30 min with a magnetic stirrer. The chosen initial dye concentrations in the experiments were 100 mg/L, 200 mg/L and 400 mg/L. Buffer solutions of $K_2HPO_4/KH_2PO_4/H_3PO_4$ were used for the adjustment of pH to 2.5 and 7 in the reaction medium. The aqueous solution to be ozonated was prepared by adding 900 mL of distilled water and 50 mL of buffer solution at the desired pH into the reactor. Then, the buffered solution in the reactor was ozonated for about 20 min to reach an equilibrium concentration of ozone at the operating conditions in the reactor. After 20 min of ozonation, 50 mL of the solution containing dissolved dye was added into the reactor while continuously ozonating the reactor. For the analyses of COD, O_3 and dye concentrations at specific time intervals, the samples were withdrawn from the reactor into the sample bottles operated by vacuum in order to prevent the escape of O_3 into the gas phase. One millilitre of 0.025 M sodium thiosulphate ($Na_2S_2O_3$) solution was added into each sample bottle in order to remove any residual ozone in the sample. For the experiments at pH 13, instead of 50 mL buffer solution, 4.5 g NaOH was added into 950 mL of distilled water. Then, this sample was ozonated in the reactor by following the same procedure explained above.

The same procedure was followed also in the catalytic ozonation experiments. Only, before starting to ozonate the aqueous solution, the chosen amount of catalyst was added into the reactor, which formed a heterogeneous phase in the system. The received samples from the reactor were kept waiting about an hour to ensure the settling of the turbid portion in the samples; thus, the accuracy in the results was guaranteed. The reaction pH, types of catalysts, types of dyes, initial dye and ozone concentra-



1. Dry air tube, 2. O_3 generator, 3. O_3 inlet, 4. O_3 outlet, 5. KI traps,
6. Reactor, 7. Water bath, 8. pH electrode, 9. Sampling point, 10. Stirrer

Fig. 2. The schematic of the experimental set-up.

tions, and ozone production rate are the experimental parameters in the experiments. The ranges of the experimental variables are shown in Table 2.

Table 2
The experimental parameters

Parameter	Value
$C_{d,i}$ (mg/L)	100, 200, 400
PR_{O_3} (g/h)	1.17, 1.70, 2.21
pH	2.5, 7, 13
Dye type	AR-151, RBBR
Q_G (L/h)	150
Stirrer rate (rpm)	300
Catalyst type	Alumina, (25%, 50%, 100%) PFOA
COD_i (mg/L)	AR-151: 200; RBBR: 232
T (°C)	25
m_{cat} (g)	5

2.4. Analytical determinations

The samples were analyzed for the absorbance of the dyes at their maximum wavelengths. For this purpose, Hitachi U-3010 type UV–vis spectrophotometer was used and the absorbance values of AR-151 and RBBR were determined at 512 nm and 591 nm, respectively. Chemical oxygen demands (COD) of the samples were measured by adding 2 mL of the sample solution into a glass vial containing 3 mL of COD solution and digesting the sample in a WTW Cr-3000 type thermo-reactor for 2 h at 150 °C according to the standard methods [16]. After the sample was cooled, its COD was determined directly by a Hach DR-2010 type portable spectrophotometer. The ozone concentrations in the inlet and outlet gas streams were determined by the iodometric method [16]. Indigo method [17] was used to measure the residual O_3 concentration in the liquid phase using a Hitachi spectrophotometer.

3. Results and discussion

3.1. Ozonation experiments

Ozonation experiments, without using catalysts, were carried out at different pH. At the acidic pH (pH 2.5), direct reaction of ozone with dye molecule was observed. Since, the concentration of hydroxyl ion (OH^-), the initiator of radical reactions of ozone, was low in the aqueous phase at low pH, radical reactions of ozone with the dye could be neglected. At alkaline pH (pH 13), O_3 molecules were decomposed into ions and radicals, therefore ozonation of dye molecules took place mainly by radical reactions. Also, direct ozonation could be important with the undecomposed O_3 as well. Therefore, it was difficult to differentiate the effects of direct and radical reactions on the removal efficiencies of the dye and COD. At neutral pH (pH 7), the status became much more complicated since the concentrations of both the O_3 and OH^- were lower [18–20].

In this study, more than 90% dye removals were achieved by the ozonation of AR-151 and RBBR solutions at the studied pH values. As seen in Fig. 3, initial dye removal rates were almost the same at pH values of 2.5 and 7 for the dye RBBR. At pH 13, an increase in the initial reaction rate was observed which was greater in the ozonation of AR-151 than in that of RBBR. Because the increment of initial reaction rate at pH 13 was higher in the case of RBBR than in the case of AR-151 where the initial reaction rates at pH 2.5 and 13 were very similar or same and the initial reaction rate at pH 7 was slightly lower (Fig. 3). This observation might indicate that the direct oxidation of AR-151 by ozone molecules was probably accompanied with the indirect oxidation by reactive hydroxyl radicals formed due to the higher decomposition rate of ozone at an alkaline pH of 13. In RBBR ozonation, the occurrence of the highest initial dye removal rate at pH 13 might suggest that radical reactions played relatively a more significant role in the oxidation mechanism. Ozonation time period of 30 min was sufficient to achieve more than 90% dye removal efficiencies for both of the dyes at the end of the reaction time, regardless of pH. In other words, the overall dye removal efficiency, after 30 min of reaction time, did not depend on solution pH significantly.

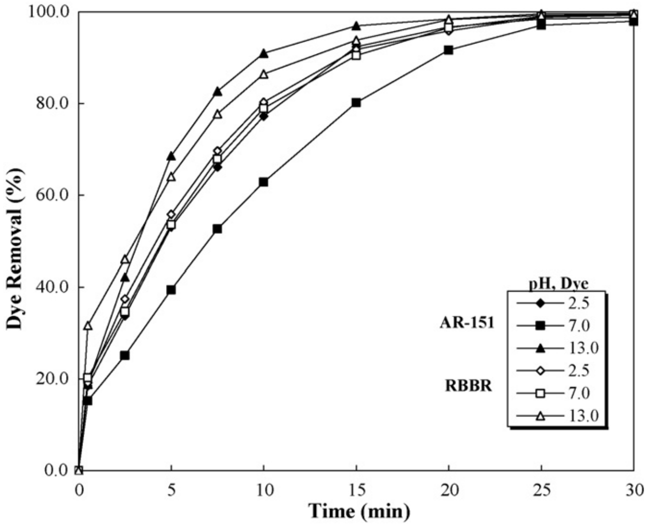


Fig. 3. Dye removals with ozonation at different pH values. Conditions: $C_{d,i}$ = 200 mg/L; T = 25 °C; stirrer rate = 300 rpm; Q_G = 150 L/h; PR_{O_3} = 2.21 g/h; reaction time = 30 min. Bold shapes: AR-151; apparents: RBBR.

The effects of pH on COD removals in the ozonation of AR-151 and RBBR are presented in Fig. 4, where the highest COD removals are observed at pH 13 in concordance with the results of dye removal efficiencies (Fig. 3). For RBBR, COD removal increased with the increasing pH. The increment was linear and it showed that the COD removal was mainly due to the radical reactions in the ozonation of RBBR. The COD removal showed a slight decrease at pH 7 with respect to that at pH 2.5 for AR-151, then increased again with the increasing pH; but COD removal at pH 13 was still slightly lower than that at pH 2.5. In a previous work of the authors [15], it was understood that the main mechanism in the ozonation of AR-151 in a batch reactor was direct oxidation of the dye with ozone molecules; because the highest dye and COD removals were obtained at pH 2.5. In accordance with the present results, both the dye and COD removals decreased at pH 7, then they increased again with pH. In spite of this increasing trend of efficiencies between pH 7 and 10, the

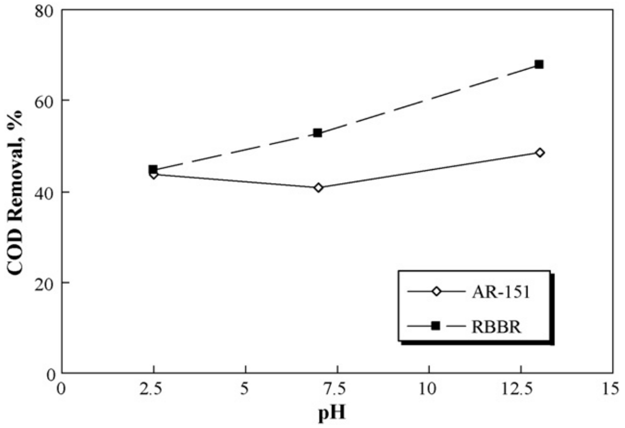


Fig. 4. COD removals with ozonation for AR-151 and RBBR at different pH values. Conditions: $C_{d,i} = 200$ mg/L; $T = 25\,^{\circ}$C; stirrer rate = 300 rpm; $Q_G = 150$ L/h; $PR_{O_3} = 2.21$ g/h; reaction time = 30 min.

removal efficiencies at pH 10 were slightly lower than those at pH 2.5. This could be attributed to the limitation of the dissolved ozone concentration in the batch reactor [15]. In the present set-up, due to the continuous feed of ozone gas to the semi-batch reactor, dissolved ozone concentration was not limited; besides, the decomposition rate of ozone at pH 13 was slightly greater than that in the batch study at pH 10. These arguments suggested that the contribution of radicals to the dye-oxidation was more significant in the semi-batch reactor compared to that in the batch reactor [15].

3.2. Catalytic ozonation experiments

3.2.1. Dye removals

The catalytic ozonation experiments with AR-151 and RBBR were conducted in the presence of Al_2O_3, 25%, 50% and 100% PFOA and the most efficient conditions were determined according to the dye and COD removal percentages. In catalytic ozonation, adsorption of dye molecules on catalyst surface was an important phenomenon and the adsorption capability of the catalyst depended on its type, properties, groups attached to its surface and solution pH. For alumina, pH of point zero charge (pH_{PZC}) at which the net surface charge was zero, characterized its surface charge at a certain pH. At acidic pH, where pH was less than the pH_{PZC} value, surface of alumina was positive, and therefore anions could be adsorbed on its surface. On the other hand, at basic pH ($pH > pH_{PZC}$), the surface was negative permitting the adsorption of cations [21]. An azo dye (an acid dye) such as AR-151, is negatively charged in the solution and is adsorbed easily on the surface of alumina at acidic pH; however, it becomes difficult for a positively charged basic dye to be adsorbed on alumina surface at the acidic pH. In the case of PFOA catalyst prepared from bare alumina, the surface properties of the catalyst are changed. A bond is formed between the surface of alumina and PFO acid [21]. Due to the formation of perfluorinated alkyl chains on the surface, the latter turns from acidic or basic character to the hydrophobic non-polar character. This might be the main reason for the easy adsorption of organic molecules, which are hydrophobic in character.

Table 3
Dye removal percentages for AR-151 and RBBR for different pH values and catalyst types

Treatment	pH	Dye removal (%)	
		AR-151	RBBR
	2.5	98.8	99.3
O_3 only	7	98.0	99.4
	13	99.7	99.5
	2.5	97.4	97.5
O_3 + alumina	7	94.9	98.1
	13	98.4	98.3
	2.5	96.2	97.3
O_3 + 25% PFOA	7	91.3	99.6
	13	96.3	98.4
	2.5	96.1	97.6
O_3 + 50% PFOA	7	90.3	99.0
	13	97.9	97.7
	2.5	98.3	97.6
O_3 + 100% PFOA	7	94.8	99.4
	13	98.8	97.4

Conditions: $C_{d,i} = 200$ mg/L; $T = 25\,^{\circ}$C; stirrer rate = 300 rpm; $Q_G = 150$ L/h; $PR_{O_3} = 2.208$ g/h; reaction time = 30 min.

Ozonation of the present dye solutions in the presence of alumina, or PFOA catalysts containing different amounts of PFO acid provided dye removal efficiencies up to 98–99%, depending on the catalyst type and solution pH (Table 3). Almost the same dye removal efficiencies had been achieved in the non-catalytic ozonation of Acid Red-151 [15]. Therefore, no further improvement was observed in the dye removal efficiency with the usage of any catalyst type in the system. The observed total dye removals (at the end of 30 min) in the catalytic ozonation were even less than those in the sole ozonation at all the studied pH values (Table 3). At low pH value (2.5) adsorption of the dye molecules on alumina seemed to be an important mechanism during ozonation, as stated above. Since AR-151 had an acidic character, its adsorption on the alumina surface became easier at pH 2.5 and 7 which were the pH values lower than the pH_{PZC}; similarly, the protonation of RBBR molecules at acidic pH made the adsorption of these molecules on the alumina surface easier [4,21,22]. The observation of red- or blue-dyed catalyst particles at the end of 30 min of reaction time was a strong sign of adsorption of AR-151 or RBBR, respectively. The intensity of the color decreased with the increase of PFO acid amount in the PFOA catalyst. At the end of 30 min of ozonation, presence of a catalyst or its types did not affect the total percent dye removal significantly for both the AR-151 and RBBR dyes. The possible explanations are provided below for the slight differences in the dye removal values depending on the experimental conditions.

Since the dye removal mainly occurred by direct oxidation with ozone molecules in the aqueous phase besides by adsorption on the catalyst surface, the dye removal efficiency was higher at pH 2.5. However, ozone direct and radical reactions became more important than the effect of adsorption at a pH of 13; because the color intensity of the catalyst particles was lower at this pH. The decreasing effect of adsorption seemed to be compensated by the increasing contribution of radical reactions at pH 13; thus the overall dye removal efficiency became almost the same as that at pH 2.5 for both of the dyes with each catalyst type. Ni and Chen [8] also emphasized the contribution of radical reactions in the removal of organics by the catalytic ozonation at alkaline pH of 9. In addition, it was shown by Thomas et al. [23] that hydroxyl radicals were produced on the alumina surface at basic pH, enabling radical reactions to occur both in the liquid phase and also on the catalyst surface.

In the catalytic ozonation of AR-151 with PFOA, the total dye removals in 30 min were found to be lower at pH 7 than those obtained at pH 2.5 and 13; the same trend of dye removals with respect to pH was also previously determined in the non-catalytic ozonation of AR-151 [15]. This may be attributed to the lower dissolved ozone concentration at pH 7 than that at pH 2.5 due to the slightly greater decomposition rate of ozone at the former pH compared to that at the latter. Furthermore, the oxidation of dye molecules by hydroxyl radicals might be insignificant due to the smaller concentration of radicals at pH 7 compared to that at pH 13 because of the faster decomposition of ozone at pH 13. However for RBBR, the dye removal at pH 7 was higher than those at pH 2.5 and pH 13. Most probably, the chemical structure of RBBR was more compatible with the surface of PFOA catalyst than that of AR-151. Some authors have observed that at pH 7 (a pH value close to $\mathrm{pH_{PZC}}$) alumina becomes neutral and more hydrophobic. Hence, the formation of non-polar perfluorooctyl chains on alumina surface increased the efficiency of PFOA. Besides, RBBR molecules were known to be more rigid and hydrophobic than AR-151 due to its aromatic anthraquinone structure highly stabilized by resonance [24,25]. These arguments could justify the high dye removal percentages of RBBR at pH 7; therefore, a pH of 7 could be accepted as an optimum value in the treatment of RBBR solutions, not requiring a pH adjustment by using additional chemicals to satisfy the wastewater discharge standards to environment.

At pH 13, the total dye removal percentage was found to be less than those found with ozonation alone for all the catalysts used. The removal percent was increased by the change of the catalyst from alumina to 100% PFOA for AR-151. This indicated that the use of PFOA containing higher amounts of PFO acid would be more advantageous in the ozonation of AR-151. On the contrary, alumina and PFOA containing lower amounts of PFO acid was observed to give higher dye removal efficiencies for RBBR at pH 13. Carlos et al. [22] claimed that at high pH values (pH > 7), the structure of RBBR changed due to the deprotonation of the molecules with the effect of pH creating a higher adsorption capability on the alumina surface. This might be the cause of higher efficiencies with alumina and 25% PFOA.

Comparing the ozonation efficiencies of the two dyes, the removal rates of RBBR were found to be the highest at all the pH studied. Due to two sulphonic acid groups in the structure of RBBR, the dissolution process of this dye in the aqueous phase was faster than the dissolution of AR-151, which had only one sulphonic group. Furthermore, the degradation of RBBR molecules in a specified time period was higher than the reaction of AR-151 molecules at pH 2.5. Therefore, results showed that ozone molecules oxidized RBBR with a higher efficiency than in the case of AR-151 removal.

3.2.2. COD removals

For the studied pH range, the COD reduction increased with the addition of each catalyst type compared to the ozonation alone as seen in Table 4. The increased amount of COD removal demonstrated the differences among the behavior of different catalyst types and pH. For pH 2.5 and 7, the COD removal percentage increased with the increase of PFO acid amount in the catalyst, and the highest removal was observed at the condition where 100% PFOA was used. For RBBR, COD removal increased linearly with the PFO acid amount on alumina at pH 2.5 and 7. Only at ozonation with alumina, the COD removal percentage was lower than that of the non-catalytic ozonation case. The behavior of COD removal with the increased amount of PFO acid could be explained by the enhancement of catalytic activity of PFOA with alkyl chains as stated by Kasprzyk-Hordern et al. [4,12]. Higher amount of PFO acid in the catalyst created longer alkyl chains on the catalyst surface. Due to the increase of catalytic activity, the most efficient PFOA type was found as 100% PFOA for AR-151 and RBBR at pH 2.5 and 7.

Table 4
COD removal percentages for AR-151 and RBBR at different pH values and catalyst types

Treatment	pH	COD removal (%)	
		AR-151	RBBR
O_3 only	2.5	43.8	44.8
	7	40.7	52.6
	13	46.3	67.7
O_3 + alumina	2.5	50.5	42.5
	7	52.5	45.1
	13	78.7	82.6
O_3 + 25% PFOA	2.5	48.5	46.7
	7	51.8	53.3
	13	70.5	94.4
O_3 + 50% PFOA	2.5	45.0	52.2
	7	53.5	55.6
	13	68.2	95.7
O_3 + 100% PFOA	2.5	53.0	56.6
	7	61.7	83.2
	13	75.7	96.6

Conditions: $C_{d,i} = 200$ mg/L; $T = 25\,°C$; stirrer rate = 300 rpm; $Q_G = 150$ L/h; $PR_{O_3} = 2.208$ g/h; reaction time = 30 min.

Due to the adsorption of the dye molecules on alumina, there would be a competition for the surface active sites among the dye molecules and the ozonation by-products. For the alumina catalyst, adsorption of the dye was more dominant than those of the by-products causing lower COD removals than those shown by the PFOA types. This behavior explained the increase in COD removal with the increase of PFO acid amount. At 100% PFOA, the catalyst preferred the adsorption of ozonation by-products due to the non-polar nature of PFOA.

Another important result was the increase of COD removal percentage with the increase of pH. Contrary to the percent dye removal results, pH 7 was more effective than pH 2.5 for the removal of ozonation by-products. In other words, ozonation with catalyst showed an opposite behavior from ozonation alone in the respect of COD removals at pH 2.5 and 7. The increase of the discrepancies between the COD removal percentages with the increasing pH from 2.5 to 7 showed the importance of $^{\bullet}$OH radicals in the ozonation with PFOA. As expected, the highest COD removal percentages were observed at pH 13 in accordance with the existence of more $^{\bullet}$OH radicals. However, when the percentages of COD reductions for the dye AR-151 with the increase of PFO acid amount on alumina were considered, they were 78.7% by ozonation in the presence of alumina (0% PFO) compared to 46.3% by sole ozonation, and 75.7% by ozonation with 100% PFOA catalyst (Fig. 5). At pH 13, no significant color change of the catalyst particles due to the adsorption of the dye molecules was observed for either alumina or any type of PFOA. This meant that the dye molecules were degraded in the aqueous phase only at that pH, but the ozonation by-products might possibly be degraded both in the aqueous phase and on the catalyst surface. Further investigation about the functional groups and ligands on the catalyst surface before and after the treatment was needed to clarify this point.

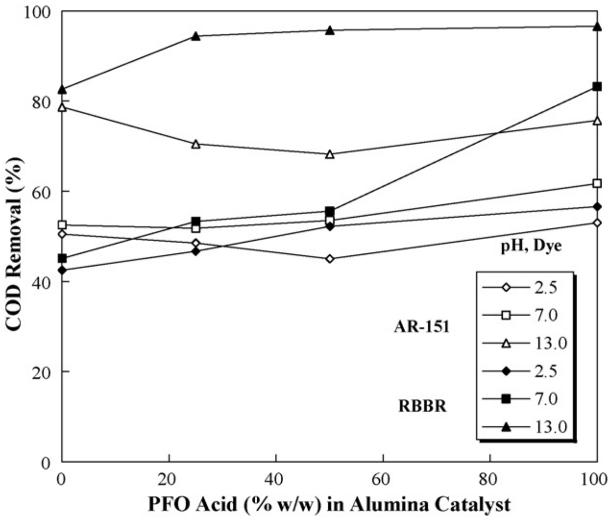


Fig. 5. The change of COD removal percentage for the dyes by catalytic ozonation. Conditions: $C_{d,i} = 200$ mg/L; $T = 25\,^{\circ}$C; stirrer rate = 300 rpm; $Q_G = 150$ L/h; $PR_{O_3} = 2.21$ g/h; reaction time = 30 min. Bold shapes: AR-151; apparents: RBBR.

In the ozonation of RBBR, the adsorption of the dye molecules on the catalyst surface was limited as observed by the less intense blue color of the catalyst surface after the catalytic ozonation treatment. In other words, RBBR molecule showed less affinity to attach the catalyst surface than that of AR-151 molecule. Thus the surface became less occupied with the dye molecules enabling the ozonation by-products to attach easily on the surface. This was most probably the reason for the higher COD reduction percentages observed in the ozonation of RBBR solutions with respect to AR-151 solutions. The percent COD removals at pH 7 in the ozonation of RBBR, as seen in Fig. 5, are slightly above those at pH 2.5 for alumina, 25% and 50% PFOA. However, COD removal value at pH 7 with 100% PFOA is much higher than that at pH 2.5. The limited effect of PFO acid amount on COD removal efficiency at pH 2.5 and 7 suggested that a relatively higher percentage of the reaction occurred in the aqueous phase rather than on the catalyst surface. At pH 13, the reduction of COD was more efficient especially in the case of RBBR than those at the lower pH values. Even without catalyst, 67.7% COD removal could be achieved. At that pH, %COD removal for RBBR was increased from 82.6% to 94.4%, 95.7% and 96.6% by changing the catalyst type from alumina to 25%, 50% and 100% PFOA, respectively. As it was understood from these values, the COD removal stayed almost unaffected by the amount of PFO acid in alumina after 25%. In other words, the catalytic sites and alkyl chains on the surface provided by PFAO (25%, w/w) were sufficient to remove the remaining COD; therefore further increase in the amount of PFO acid in alumina did not affect the process significantly.

3.2.3. Effect of ozone production rate on dye and COD removals in catalytic ozonation

The effect of ozone production rate on dye and COD removals in the catalytic ozonation (with 100% PFOA catalyst) was investigated by regulating the dial-up setting of the ozone generator while keeping the gas flow rate constant. The ozone production rate then was determined by iodometric method [16]. These experiments were carried out preferably at pH 2.5 for AR-151 and at pH 7 for RBBR which corresponded to the cases yielding the highest dye removals for both of the dyes in the presence of 100% PFOA; because the catalytic activity of PFOA increased with the increase of PFO amount in it [4,12]. Besides, catalytic activity of 100% PFOA was observed to be the highest at pH values of 2.5 and 7 for both of the dyes, as stated previously in the paper. Although the percentage of dye removal for AR-151 at pH 2.5 was slightly lower than that at pH 13 (98.3% compared with 98.8%, respectively), the small difference was within the limits of experimental error. An alkaline pH of 13 was not preferred because of the necessity for observing the catalytic effect of 100% PFOA on dye degradation reactions occurring mainly on the catalyst surface, but not in the liquid phase; because as Thomas et al. [23] reported, dye degradation occurred both in the aqueous phase and also on the catalyst surface by indirect oxidation due to hydroxyl radicals at alkaline pH values (pH > 9).

The studied ozone production rates were 1.17 g/h, 1.70 g/h and 2.21 g/h. The results showed that all the chosen ozone generation rates were sufficient to complete the removal of each dye with almost 100% efficiency so that it would be possible to observe the extent of by-product oxidation by measuring the total COD removals achieved in 30 min of ozonation. As seen in Fig. 6, the slowest dye removal cases are observed at the lowest production rate of ozone for both of the dyes. But, in 30 min of ozonation, the overall dye removal percentage is almost independent of the production rate. Actually, during the first 15 min of ozonation, the reaction follows a different pattern from each other at different production rates of ozone. For the ozonation of RBBR, “% dye removal versus time” curves are closer to each other than those for AR-151 showing a less significance of the ozone production rate. Since, the degradation of RBBR molecules by ozone is easier than that of AR-151 molecules, the

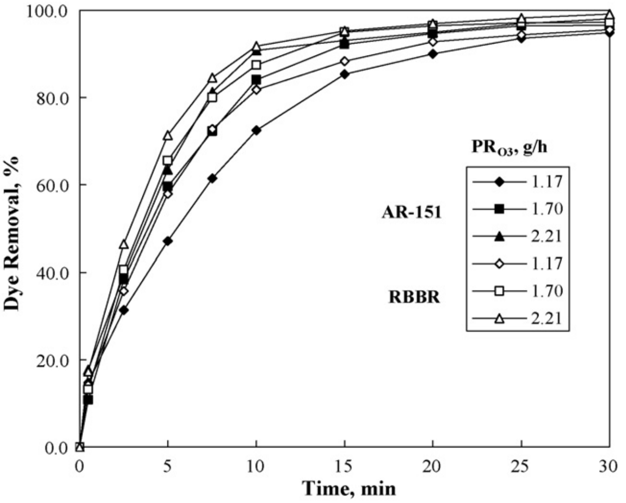


Fig. 6. The effect of ozone production rate on the dye removal. Conditions: catalyst = 100% PFOA; $C_{d,i}$ = 100 mg/L; T = 25 °C; stirrer rate = 300 rpm; Q_G = 150 L/h; reaction time = 30 min. Bold shapes: AR-151, pH 2.5; apparents: RBBR, pH 7.

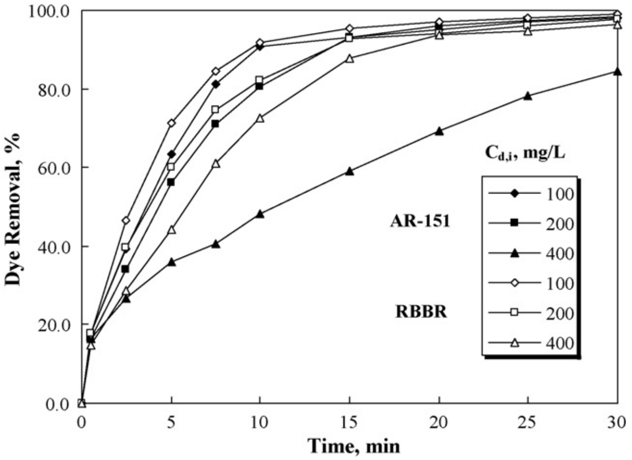


Fig. 7. The effect of initial dye concentration on dye removal. Conditions: catalyst = 100% PFOA; PR_{O_3} = 2.21 mg/h; T = 25 °C; stirrer rate = 300 rpm; Q_G = 150 L/h; reaction time = 30 min. Bold shapes: AR-151, pH 2.5; apparents: RBBR, pH 7.

amount of O_3 has a lower effect on the process. The dye removal rate increases with the ozone production rate, except the initial ozonation rate of both AR-151 and RBBR, which shows a low dependence on the ozone input.

Table 5 shows that COD reduction efficiency increases with the ozone input to the reactor, because of the higher amount of ozone available for the degradation of ozonation by-products. However, the increase of ozone production rate from 1.17 g/h to 1.70 g/h shows a small improvement on the COD reduction for AR-151. During ozonation of dye molecules, double bonds and aromatic structure are broken first to yield smaller structured organics such as aldehydes. These organics also have a remarkable COD. Therefore in the second step, these aldehydes need more ozone to be converted to carboxylic acids and may be partly transformed into gaseous products by further oxidation. Occurrence of relatively lower improvement on COD reductions, with the increase of ozone production rate from 1.17 g/h to 1.70 g/h, may be due to the oxidation of dye molecules to intermediates having different molecular weights. With a further increase in the ozone generation rate to 2.21 g/h, a result of the higher increment in COD reduction may possibly be due to the relatively easier and faster oxidation of some ozonation by-products having the small molecular weights. In the case of RBBR ozonation contrary to the case of AR-151, COD reductions are increased considerably with the increasing amount of dissolved O_3 in the reactor. This may be attributed to the greater degradation rate of RBBR compared to that of AR-151 as explained previously in the paper.

Table 5
COD removal percentages of AR-151 or RBBR by ozonation with 100% PFOA catalyst

Type of the dye	PR_{O_3} (g/h)	$C_{d,i}$ (mg/L)	COD reduction (%)
AR-151	1.17	100	44.9
	1.70	100	48.3
	2.21	100	57.3
		200	53.0
		400	15.0
RBBR	1.17	100	32.1
	1.70	100	46.9
	2.21	100	65.6
		200	61.4
		400	35.2

Conditions: pH 2.5 for AR-151; pH 7 for RBBR; T = 25 °C; stirrer rate = 300 rpm; Q_G = 150 L/h; reaction time = 30 min.

3.2.4. Effect of initial dye concentration on dye and COD removals

Fig. 7 shows the effect of initial dye concentration on percent dye removals for both of the dyes in the catalytic ozonation process. It is observed that the effect of initial dye concentration is considerable after the first minute of the reaction.

The removal of the dyes follows similar trends for the concentrations of $C_{d,i}$ = 100 mg/L and 200 mg/L. After a reaction time of 30 min, the total dye removal percentages when the initial dye concentration is 100 mg/L or 200 mg/L become very similar, 98.1% or 98.2%, respectively. The results demonstrate that the overall dye removal percentage after 30 min of ozonation is almost independent of the initial dye concentration at relatively low values whereas at higher dye concentrations, it depends significantly on the initial dye concentration.

In the ozonation of RBBR, the overall dye removal percentages after a reaction time of 30 min decrease slightly with the increasing initial dye concentration (Fig. 7). However, although when the initial dye concentration is 200 mg/L the COD reduction, after 30 min of reaction time, is very close to the value achieved at 100 mg/L, it decreases notably when the initial dye concentration is doubled from 200 mg/L to 400 mg/L (Table 5). Results reveal that when the initial dye concentration is 100 mg/L or 200 mg/L, ozonation with 100% PFOA removes both the dye and COD from the aqueous solutions of AR-151 or RBBR with similar efficiency with low effect of the initial dye concentration. Then, the increase of initial dye concentration to

400 mg/L decreases the %COD reduction to the half of those at 100 mg/L and 200 mg/L. This means that at the highest initial dye concentration, catalytic ozonation achieves only a limited amount of dye and COD removal, because an increase in the initial dye concentration corresponds to an increase of by-product concentration in the solution. Then, the available ozone will start to be consumed both for oxidation of intermediates and also for the continuing degradation of original dye. Thus, this will cause a decrease in the degradation rate of the dye in time, yielding a lower overall dye removal in 30 min of reaction than that of the case with a lower initial dye concentration. However, the overall dye and COD removals could be higher with the increasing time of ozonation; because it was reported that after the adsorption of non-polar organics on the catalyst surface took place, subsequently oxidation reaction with ozone molecules started and an increasing amount of by-products were obtained with the time of ozonation [4].

3.3. Ozonation kinetics

In the experiments before the addition of the dye, the aqueous solution was ozonated about 20 min to achieve the equilibrium concentration of ozone at the operating conditions. The rate of dye ozonation reactions was shown to follow a second-order reaction, being first order both with respect to the dye and ozone concentrations [26–28]. Since the concentration of ozone in aqueous phase was uniform during the ozonation of dye molecules, therefore the reaction rate can be assumed to follow a pseudo-first order as shown in the following equations:

$$C_{O_3}(t) = C_{O_3,s} \tag{1}$$

$$-r_{d,i} = -\frac{dC_d}{dt} = kC_{O_3}C_d \tag{2}$$

$$-r_{d,i} = -\frac{dC_d}{dt} = k'C_d \tag{3}$$

$$k' = kC_{O_3,s} \tag{4}$$

where k' (min^{-1}) is the pseudo-first-order kinetic constant, and k (mM^{-1} min^{-1}) is the overall reaction kinetic constant. The pseudo-first-order kinetic constant, k', can be determined from the slope of the line obtained by $\ln(C_d/C_{d,i})$ versus time. Then, the overall kinetic constant (k) can be calculated from Eq. (4). The results of the experiments were evaluated to find k' and k for the ozonation and catalytic ozonation of both the AR-151 and RBBR. The reaction kinetics was shown to follow a pseudo-first-order reaction rate. The effect of the catalyst, ozone dose, initial dye concentration and pH on the kinetic constant of the dye ozonation was investigated.

3.3.1. The kinetics of ozonation of AR-151 and RBBR

The reaction kinetics of ozonation at pH 2.5, 7 and 13 were investigated for AR-151 and RBBR, respectively. $\ln(C_d/C_{d,i})$ versus t curves (Figs. 8 and 9) were found to be linear indicating a pseudo-first-order reaction at the equilibrium concentration of ozone in the aqueous phase for each pH (for the studied pH range) and for both of the dyes. The pseudo-first-order kinetic constant (k') decreased by changing pH from 2.5 to 7 and then, it increased by the increase of pH to 13 showing a minimum value at pH 7 for AR-151 ozonation. In the case of RBBR ozonation, a linear increase of k' was observed with the increasing pH. The values of pseudo-first-order and overall kinetic constants for the ozonation of AR-151 and RBBR are summarized in Table 6. The overall kinetic constants (k) were found to increase with the increase of pH from 2.5 to 13 for both of the dyes showing the effect of radical reactions on the dye ozonation kinetics.

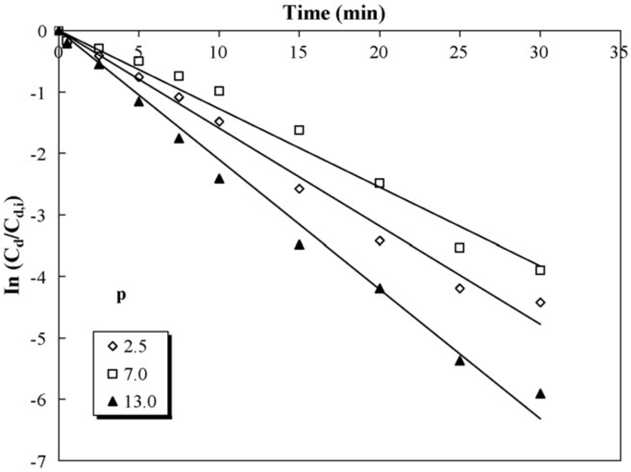


Fig. 8. The pseudo-first-order kinetic constants of AR-151. Conditions: ozonation only; $C_{d,i} = 0.440$ mmol/L; $PR_{O_3} = 2.21$ g/h.

At pH 2.5 and 7, the reaction followed very close rates and similar paths for the ozonation of RBBR to conclude that the reaction mechanisms were almost the same at those pH values for the ozonation of RBBR. The reaction rate followed a faster mechanism at pH 13, showing the effect of radical reactions at this pH.

3.3.2. Effect of alumina and PFOA types on ozonation kinetics of AR-151 and RBBR

The reaction kinetic was investigated for the catalytic ozonation process in the presence of alumina and the PFOA types

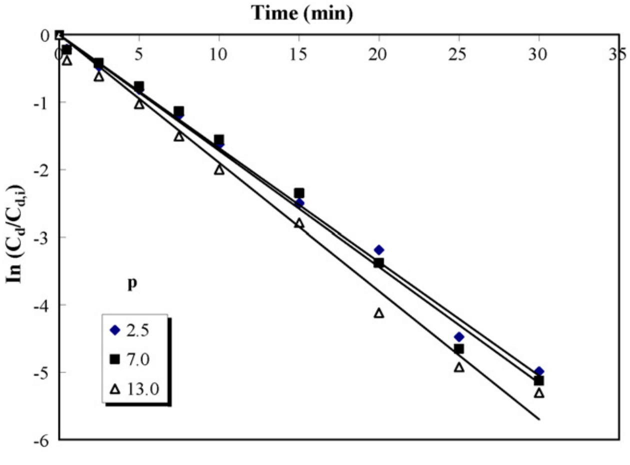


Fig. 9. The pseudo-first-order kinetic constants of RBBR. Conditions: ozonation only; $C_{d,i} = 0.440$ mmol/L; $PR_{O_3} = 2.21$ g/h.

Table 6
Pseudo-first order and overall kinetic constants for AR-151 or RBBR, in cases of sole ozonation and catalytic ozonation

Type of the dye	pH	Catalyst	k' (min^{-1})	k (mM^{-1} min^{-1})
AR-151	2.5	–	0.159	1.81
		Alumina	0.125	1.42
		25% PFOA	0.121	1.38
		50% PFOA	0.126	1.43
		100% PFOA	0.150	1.70
	7	–	0.128	2.16
		Alumina	0.101	1.71
		25% PFOA	0.080	1.36
		50% PFOA	0.085	1.43
		100% PFOA	0.090	1.52
	13	–	0.210	5.99
		Alumina	0.136	3.86
		25% PFOA	0.128	3.64
		50% PFOA	0.130	3.72
		100% PFOA	0.132	3.75
RBBR	2.5	–	0.168	1.91
		Alumina	0.135	1.53
		25% PFOA	0.161	1.83
		50% PFOA	0.181	2.06
		100% PFOA	0.194	2.20
	7	–	0.172	2.91
		Alumina	0.135	2.28
		25% PFOA	0.194	3.28
		50% PFOA	0.158	2.67
		100% PFOA	0.168	2.84
	13	–	0.190	5.41
		Alumina	0.132	3.77
		25% PFOA	0.152	4.32
		50% PFOA	0.155	4.41
		100% PFOA	0.158	4.50

Conditions: $C_{\mathrm{d,i}} = 0.440$ mM; $\mathrm{PR}_{\mathrm{O_3}} = 2.21$ g/h; $m_{\mathrm{cat}} = 5$ g.

prepared. Catalytic ozonation followed a pseudo-first-order reaction. But, the presence of the catalyst changed the pseudo-first order and overall reaction kinetic constants as seen in Table 6. The effect of the catalysts on pseudo-first order and overall reaction kinetic constants depended on the pH; but as a general observation, the kinetic constants decreased by the addition of the catalysts into the system, especially at pH 13. In this case, a very high reaction rate of non-catalyzed ozonation ($k = 5.99$ mM^{-1} min^{-1}) with respect to those with the catalysts ($k = 3.75$ mM^{-1} min^{-1}, with 100% PFOA) indicates that the presence of the catalysts causes a decrease in the efficiency of the radical reactions.

The highest reaction rates of catalytic ozonation of RBBR at pH of 2.5, was found in the presence of 100% PFOA and it was higher than the one without catalyst, giving overall kinetic constants of 2.20 mM^{-1} min^{-1} with 100% PFOA, and 1.91 mM^{-1} min^{-1} without catalyst. However, at pH 13, the non-catalytic reaction kinetic constant (5.41 mM^{-1} min^{-1}) was the highest. Chu and Ma [29] reported that at the acidic pH, ionization of the amine groups of an anthraquinone dye promoted the dye solubility increasing the rate of non-catalyzed dye degradation. Therefore at pH 2.5, a high rate constant for the degradation of RBBR (an anthraquinone dye) by ozonation without catalyst might be expected. However, a slightly higher kinetic constant of 2.20 mM^{-1} min^{-1} was obtained in the catalytic ozonation of RBBR with 100% PFOA at pH 2.5. This might be attributed to the higher affinity of RBBR molecules, having relatively lower polarity due to their dipole moment of 3.3 [30], to the organic phase saturated with molecular ozone on the surface of PFOA catalyst, where the oxidation reaction took place. The higher kinetic constant in the removal of RBBR by sole ozonation at pH 13 showed that more powerful hydroxyl radicals degraded the dye molecules faster, while PFOA/O_3 system was based on molecular ozone reactions occurring at a slower rate; because ozone decomposition reactions were inhibited by PFOA catalyst [31]. Although the reaction rate was lower, the overall removal efficiency would be higher, because PFOA was regarded as being capable of adsorbing ozone, stabilizing it, and thus causing it to have a longer half-life time in aqueous solution [12].

At pH 2.5, the values of the pseudo-first order and overall kinetic constants were higher in the presence of 100% PFOA compared to the cases of using alumina and the other types of PFOA catalysts, showing that the most effective catalyst was 100% PFOA for AR-151 and RBBR ozonations (Table 6). The reason for the lower kinetic constants in Al_2O_3/O_3 system at pH 2.5 and 7 might be due to using phosphate buffer to adjust the solution pH to the desired value in the experiments. It was reported that phosphate anions in the buffered solution had a high affinity to be adsorbed on the surface of alumina reducing its catalytic activity [6]; this effect was less significant at pH of 7 compared to the case at pH 2.5, but still it was obvious. Also some ozonation by-products (oxalic acid, formic acid, etc.) were adsorbed on the surface of alumina deactivating the surface-active groups at acidic medium [6]. The lower kinetic constants for ozonation of AR-151 with 100% PFOA catalyst compared with those for RBBR might be due to the relatively higher polarity of AR-151 having a higher dipole moment of 50.1 than that of RBBR with a dipole moment of 3.3 [30]. Only at pH 13, alumina catalyst yielded higher kinetic constant and COD removal in the ozonation of AR-151 than those of RBBR; because catalytic activity of alumina was known to be based on the catalytic decomposition of ozone and the enhanced generation of hydroxyl radicals [21]. However, PFOA catalyst did not decompose ozone but only enhanced its stability and solubility [11]. Therefore PFOA was found as a more effective catalyst for the dye RBBR, having a relatively low polarity (dipole moment = 3.3), and this finding was in agreement with the literature.

3.3.3. Effect of initial dye concentration on catalytic ozonation kinetics of AR-151 and RBBR

The pseudo-first order and overall kinetic constants were found at different initial dye concentrations by keeping ozone concentration in the aqueous phase constant (Table 7). The kinetic constant decreased from 1.99 mM^{-1} min^{-1} at $C_{\mathrm{d,i}} = 0.22$ mM to 0.70 mM^{-1} min^{-1} at $C_{\mathrm{d,i}} = 0.88$ mM for AR-151. Similarly, the kinetic constants were changed from 3.33 mM^{-1} min^{-1} to 2.27 mM^{-1} min^{-1} by changing $C_{\mathrm{d,i}}$ from 0.16 mM to 0.64 mM. The pseudo-first order and overall kinetic constants were decreased with the increasing initial dye concentration. The reaction rates were affected by the change of

Table 7
Effect of ozone production rate and initial dye concentration on kinetic constant in catalytic ozonation of AR-151 or RBBR

Dye	PR_{O_3} (g/h)	$C_{d,i}$ (mM)	k' (min^{-1})	k ($mM^{-1}\ min^{-1}$)
AR-151	1.11	0.22	0.109	2.45
	1.70	0.22	0.140	1.88
	2.21	0.22	0.175	1.99
		0.44	0.150	1.70
		0.88	0.062	0.70
RBBR	1.11	0.16	0.134	4.96
	1.70	0.16	0.172	3.25
	2.21	0.16	0.197	3.33
		0.32	0.168	2.84
		0.64	0.135	2.27

Conditions: pH 2.5 for AR-151; pH 7 for RBBR; catalyst type = 100% PFOA; $m_{cat} = 5$ g.

$C_{d,i}$ strongly in AR-151 ozonation, whereas the decrease in the constants with the increase of $C_{d,i}$ was smaller in the case of RBBR.

3.3.4. *Effect of ozone production rate on catalytic ozonation kinetics of AR-151 and RBBR*

The ozone production rate (PR_{O_3}) affected the equilibrium concentration of dissolved ozone in aqueous phase due to the changing percentage of O_3 in the inlet gas; because power level of the ozone generator was increased at a constant inlet air flow rate ($Q_G = 150$ L/h) which increased the partial pressure of ozone in the inlet gas. Thus its mole fraction in the aqueous phase increased according to the Henry's law [32]. Its effect on the reaction kinetics was investigated, and the kinetic constants were determined as given in Table 7. The pseudo-first-order rate constant k', being equal to kC_{O_3}, increased with the increasing ozone production rate, since the dissolved ozone concentration increased; but the overall kinetic constant, k, decreased. Therefore the overall kinetic constant was found to be the highest at the lowest PR_{O_3} (1.11 g/h). Afterwards, k value did not change significantly by the slight increase in PR_{O_3}.

4. Conclusions

The catalytic ozonation experiments for the aqueous solutions of the dyes, namely Acid Red-151 (AR-151) and Remazol Brilliant Blue R (RBBR) were conducted to find the dye and COD removal efficiencies in a semi-batch reactor at different operating conditions. Catalyst type, pH, initial dye concentration and ozone production rate (ozone dosage) were experimental variables. Generally it can be concluded that the efficiency of catalytic ozonation depended to a great extent on the pH of the solution, surface properties of the catalyst and characteristics of dyes, which affected ozone decomposition rate and interaction between the species in solution and surface active sites on the catalysts. The specific findings can be listed as follows:

- Overall dye removal efficiency, after 30 min of reaction time, did not depend on solution pH significantly.
- The contribution of radicals to the dye-oxidation was more significant in the semi-batch reactor compared to that in the batch reactor [15] in the sole ozonation of AR-151.
- Catalytic ozonation using alumina or perfluorooctylalumina (PFOA) as a catalyst did not further improve the overall dye removals in 30 min of ozonation over those obtained in the ozonation alone for both of the dyes.
- For RBBR, pH 7 was found as the optimum value in removing the dye with best efficiency at the studied experimental conditions for both alumina and 100% (w/w) PFOA catalysts.
- The dye removal rates increased with the ozone production rate, except the initial ozonation rate of both AR-151 and RBBR, which showed a low dependence on the ozone input.
- In the ozonation of RBBR with PFOA catalyst, catalytic sites and alkyl chains on the surface provided by 25% (w/w) PFAO were sufficient to remove COD with an efficiency of about 95%, and further increase in the amount of PFO acid in alumina did not improve the efficiency significantly, at pH 13.
- At pH 13, ozone decomposition was enhanced by alumina catalyst yielding the highest value of COD removal for AR-151, where the removal mechanism was based on the high reactivity of hydroxyl radicals.
- The results indicated that both the total dye and COD removals after 30 min of ozonation were almost independent of the initial dye concentration at its relatively low values while at higher concentrations, they changed with the initial dye concentration for both of the dyes.
- In the sole ozonation of AR-151 at a high initial dye concentration of 400 mg/L and at pH 2.5, the total dye and COD removals in 30 min of ozonation were much lower than those at the lower initial concentrations of 100–200 mg/L. These removal efficiencies could be improved by increasing the time of ozonation, which would be necessary for the oxidation of all the intermediates produced at higher concentrations due to the high initial concentration of the original dye.
- Phosphate anions from buffer solutions used in the experiments to adjust pH value to 2.5 or 7 had high affinity to be adsorbed on the surface of alumina catalyst, and apparently decreased its catalytic activity causing relatively low kinetic constants and COD removals; this was in agreement with the literature.
- The results showed that catalytic ozonation with alumina or a type of PFOA catalyst was a very effective method to remove both the dye and COD from the wastewaters containing high concentrations of dyes. At pH 13, alumina catalyst yielded higher kinetic constant and COD removal in the ozonation of AR-151 than those of RBBR; 100% PFOA was found to be the most effective catalyst for RBBR at pH 13 with respect to COD removal percentages.
- Increasing amount of perfluorooctanoic (PFO) acid in PFOA catalyst enhanced its catalytic activity with alkyl chains.
- It was observed that the effect of supplied ozone did not significantly affect the total dye removal in 30 min at different ozone production rates studied. However, the COD reduction percentage was increased by the increment of ozone input to the reactor.

References

[1] H.Y. Shu, M.C. Chang, Pre-ozonation coupled with UV/H_2O_2 process for the decolorization and mineralization of cotton dyeing effluent and synthesized C.I. Direct Black 22 wastewater, J. Hazard. Mater. B 121 (2005) 127–133.

[2] D.R. Hitchcock, S.E. Law, J. Wu, P.L. Williams, Determining toxicity trends in the ozonation of synthetic dye wastewaters using the Nematode, *Caenorhabditis elegans*, Arch. Environ. Contam. Toxicol. 34 (1998) 259–364.

[3] E. Oğuz, B. Keskinler, Z. Çelik, Ozonation of aqueous Bomaplex Red CR-L dye in a semi-batch reactor, Dyes Pigments 64 (2005) 101–108.

[4] B. Kasprzyk-Hordern, A. Dabrowska, J. Swietlik, J. Nawrocki, Ozonation enhancement with non-polar bonded alumina phases, Ozone Sci. Eng. 26 (2004) 367–380.

[5] B. Kasprzyk-Hordern, P. Andrzejewski, A. Dabrowska, K. Czaczyk, J. Nawrocki, MTBE, DIPE, ETBE and TAME degradation in water using perfluorinated phases as catalysts for ozonation process, Appl. Catal. B: Environ. 51 (2004) 51–66.

[6] M. Ernst, F. Lurot, J. Schrotter, Catalytic ozonation of refractory organic model compounds in aqueous solution by aluminum oxide, Appl. Catal. B: Environ. 47 (2004) 15–25.

[7] C. Cooper, R. Burch, An investigation of catalytic ozonation for the oxidation of halocarbons in drinking water preparation, Water Res. 33 (1999) 3695–3700.

[8] C.H. Ni, J.N. Chen, Heterogeneous catalytic ozonation of 2-chlorophenol aqueous solution with alumina as a catalyst, Water Sci. Technol. 43 (2001) 213–220.

[9] H. Einaga, S. Futamura, Catalytic oxidation of benzene with ozone over alumina-supported manganese oxides, J. Catal. 227 (2004) 304–312.

[10] C. Volk, P. Roche, J. Joret, H. Paillard, Comparison of the effect of ozone, ozone-hydrogen peroxide system and catalytic ozone on the biodegradable organic matter of a fulvic acid solution, Water Res. 31 (1997) 650–656.

[11] B. Kasprzyk-Hordern, M. Ziolek, J. Nawrocki, Catalytic ozonation and methods of enhancing molecular ozone reactions in water treatment, Appl. Catal. B: Environ. 46 (2003) 639–669.

[12] B. Kasprzyk-Hordern, A. Dabrowska, J. Swietlik, J. Nawrocki, The application of the perfluorinated bonded alumina phase for natural organic matter catalytic ozonation, J. Environ. Eng. Sci. 3 (2004) 41–50.

[13] C. Lai, J.H. Harwell, E.A. O'Rear, S. Komatsuzaki, J. Arai, T. Nakakawaji, J. Ito, Adsorption isotherms of perfluorocarbon surfactants from aqueous and non-aqueous solutions and friction measurements of perfluorosurfactant-adsorbed alumina, Colloid Surf. A 104 (1995) 231–241.

[14] L.F. Wieserman, K. Cross, E.S. Martin, US Patent 4,983,566 (1991).

[15] T.A. Özbelge, F. Erol, H.Ö. Özbelge, A kinetic study on the decolorization of aqueous solutions of Acid Red-151 by ozonation, J. Environ. Eng. Sci. Health: Part A 38 (2003) 1607–1623.

[16] M.C. Rand, A.E. Greenberg, M.J. Taras, Standard Methods for the Examination of Water and Wastewater, 18th ed., APHA, Washington, DC, 1992, pp. 455–460.

[17] H. Bader, J. Hoigne, Determination of ozone in water by the indigo method, Water Res. 15 (1981) 449–455.

[18] H.Y. Shu, C.R. Huang, Degradation of commercial azo dyes in water using ozonation and UV-enhanced ozonation process, Chemosphere 31 (1995) 3813–3825.

[19] J. Hoigne, H. Bader, Role of hydroxyl radical reactions in ozonation processes in aqueous solution, Water Res. 10 (1976) 376–386.

[20] R.G. Rice, Applications of ozone for industrial wastewater treatment—a review, Ozone Sci. Eng. 19 (1997) 477–515.

[21] B. Kasprzyk-Hordern, Chemistry of alumina, reactions in aqueous solution and its application in water treatment, Adv. Colloid Interf. Sci. 110 (2004) 19–48.

[22] A.K. Carlos, F. Wypych, S. Moraes, N. Duran, N. Nagata, P. Peralta-Zamora, Semiconductor-assisted photocatalytic degradation of reactive dyes in aqueous solution, Chemosphere 40 (2000) 433–440.

[23] K. Thomas, P.E. Hoggan, L. Mariey, J. Lamote, J.C. Lavalley, Experimental and theoretical study of ozone adsorption on alumina, Catal. Lett. 46 (1997) 77–82.

[24] R.G. Harris, J.D. Wells, B.B. Johnson, Selective adsorption of dyes and other organic molecules to kaolinite and oxide surfaces, Colloid Surf. A 180 (2001) 131–140.

[25] A.H. Gemeay, G.R. El-Ghrabawy, A.B. Zaki, Kinetics of the oxidative decolorization of reactive blue 19 by acidic bromate in homogeneous and heterogeneous media, Dyes Pigments 73 (2007) 90–97.

[26] S.J. Masten, J. Hoigne, Comparison of ozone and hydroxyl radical-induced oxidation of hydrocarbons in water, Ozone Sci. Eng. 14 (1992) 197–214.

[27] F. Saunders, J.P. Gould, C.R. Southerland, The effect of solute competition on ozonolysis of industrial dyes, Water Res. 17 (1983) 1407–1419.

[28] M. Trapido, Y. Veressinina, J.K. Hentunen, A. Hirvonen, Ozonation of chlorophenols: kinetics, by-products and toxicity, Environ. Technol. 18 (1997) 325–332.

[29] W. Chu, C.W. Ma, Quantitative prediction of direct and indirect dye ozonation kinetics, Water Res. 34 (12) (2000) 3153–3160.

[30] R.W. Dapson, Dye–tissue interactions: mechanisms, quantification and bonding parameters for dyes used in biological staining, Biotech. Histochem. 80 (2) (2005) 49–72.

[31] B. Kasprzyk-Hordern, J. Nawrocki, The feasibility of using a perfluorinated bonded alumina phase in the ozonation process, Ozone Sci. Eng. 25 (2003) 185–197.

[32] W.L. McCabe, J.C. Smith, Unit Operations of Chemical Engineering, 6th ed., McGraw-Hill Inc., Tokyo, 2000.