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Assessment of degradation of eight commercial reactive azo dyes individually and in mixture in aqueous solution by ozonation

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Abstract

Degradation of eight commercial reactive azo dyes with different structures containing different substituted groups has been investigated in a semi-batch reactor by ozonation individually and in mixture. The results showed that pH 10 was effective for color and COD removal of these dyes. Different dyes needed different time of ozonation for decolorization. Dyes even if decolorized to 95–99%, COD removal was different for different dyes indicating that the complexicity of structures play a major role. Oxidation and cleavage of substituent groups were evidenced by the release of chloride, nitrate and sulfate during ozonation. Increase in biodegradability was observed after ozonation, as measured by the BOD_5/COD ratio. The ozonation reaction followed a pseudo first order kinetics. The study revealed that ozonation of reactive dye is a viable technique for dye containing wastewater treatment.

Keywords: Ozonation; Decolorization; COD removal; TOC removal

1. Introduction

Synthetic dyes and pigments released to the environment in the form of effluents by textile, leather and printing industries cause severe ecological damages. Wastewater from these industries is highly colored and contains organics which contaminate ground water. Synthetic dyes include several structural varieties of dyes such as acidic, reactive, basic, azo, diazo, anthraquinone based and metal complex dyes [1]. Neither simple chemical nor biological treatment alone has proved adequate in decolorization and sufficient depletion of inorganic matter [2]. Due to the inhibitory nature of many compounds for biological oxidation, the need for pretreatment by advanced oxidation process (AOP) has become essential. One of the AOP processes is ozonation, which is versatile and environmentally sound. Ozonation of water is a well known technology and the strong oxidative properties of O_3 and its ability to effectively oxidize many organic compounds in aqueous solution have been well documented [3]. Ozone treatment of several types of wastewater has resulted in considerable COD reduction and has been used for treatment of dyes, phenols, pesticides, etc. [4,5]. In recent years, ozonation is emerging as a potential process for color removal of dyes, since the chromophore groups with conjugated double bonds, which are responsible for color can be broken down by ozone either directly or indirectly forming smaller molecules, thereby decreasing the color of the effluents [4,6]. Due to its high electrochemical potential (2.08 V), O_3 is the strongest oxidant available and applicable as compared to H_2O_2 (1.78 V) [7] and can react with several classes of compounds through direct or indirect reaction. Unlike other oxidizing agents such as Cl_2, oxidation with O_3 leaves no toxic residues that have to be removed or disposed [8]. Studies carried out by Bowers [9] have shown that ozone generally produces nontoxic end products which are converted to CO_2 and H_2O depending on the conditions.

The mechanism of O_3 reaction was studied by Hoigne and co-workers [10,11]. Ozone reacts directly with pollutants via ozonolysis and through radical chain reaction. The reaction

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of ozone with OH^- ions to intermediate radicals and to OH radicals is important for the oxidation of saturated organic compounds where no molecular ozonolysis is possible [12]. Typically, ozonation rarely produces complete mineralization to CO_2 and H_2O, but leads to partial oxidation products such as organic acids, aldehydes and ketones where oxygen is introduced into carboneous sites within the product molecules [13]. It has been reported that the rate-limiting step in the ozonation of dye containing wastewater is the mass transfer of ozone from the gas phase to the wastewater [14,15].

Textile preparation, dying and finishing plants are currently been forced to treat their effluents at least partially prior to discharge, due to high organic load, strong and resistant color, as well as high dissolved solids of the wastewater [6,16]. The commercial dyestuff which is imparting color is intentionally designed to be recalcitrant under typical usage condition, and a marked resistance of these dyes to biological treatment is not unusual [17]. Many studies have confirmed that incomplete degradation product of dyes are carcinogenic and mutagenic in nature [18].

The objective of the present investigation is to study the feasibility of the degradation of eight commercial dyes with different chemical structure for color and COD removal individually as well as in mixture. Changes intended by ozonation on biodegradability of dyes in terms of COD, BOD and TOC are also evaluated.

2. Materials and methods

2.1. Reagents and chemicals

Commercial grade reactive dyes were used in the study without purification. Known concentration of azo dye solution was prepared in deionized water and used for all studies. Other chemicals used were of A.R. grade. Table 1 presents the characteristics of commercial azo dyes used in the study. They are Red RB (RRB), Remazol Red (RR), Remazol Blue (RB), Remazol Black (Rbla), Remazol Violet (RV), Remazol Orange (RO), Golden Yellow (GY) and Remazol Yellow (RY).

2.2. Ozonation experiment

Ozone was generated from dry air in a laboratory model of ozonator with a maximum capacity of 20 g h^{-1}. Ozonation experiments were conducted in 1 l borosilicate glass reactor. Ozone was supplied at the bottom of the reactor through a glass diffuser. All connections from the ozone generator to the reaction vessel were made through Teflon tubing. The ozone concentration in the feed gas stream and outlet gas stream was measured by iodometric Standard Method [19]. The unreacted ozone leaving the column was collected in three gas washing bottles filled with 2% KI solution. The KI solution reacts with excess ozone liberating I_2 and the resulting I_2 was titrated against standard thiosulfate using starch as indicator. All experiments were conducted at room temperature and in semi-batch mode by sparging the ozone continuously into solution. Samples were withdrawn at definite time intervals to analyze all parameters.

Table 1
Commercial monoazo dyes used in the study

Name of commercial dyes	CI number	λ_{max}	COD (mg l^{-1})
Red RB	18 055	520	144
Remazol Red	11 460	511	147
Remazol Blue	62 125	610	169
Remazol Black	11 815	576	162
Remazol Violet	42 650	541	90
Remazol Orange	60 700	494	54
Golden Yellow	22 910	412	108
Remazol Yellow	13 065	418	90

2.3. Analysis

pH, COD, chloride, nitrate and sulfate were measured as per Standard Methods [19] . TOC was analyzed using a TOC analyzer (Beckmann Model 925-A). The UV scans of the samples were done using UV–vis spectrophotometer (Shimadzu Model UV 160A) at 200 nm to 800 nm. Decolorization was determined by measuring the absorbance of the solution at the wavelength in the visible range, where maximum absorbance was obtained.

3. Results and discussion

3.1. Effect of pH on ozonation

Solution pH plays a major role in the formation of OH radicals during ozonation. The experiments were carried out at various pH values for one of the dyes, Remazol Red (100 mg l^{-1}), at an ozone dose of 4.33 mg l^{-1} and the data are presented in Fig. 1. Boncz et al. [20] indicated that pH value is the most important factor in the ozonation of chlorophenol, since pH determines the dissociation of organic compounds. Hsu et al. [21] reported that increase in COD removal with increase in pH might be due to the self-decomposition of ozone to generate hydroxyl free radicals which can oxidize the organic compounds more efficiently. It could be seen from the figure that as the pH was increased from 5.0 to 10, COD removal (COD_t/COD_0) increased from 0.2 to 0.8 indicating that the alkaline pH is favorable for decomposition by

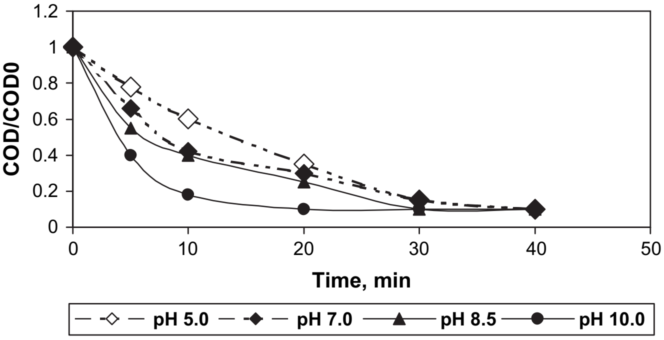


Fig. 1. Degradation of Remazol Red at various pHs.

ozonation which is initiated by the formation of hydroxyl radicals at higher pH values [22,23]. The applied ozone dose was able to decolorize dyes within 30 min of ozonation turning the solution colorless. Color removal also showed increasing trend with increase in pH and was observed to be 90% at pH 10. The solution also turned from dark red to colorless. Balcioglu and Arslan [24] reported similar observation during the ozonation of synthetic dye wastewater. During ozonation, at initial pH of 10, the pH of the solution decreased gradually during the degradation process, while at lower initial pH, the solution rapidly became acidic. At lower pH, oxidation by ozone became significant and oxidation by more reactive hydroxyl radical was less, therefore dye degradation was slower in acidic solutions as observed by steady COD removal. The pH decrease was caused by both the formation of acidic degradation products and by consumption of OH^- in the decomposition of ozone [5].

3.2. Color removal

The color removal during ozonation was studied for all the dyes individually. Fig. 2a and b shows the color removal with reaction time for 500 mg l^{-1} of initial dye concentration. The result indicates that the decolorization pattern of studied dyes is different and each dye presents a behavior according to its chemical structure. Ozonation was carried out for 30–40 min. Color removal was between 60 and 90% for all the eight dyes. Decolorization was slow for dyes, namely RY, RRB, RV, as compared to other dyes. pH decreased during color removal from 10 to 3.0.

Decolorization of some of the dyes, RR, RY, GY, RO and RB beyond 500 mg l^{-1} was not possible even after 1 h of ozonation, whereas Red RB, RV and RB were able to decolorize even at a higher concentration of 1000 mg l^{-1} (Fig. 2c). This may be due to the structural differences existing between the dyes. The color removal was probably due to the fact that ozone is able to cleave the azo bond from dye. Nematu et al. [25] have obtained only 29.3% decolorization for Disperse Red 354, after 30 min of ozonation at an ozone concentration of 8.2 mg l^{-1}. Banat et al. [1] have shown inability to remove color from dyes which are highly recalcitrant and unbiodegradable because of the diverse chromophoric groups.

3.3. COD removal

The COD removal during ozonation was studied for all the dyes individually. Fig. 3a and b shows COD removal during ozonation at an initial dye concentration of 500 mg l^{-1}. COD removal was 22–70% after the same reaction time of ozonation. This may be due to the production of small organic molecular fragments along with the destruction of dyestuff, not being completely mineralized under prevailing oxidation conditions. GY, RR, RY have shown only 20–40% COD removal as compared to other dyes.

Fig. 3c represents COD removal for Red RB, RV, and RB at 1000 mg l^{-1} of dye concentration. COD removal was only 40% for Red RB and RV, whereas RB has 75%. Small organic molecules contribute considerably to the COD that cannot be completely removed by ozonation reaction. However, they are easily digested by activated sludge processes [26]. Singer [27] has also observed that even in the presence of excess ozone, the reaction does not result in complete mineralization to carbon di oxide.

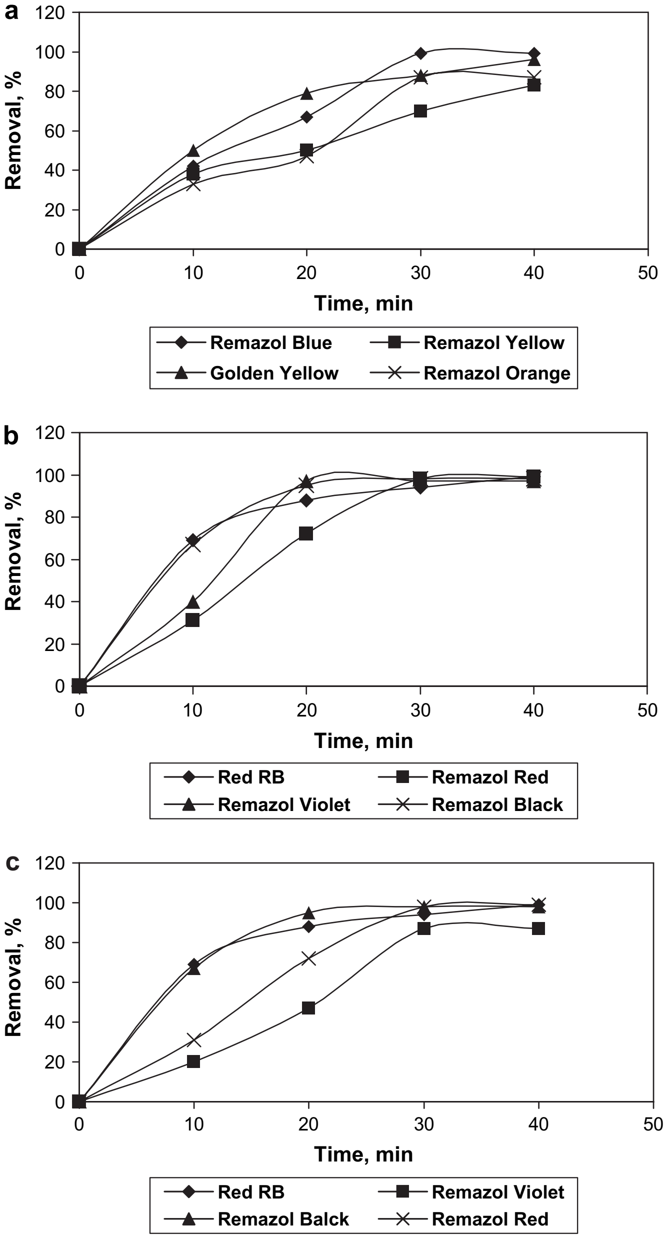


Fig. 2. Color removal during ozonation of azo dyes (concentration: 500 mg l^{-1} (a), 500 mg l^{-1} (b) and 1000 mg l^{-1} (c)).

3.4. Mixed dyes

Once the ozonation treatment has been tested on monocomponent solutions, an attempt was made to determine the efficiency of decolorization in a mixture. Real effluents often include more than one component and study of the possible interaction between different chromophores will be very

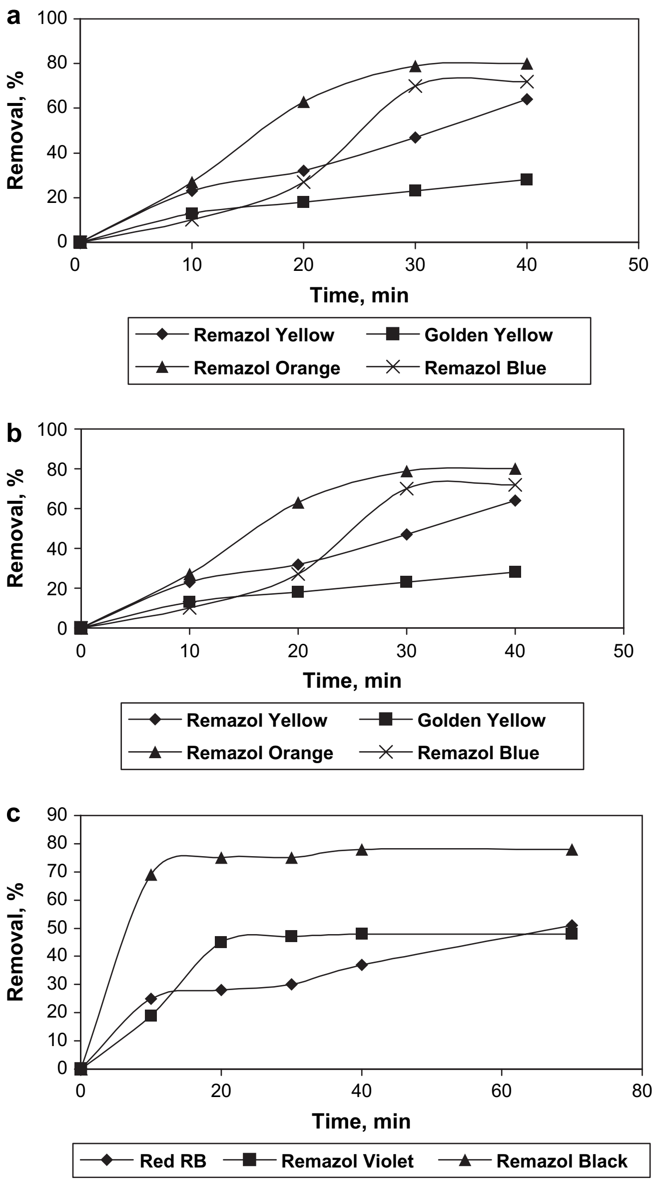


Fig. 3. COD removal during ozonation of azo dyes (concentration: 500 mg l^{-1} (a), 500 mg l^{-1} (b) and 1000 mg l^{-1} (c)).

useful for the treatment of real effluents. All the eight dyes were mixed together in equal proportion to formulate synthetic wastewater. The concentrations of dyes in the mixture ranging from 50 to 500 mg l^{-1} were ozonated and the efficiencies of decolorization and COD removal are given in Fig. 4a and b, respectively. At lower concentrations of dyes, the color removal from synthetic wastewater was quite fast, but when dye concentration increased to 200–500 mg l^{-1}, it requires a longer time for color removal. Fig. 5 represents UV–Vis absorbance spectrum of mixed dyes after ozonation. The peak corresponding to 510 nm disappeared in the ozonated samples. Increase in organics, estimated by peak in UV region, indicates that degraded organic intermediates were formed during ozonation. It is remarkable that the decolorization rate of each dye clearly changed in the mixture. Similar was the case with COD removal. At lower concentration, COD removal was fast. Fig. 6 depicts the TOC removal during ozonation of synthetic wastewater at different dye concentrations. At a concentration of 50–100 mg l^{-1}, TOC removal was 55%, but it has reduced at a higher concentration of 200–500 mg l^{-1}. COD removal was more efficient than TOC reduction throughout the ozonation process (Figs. 4b and 6). COD removal rate was 40–80% after 30 min of ozonation. The corresponding TOC removal rate was 44–80% under identical operation conditions. Wang et al. [28] have also observed that for the azo dye Remazol Black 5, COD reduction was more efficient (65%) than TOC (25%) under identical operation conditions.

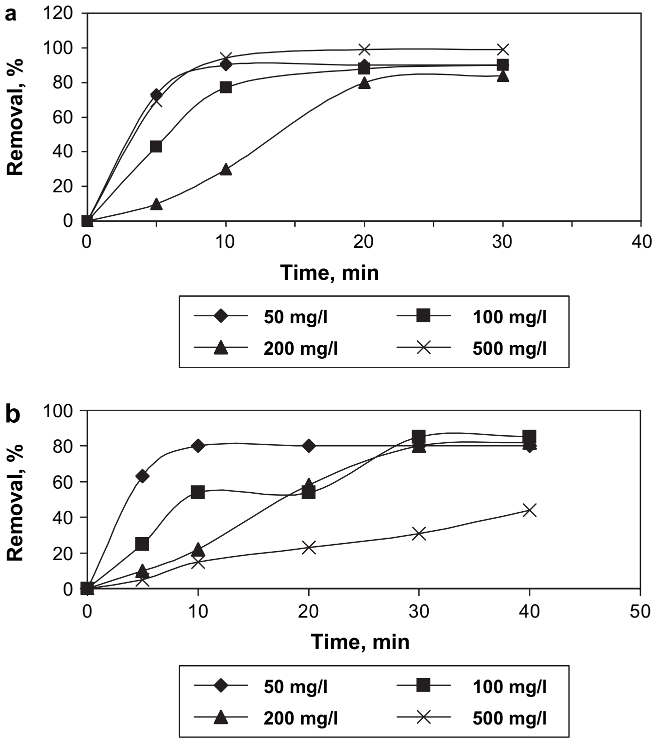
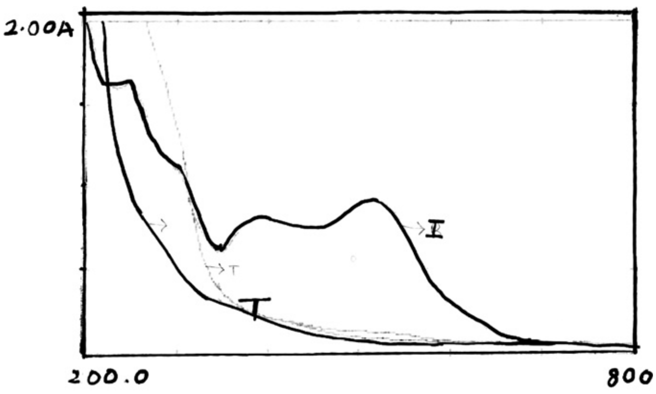


Fig. 4. (a) Color removal during ozonation at different concentrations of mixed dyes; (b) COD removal during ozonation at different concentrations of mixed dyes.



(I-Initial, T –After ozonation)

Fig. 5. UV–vis scan data of mixed dyes during ozonation.

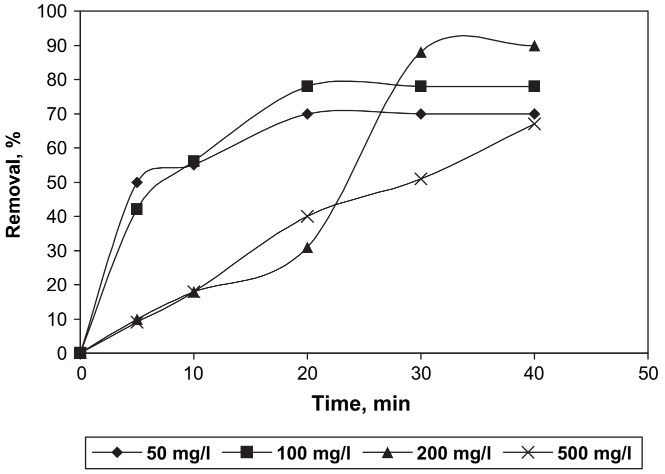


Fig. 6. Removal of TOC during ozonation at different concentrations of mixed dyes.

3.5. Biodegradibility of dyes

Parallel to decrease of the COD, biodegradability was measured as BOD_5 for raw and treated dyes. The COD, BOD and TOC for raw and treated samples of all the dyes individually and for the mixture are given in Table 2. TOC values may not present the total TOC concentrations due to loss of volatile compounds formed during ozonation. Considering extremely low BOD_5/COD ratio (0.196) for mixed dyes can be regarded as almost resistant to biological degradation. The BOD_5/COD ratio for RRB, RV, RY, RO, GY, RB, Rbla, etc. was more than 0.3 after ozonation of dyes. The biodegradability test in terms of BOD_5/COD ratio for dyes after ozonation have increased may be probably as a result of metabolic activity due to the presence of more easily degradable compounds. Wang et al. [28] have also shown that first by-product after partial ozonation (10–150 min) of Remazol Black 5 was more biodegradable than the parent compound and ozonation can enhance the biodegradability of the azo dyes.

3.6. Ozonation product

To obtain detailed invention on the reaction process during ozonation, the resulting oxidation product analysis of organic and inorganic anions were performed. The main oxidation products were identified to be acetate, formate, sulfate and in some dyes, chloride. Oxidation and cleavage of the sulfonic groups lead to the increasing amount of sulfate during ozonation. Table 3 represents the concentration of inorganic/organic ions formed during ozonation of dyes. The pH of the solution decreased from 10 to 3.0 during 30 min of ozonation indicating the formation of acids and other ions due to the reaction of ozone with nucleophilic centers [7]. Decrease in pH of the solution from 6.1 to 2.3 was observed on ozonation of reactive dyes [28]. Sulfate values increased to 380 $mg\,l^{-1}$ after 30 min ozonation. Concentration of nitrate increased from 8 to 20 $mg\,l^{-1}$. These observations indicate that during ozonation, the aromatic ring of dye is broken down leading to the generation of inorganic ions. Oxidation and cleavage of amino groups results in the formation of nitrate, and cleavage of sulfonic group leads to increasing amount of sulfate. Koch et al. [2] reported that ozonation of Reactive Yellow 84 resulted in decolorization of the dye and 50% COD removal with increase in concentration of nitrate and sulfate. These observations show that dyes are decomposed by ozonation into smaller molecules, which are biodegradable. Therefore BOD_5/COD ratio is increased after ozonation. Due to the decreasing value of pH during ozone treatment it can be assumed that the ozonated solution contains the analyzed organic anions in the form of their corresponding acids.

Table 2
Biodegradability of commercial azo dyes

Dyes	COD ($mg\,l^{-1}$)		BOD ($mg\,l^{-1}$)		TOC ($mg\,l^{-1}$)		Initial BOD_5/COD	Treated BOD_5/COD
	I	E	I	E	I	E		
Red RB	261	90	88	40	64	28	0.366	0.444
Remazol Red	551	385	120	90	99	65	0.217	0.233
Remazol Black	290	199	80	70	23	19	0.275	0.301
Remazol Orange	423	91	110	50	120	79	0.260	0.549
Remazol Blue	329	172	100	70	37	31	0.303	0.406
Remazol Violet	588	136	190	70	75	47	0.323	0.515
Remazol Yellow	423	151	70	50	94	62	0.165	0.331
Golden Yellow	306	235	100	80	–	–	0.326	0.340
Mixed Dyes	306	212	60	25	184	60	0.196	0.212

Dye concentration, 500 $mg\,l^{-1}$; ozonation time, 30 min; I, influent; E, effluent.

3.7. Kinetics of ozonation

The direct reaction of ozone is assumed to be first order with respect to the dye and ozone. If ozone concentration is assumed to reach a stationary concentration at the interface, the oxidation rate follows a pseudo first order kinetics with respect to the concentration of the organic substance [14] and is as follows:

$$-\frac{dC_A}{dt} = k'\,dC_A$$

where k'd is the pseudo first rate constant and C_A concentration of organic substance. This coefficient takes into account the concentration of dissolved ozone. According to the equation above, a plot of ln $[COD_t/COD_0]$ vs reaction time has to provide straight line whose slope is the pseudo first order kinetic constant. Fig. 7 represents experimental data for dyes GY, RY and mixed dyes. The pseudo first order kinetic k' values for

Table 3
Concentrations of inorganic/organic ions formed during ozonation of mixed azo dyes

Inorganic/organic ions	Concentration ($mg\,l^{-1}$)
Sulfate	380
Nitrate	25
Chloride	9
Formate	30
Oxalate	5

Dye concentration, 500 $mg\,l^{-1}$; ozonation time, 30 min.

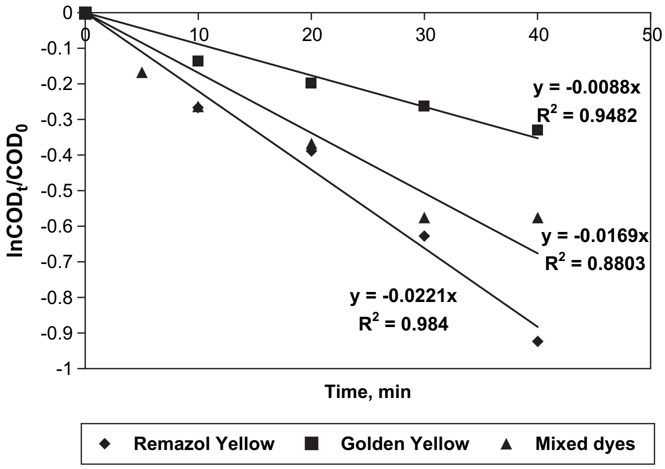


Fig. 7. Pseudo first order kinetics of some dyes by ozonation.

other dyes are given in Table 4. Least square regression analysis was used to determine the values of slope. This suggests that the decolorization reactions are kinetically controlled. It could be seen from Table 4 that the data fitted linearly with coefficient values ranging from 0.902 to 0.9598. The rate constants obtained for O_3, as given in Table 4, indicate that the order of degradation was RR > RV > RO > RY > RB > Rbla > mixed dyes > RRB > GY. Wu and Wang [29] have also observed pseudo first order trend during ozonation of Reactive Black 5. RR was almost completely decolorized within 30 min with a rate constant value of 12.3×10^{-2} min^{-1}. An azo dye such as RO, RV, RRB, RY and RB showed decolorization percentage of about 95.5–98.0% after 30 min of ozonation. The rate constant for mixed dyes was 1.69×10^{-2} min^{-1} with 98% decolorization within 30 min. The rate constant in mixture was much lower as compared to individual dyes. The behavior can be explained in terms of the nature of the substituent groups in dyes. It is known that structural differences component reactivity. Sanromain et al. [30] observed that dyes Bromophenol Blue (BPB) and Phenol Red have same structure but BPB has four bromo substituents, thus making it more reactive and can be easily decolorized by electrochemical treatment. Mostly, the decolorization rate was enhanced by indirect oxidation, degrading first the dye with a small size (low number of aromatic rings). In this way dyes with simpler molecular structure was more rapidly degraded than a much more complex molecule such as GY, Rbla. Dyes RR, RRB were decolorized by 98–99.4% in 30 min whereas RY, RO reached a value as high as 50% and 80%, respectively, in the same time. When all the dyes were mixed together they gave 98% decolorization within 30 min of ozonation at 500 mg l^{-1} concentration. Therefore, dyes difficult to be decolorized in monocomponent system can be satisfactorily treated in a mixture.

Table 4
Influence of ozonation on decolorization of pseudo first order reaction rate constants

Dyes	k' ($\times 10^{-2}$ min^{-1})	r^2	Color removal (%)
Red RB	3.2	0.78	98.0
Remazol Red	12.3	0.96	99.4
Remazol Black	1.91	0.68	97.1
Remazol Orange	4.35	0.96	95.5
Remazol Blue	2.19	0.018	96.7
Remazol Violet	4.55	0.56	97.2
Remazol Yellow	2.21	0.98	95.5
Golden Yellow	0.88	0.95	95.7
Mixed Dyes	1.69	0.88	98.0

4. Conclusions

The present study demonstrated that nearly complete decolorization of various azo dyes could be accomplished by ozonation. Maximum color and COD removal could be achieved at an ozone dose of 4.33 mg l^{-1} at 30 min. The study also revealed that the applied ozone dose has a positive effect on decolorization and degradation. The sulfate, nitrate, and chloride group from azo dyes were released from the structure group early during the decomposition reaction followed by mineralization to simpler organic intermediates such as formate and oxalate. The decomposition of reactive azo dyes followed a pseudo first order kinetics with rate of reaction being highest during ozonation with RR. The results of the present study have clearly demonstrated that ozonation proes to be a viable technique for the treatment of highly recalcitrant azo dyes containing wastewater.

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