Integrated Treatment of Ozonation and Aerobic Biodegradation for Mixed Azo Dyes

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Abstract: There are several studies on decolorization and degradation of azo dyes by ozonation. However, the combined treatment of ozonation followed by aerobic biodegradation for mixed azo dyes has not been reported much. As prolonged ozonation alone is costly so aerobic degradation which is cheaper has been studied after ozonation to make overall treatment economic. The effect of ozonation on the degradation process of mixed azo dye solution, containing four azo dyes, CI Acid Red14 (AR14), Congo Red (CR), CI Reactive Black 5(RB5), CI Reactive Violet 5(RV5) each of 250 mgl^{-1} has been studied in the semi batch rector. The parameters such as pH, absorbance (at maximum wavelength), conductivity, COD, TOC and BOD_5 were monitored during the ozonation process at different time intervals with influent ozone dose of 55.8 g, O_3m^{-3}. The results obtained indicate that ozonation is highly effective way to remove the color of synthetic dye solutions but still lots of organic contents remain at that time. Determination of coefficients of decay for individual dyes from ozonated samples of mixed dye by high performance thin layer chromatography (HPTLC) showed that decay rates of reactive dyes as well as di-azo dyes were less compared to other dyes and mono azo dyes. BOD_5 data revealed that partial oxidation of mixed azo dyes by ozonation increases the biodegradability (BOD_5/COD ratio increases from .01 to 0.42) after 80 min ozonation. More then 90% reduction in COD and TOC takes place for mixed dye after 60 min ozonation followed by aerobic biodegradation. Results of integrated treatment indicate that treated wastewater may be disposed in water bodies or may be considered for reuse.

Keywords: Azo dyes; Ozonation; Biodegradability; HPTLC; Mixed dye

I. Introduction

Wastewaters from dye manufacturing and textile dyeing and finishing factories are complex waste products, characterized by their deep color and high concentration of environmental pollutants. In the past, a chemical coagulation process in combination with activated sludge process was widely adopted for the treatment of this type of wastewater. The effects were ineffective because of the wide variations in the quantity and wastewater composition and the very low biodegradability of dyes. Ozonation may prove to be a potential alternative to solve this problem (Hsu et al., 2001). In general, 40-90% of the dye is fixed to the fabric during the dyeing process, depending on the fixation rate of the applied dyestuff. Large amount of unfixed azo dye remain in effluent after completion of dyeing process, which leads to decrease in transparency of water and inhibition of sunlight if discharged in water body (Gomes et al., 2000; Wang et al., 2003).

Azo dye molecules are highly structured polymers, characterized by nitrogen to nitrogen double bonds (N=N) which are mainly bound to benzene or naphthalene rings (Sarasa et al., 1998), hence they are very difficult to breakdown biologically and can not be treated efficiently by conventional methods like an activated sludge process (Lin and Lin, 1993; Arslan and Balcioglu, 1999; Wu and Wang, 2001). It is known that reactive and acid dyes are the most problematic, as they tend to pass through conventional treatment system unaffected (Robinson et al., 2001; Wang et al., 2003). The mechanism of microbial decolorization of azo dyes involves the reductive cleavage of azo linkages under anaerobic conditions resulting in the formation of colorless aromatic amines, which are more toxic than parent dyes and resist further anaerobic degradation (Kherha et.al., 2005)

Ozone as one of the good oxidation agent (oxidation potential 2.08V) has been applied to many fields of water and wastewater. There are many processes by which decolorization is possible: adsorption, precipitation, chemical degradation, photo-degradation and biodegradation. Of the chemical processes for color removal oxidative degradation by ozone is the most important and effective. High color removal efficiency, enhanced biodegradability, destruction of phenolic compounds as well considerable reduction in chemical oxygen demand can be attained by ozonation for textile mill effluents (Koch et al., 2002). Ozone is very effective for complete removal of color, because it attacks conjugated double bonds which are associated with color but provides only partial reduction of COD and TOC. The mechanism of reaction of ozone follows two main paths: a direct path corresponding to the action of molecular ozone, and an indirect path resulting from the decomposition ozone to radicals, initiated by hydroxyl ions (Gural& Singer, 1982; Sarasa et al, 1998). Ozone and hydroxyl radicals ($OH^{.}$) generated in the aqueous solution are able to open the aromatic rings (Oguz et al., 2005). Dye molecules are oxidized to small molecules such as organic acids, aldehydes, ketones etc, instead of completely mineralized by ozonation (Lin and Lin, 1993; Alvares et al., 2001;Wang et al., 2003). Thus ozonation is capable of decomposing the highly structured dye molecules into smaller ones, which can easily be biodegraded in an activated sludge process (Gökçen and Tülay, 2005).

Most of the wastewater from actual dye manufacturing and textile dyeing and finishing factories is composed of mixed dye solutions. The ozonation of a mixed-dye solution is considerably more complicated than that of a single –dye solution. The mixed dye solution could have effects on the rate and degree of single-dye decolorization (Hsu et al., 2001). Ozonation could be competitive in spite of its high energy costs, if partial effluents were to be treated (Koch et al., 2002). Therefore, a combined treatment of ozonation and biological degradation might be a choice for the treatment of dye bath effluents (Wang et al., 2003; Zhange et al., 2004).

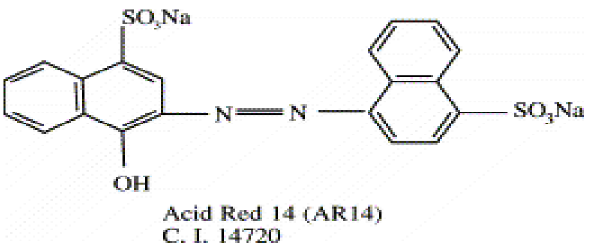
It has been confirmed that rate limiting step in the ozonation of dye containing wastewater is the mass transfer of ozone from gas phase to the wastewater (Wu and Wang, 2001). Researchers have also observed that the decolorization of the azo dye by ozone is a pseudo-first-order reaction with respect to dye and the rate constants decreased as the dye/ozone ratio increased (Chu and Ma, 2000; Wu and Wang, 2001). Time for complete decolorization increases with increase in number of azo groups (Shu and Hung, 1995) and salt concentration in azo dyes while it decreases with increase in number of sulphonic acid groups in the dye structure (Muthukumar et al., 2005).At higher dye concentrations ozonation may become less efficient because of increased competition for ozone between parent molecules and reaction by-products (Alvares et al., 2001).

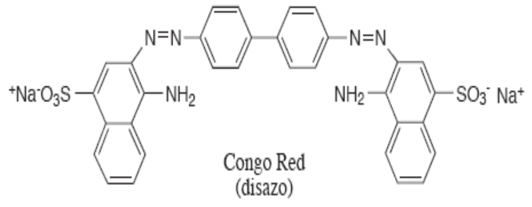
This study include the ozonation of mixed aqueous azo dyes containing four azo dyes AR 14, CR, RB 5 and RV 5 in semi batch reactor followed by aerobic biodegradation after different ozonation time. Determination of coefficients of decay of individual dyes as well as decay coefficients after separating individual dyes from mixed dye solutions have also been done. The objective of the study was to investigate the integrative effect of ozonation and aerobic biodegradation on synthetic mixed dye wastewater of mostly used azo dyes of acid, direct and reactive groups, to meet the final effluent standards for disposal and/or possible reuse.

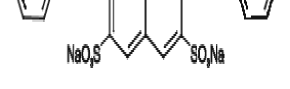
II. Material and Methods

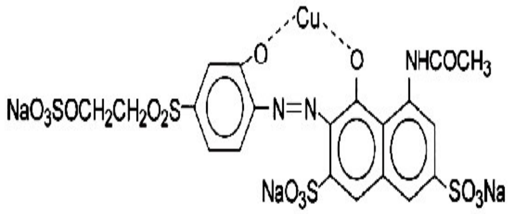
The azo dyes CI Acid Red 14, Congo Red, CI Reactive black 5 and CI Reactive violet 5, used for the experiments were obtained from Colour Chem Ltd. Mumbai (India) as a commercially available dye. Structures of these dyes are as in Figure 1.0 and characteristics are as follows:

C.I. Name and number	azo group	Molecular Weight (g)	λ_{max} (nm)	%Carbon (theoretical)	%Carbon (actual)
Acid Red 14 (14720)	mono azo	502	510	47.8	41.232
Congo Red (22120)	di-azo	696.7	495	55	31.734
Reactive black 5 (20505)	di-azo	991.8	597	31.5	19.798
Reactive Violet 5	di-azo	749	560	32	13.06









Reactive Black 5 (RB5)
Reactive Violet 5 (RV5)

Figure 1.0 Chemical structures of the Acid Red 14, Congo Red, Reactive Black 5 and Reactive Violet 5.

Elemental analyzer (CHNOS analyzer, model CE-440, Leemans Lab. Inc. USA) was used to determine actual carbon, hydrogen and nitrogen content. On the bases of carbon content the purity of AR 14, CR, RB5 and RV5 were around 86%, 57%, 62% and 40%. All the dyes were used as available without any further purification.

The experimental setup used for ozonation consists of a bubble contactor operated in the semi-batch mode. The shape of the reactor was cylindrical with diameter of 6.4 cm and height 39 cm. The rector was fitted with porous ceramic plate at bottom to form bubbles of 1 mm average size. Ozone was generated in gas phase by passing pure dry oxygen through the ozone generator (INDIZONE, CDS/4C/AF, India). Arrangements were made for applying this gas mixture to the bottom of the reactor, where it bubbled through a porous ceramic plate and moved upwards through the reactor. The gas flow into the reactor was controlled using an on-line mass flow controller (AALBORG, GFC171S, USA). Ozone concentrations in the gas influent and effluent to the reactor were measured using online UV absorbance based ozone monitors (ANSEROS, OZOMAT GM-6000-OEM; Germany). All components of the experimental setup and the reactor were made of glass, Teflon or stainless steel to eliminate ozone consumption due to corrosion of components by ozone. It was assumed that due to the agitation caused by gas bubbles and due to low reactor height: diameter ratio, the aqueous contents of the reactor were well mixed.

An aerobic reactor essentially conical flask of 500 ml capacity, with a retention time of 8 days was operated with objective to produce microbial seed acclimatized to ozonated mixed dye solution, to be used for aerobic degradation. Aerobic reactors were fabricated for aerobic biodegradation, from glass columns of 130 ml capacity, equipped with a porous bottom plate made of sintered glass. Four reactors of this type were kept in a wooden box and oxygen was supplied to each reactor through a manifold system connected to the air compressor (Model: Comair NF264, India).

Mixed dye solution of concentration 1000 mg/l was prepared in double distilled water by using equal contents of 250 mg/l of all four dyes(AR 14, CR, RB 5 and RV 5) in order to investigate the effect of ozonation on color, COD, TOC ,biodegradability and effect of aerobic biodegradation on ozonated mixed dye solutions. Mixed dye solutions were suitably buffered with 0.2 M phosphate buffer to prevent reduction in pH, as for subsequent aerobic degradation pH should be around 7.0. Mass flow controller and both ozone monitors were switched on for at least 30 minutes for warming up and zero reading setting. Rector was filled with 500 ml dye solution, prepared in BOD dilution water and flow of oxygen to ozone generator was set to 0.5 l min^{-1}. At least for 5 min only oxygen was supplied just to make sure that no residual ozone present in cuvette of ozone monitors. Ozone generator was then switched on and readings of influent and effluent ozone monitors were recorded at 5 min intervals. Average ozone dose recorded in the influent ozone monitor was 58.5 gO_3m^{-3} and cumulative ozone consumptions were calculated from influent and effluent ozone monitors readings taken at 5 min interval. Samples (20ml) were collected after 10, 20, 30, 40, 60, 80 min intervals. Sample pH was measured using a combination pH electrode (Toshiwal CL-51, India) connected to a digital pH meter (Toshiwal CL-54, India).COD of the samples were analyzed by using closed reflux method as described in Standard Methods (Method No. 5220 C, APHA et al., 1995).BOD of the samples was analyzed on BOD Trak. Samples were analyzed for TOC on the Carbon Analyzer, model TOC-V $_{CPN}$, Shimadzu Make as per Standard Methods (APHA et al., 1995). Scanning (range 200-700 nm) and Absorbance determination was done as described in Standard Methods (Method No. 5910 B., APHA et al., 1995) by using UV- Visible Spectrophotometer (Varian CARY 50 Conc.), and 1 cm quartz cell. The samples were suitably diluted when absorbance values of samples were greater than one. For aerobic biodegradation, dye solutions were ozonated for 20, 40, 60 and 80 min separately. Four aerobic reactors were operated simultaneously and each rector was fed with 100 ml ozonated feed and 5 ml of acclimatized seed and aeration started. Reactors were maintained at average retention time of 2.5 days, i.e., 40 ml of effluent was extracted and 40 ml of feed added each day. Reactors were operated at these final influent COD concentrations for more than 40 days and steady-state COD removal in each reactor was recorded.

TLC was performed on 10×10 cm Aluminium-backed silica gel 60F$_{254}$ HPTLC plates (Merck article 1.05641, Darmstadt, Germany) prewashed with methanol. All the standards and the samples were applied to the plates by means of the Linomat 5 applicator (Camag, Muttenz, Switzerland) equipped with a 100-µl syringe. The band length was 6 mm, the application volume for the standards was 2, 3 and 4 µl and 3 µl for the samples. Eight to nine bands per plate were applied, 10 mm from the bottom edge and 10 mm centre to centre apart by using WINCATS software and Linomat 5. The plates were developed in a saturated glass twin-trough chamber (Camag) with mobile phase of phenol-water (8:2 v/v) up to the migration distance of 7 cm. After the separation, the plates were dried in a stream of warm air for about 2 min and then scanned in scanner 3 with W visible lamp and Chromatograms were evaluated for the concentration using calibration via peak area.

III. Results and Discussion

Concentration of the mixed dye solution was 1000 mg/l which was mixer of 250 mgl^{-1} each of four azo dyes AR 14, CR, RB5 and RV5. Generally concentrations of dyes in dye bath are considered to be between 0.8 – 2.6 gl^{-1} (Arslan and Balcioglu, 2000). Dye solutions were buffered for doing ozonation by 0.2 M phosphate buffer to keep pH around 7.0, even after 80 min of ozonation, required for further aerobic degradation process. As per literature production of organic and inorganic acid anions due to ozonation cause decrease in pH (Adams and Gorg, 2002; Koch et al., 2002; Wang et al., 2003) but the pH was around 7.0 during ozonation as buffer prevented decrease in pH. Graph A of Figure 2.0 shows variations of percentage ozone absorbed during ozonation with ozone consumed in mg/mg initial TOC. Initially percentage ozone absorbed was found more because of high concentration of dye and mass transfer of ozone to reach saturation concentration in liquid medium but percentage ozone absorbed decreases as ozonation prolongs. Sharp reduction in absorbed ozone was observed around ozone dose of 10 mg/mg initial TOC which could be due to almost complete decolorization and substantial reduction in COD at that level. Color on the Pt-Co scale was measured for samples of mixed dye solutions after 20, 40, 60, and 80 min of ozonation as shown in Graph B of Figure 2.0. Decolorization was almost complete after ozone dose of 11.14 mg/mg initial TOC (60 min of ozonation) for mixed dye solution. Conductivity increases with ozonation due to formation of ions while pH was almost constant because samples were buffered as shown in Graph C and D of Figure 2.0.

COD was seen to decline for mixed dye solution with ozonation time, which may be partly attributed to mineralization of organic carbon and partly to conversion of the remaining organic carbon to higher average oxidation stage. Further reductions in TOC suggest considerable mineralization of compounds due to ozonation, but the obtained TOC values may not represent actual TOC concentrations due to the losses of volatile compounds (formaldehyde, acetaldehyde) during ozonation. Variations in COD/CODo and TOC/TOCo for mixed dye solution are as Graph E of Figure 2.0. The COD reduction seems more efficient then reduction in TOC as sighted in literature (Wang et al., 2003; Koch et al., 2002). About 86% COD reduction as well as 79% TOC reduction was found for mixed dye solution of concentration 1000mg/l corresponds to ozone consumption of 13.64 mg per each mg of organic carbon initially present (80 min ozonation). While About 79% COD reduction as well as 68% TOC reduction was found for mixed dye solution of concentration 1000mg/l corresponds to ozone consumption of 11.14 mg per each mg of organic carbon initially present (60 min ozonation). Ozonation of dyes results conversion of complex organic matter to simpler organic matter and so oxidation state improves which may be justified by decrease in COD/TOC ratio with ozonation time as shown in Graph F of Figure 2.0. Biodegradability (measured as BOD_5/COD ratio), improved significantly after ozonation because dye molecules are oxidized by ozonation to small organic molecular fragments which are more biodegradable than parent compound. Changes in BOD_5 (mg/l) and BOD_5 /COD ratio after different time of ozonation of mixed dye solution was plotted with ozone consumed in mg/mg initial TOC as shown in graph G and H of Figure 2.0.

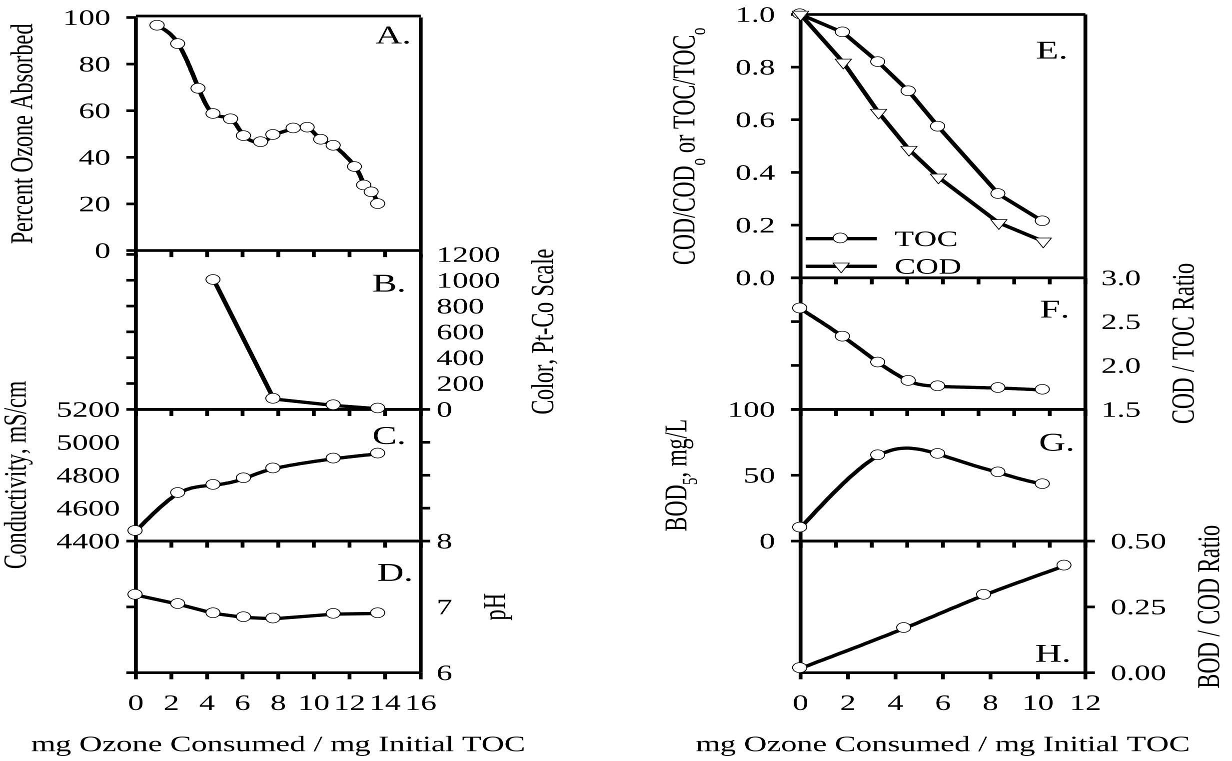
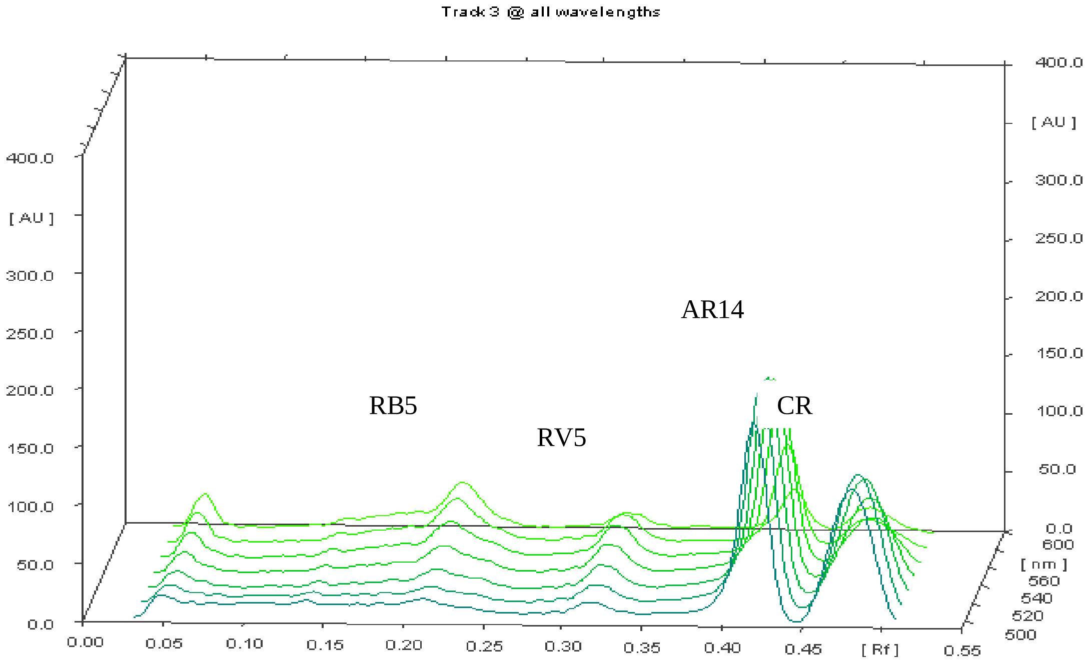


Figure 2.0 Impact of Ozonation on Physical and Chemical Properties of a 1000 mg/L Mix Dye Solution

Quantitative estimation of decrease in dye concentration by ozonation was studied by separating the individual dyes from mixed dye solution using precoated silica gel 60 F_{254} aluminum TLC plates by high performance thin layer chromatography(HPTLC). The separation of individual dyes from mixed dye solution at different wavelength is shown in Figure.3.0.



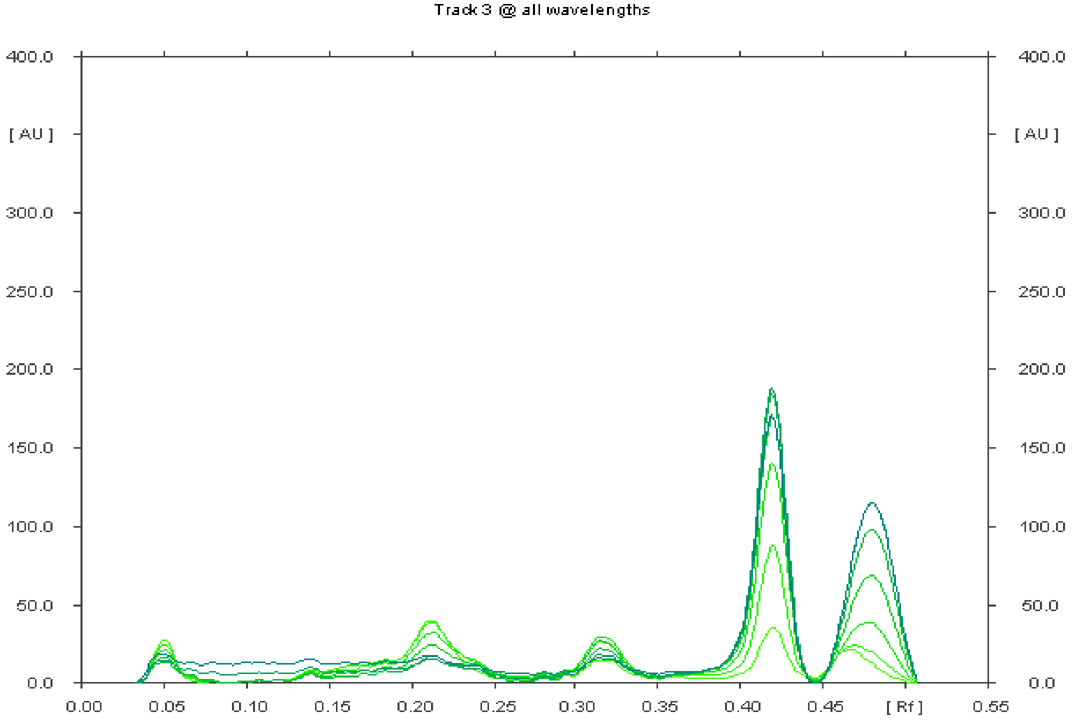


Figure 3.0 Separation of dyes from mixed dyes(1000 mg/l) using HPTLC at different wavelength with mobile phase of phenol:water(8:2).

Kinetic study for individual dyes after separating dyes from mixed dye solution of 1000 mg/l(fig 4.0 a) as well as kinetic study for individual dyes for concentration of 250 mg/l (fig 4.0 b) was done using HPTLC as shown in fig. 4.0. Determination of coefficients of decay for individual dyes as well as for mixd dyes showed that rates of decay for reactive dyes as well as for di-azo dyes are low. Decay of reactive dyes becomes very slow during ozonation of mixed dyes compared to ozonation of individual dyes (fig.4.0).

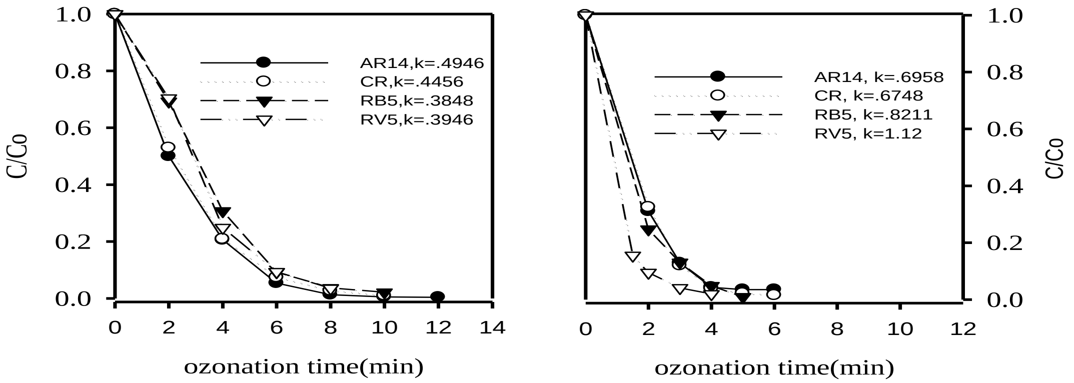


Figure 4.0 Impact of Ozonation on kinetics of (a) individual dyes separated from mixed dyes (1000 mg/l) (b) Individual dyes of concentration 250 mg/l studied separatety using HPTLC

Ozonated samples after 20, 40, 60, 80 min were treated in aerobic reactors. Aerobic reactors were run for more than 40 days till COD reduction got stabilized. Results of aerobic biodegradation indicate that reductions in COD were further 37%, 54%, 52% and 50% while TOC reductions were further 47%, 66%, 69% and 58% for mixed dye solutions after aerobic biodegradation of ozonated samples (20, 40, 60, 80 min) of mixed dyes as shown in Graph A and B of Fig 5.0 as variations in COD and TOC with ozone dose in mg of ozone consumed per mg of initial TOC. Reductions in COD and TOC indicate partial mineralization which is justified by decrease in COD/TOC ratio with ozonation time. Improvement in COD/TOC ratio after aerobic biodegradation is due to more percentage reduction in TOC by aerobic treatment. Reductions in COD/TOC ratios and COD removal after ozonation and aerobic biodegradation are shown in Graph C and D of Fig 5.0 with ozone dose in mg of ozone consumed per mg of initial TOC. Percentage of COD reduction after 80 min ozonation was found 86% while total reduction after aerobic biodegradation of ozonated samples was 93% for mixed dyes solution (Graph E of Fig 5.0). After 80 min ozonation 79%, TOC reduction was found for mixed dye while total reduction after aerobic biodegradation of ozonated sample was 91% (Graph F of Fig 5.0). The COD reduction seems more efficient then reduction in TOC for mixed dyes especially after ozonation as sighted in literature also (Wang et al., 2003; Koch et al., 2002). More than 90 % COD and TOC reduction was found for mixed dye after 60 min of ozonation followed by aerobic biodegradation which suggest that 60 min ozonation may be sufficient before disposal or reuse.

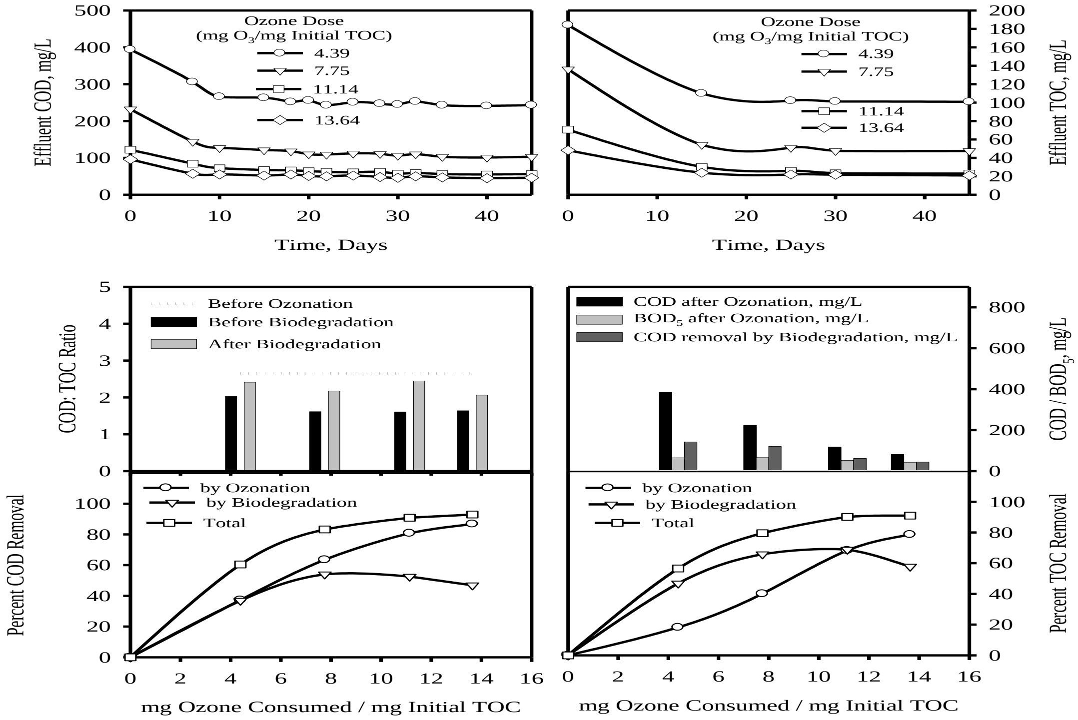


Figure 5. Effects on COD, TOC and COD/TOC ratio after aerobic biodegradation of ozonated samples of mixed dyes(1000 mg/l)

IV. Conclusions

Reductions in color and absorbance spectra for mixed dye solutions suggest that ozone treatment is efficient for complete decolorization of mixed dye solution of acid, reactive and direct dyes. BOD_5 data reveal that partial ozonation of mixed dye solution increases the biodegradability of the dye solution. After 80 min of ozonation (ozone dose of 13.64 mg/mg initial TOC) the ratio of BOD5/COD increased from 0.016 to 0.51. Results obtained by experimental study confirm that ozone treatment is an effective treatment for color removal and biodegradability enhancement but gives partial reduction of TOC and COD for all the compounds. More then 90% reduction in COD and TOC takes place for mixed dye solution after 60 min ozonation followed by aeration. Around 93% reduction in COD and 91% reduction in TOC take place after 80 min ozonation followed by aeration. Reductions in COD were found more efficient then reductions in TOC specifically after ozonation. Results of combined treatment of ozonation and aerobic biological treatment indicates its potential from economic and ecological point of view, and thus may be the choice for the treatment of mixed dyes containing acid ,direct and reactive dyes. Synthetic mixed dye solution can be disposed or may be considered for reuse after ozonation for 60 min (ozone dose of 11.14 mg/mg initial TOC) followed by aerobic biodegradation. It is concluded that in spite of high energy cost of ozonation, the combined treatment of such type may be useful not only for achieving water body discharging standards but also for reuse of water in the textile industries.

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