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Integrated Ozonation and Aerobic Biodegradation of Acid Red 14 and Congo Red Azo Dyes

Umesh Kumar Khare[a] and Purnendu Bose[b]
[a]Associate Professor, Department of Civil Engineering, Government Engineering College Dahod, Gujarat, India
[b]Purnendu Bose , Professor, Department of Civil Engineering, Indian Institute of Technology, Kanpur, India

ABSTRACT:
The effect of ozonation on the degradation process of azo dyes CI Acid Red14(AR14) and Congo Red(CR) has been studied in the semi batch rector and parameters such as pH, Color, Absorbance(at maximum wavelength, λ_{max}), COD, TOC, BOD_5 were monitored during process at different time intervals. The results obtained indicate that ozonation is highly effective way to remove the color of synthetic dye solutions. COD and TOC removals were however less complete, suggesting production of colorless ozonation by-products. Ozonation increased the biodegradability of both the studied dyes, as observed by increase in BOD_5/COD ratio from zero to 0.46 and 0.48 for AR14 and CR respectively, after 80 min ozonation. Aerobic biodegradation of these ozonated dye solutions resulted more then 90% reduction in COD and TOC. Results of this study demonstrate the potential of integrated ozonation and aerobic biodegradation for treatment of azo-dyes from economic and ecological point of view.

Keywords: Azo dye; Ozonation; Biodegradability; BOD_5/COD; Aerobic treatment

I. INTRODUCTION

Azo dyes are an abundant class of synthetic, colored, organic compounds, characterized by nitrogen to nitrogen double bonds (N=N) which are mainly bound to benzene or naphthalene rings [1]. They are most used dyes in textile industry [2]. There are at least 3000 of these dyes currently in use worldwide (they account for more than 50% of the commercial dye market), and they are used to color a wide variety of consumer goods and pharmaceutical products, e.g. fabrics, cosmetics, mouthwashes, drugs, etc. 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[3] .

Azo dye molecules are highly structured polymers, hence they are very difficult to breakdown biologically and cannot be treated efficiently by conventional methods like an activated sludge process [4]. Under anaerobic conditions, many bacteria reduce azo bond in the dye molecule, to produce colourless aromatic amines which can be toxic and carcinogenic [5].

Acid dyes are water-soluble anionic dyes and are applied to nylon, wool, silk, and modified acrylics [6]. Direct dyes are applied to the cotton in solution and are held to the fibres by hydrogen bonds and instantaneous dipole-induced dipole forces. It is known that reactive and acid dyes are the most problematic, as they tend to pass through conventional treatment system unaffected [7].

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 [1][7]. 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 [8]. 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 [1]. Ozone and hydroxyl radicals (OH.) generated in the aqueous solution are able to open the aromatic rings [9]. Dye molecules are oxidized to small molecules such as organic acids, aldehydes, ketones etc, instead of completely mineralized by ozonation[4][7] .

Thus dye molecules are oxidized by ozonation to small organic molecular fragments causing increase in ratio of BOD_5/COD which indicates an improved biodegradability of dye wastewater [10]. Ozonation could be competitive in spite of its high energy costs, if partial effluents were to be treated. Therefore, a combined treatment of ozonation and biological degradation might be a choice for the treatment of dye bath effluents [10][11].

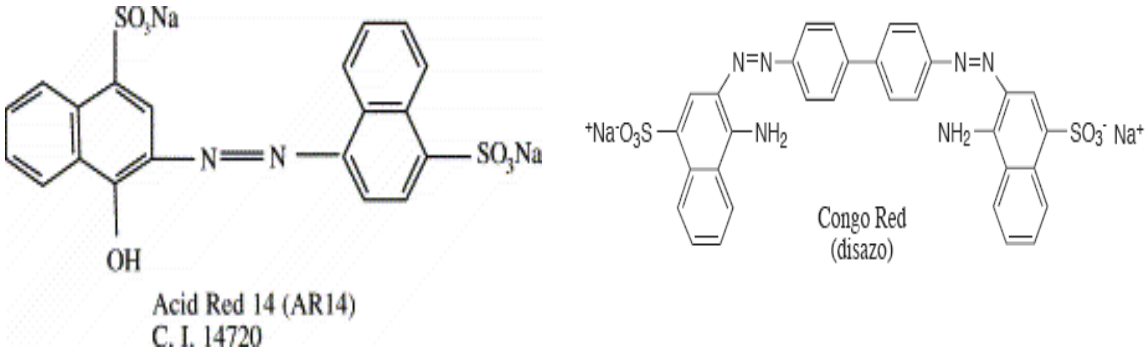
It has been confirmed that rate limiting step in the ozonation of dye containing wastewater is the mass transfer of ozone from gas phase to the wastewater. Time for complete decolorization increases with increase in number of azo groups and salt concentration in azo dyes while it decreases with increase in number of sulphonic acid groups in the dye structure[12]. At higher dye concentrations ozonation may become less efficient because of increased competition for ozone between parent molecules and reaction byproducts[13].

This study include the ozonation of aqueous azo dyes AR14 and CR solutions in semi batch reactor followed by aerobic biodegradation of same compounds after different ozonation time. The objective of the study was to investigate the integrative effect of ozonation and aerobic biodegradation on synthetic dye wastewater of mostly used azo dyes-Acid red 14 and Congo red, to meet the final effluent standards for disposal and/or possible reuse.

II. MATERIAL AND METHODS

The azo dyes CI Acid Red 14 and Congo Red, used for the experiments were obtained from Colour Chem Ltd. Mumbai (India) as a commercially available dye. Structures of these dyes are as in Figure1.0 and characteristics are as follows:

C.I. Name and number	azo group	Molecular Weight (g)	λmax (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



"Figure 1. Chemical structures of dyes AR14 and CR"

Elemental analyzer (CHNOS analyzer, model CE-440, Leemans Lab. Inc. USA) was used to determine actual carbon content. On the bases of carbon content the purity of AR 14 and CR were around 86% and 57%. Both 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.

Four aerobic reactors essentially conical flasks of 500 ml capacity, with a retention time of 8 days were operated with objective to produce microbial seed acclimatized to ozonated model compounds, to be used for aerobic biodegradation. For aerobic biodegradation aerobic reactors were fabricated from glass columns of 130 ml capacity, equipped with a porous bottom plate made of sintered glass. 10 reactors of this type were kept in a wooden box and arrangement for oxygen supply was made to each reactor through a manifold system connected to the air compressor (Model: Comair NF264, India).

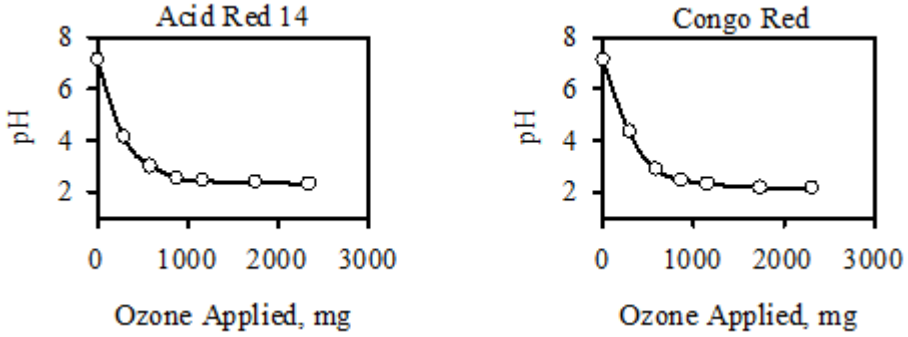
Relatively high dye concentrations of 1000 mgl^{-1} for AR14 and CR aqueous solutions were prepared in double distilled water in order to investigate the effect of ozonation on color, COD, TOC ,biodegradability and effect of aerobic biodegradation on ozonated dye solutions. Dye solutions were suitably buffered with 0.2 M phosphate buffer to prevent reduction in pH, as for subsequent aerobic biodegradation pH should be around 7. Mass flow controller and both ozone monitors were switched on for at least 30 minutes for warming up before start of experiment. 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 and then if required zero readings were set in 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.

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 [14]. BOD of the samples was analyzed using Hach, 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 [14] by using UV- Visible Spectrophotometer (Varian CARY 50 Conc.), and 1 cm quartz cells. The samples were suitably diluted when absorbance values of samples were greater than one.

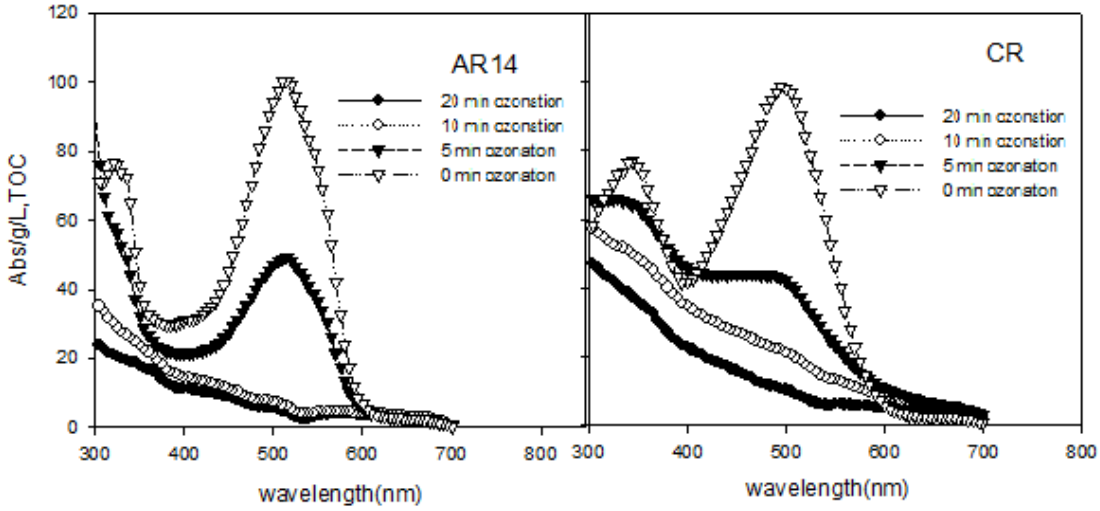
To prepare microbial seed acclimatized to ozonated compounds, for first 10 days domestic wastewater (volume 400ml) was aerated with 50 ml fresh domestic wastewater replaced each day after 30 min settling of biomass, to ensure rapid biomass growth. From 11 th day onwards 25% of influent to the reactor was replaced by corresponding 30 min ozonated compound. This proportion was increased to 50%, 75% and 100% at interval of 5 days. For 100 % proportion of compound feed solutions were prepared with BOD dilution water to maintain required nutrient for biomass growth. Two similar aerobic reactors were also run for at least one month for biodegradability study of model compounds AR14 and CR. For aerobic biodegradation, dye solutions were ozonated for 20, 40, 60 and 80 min separately. Ten aerobic reactors were operated simultaneously (five for each AR14 and CR). Each reactor fed with 100 ml ozonated feed and 5 ml of acclimatized seed of the appropriate type 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 recorded.

III. RESULTS AND DISCUSSION

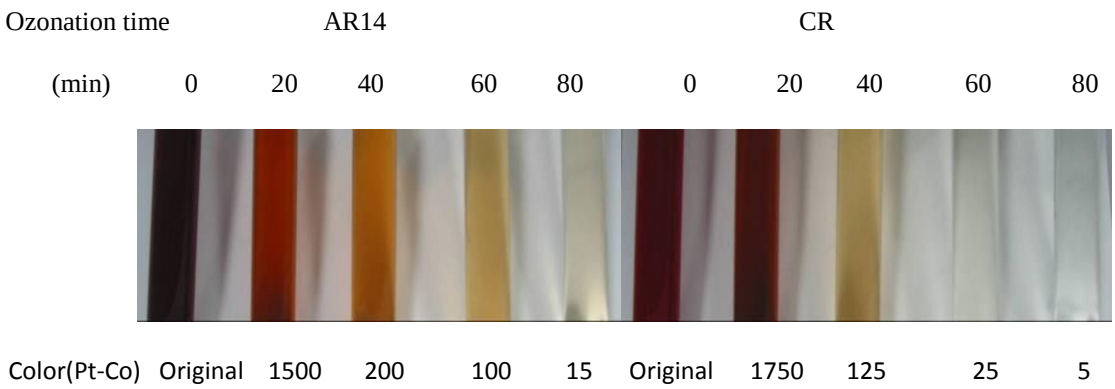
Different concentrations of the compounds were chosen because of different purity of dyes and rather high dye concentrations were chosen to make sure about availability of organic matter even after prolonged ozonation for aerobic biodegradation. As degradation rate of azo dye depends upon dye concentration and ozone dose, much higher ozone dose(55.8 mgl^{-1}) was chosen than commonly applied dose(8.9 -20.5 mgl^{-1}) in the related literature [2][7][10][11]. On the other hand slightly lower ozonation periods (20-80 min) were chosen to facilitate aerobic treatment after ozonation also described in literature[2][3][11]. 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 biodegradation process. As per literature production of organic and inorganic acid anions due to ozonation cause decrease in pH[7][11]as also shown in ozonation of un-buffered samples of both dyes(Figure2.0), but in all cases pH was around 7.0 during ozonation as buffer prevented decrease in pH. The absorbance corresponding to maximum absorption wavelength for aqueous solutions of all dyes measured at different intervals of ozonation time indicates reduction in absorbance with increase in ozonation time. Disappearance of original compounds was seen even after 10 min of ozonation (Figure 3.0) but still there was some color which could be due to organic by-products formed during ozonation. Pictures of reductions in color with values, measured on Pt-Co scale are shown in Figure4.0.



"Figure 2. Decline in pH during Ozonation process without buffer for AR14 and CR"



"Figure 3.0. Disappearance of absorbance spectra of dyes during ozonation"



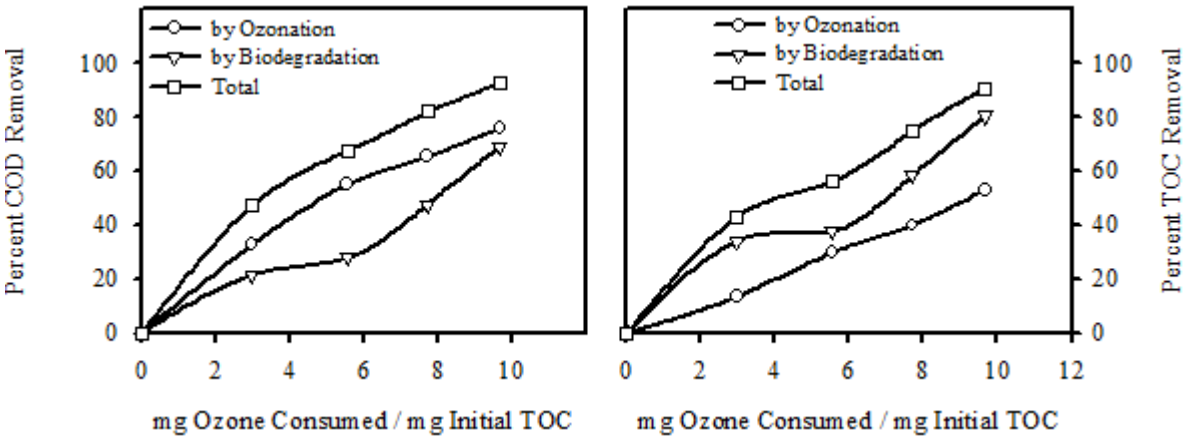
"Figure 4.0. Disappearance of color on Pt-Co Scale of dyes during ozonation"

Reductions in COD and TOC with ozonation time for both the dyes are shown in Table 1.0. COD was seen to decline for all the compounds with ozonation time, which could 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. The samples containing the parent compounds almost resist biodegradation. But parallel to reduction in the COD, biodegradability (measured as BOD_5/COD ratio), improves significantly after ozonation. Changes in BOD_5/COD ratio after different time of ozonation of selected dyes are also shown in Table 1.0.

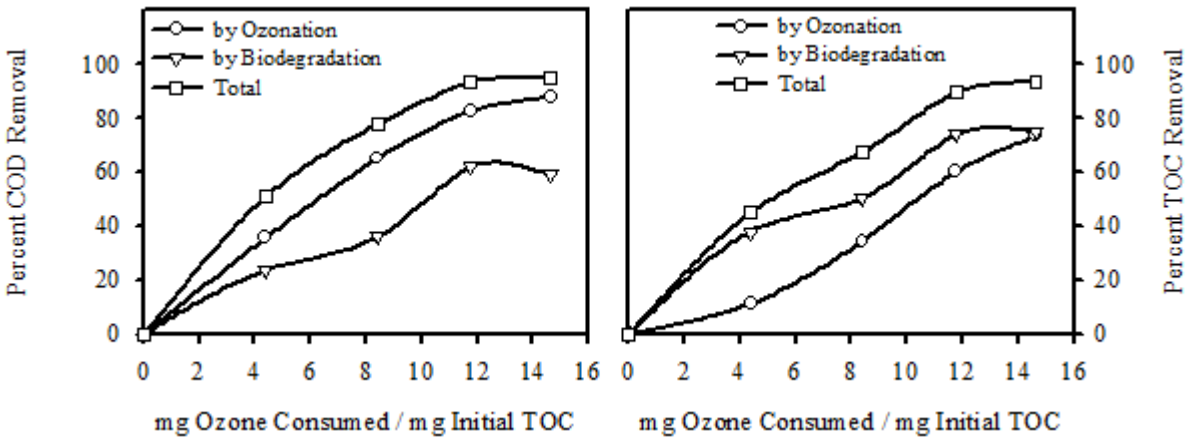
"Table 1.0. Effects on COD, TOC and BOD_5/COD ratio during ozonation of both dyes"

	AR14 (1000 mg/l)				CR (1000 mg/l)			
Ozonation Time	COD (mg/l)	TOC (mg/l)	BOD (mg/l)	BOD_5/COD	COD (mg/l)	TOC (mg/l)	BOD (mg/l)	BOD_5/COD
0 min	1083	403	10	0.01	681	240	12	0.02
20 min	728	349	72	0.10	439	213	52	0.12
40 min	488	283	90	0.19	237	157	80	0.34
60 min	374	242	112	0.30	118	96	48	0.41
80 min	259	189	120	0.46	83	64	40	0.48

Ozonated samples after 20, 40, 60, 80 min were treated in aerobic reactor, as stated in materials and methods. Aerobic reactors were run for more than 40 days till COD reduction got stabilized. Percentage of COD reductions after 80 min ozonation were found 76% and 88% for AR14 and CR while total reductions after aerobic biodegradation of ozonated samples were 93% and 95% respectively(Figure 5.0). After 80 min ozonation 53% and 73% TOC reduction was found for AR14 and CR while reductions after aerobic biodegradation of ozonated samples were 91% and 94% respectively (Figure 6.0). The COD reduction seems more efficient then reduction in TOC for all the compounds especially after ozonation as sighted in literature also[7][11].



"Figure 5. Effects on COD and TOC after aerobic biodegradation of ozonated samples of AR14 (1000 mg/l)"



"Figure 6. Effects on COD and TOC after aerobic biodegradation of ozonated samples of CR (1000 mg/l)"

IV. CONCLUSIONS

Reductions in color and absorbance spectra of dye solutions confirm that ozone treatment is an effective treatment for color removal for selected acid and direct azo dyes. BOD_5 data reveal that partial ozonation of all selected dyes increases the biodegradability of the dye solutions. Experimental study showed 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 AR14 dye after 80 min ozonation followed by aerobic biodegradation. About 90% reduction in COD and TOC takes place for CR dye after 80 min ozonation followed by aerobic biodegradation Decolorization as well as reduction in COD and TOC was found faster in direct dye (CR) compared to acid dye (AR14). 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 of the treatment of acid and direct dyes. It is concluded that integrated treatment of ozonation, followed by aerobic biodegradation may be choice of treatment for dye wastewater in the textile industries.

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