ELSEVIER

Chemical, Civil and Mechanical Engineering Tracks of 3rd Nirma University International Conference (NUiCONE 2012)

Studies on Degradation of Reactive Red 135 Dye in Wastewater using Ozone

Sandip Sharma[a], Jimit Buddhdev[b], Manish Patel[c], Jayesh P Ruparelia[d]

Department of chemical Engineering, Institute of technology, Nirma University-382481

Abstract

An attempt has been made in this paper to identify effects of efficient ozonation processes for decolorization and/or degradation of organic pollutants for environmental protection. In dyes, since the chromosphere 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. Ozonation and its combinations are effective for wastewater treatment. In the present study 99.9% decolorization of RR 135 was accomplished by ozonation. The time required for the complete decolorization gradually increase with increase in the initial dye concentration. For RR135 after 48, 55 and 67 min reaction time, complete decolorizaton was achieved at initial dye concentrations of 500, 1000 and 1500 mg/L, respectively. The COD removal efficiency gradually decreased with an increase in the initial concentration. For RR135 after 60, 65 and 87 min reaction time, the COD removal percentage was 66.66%, 61% and 56.64% at initial dye concentrations of 500, 1000 and 1500 mg/L, respectively.

Keywords: Advanced oxidation processes, Chemical oxygen demand, Decolorization, Ozonation, Ozone demand, Reactive red 135.

1. INTRODUCTION

In the last 10 years, a rather fast evolution of the research activities devoted to environment protection has been recorded as the consequence of the special attention paid to the environment by social, political and legislative international authorities leading in some cases to the delivery of very severe regulations [1]. The fulfilment of severe quality standards is especially claimed for those substances exerting toxic effects on the biological sphere preventing the activation of biological degradation processes. The destruction of toxic pollutants as also that of the simple biologically recalcitrant compounds must be therefore demanded to other, non-biological technologies. These technologies consist mainly of conventional phase separation techniques (adsorption processes, stripping techniques) and methods which destroy the contaminants (chemical oxidation/ reduction).

Chemical oxidation aims at the mineralization of the contaminants to carbon dioxide, water and inorganics or, at least, at their transformation into harmless products. Obviously the methods based on chemical destruction, when properly developed, give complete solution to the problem of pollutant abatement differently from those in which only a phase separation is realised with the consequent problem of the final disposal. It has been frequently observed [1] that pollutants not amenable to biological treatments may also be characterised by high chemical stability and/or by strong difficulty to be completely mineralized. In these cases, it is necessary to adopt reactive systems much more effective than those adopted in conventional purification processes.

AOPs can provide effective technological solutions for water treatment. Such solutions are vital for supporting and enhancing the competitiveness of different industrial sectors, including the water technology sector, in the global market. The main goals of academic, research and industrial communities through the development and implementation of environmental

Conventional wastewater treatment methods, such as biological processing, coagulation, and flocculation, are successful for color removal, but they also cause new problems. Excess sludge production due to pollution is not degraded and only changes phase from wastewater to biomass or sludge. In recent years, advanced oxidation processes (AOPs) have been used as an alternative technology based on the degradation of organic pollutants, ozone analysis, and Fenton, photo catalytic, and wet-air oxidation. Among the AOPs, treatment with ozone processes has yielded the most favorable results.

Most studies have focused on decolorization, degradation mechanisms, and mineralization reactions in dye- ozone reactions, and few have reported the relationship between ozone-substrate and the stoichiometry of the degradation reaction

during ozonation processes.

Ozonation is one method that gives the best results in the degradation of dyes and eliminates any problem to a great extent [12]. Oxidation with ozone is known to be a powerful method for decolorizing reactive dyes by destroying the chromophoric system. The reaction mechanisms of ozonalytic decomposition follow two possible degradation pathways. Both molecular ozone attack (i.e. direct reaction) and the free radical mechanism (i.e. indirect reaction) have been found to simultaneously exist during the reaction processes [7]. The oxidation potential of ozone is 2.07 V and its high oxidation potential allows it to degrade most organic compounds [8].

The objective of this study was to investigate the effects of ozonation on the decolorization, degradation and ozone demand for the RR135 in wastewater. The majority of color removal techniques work either by concentrating the color into sludge, or by partial or complete breakdown of the colored and soluble molecule. Other factors involved in reduced degradation include high water solubility, high molecular weight and fused aromatic ring structure. Therefore there is a need of developing a process that offers solution for this problem as it leads to complete degradation and Mineralisation of dyes. The scope of this report is to review recently published work in the field of advanced oxidation processes on wastewater treatment. It has been reported that Ozonation process does not lead to any secondary sludge production. Present work shows the comparison of the parameter like Chemical oxygen demand (COD), Color removal and Ozone demand for the treatment of waste water by using ozonation as an advanced oxidation process.

Advanced oxidation processes (AOPs) are alternative methods for decolorizing and reducing recalcitrant wastewater loads from textile companies. AOPs are based on the generation of hydroxyl radicals in water, which are highly reactive and non-selective oxidants that can oxidize organic compounds. Hydroxyl radicals have an oxidation potential that exceeds that of ozone and H_2O_2 – 2.80 V for hydroxyl radicals, 2.07 V for ozone and 1.78 V for H_2O_2. Ozone may either react directly with organic compounds or decompose highly reactive species, such as hydroxyl radicals. Ozonation has potential in decolorization for the following reasons: (1) no sludge remains; (2) danger is minimal; (3) decolorization and degradation occur in one step; (4) it is easily performed; (5) little space is required, and (6) all residual ozone can be easily decomposed to oxygen and water. Accordingly, the ozone-based systems are feasible for decolorizing azo dyes.

2.   LITERATURE REVIEW

2.1 Ozone for Wastewater Treatment

Ozone is a molecule that consists of three negatively charged oxygen atoms. The ozone molecule is very unstable and has a short half-live, causing it to fall back into its original form after a while, according to the following reaction mechanism:

$$2O_3 \rightarrow 3O_2$$
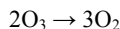
Principally, an ozone molecule is nothing but an oxygen molecule that has received an extra oxygen atom by electric high voltage. Ozone is naturally produced through certain types of chemical reactions. The most commonly known example is the ozone layer, in which ozone is produced by ultra violet rays (UV), which derive from the sun. Ozone is also formed during thunderstorms, in waterfalls and – although this is a less natural process – in photochemical smog which forms in summer. In thunderstorms, ozone forms as a result of the high voltages that are involved. The specific fresh scent after a thunderstorm is caused by ozone formation.

When one speaks of ozone, the above-mentioned examples are immediately associated with it. It is however less known that ozone can be artificially produced, so that it can be used for water treatment. Ozone generators can create ozone artificially by means of extremely high voltages or by means of UV-light. Both methods involve the decomposition of the oxygen molecule. This causes oxygen radical formation. These oxygen radicals can bind to oxygen molecules, forming ozone (O_3).

Using ozone to treat wastewater has many benefits:

The reaction rate of ozonation is very rapid. Small foot print and potential to reduce toxicity and possibly complete mineralization of organics treated. It does not concentrate waste for further treatment with methods such as membranes. It does not produce materials that require further treatment such as "spent car- bon" from activated carbon absorption. It does not create sludge as with physical chemical process or biological processes (wasted biological sludge). The ozone is Kills the bacteria effectively. Oxidises substances such as iron and sulphur so that they can be filtered out of the solution. There are no nasty odours or residues produced from the treatment. Ozone converts back into oxygen quickly, and leaves no trace once it has been used.

The disadvantages of using ozone as a treatment for wastewater are:

The Capital cost is very high. The complex chemistry must be trilored to specific application. For some applications quenching of excess peroxide is require. The treatment of ozone requires energy in the form of electricity; this can cost money and cannot work when the power is lost. The treatment cannot remove dissolved minerals and salts. Ozone treatment can sometimes produce by-products such as bromate that can harm human health if they are not controlled.

3. **Materials and Method**

3.1 Materials

Reactive Red 135 was taken from local vender and used without further purification. The experiment is carried out in a batch mode. 1.5 L of 500, 1000 and 1500 ppm dye solution was taken into the reactor for the experiment. Fig. 1 shows the experimental setup of Reactive Red 135 for an ozonation process. Potassium Iodide (LR grade, Ranbaxy Laboratory Limited), Sodium Thiosulphate ($Na_2S_2O_3$) (LR grade, High Purity Laboratory Chemical), Sulphuric Acid (LR grade, S.D. Fine Chem. Limited)

3.2 Analysis

3.2.1 Decolorization

The UV scans of the samples were done using UV-visible spectrophotometer (UV-1800 SHIMADZU) 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.

The decolorization of RR135 was detected using a spectrophotometer and the decolorization ratio was calculated from the following equation.

$$\text{Decolorization ratio} = (A_i - A_0) / A_t$$

3.2.2 Chemical oxygen demand (COD)

Chemical Oxygen Demand (COD) of the samples were found by using HACH (DRB 200 Reactor). HACH's USEPA approved dichromate COD Method is the most widely used chemical oxygen demand method in the world for NPDES reporting and for easy process monitoring [9].

$$\text{COD} = \frac{(A-B)*M*8000}{7.5}$$

Where A = mL FAS used for Blank
B = mL FAS used for sample
M = Moles of FAS

3.3 Experimental Method

Ozonation studies were done using an experimental setup consisting of ozonator, oxygen concentrator and bubble column reactor and air diffuser as depicted in Figure 2. [10]

Reactive red 135 was selected to prepare waste water having initial dye concentration of 500 ppm, 1000 ppm and 1500 ppm. The decolorization of RR135 was detected using a spectrophotometer.

Ozone was generated from oxygen by Corona Discharge Ozone generator. Oxygen cylinder is used as a source of Oxygen. Silicon tubing was used for the connection between ozone generator and reactor column. A circular porous diffuser was connected to the silicon tube and placed at the bottom of the reactor to transfer ozone gas into aqueous solution. Two impingers containing 200 ml of 20% KI solution were used to trap the unreacted ozone. Sodium thiosulphate titration procedure was performed to measure the ozone concentration, trapped in the KI solutions from which the ozone dose required for complete decolorization of dye bath was determined.

All experiments were performed at ambient temperature. 1.5 liter of the reactive dye samples was initially subjected to ozonation at an ozone dose of 0.45 g/hr.
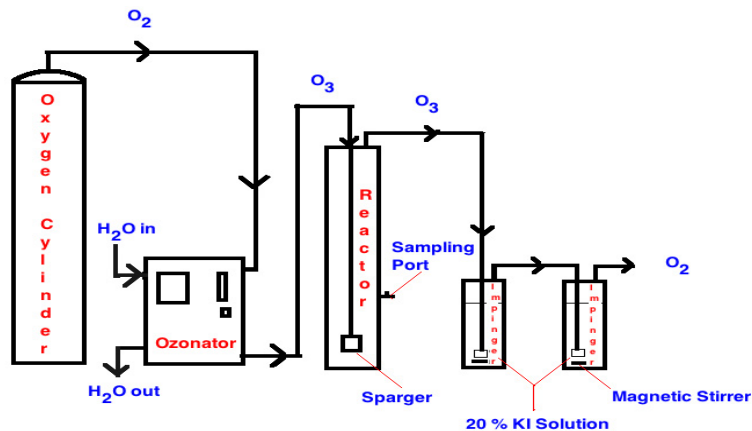

Fig.1 Experimental Setup for Ozonation of waste water treatment

4. Result and Discussion

1.1 Effect of dye concentration

The decolorization of RR135 in the ozonation system was conducted with initial dye concentrations in the range of 500, 1000 and 1500mg/L.

As shown in Figure 2, the time required for the complete decolorization gradually increase with increase in the initial concentration. As shown in Figure 3, the COD removal efficiency gradually decreased with an increase in the initial concentration.
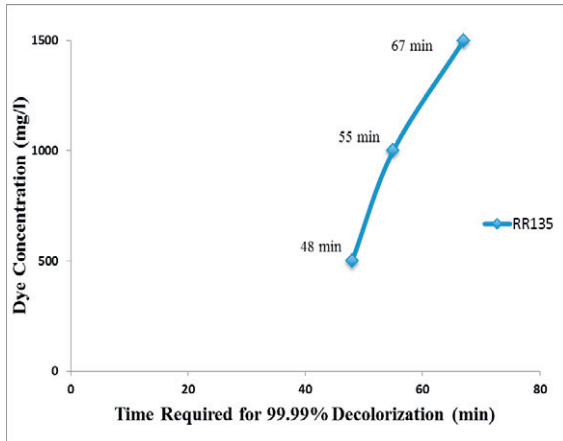

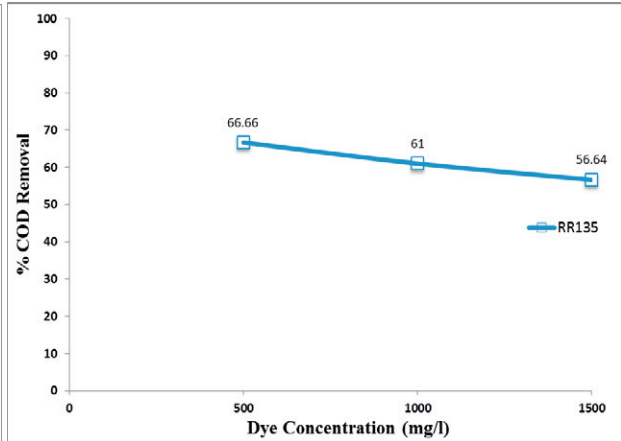Fig. 2 Effect of initial dye concentration on color removal

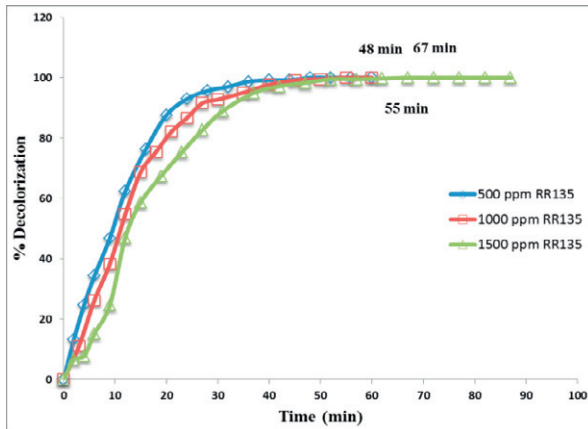Fig.3 Effect of initial dye concentration on COD Reduction

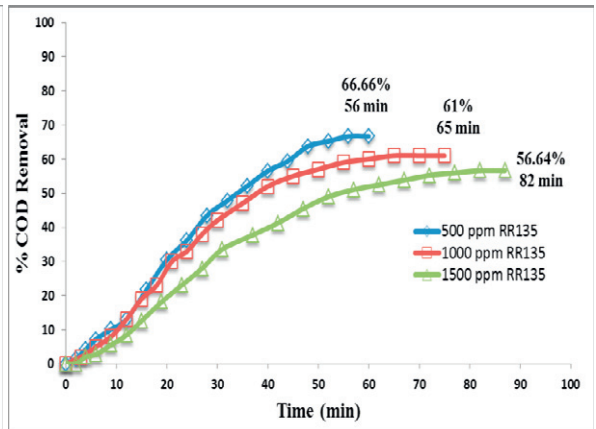Fig. 4 Removal of color during ozonation of 500, 1000 and 1500 ppm of RR135 Fig.5 Removal of COD during ozonation of 500, 1000 and 1500 ppm RR135

The results in Figure 4 show that for RR135 the time required for complete decolorization from 48 min to 67 min with increase in initial dye concentration from 500 gm/L to 1500 gm/L.

The results in Figure 5 show that for RR135 COD removal decrease from 66.66% to 56.64% with increase in initial dye concentration from 500 gm/L to 1500 gm/L.

4.2 Ozone demand

The results in Figure 6 shows that for RR135 ozone demand increase from 0.277 to 1.056 gm with increase in dye concentration from 500 gm/L to 1500 gm/L.
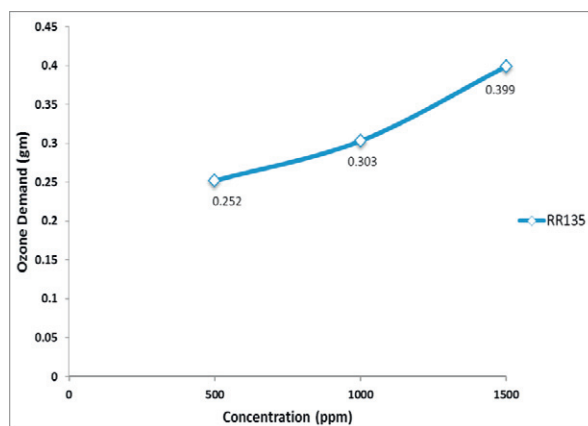
Fig. 6 Ozone demand for ozonation

4.3 Factors affecting Ozonation

Size of the ozone bubble plays important role. If the size of bubbles is small then it will provide higher surface area for the reaction. For said ozone flow rate, initial concentration of dye is one of the important parameter. If concentration is higher than consumption of ozone is higher. Effective contact time between ozone bubbles and dye molecules should be provided so that pollutants can easily interact with O_3 and get degraded. Ozone is a highly unstable gas at normal temperature. The solubility of ozone decreases at higher temperatures and is less stable. Principally, ozone dissolved in water cannot be applied when temperatures are above 40 °C, because at this temperature the half-life of ozone is very short. So for better results install cooling system that can increase the efficiency of the ozone gas [15].

5   CONCLUSION

The major conclusions derived from the present work are as follows:

- The present study demonstrated that 99.99% decolorization of RR 135 could be accomplished by ozonation. The time required for the complete decolorization gradually increase with increase in the initial dye concentration. For RR135 after 48, 55 and 67 min reaction time, 99.99% decolorization was achieved at initial dye concentrations of 500, 1000 and 1500 mg/L respectively.

- The COD removal efficiency gradually decreased with an increase in the initial concentration. For RR135 after 60, 65 and 87 min reaction time, the COD removal percentage was 66.66%, 61% and 56.64% at initial dye concentrations of 500, 1000 and 1500 mg/L respectively.

6   REFERENCES

[1] R. Andreozzi, V. Caprio, A. Insola, R. Marotta, 1999, Advanced oxidation processes (AOP) for water purification and recovery, Cat. Today 53, p.51.
[2] F. Haber, J. Weiss, 1934, the catalytic decomposition of hydrogen peroxide by iron salts, Proc. R. Soc. Series A 147, p.332.
[3] A. Wang, J. Qu, J. Ru, H. Liu, J. Ge, 2005, Mineralization of an azo dye Acid Red 14 by electro- Fenton's reagent using an activated carbon fiber cathode, Dyes and Pig. 65, p. 227.
[4] M. P. Titus, V. G. Molina, M. A. Banos, J. Giménez, S. Esplugas, 2004, Degradation of chlorophenols by means of advanced oxidation processes: a general review, App. Cat. B: Env. 47, p. 219.
[5] S. Trasatti, Electrochemistry and environment: the role of electro catalysis, Dep. of Physical Chemistry and Electrochemistry, Uni. of Milan, Via Venezian 21, Milan. Italy.
[6] M. S. Lucas, J. A. Peres, 2006, Decolorization of the azo dye Reactive Black 5 by Fenton and photo- Fenton oxidation, Dyes and Pig. 7, p.236
[7] Shu H, Huang C., 1985, Degradation of commercial azo dyes water using ozonation and UV enhanced ozonation processes. Chemosphere 31, p. 3813
[8] Garu P., 1991, Textile industry wastewater treatment, Water Sci. Tech. 24, p. 97.
[9] APHA, AWWA, WPCF, 1998, "Standard Methods for examination of water and wastewater", American Public Health Association, 20th Edition, Washington, DC, US.
[10] Kusvuran E., Gulnaz O., Samil A., Yildirim O., 2011, Decolorization of malachite green, decolorization kinetics and stoichiometry of ozone-malachite green and removal of antibacterial activity with ozonation processes, Jr. of Haz. Mat. 186, p. 133.
[11] Baban A., Yediler A., Lienert D., Kemerdere N., Kettrup A., 2003, Ozonation of high strength segregated effluents from a woollen textile dyeing and finishing plant, Dyes and Pig. 58, p. 93.
[12] Iranifam M.,Zarei M.,Khatace A.R., 2011, Decolorization of C.I. Basic Yellow 28 solution using supported ZnO nanoparticles coupled with photoelectron-Fenton process, Jr of Electro analytical Chemistry 659, p. 107.
[13] Ruiz E.J., Hernández-Ramírez A., Peralta-Hernández J.M., Arias C., Brillas E., 2011, Application of solar Photo electro-Fenton technology to azo dyes mineralization: Effect of current density, Fe^{2+} and dye concentrations, Chem. Eng. Jr. 171, p. 385.
[14] Salazar R., Garcia-Segura S., Ureta-Zanartu M.S., Brillas E., 2011, Degradation of disperse azo dyes from waters by solar Photo electro-Fenton, Electrochimica Acta 56, p. 6371.
[15] C.Gottschalk, J.A. Lobra, A.saupe, 2000, Ozonation of Water and Wastewater, Wiley-VCH, p. 39-43.