ANALYSIS VOL. 1, 2015

ISSN 2394–3750 EISSN 2394–3769

SCIENCE & TECHNOLOGY

Advanced Oxidation and Anaerobic Biodegradation Treatment for Removal of Dye Acid Red 14

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Article History
Received: 05 September 2015
Accepted: 29 September 2015
Published: 9 October 2015

Citation
Smita Venkatesh, Quaff AR, Pandey ND. Advanced Oxidation and Anaerobic Biodegradation Treatment for Removal of Dye Acid Red 14. *Science & Technology,* 2015, 1(4), 208-213

General Note
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ABSTRACT
The degradation of azo dye wastewater containing Acid Red 14 has been investigated. Significant drop in COD and concentration of dye has been observed. The effect of ozonation time on the COD removal and mineralization of azo dye was studied and the result was analysed in terms of COD removal efficiency. From the experimental results it has been observed that with increasing the ozonation time the degradation of dye increase. The ozone concentration of 55 mg/l at flow rate 5g/hr. reduced 75% COD and degrade 95% dye after 20 minutes of ozonation at the dye concentration was 1500mg/l. To reduce the cost of ozonation for maximum dye degradation, ozonation followed by anaerobic biodegradation was carried out.

Keywords: Acid Red 14, Degradation, Decolourization, Ozonation, Anaerobic Biodegradation

1. INTRODUCTION

The generation of highly coloured wastewater by the textile dyeing industry is considered as one of the highest toxic wastewater in India. In textile industry, complex dyes are used as colouring agents. Textile industry generates highly polluting wastewater because it contains dyes, typical organic compounds with complex structures that are highly soluble in water and easily hydrolysed (Peternal et al., 2007; Behnajady et al., 2009). Azo dyes mostly used in textile dyeing industry, are one of the largest groups of synthetic colourants and most common synthetic dyes released in to the environment (Chang et al., 2001b; Saratale et al., 2009a). The release of coloured compounds into water bodies is undesirable because of their impact on photosynthesis of aquatic plants, the carcinogenic nature of many of these dyes and their break-down products (Gomez et al., 2007) and affects the aesthetic merit, water transparency, gas solubility and may be toxic to aquatic life in water bodies, these characteristics of the dyes affects the methods of cleaning water.

Advanced oxidation process is useful technology for its many applications such as organic pollutant destruction in the form of toxicity reduction, biodegradability enhancement, COD removal as well as odour and colour removal. Ozonation is one of the most effective means of decolourizing dye wastewater up to 97% (Amat et al., 2007; Srinvasan et al., 2009). Researcher reported that ozonation effectively decolourize Reactive Red 120 azo dye by ozonation (Fahmi et al., 2010). Several combinations of treatment methods have been developed in order to effectively process textile wastewater; recently chemical oxidation becomes an important pre-treatment of biological treatment (Tehrani-Bagha et al., 2010). Antonio Marco et al., (1997) reported that total mineralization through oxidation process is highly expensive whereas a combination of the oxidation process and biological option would be a cheaper method for degradation of total organics from toxic wastewater. The present study is designed to see the effect of combination of ozonation and anaerobic biodegradation in dye wastewater treatment.

2. MATERIALS AND METHODS

2.1. Preparation and characterization of Azo Dye Solutions

Acid Red 14, as monoazo dye was purchased from commercial market and used without any further purification. Azo dye solution is prepared by dissolving dye in Milli Q water. The initial pH and concentration of Acid Red 14 dye solution was 10.7 and 1500mg/L. Figure 1 shows the chemical structure of Acid Red 14. Table 1 shows the characteristics of Acid Red 14 dye solution. Dye degradation has been studied in a semi-batch system.

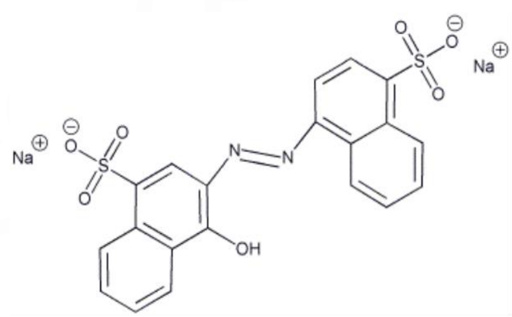

Figure 1 Chemical structure of Acid Red 14

Table 1 Characteristics of Acid Red 14 Dye Solution

Parameters	Values	Unit
pH	10.7 at 25˚C	-
Colour	Dark reddish	
COD	426	mg/L
TDS	1660	mg/L
Total Fixed Solids	954	mg/L
Total Volatile Solids	706	mg/L
Colour (Absorbance)	5(at 507 nm)	-
TOC	209.5	Mg/L

Conductivity	1.543 at 25ºC	mS/cm
Dye Concentration	1500	mg/L

2.2. Ozonation Procedure

Ozonation of dye solution was carried out in a batch mode. Figure 2 shows the schematic diagram of ozonation apparatus. Ozone was generated by corona discharge type ozone generator model Eltech el-5g/hr.-A with flow rate of 5gm/hr. from pure oxygen as feed gas. Oxygen was fed to the ozonator with a regulated pressure in the cylinder of 120 kg/cm^2, before entering the ozone generator cell. The pressure was adjusted to 2kg/cm^2 using the pressure regulator of the ozonator. The oxygen gas was circulated through Rota meter. Initial ozone concentration and ozone-oxygen flow rate were 55.5 mg/L and 1.5LPM respectively. The initial dye concentration was 1500mg/L. The equipment was cooled through air. All the experiments were conducted at room temperature. Ozonation was carried out in cylindrical plexiglass bubble column reactor with an internal diameter 9.2cm and height 60cm. The volume of synthetic dye sample was used 500 ml to avoid agitation caused by gas bubbles. Ozone-oxygen mixture was introduced through a porous diffuser that generates fine bubbles at the bottom of the reactor. The residual ozone in the off-gas was distracted by anhydrous MnO_2.

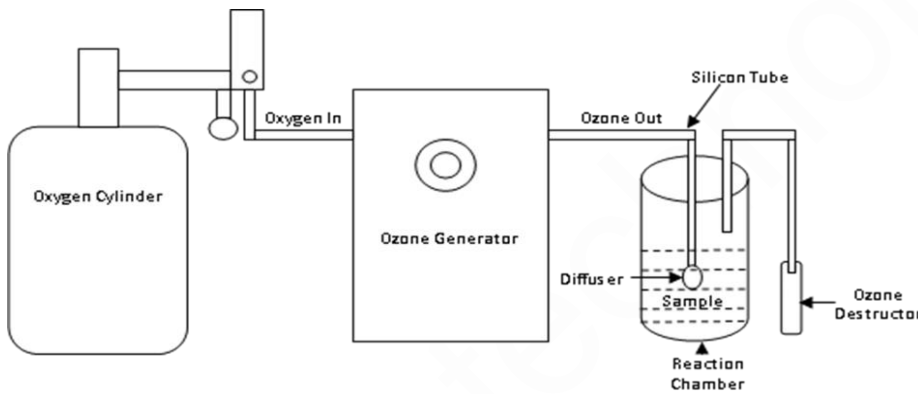

Figure 2 Schematic diagram of ozonation apparatus

2.3. Anaerobic Biodegradation

The experiments were conducted with a lab scale upflow anaerobic sludge blanket (UASB) reactors. Initially, the reactor was fed with synthetic wastewater containing some nutrients and sucrose as carbon source whose strength was 534mg COD/l till steady state condition achieved. The flow rate was 25ml/h, which translated to up flow velocity 0.16 m/hr. and hydraulic retention time (HRT) of 40 hrs. The reactor was operated at room temperature with this synthetic feed till steady state condition achieved. After achieving a steady state condition the reactor was continuously running on synthetic medium strength domestic wastewater. After that, the reactor was subjected to ozonated synthetic dyes solutions. The ozonated azo dye solutions were mixed with synthetic wastewater in a 1:1 ratio. For determination of the extent of anaerobic biodegradation, mixed ozonated azo dye solutions were used as feed for anaerobic bacteria and assessed for the extent of biodegradability in UASB reactor. Table 2 is mean and standard deviation of the daily measurements conducted during the study.

Table 2 Average value of reactor monitoring parameter during steady state

Reactor Performance	Value
pH	7.45±0.12
Influent Alkalinity, mg/L as $CaCO_3$	334.62±14.11
Effluent Alkalinity, mg/L as $CaCO_3$	343.68±12.8
VFA, mg/L as CH_3COOH	7.02±3.02
Total COD Removal Efficiency, %	79.34±1.25
Sludge TSS (g/L)	97.72±1.93
Sludge VSS (g/L)	42.67±1.97
VSS/TSS	0.436±0.011

2.4. Analytical Methods

Characterization of such dyes carried out e.g. dyes concentration and chemical properties. Ozone concentration in feed gas was determined by KI starch titration method (APHA 1985). 500 ml of dye solution prepared using Milli Q water to minimize interference, and an initial dye concentration 1500 mg/L was added into the reactor before starting the reaction at pH 10.7. Decolourization and COD reduction of dye sample performed at a certain time interval i.e. experiments were conducted consecutively for contact times of 5, 10, 15, 20, 25 minutes, and analysed immediately. The synthetic dye samples were drawn at desired intervals to analyse the dye concentration and COD. After ozonation, the ozonated dye solution was biodegraded by an upflow anaerobic sludge blanket (UASB) reactor. COD removal efficiencies were determined by the following equation:

$$C_{COD\%} = \left(\frac{COD_i - COD_f}{COD_i}\right) \times 100$$

Where C_{dye} (mg/L) is COD (mg/L) is the chemical oxygen demand of the solution, whereas C_i and C_f correspond to initial time and final sampling time, of the treatment.

3. RESULTS AND DISCUSSION

3.1. Effect on Dye concentration and COD by ozonation

Figure 3 presents the reduction in the dye concentration and COD decline during ozonation of Acid Red14 dye solution. After 25 minutes of ozonation at the initial concentration 1500mg/L, result indicates that the final dye concentrations of dye solution were 98mg/L. In the dye molecules ozone selectively attacks the electron–rich sites, i.e. the aromatic rings and azo bonds, resulting dyes degradation (Robinsion et al., 2001). It can be observed that for a longer ozonation times there is a greater reduction in the Acid Red 14 dye concentration, while for shorter ozonation times less reduction in the dye concentration occurs. The degradation of high concentration Acid Red 14 dye molecules required longer ozonation time.

Ozonation of dye solution resulted decline in COD concentration. The results show that ozonation contact time had a significant effect on COD removal. From figure 3, we can observe that decrease in COD with increasing ozonation time. 75% COD removal occurred in 20 min of ozonation time, although in some cases the values of COD increase with ozonation time. In this study COD increases after 20 min. Fahmi et al., (2011) and Venkatesh et al., (2015) reported that increases of COD were observed in the ozonation process due to dye molecules being oxidized resulting in formation of small organic molecular fragments, such as acetic acid, aldehydes, ketones, which are not completely mineralized under the oxidative conditions, contributing to the increase in COD during ozonation. An increase in COD value was mainly because of an organic species produced due to destruction of the molecular structure of azo dye by ozone (Zou et al., 2007; Constapel et al., 2009).

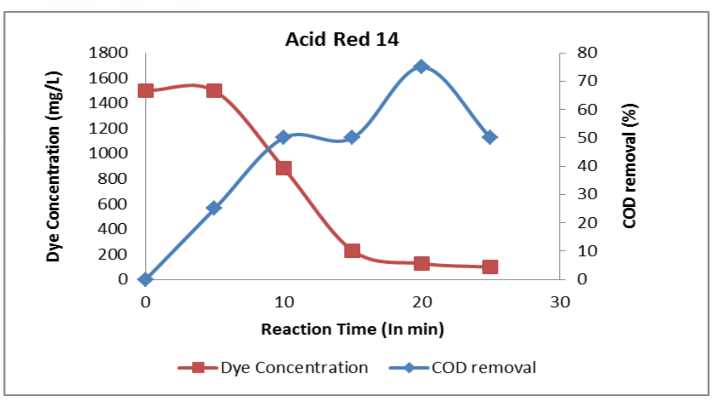

Figure 3 Reduction in the dye concentration and COD during ozonation of Acid Red 14 dye solution

3.2. Mineralization of ozonated azo dye Solutions by anaerobic process using UASB reactor

Ozonated azo dye solutions were passed through UASB reactor to assess the anaerobic biodegradation. The ozonated azo dye solutions were mixed with synthetic wastewater in a 1:1 ratio. For determination of the extent of anaerobic biodegradation, mixed ozonated azo dye solutions were used as feed for anaerobic bacteria and assessed for the extent of biodegradability in UASB reactor. Table 3 shows organic contents removal after anaerobic process.

Table 3 Organic contents removal after anaerobic process

Acid Red 14	Influent (mg/L)	Effluent (mg/L)	Removal (%)
COD	374	64	83

**Dye Concentration: 1500 mg/L*

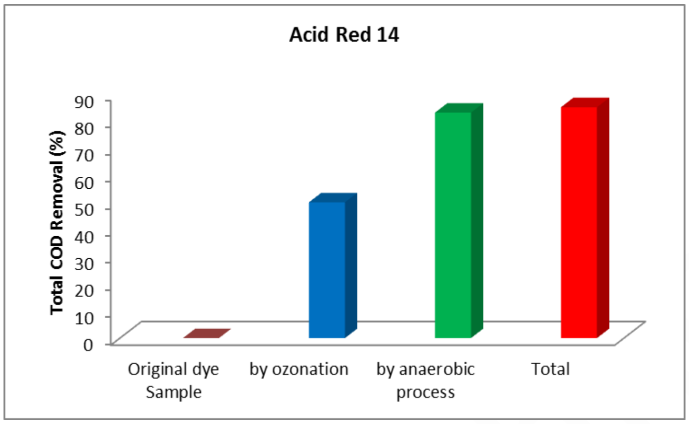

Figure 4 Decline of COD after combined process

3.3. The combination of ozonation and anaerobic biodegradation for the treatment of dye wastewater

The results of present study proved that ozonation play a significant role in COD reduction of the dye wastewater. It has been found that high ozonation time the dye degradation increases. It is also observed that the degradation of high concentration Acid Red 14 dye molecules required longer ozonation time. This is tremendously affecting the treatment cost. Thus combined treatment to reduce the cost of the wastewater treatment process by ozonation, anaerobic treatment process by UASB reactor was used along with ozonation in this study. Combined treatment reduced the COD level much more significantly, which is about 85% shown in Figure 4.

4. CONCLUSION

Acid Red 14 is a monoazo dye with long molecule and high molecular weight which are widely applied in industry. Effective, economic and efficiently treatment process is developed using ozonation and subsequent anaerobic process. This combined process has shown effective role in COD reduction of dye wastewater which is about 85% of total COD removal. COD concentration of Acid Red 14 dye decreased significantly up to ozonation time 20 min, whereas further ozonation was not efficient for COD reduction. The subsequent anaerobic process is followed by ozonation reduced COD value. It is also observed that for reduction of organic contents required maximum ozonation time which is affecting the entire cost of the process. Thus anaerobic process by an upflow anaerobic sludge blanket reactor has been tried along with ozonation to reduce COD as well as to optimize the ozonation treatment process.

ACKNOWLEDGMENT

The authors wish to acknowledge the Science & Engineering Research Board, Department of Science and Technology of India (SERB/DST) for the financial support.

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