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Removal of Colour and COD from Reactive Green – 19 Dyeing Wastewater using Ozone

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Abstract

Ozone is mainly used in the Advanced Oxidation Processes (AOP's) refers to a set of chemical treatment procedures designed to remove organic and inorganic materials in dye industry wastewater by Ozonation process. Reactive Green – 19 effluent is treated with Ozonation process. The operating parameters are Dye concentration (200, 300 & 400 ppm), time of ozone passing (20, 40 & 60 min.) & pH (4, 7 & 10). Experiments have to done for evaluated to find the optimum conditions for the Ozonation process. The contaminant materials are converted to a large extent into stable inorganic compounds such as water, carbon dioxide and salts, i.e. they undergo mineralization. The effect of Ozonation on the Decolourization, Degradation, and Mineralization of a dye, perform in a laboratory scale bubble column batch reactor. In Experiment Decolourization & Chemical Oxygen Demand (COD) will analyse. The effect of operational parameters on decolourization such as Ozone dosage and dye concentration in study.

Keywords: Ozonation, Removal of colour and COD, Reactive Green Dye wastewater

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. The fulfillment 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). [1]

Chemical oxidation aims at the mineralization of the contaminants to carbon dioxide, water and inorganic 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 realized with the consequent problem of the final disposal. It has been frequently observed that pollutants not amenable to biological treatments may also be characterized 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. [1]

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 wetair oxidation. Among the AOPs, treatment with ozone processes has yielded the most favorable results.

Most studies have focused on decolourization, 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. 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. The oxidation potential of ozone is 2.07 V and its high oxidation potential allows it to degrade most organic compounds.[1]

The objective of this study was to investigate the effects of ozonation on the decolorization, degradation and ozone demand for the RG19 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) and Color removal or the treatment of waste water by using ozonation as an advanced oxidation process.

Literature Review

Ozone Process

Ozone is formed naturally in the atmosphere as a colourless gas having a very pungent odor. Chemically, ozone is the triatomic, allotropic form of oxygen having the chemical symbol O_3 and a molecular weight of 38. Under standard atmospheric temperature and pressure, it is an unstable gas that decomposes into molecular oxygen. This very powerful oxidant, with a redox potential of 2.07, has many commercial and industrial applications. It is used commonly in potable and non-potable water treatment, and as an industrial oxidant. The considerable oxidizing power of ozone and its molecular oxygen by-products make it a first choice for oxidation or disinfection. The first drinking water plant began operations in Nice, France, in 1906. Since Nice has been using ozone since that time, it generally is referred to as the birthplace of ozonation for drinking water treatment.
In ozone treatment ozone was first used for drinking water treatment in 1893 in the Netherlands. Ozone is used in water treatment for disinfection and oxidation. Ozone exists as a gas at room temperature. The gas is colourless with a pungent odor readily detectable at concentrations as low as 0.02 to 0.05 ppm (by volume), which is below concentrations of health concern. Ozone gas is highly corrosive and toxic. Ozone is a powerful oxidant, second only to the hydroxyl free radical, among chemicals typically used in water treatment. Therefore, it is capable of oxidizing many organic and inorganic compounds in water. These reactions with organic and inorganic compounds cause an ozone demand in the water treated, which should be satisfied during water ozonation prior to developing a measurable residual.[2]

Principle:

Ozone is one of the strongest known oxidants. It can be used to technically burn dissolved compounds (oxidation). The extra oxygen radical in an ozone molecule quickly binds to each component that comes in contact with ozone molecules. This is because of the instability of ozone and its inclination to return to its original form (O_2). Both organic and inorganic substances may be oxidized by ozone (oxidation), but also microorganisms such as viruses, bacteria and fungi (disinfection). This causes the extra oxygen radical to be released from the ozone molecule and to bind to other materials, so that only pure and stable oxygen molecules (O_2) are left. Ozone is mainly applied in waste water and drinking water purification (for disinfection). The application of ozone in the industrial branch is increasing. The food industry uses ozone for disinfection and the textile industry uses ozone for colour removal. The largest benefit of zone is its pure caracter. It only oxidizes substances, and as a result byproduct formation rarely occurs.

Ozone treatment of several types of wastewater has resulted in considerable COD reduction and has been used for treatment of dyes, phenols, pesticides, etc. In recent years, ozonation is emerging as a potential process for colour removal of dyes, since the chromophore groups with conjugated double bonds, which are responsible for colour can be broken down by ozone either directly or indirectly forming smaller molecules, thereby decreasing the colour of the effluents. 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) 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. [3]

Ozone acts by direct or indirect oxidation, by ozonolysis, and by catalysis. The three major action pathways occur as follows:-

1) Direct oxidation reactions of ozone, resulting from the action of an atom of oxygen, are typical first order, high redox potential reactions.
2) In indirect oxidation reactions of ozone, the ozone molecule decomposes to form free radicals (OH•) which react quickly to oxidize organic and inorganic compounds.
3) Ozone may also act by ozonolysis, by fixing the complete molecule on double linked atoms, producing two simple molecules with differing properties and molecular characteristics.

Ozone produced commercially for oxidation reactions always is produced as a gas, from air at concentrations between 1.0 and 2.0 percent by weight, since ozone is highly reactive, and has a short half-life; it cannot be stored as a gas and transported. Consequently, ozone always is generated on site for immediate use. [4]

Advantages and Disadvantages of Ozone

Advantages:[4]

- Ozone is more effective than chlorine in destroying viruses and bacteria.
- There are no harmful residuals like iron, manganese, and sludge that not need to be removed after ozonation because ozone decomposes rapidly.
- Ozone can sometimes enhance the clarication process and turbidity removal.
- Ozone controls colour, taste, and odors.
- The ozonation process utilizes a short contact time (approximately 10 to 30 minutes).
- In the absence of bromide, halogen-substitutes DBPs are not formed.
- Biocidal activity is not inuenced by pH.
- Upon decomposition, the only residual is dissolved oxygen.

Disadvantages:[4]

- The cost of treatment can be relatively high in capital and in power intensiveness.
- The generation of ozone requires high energy and should be generated on-site.
- Ozone is highly reactive, toxic and corrosive, thus requiring corrosion resistant material such as stainless steel.
- Ozonation is not economical for wastewater with high levels of suspended solids (SS), biochemical oxygen demand (BOD), chemical oxygen demand, or total organic carbon (TOC).
- Ozone decays rapidly at high pH and warm temperatures.
- Ozone requires higher level of maintenance and operator skill.

Materials and Methods

Materials

Reactive Green 19 was taken from local vender and used without further purification. The experiment is carried out in a batch mode. 2 L of 200, 300 and 400 ppm dye solution was taken into the reactor for the experiment. Fig. 1 shows the experimental setup of Reactive Green 19 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)

Fig. 1. Experimental Setup

Analysis

Decolorization

The UV scans of the samples were done using UV-visible spectrophotometer 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 RG was detected using a spectrophotometer and the decolorization ratio was calculated from the following equation. [5]

Colour Removal (%) = $[(A_i - A_f)/A_i] \times 100$
where,
A_i= Absorbance before Treatment.
A_f = Absorbance after Treatment.

Chemical oxygen demand (COD)

Chemical Oxygen Demand (COD) of the samples were found by using approved dichromate COD Method is the most widely used chemical oxygen demand method in the world for NPDES reporting and for easy process monitoring [5].

Molarity of FAS Solution = ((vol of $K_2Cr_2O_7$) x 0.25) / (vol of FAS used)

COD as mg O_2/ Lit. = [(A−B) X M X 8000] / ml of sample
Where A = ml FAS used for Blank
B = ml FAS used for sample
M = Moles of FAS

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. [6]
Reactive Green 19 was selected to prepare waste water having initial dye concentration of 200 ppm, 300 ppm and 400 ppm. The decolorization of RG 19 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. 2 liter of the reactive dye samples was initially subjected to ozonation at an ozone dose of 0.45 g/hr.

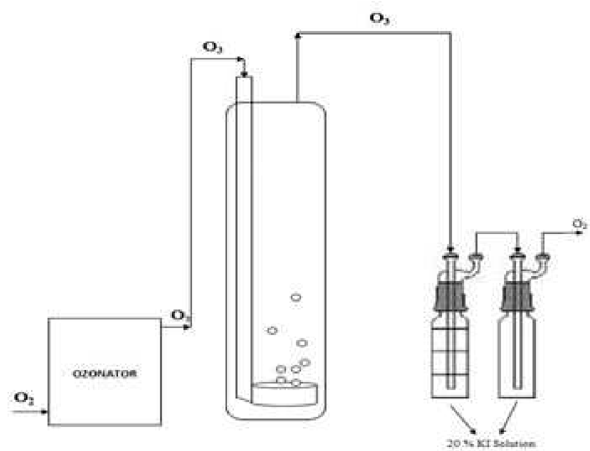


Fig. 2. Bubble Column Reactor with air diffuser

Experimental Results & Discussion

Effect of Concentration and Time at pH 10, 7 & 4

The decolourization & COD removal of RG19 in ozonation system was conducted with initial dye concentration in the range of 200, 300 & 400 ppm.

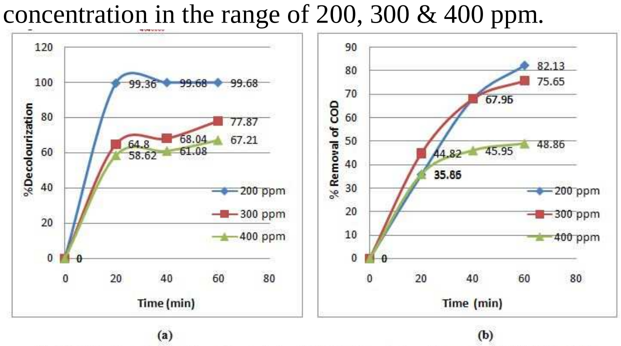
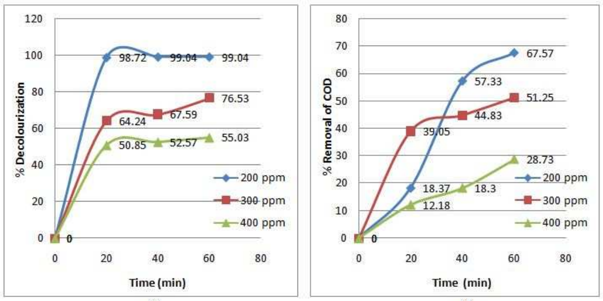
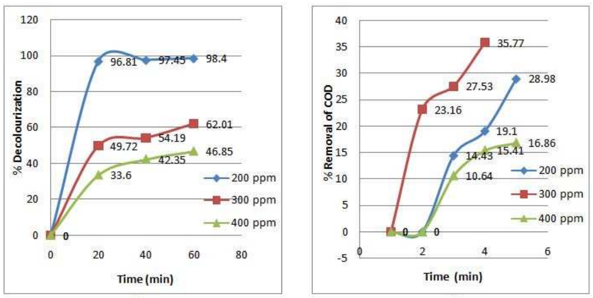


Fig.3. (a) Effect of Concentration and time on Decolourization & (b) Effect of Concentration and time on Removal of COD **(At pH 10)**



(c) (d)

Fig.4. (c) Effect of Concentration and time on Decolourization & (d) Effect of Concentration and time on Removal of COD (At pH 7)



(e) (f)

Fig.5. (e) Effect of Concentration and time on Decolourization & (f) Effect of Concentration and time on Removal of COD (At pH 4)

The result in Fig. 3 shows that for RG 19 the time requirement for maximum Decolourization (67 to 99 %) and COD removal (49 to 82 %), 40 to 60 min with increase in initial dye concentration 200 to 400 ppm at pH 10.

The result in Fig. 4 shows that for RG 19 the time requirement for maximum Decolourization (55 to 99 %) and COD removal (28 to 67 %), 40 to 60 min with increase in initial dye concentration 200 to 400 ppm at pH 7.

The result in Fig. 4 shows that for RG 19 the time requirement for maximum Decolourization (46 to 99 %) and COD removal (17 to 29 %), 40 to 60 min with increase in initial dye concentration 200 to 400 ppm at pH 4

Effect of pH on maximum time 60 min.

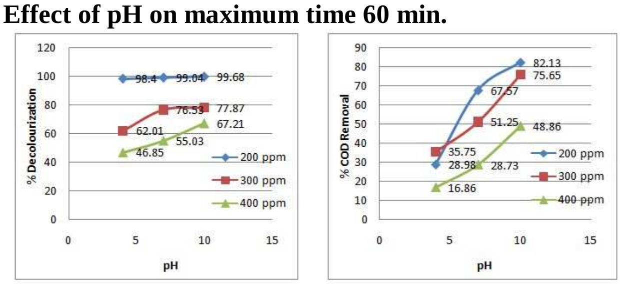


Fig.6. Effect of pH on Decolourization & Removal of COD

The result in Fig. 6 shows that for RG 19, Decolourization and Removal of COD is decrease with decrease with pH 10 to 4 cat maximum reaction time 60 min.

Conclusion

The major conclusions derived from the study are as follows:

- From the study demonstrated that 99.68 % decolourization of RG 19 could be accomplished by ozonation. The time required for complete decolourization is increase with increase concentration.
- From the study demonstrated that 82 % COD removal achieved by ozonation. The time required for removal of COD is increase with increase concentration.
- Decreasing pH, the decolurization and COD removal was also decrease. Maximum efficiency of ozonation system at pH between 10 to 11.

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