Degradation of Reactive Black 5 Azo Dye Using Catalytic Ozonation with MgO

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***Abstract*— The main aim of wastewater treatments is to dispose of wastewater safely without any adverse effect on human health and without polluting any water resources. Most of the dye molecules are toxic, recalcitrant, and chemically and photochemically stable and impart color to receiving water. Advanced oxidation processes are the most viable option to treat the wastewater. Among them catalytic ozonation allows a quicker removal of organic pollutants, because catalysts improve the oxidizing power of ozone, markedly reducing the economic cost.The catalytic ozonation of Reactive Black -5 solution in the presence of MgO catalysts was investigated in a laboratory scale batch reactor. The effects of solution pH (3–12), reaction time, MgO dosage (0.05-2 g/L), and initial dye concentration (100–500 ppm) on color and Total Organic Carbon removal were evaluated, and the findings were compared to those of ozonation without a catalyst. The results indicate that addition of MgO crystals greatly accelerate the degradation of RB-5 dye.**

***Keywords*— Wastewater Treatments, Advanced Oxidation Process, Catalytic Ozonation, MgO/O_3, TOC removal**

I. INTRODUCTION

Increasing demand and scarcity of clean water sources due to the rapid developments, increasing population have become an issue worldwide. So to meet this demand it's a necessity to develop the cost effective and efficient technology to treat wastewater.It is the leading worldwide cause of deaths and diseases and it accounts for the death of more than 14000 people daily. Water is a substance necessary for life, without water no one can imagine the life. Its link to every living beings which survive on the earth. Only few percentage of fresh water is available for living being out of which some percentage is in the form of ice. Sea water and sea ice constitutes of the 97% of the total remaining water. Due to scarcity of water, it has become a necessary means to Re-Cycle and Re-Use water [1, 2, 3].

Traditional physical and chemical methods such as adsorption, coagulation, ion exchange, and ultra-filtration can generally be used efficiently, result in the generation of solid waste which needs to be further treated. Although these methods are effectively remove the color, they were either costly to apply to actual field or they are enable to meet the discharge criteria of wastewater in term of total organic carbon (TOC) removal [4]. Dye molecule consist of two groups: Chromogen and Auxochrome. There are different 12 classes of chromogen groups like azo, carbonyl, nitro group etc. Among them azo groups are widely used in textile industries. Due to the ineffectiveness of biological treatments the new advanced oxidation processes (AOP) are used to degrade the dye molecule [5,6].AOPs are based on the in situ generation of highly reactive radicals for mineralization of refractory organiccompounds, water pathogens and disinfection by-products [1]. The end products of complete oxidation (i.e., mineralization) of organic compounds are carbon dioxide (CO_2) and water (H_2O). [7, 8, 9]Among all AOPs ozonation shows the efficient method to remove the color of dye wastewater but it has little effect on mineralization of dye. So now the research is focused on the catalytic ozonation process.

Catalytic ozonation has gained highly increasing attention during past years, because of its good effectiveness in the degradation of organic pollutants. Adding a catalyst to ozonation process improve the oxidation rate and reduce the reaction time. The effectiveness of process depends on various parameters like pH, type and dose of catalyst, structure of the target compound, ozone flow rate and reactor configuration. Catalytic ozonation may be carried out in homogeneous and heterogeneous mode. In homogeneous catalytic ozonation process the metal ions dissolve may be responsible for catalytic effect. In heterogeneous catalytic ozonation metal oxides, metal supported on oxides, activated carbon etc. are used as catalyst.The application of catalytic ozonation with transition ions significantly improved the efficiency of humic substances removal from water under the same experimental conditions. [10-12]. In this paper textile dye Reactive Black 5 (RB5) was decomposed by catalytic ozonation process using MgO as a catalyst and compared with the simple ozonation process. The parameters like solution pH, catalyst dosage, initial dye concentration, ozone flow rate were compared and discussed.

II. MATERIALS AND METHODS

A. Materials and Reagents

Reactive black-5 was obtained from Piyush Chemicals and used without further purification. Molecular weight of Reactive black - 5 dye is 991.82. Molecular formula of RB - 5 dye is $C_{26}H_{21}N_5Na_4O_{19}S_6$. It is soluble in water (550 mg/ml at 20 °C). Mg $(NO_3)_2$• $6H_2O$, WO_3 and γ-Al_2O_3 with purity of 99.9% was obtained from Piyush Chemicals. Ozone was produced by ozone generator from pure oxygen. Potassium Iodide was obtained from Piyush Chemicals.

B. Catalyst Preparation

1) Magnesium supported on γ-Al_2O_3 was prepared by wet impregnation method. The precursor saltMg $(NO_3)_2$•$6H_2O$

was dissolved in a volume of solvent equal to the catalyst pore volume and then added slowly (drop wise) to the γ-Al_2O_3. Then it was shake for two hours for better mixing. The moisture was removed by overnight drying at 110 ^{0}C and finally calcined at 450 ^{0}C for 3 hour.

2) MgOcatalysts were prepared by direct calcination of precursor salts Mg $(NO_3)_2$•$6H_2O$ at 500 ^{0}C for 3 hours [13].

C. Experimental Procedure

The experimental set-up was composed of a cylindrical glass columnin which ozone is bubbled through wastewater, an ozone generator, a glass sparger to distribute the ozone to the solution, an ozone off-gas destruction system, and tubing. The catalytic ozonation reactor was a magnetically stirred column with a total volume of 1.5 L. The experiments were performed at a room temperature, with 1L of dye solution in each run throughout the study. Different operational variables, including pH of the dye solution, dye concentrations, catalyst dose were investigated.MgO nanocrystalswere used as the ozonation catalyst for oxidation of the RB5 dye. In addition, experimentswere performed with ozonation alone to verify the catalytic nature of the catalyst. The ozone in the off-gas stream of the reactor was quenched and destructed in a 2% KI solution.

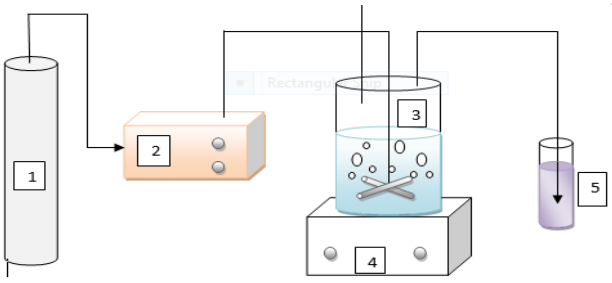

Figure 1. Experimental Setup for catalytic ozonation

1. Oxygen cylinder 2. Ozone generator 3. Reactor 4. Magnetic stirrer 5. KI solution

II. RESULT AND DISCUSSION

Simple ozonation experiment was carried out with 100 ppm RB–5 dye solution for 120 minute. Experiment was carried out by passing the ozone gas through the dye solution at the flow rate of 30 LPH. Here volume of the dye solution was 1000 ml. All the experiment were carried out at room temperature and pressure. Simple ozonation of 100 ppm RB - 5 dye solution gives 99.9 % color removal and 32.9 % TOC removal after 120 min shown in Fig. 2.

Catalytic ozonation experiments were carried out by using different catalyst and results were tabulated in Table I.

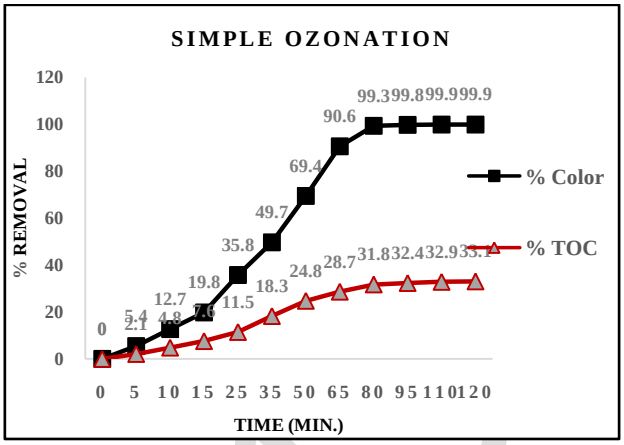

Fig. 2 Color and TOC removal in simple ozonation

Table I

Catalytic Ozonation of RB-5 Dye Using Various Catalysts

Process	Catalyst Weight (gm)	Dye Concentration	Time (min)	% Color removal	% TOC removal
O_3	-	100 ppm	110	99.9	33.9
O_3+Mg supported on γ-Al_2O_3	0.2	100 ppm	95	99.9	41.1
O_3+WO_3	0.2	100 ppm	95	99.9	39.1
O_3+MgO	0.2	100 ppm	95	99.9	**48.8**

Table I shows that MgO catalyst gives overall better color removal as well as TOC removal so for further experimental work MgO catalyst is used.

A. Parametric Study with MgO catalyst

1) *Effect of pH*: Solution pH plays significant role in the contaminant degradation mechanism during an oxidation process, it is important to evaluate the effect of pH in catalytic ozonation of the selected model dye. Therefore, the effect of

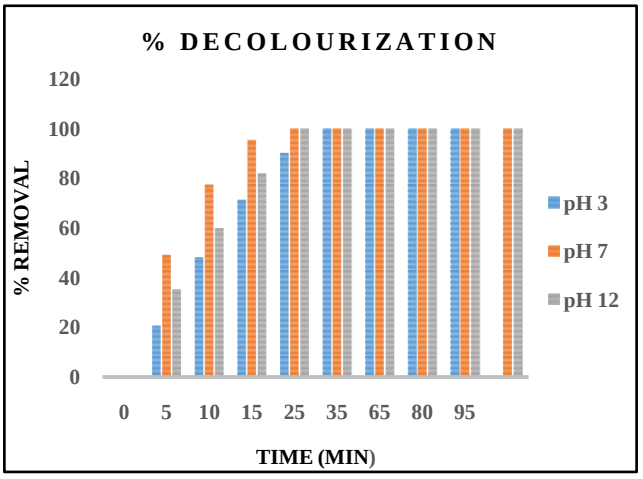

Fig. 3 Effect of pH on % color removal

the dye solution's initial pH on degradation and TOC removal of RB5 was studied at pH values of 3, 7 and 12, under constant reaction time and ozone dosing, in catalytic ozonation with MgO nanocrystals. Fig. 3& 4 shows the removal percentages of color and TOC as a function of initial pH in catalytic ozonation, respectively. As seen in Fig. 3, the percentage of color removal increases from the solution for a pH 7 compared to pH 3. As the pH increases from neutral to alkaline the color removal efficiency is decreased. This was due to the formation of different dominant oxidant under different pH condition. So in this case the degradation is not due to the OH radicals, as OH radicals are predominant in alkaline solution. So the RB5 is degraded directly by ozone molecule rather than the OH radicals [14]. Fig. 4 shows the trend of COD removal of RB5 as a function of the solution pH. It has almost the same trend as color with the value around 74.1% at a pH of 7. The maximum color and TOC removal is observed at pH 7 can be explained by the formation of radical species other than the hydroxyl radicals [13].

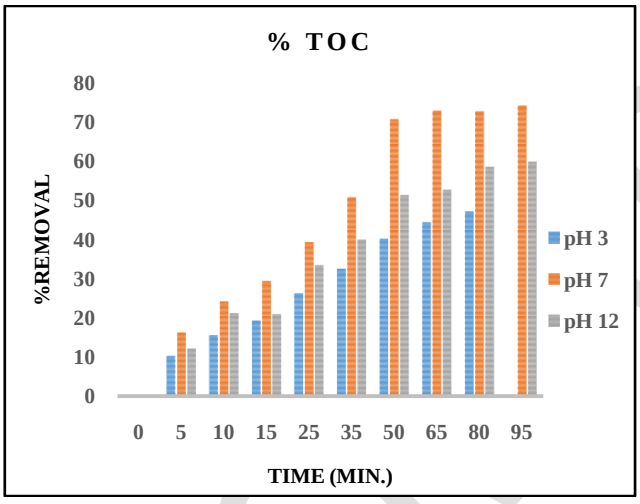

Fig. 4 Effect of pH on % TOC removal

*II) Effect of Catalyst Dosage:*The catalytic ozonation of RB - 5 dye solution in the presence of various concentration of Magnesium Oxide (ranging between 0.05 and 2 g/L) was carried out. The performance in the color degradation and TOC removal of RB5 was determined. All experiments in this phase were carried out at the constant reaction time, at RB5 concentration of 100mg/L, and at the neutral pH. Fig. 5 & 6 shows color and TOC removal of RB5as a function of catalyst concentration in the solution. As shown in Fig. 5 the color removal time is gradually decreased as we increase the weight of MgO catalyst from 0.05g/L to 1 g/L. Further increase in MgO dosage to 2g/L did not have increase the color removal. The removal of TOC showed in Fig.6. The removal of TOC increased from 36.4% to 93.1% as catalyst dosage was increased from 0.05g/L to 1g/L. Thus the optimum dosage of MgO selected for color and TOC removal was 1g/L for further experimental work. Other researchers have also reported increased oxidation efficiency with increased catalyst dosage. However the optimum catalyst dosage depends on the type of catalyst, type of pollutant, and the reaction condition [13].

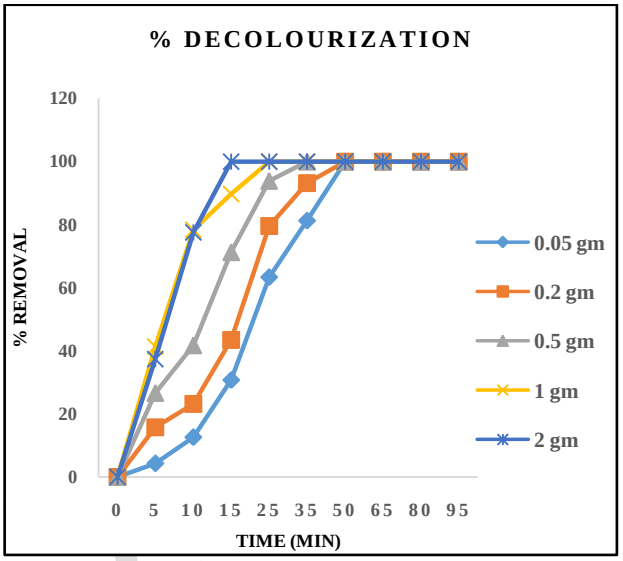

Fig. 5 Effect of Catalyst Dosage on % Color Removal

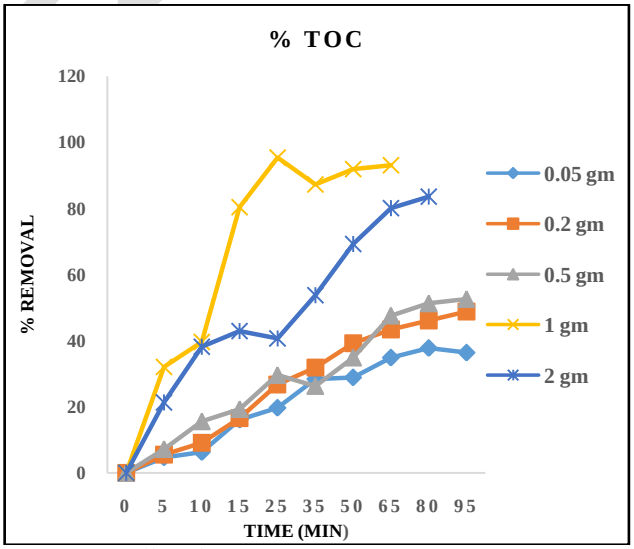

Fig. 6 Effect of Catalyst dosage on % TOC Removal

III) Effect of Dye Concentration: Industrial wastewater contain different concentration of dye, so it is important to study how the initial dye concentration affects removal of color and TOC. The effect of initial RB5 concentration of 100-500 mg/L on color and COD removal was investigated at an initial pH of 7 and catalyst dosage of 1gm/L. As shown in Fig. 7 to get the 99.99% color removal efficiency for initial concentration of 100, 200 and 500 mg/L were 25min, 35 min and 65 min respectively which shows a trend of reduced removal with increasing initial dye concentration. The TOC removal efficiency for the corresponding dye concentration were 93.1%, 71.1% and 48.3% respectively as shown in Fig. 8.

The rate of reduction in TOC removal efficiency suggests that more ozone is required to mineralize the intermediates from thedye degradation. This can be fulfilled by increasing the ozone flow rate or by increased ozonation time.

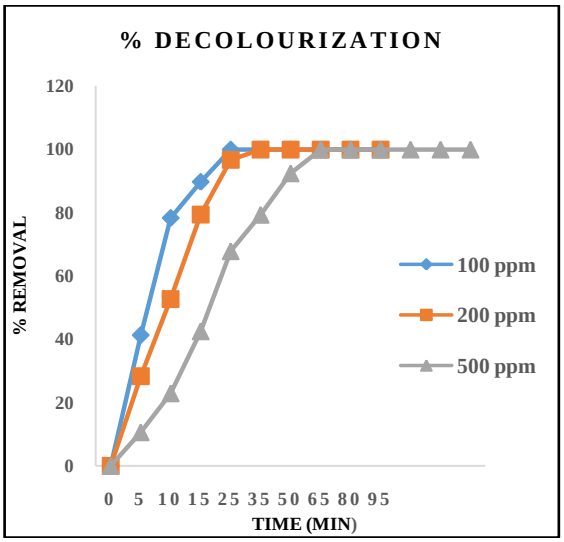

Fig. 7 Effect of Dye Concentration on % Decolourization

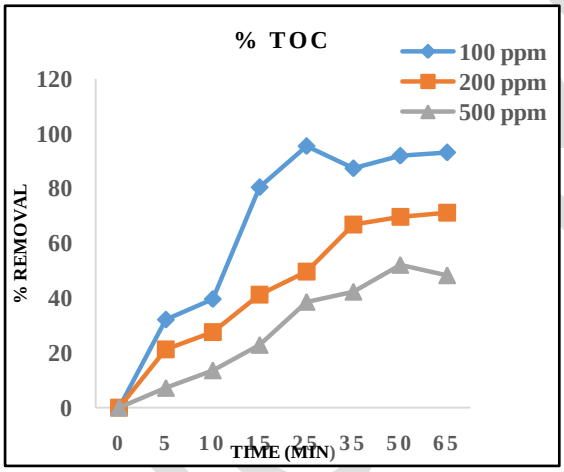

Fig. 8Effect of Dye Concentration on % TOC Removal

IV) Effect of Ozone Concentration: Color and TOC removal efficiency of the RB5 solution as a function of the ozonation time was studied with different ozone flow rates (30LPH, 40 LPH and 50 LPH). The results are shown in Fig. 9 and 10 respectively. The time required for 99.9% color removal is decreased as the ozone flow rate increased. The TOC removal trend is different than color removal. As the ozone flow rate increases the TOC removal is decreases. The maximum TOC removal is observed at 30 LPH as shown in Fig. 10. Tabrizi[15] observed that increasing ozone flow rate did not increase the decolourization efficiency.

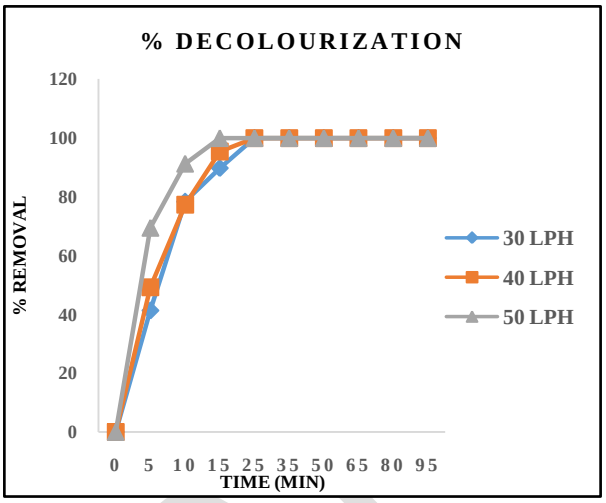

Fig. 9 Effect of Ozone Flow rate on % Decolourization

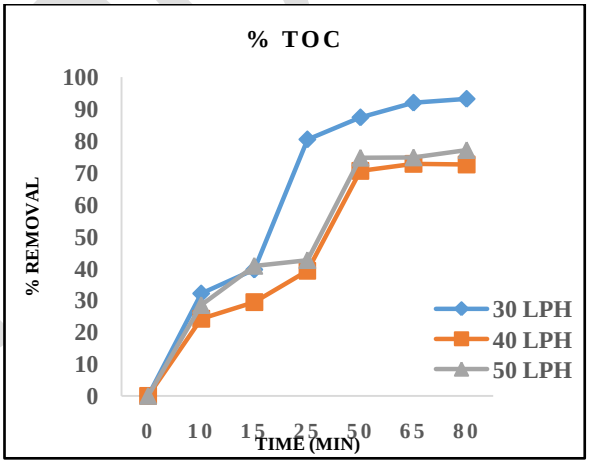

Fig.10 Effect of Ozone Flow rate on % TOC Removal

IV.CONCLUSIONS

This paper represents the results of experiments performed using MgO as a catalyst in ozonation process for degradation of RB5 dye. MgO catalyst were demonstrated to be effective catalysts in the catalytic ozonation of dye-containing solutions since it notably accelerates decolourization and TOC removal and reduces the required oxidation time compared to simple ozonation.

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