International Journal of ChemTech Research
CODEN (USA): IJCRGG, ISSN: 0974-4290, ISSN(Online):2455-9555
Vol.10 No.9, pp 402-409, 2017

Heterogeneous catalytic ozonation of Reactive Black 5 with cobalt oxide

Nikita P. Chokshi*, Himanshu Bhutia, Abhishek Chotalia, Anish Kadiwala, J. P. Ruparelia

Chemical Engineering Department, Institute of Technology, Nirma University, Ahmedabad-382481, India

Abstract : Textile wastewater needs to be treated well before the discharge as it is very harmful to environment. A well accepted technique, catalytic ozonation was applied to remove the color and recalcitrant compounds from dye solution containing Reactive Black 5 (RB5). In the study, the cobalt oxide used as a catalyst to improve degradation by ozone. The catalytic activity of cobalt oxide is studied under various experimental conditions. Results show that RB5 removal is considerably enhanced by using catalyst due to generation of hydroxyl radical as compared to ozonation alone. The influence of different variables like initial RB5 concentration, catalyst dosage, pH of the solution has been investigated at room temperature. COD removal in 80 minute can reach up to 67% while only 30% with ozonation alone.

Key Words : Wastewater, Advanced Oxidation Process, Catalytic Ozonation, Decolourization, Degradation.

Introduction:

Gujarat is considered as a hub of textile industries. The fact about the textile industries is that they consume a huge quantity of water and finally generate the wastewater. Due to the presence of the toxic substances, this will create serious environmental and health issues. The general methods which are used for the treatment of textile effluent are the combination of physical, chemical and biological processes. One of the major problem with these processes is they are generating sludge and other solid wastes. And even by using these techniques complete decolourization and mineralization of the effluent is not possible. So now a days researchers are focusing on resolving this problem using advanced oxidation processes (AOP) [1][2]. In literature different AOP's are suggested like ozonation, UV irradiation, Fenton, catalytic ozonation etc. AOPs are generally means for generating the hydroxyl radicals, which are nonselective and highly reactive oxidant [3]. As per literature, ozonation has excellent potential to remove the color but the main limitation is that it cannot degrade the recalcitrant compounds. So an improvement in ozonation process nowadays is the ongoing research on catalytic ozonation process. Basically, there are two types of catalytic ozonation: homogeneous catalyst system and heterogeneous catalyst system. In this study, the main focus is on the heterogeneous catalyst systems. In heterogeneous catalytic ozonation, the reaction may proceed in a bulk water or on the surface of catalyst [4]. The catalysts generally used in catalytic ozonation are metal oxides (MnO_2, CeO_2, TiO_2), metal and metal oxides on supports (Co- γ Al_2O_3, Cu- TiO_2, Ru- γ Al_2O_3, Ni- γ Al_2O_3). The main role of the catalyst is to help in decomposition of ozone and boost the generation of $HO^{\cdot}$radicals. The surface properties of catalyst and pH of the solution affect the effectiveness of the process[5]. Several metal oxides (especially Manganese dioxide, Cerium oxide, Magnesium oxide, Cobalt oxide) are used in catalytic ozonation process [6], [7], [8], [9].

The acidity and basicity are the basic factors that help in determining the catalytic properties of metal oxides. All the metal oxides have hydroxyl groups on their surface in varying amount [5], [4]. Both Bronsted and Lewis acid sites should be present on metal oxides.

In this work, the aqueous solution of Reactive Black 5 (RB5) using cobalt oxide catalyst is presented. The kinetics of catalytic ozonation were investigated. The different parameters affect the effectiveness of the process were analysed and optimization of parameters has been done. The experimental study was conducted using a glassbubble column. The possible pathway of degradation of the RB5 is also suggested.

2. Experimental

2.1 Materials:

Cobalt nitrate, sodium hydroxide, hydrochloric acid, Reactive black 5 (RB5) dye are purchased from Piyush chemicals and all the chemicals are of analytical grade. The chemicals are used as it is without any further purification. Fig.1 shows the chemical structure of RB5 dye.

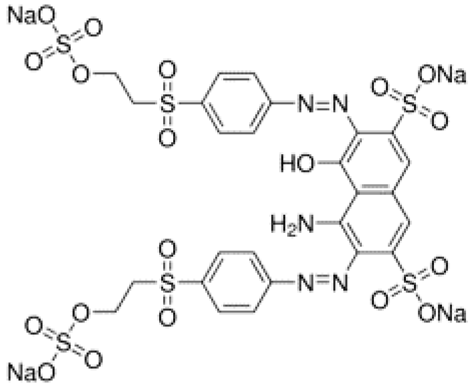

Fig. 1 Chemical structure of RB5

2.2 Preparation and Characterization of Catalyst:

The cobalt nitrate, in required amount was diluted and the solution was dried overnight at around 110 ^{o}Cto evaporate the water and finally it is calcined at around 500 ^{o}C for 3 hours [9]. The study the morphology and phases of synthesized catalyst, SEM (scanning electron microscopy) and X-ray powder diffraction (XRD) analysis was done respectively[10].

2.3 Experimental Procedure:

The experimental set up for ozonation and catalytic ozonation is shown in Fig.2. A cylindrical shaped glass column reactor with a height of 45 cm and diameter of 8 cm was used. The 100 ppm RB5 dye solution was prepared using tap water. The ozone gas was generated from pure oxygen cylinder by the ozone generator. Ozone gas was bubbled into the solution at a flow rate of 30 LPH through the bottom of the reactor with the help of gas sparger. The outlet ozone gas was treated by KI solution. The samples were taken out at different time intervals, filtered through quantitative ashless filter paper to remove any suspended particles[11]. The absorbance of the samples was measured at a wavelength of 599nm using a Shimadzu UV-1800 spectrophotometer. The decolourization efficiency was calculated as:

$$\textbf{\% Color removal} = (C_0 - C_t/C_0) * 100 \qquad (1)$$

Where C_0 and C_t are absorbances at time 0 and t, respectively.The Chemical Oxygen Demand (COD) analysis was done by closed reflux method by Hach (DBR 200, USA) COD test kit with standard method 5220B in APHA, 2005.

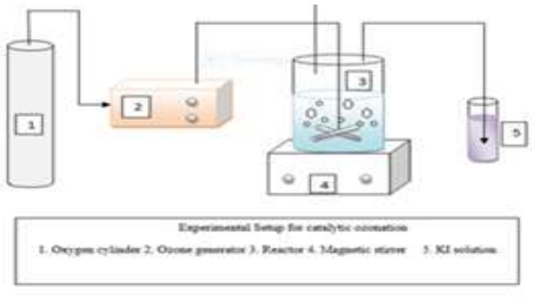

Fig. 2 Experimental setup

3. Results and Discussion:

As per the information retrieved from literature, the decolourization of many dyes involve the reaction of ozone with the chromophoric group which is responsible for color. In this study almost all color disappears in the first 10 min of ozonation, so that water can be reused for coloration of materials in industries[1]. Fig. 3 shows the UV-Vis absorption spectrum for 80 min of the experiment. The chromophoric groups which are responsible for color are destroyed in the first 10 minutes of the experiment. But the intermediates generated require the longer time for complete mineralization [1].

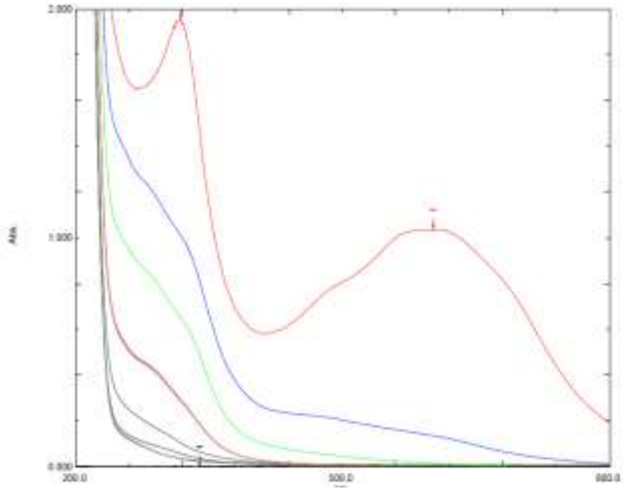

Fig. 3 UV-Vis spectra variation on the ozonation time of the RB5 solution

3.1 Catalyst Characteristics

The XRD graph of the prepared cobalt oxide catalyst is shown in Fig.4. For cobalt oxide, there are six peaks at 2θ= 19.0974, 31.3712, 36.9362, 44.8935, 59.4246 and 65.3082 corresponding to Co_3O_4 phase (JCPDS No. 04-002-2531). The SEM images are shown in Fig.5 is used to imagine the surface morphology of the catalyst. SEM and EDX analyses of a sample of cobalt oxide showed the presence of distinct layers enriched in cobalt and oxygen. In the images with magnifications shows the zones of more homogeneously distributed state/phase of cobalt. From Fig. 5, in the range 10μm, it can be observed that the agglomeration of catalyst particles takes place. So there may be chances of reduction in the activity of catalyst due to the reduction in surface area. From the EDX analyses, the spectrum shows two peaks of Cobalt particles in K and L-shell and there is no other compound or impurities present.

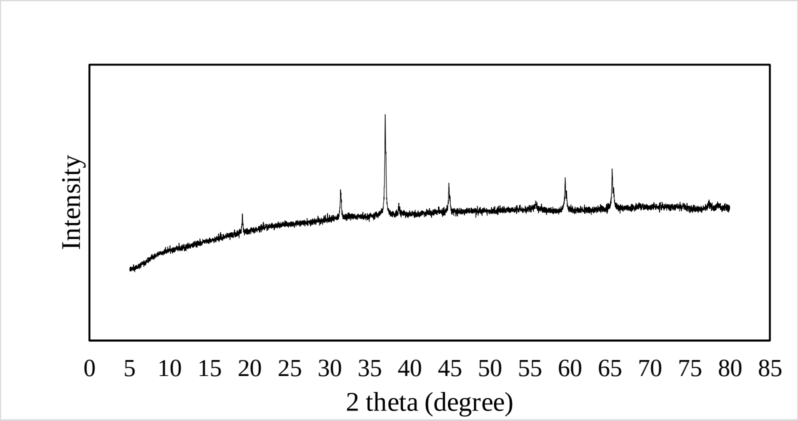

Fig. 4 XRD pattern of synthesized catalyst

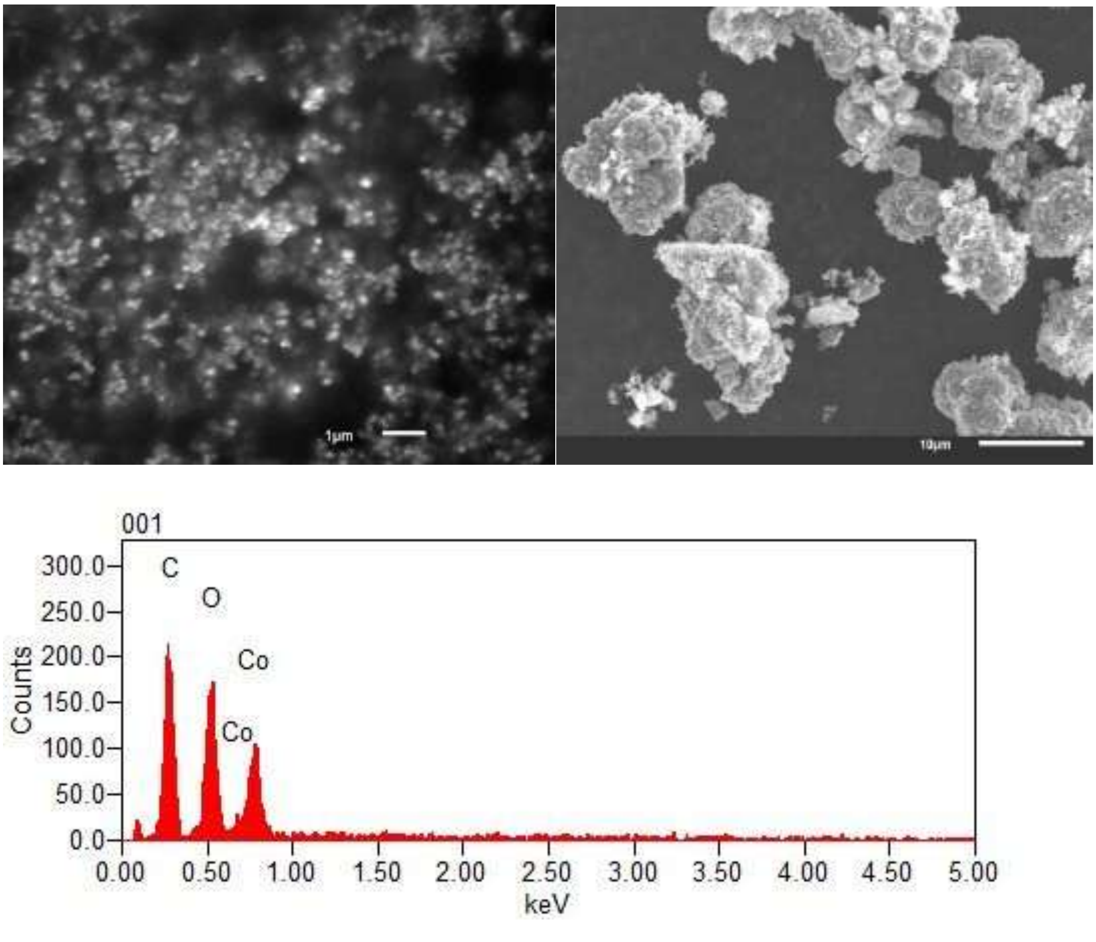

Fig. 5 SEM images and EDX analyses of Cobalt Oxide sample

3.2 Influence of Catalyst Dosage

The experiment was conducted using different concentration of cobalt oxide catalyst ranging from 0.2 and 1 g/L. All experiments were conducted at room temperature, 100 ppm dye concentration and at neutral pH. Figure 6 display the influence of catalyst dosage on color and COD removal of RB5 dye.

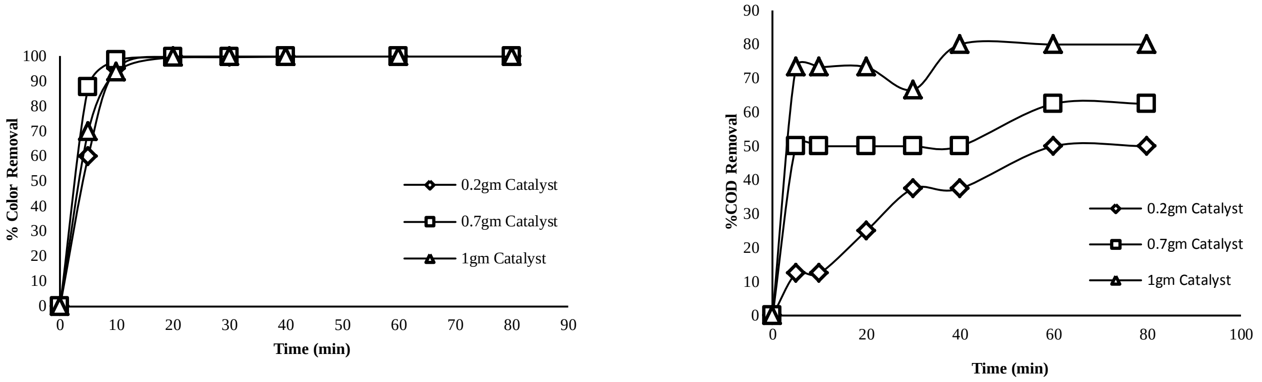

Fig. 6 Influence of catalyst dosage on color and COD removal of RB5 solution

As shown in Fig. 6, the time required for 99.99% color removal is decreasing as the weight of the catalyst increases. There is not much more difference in time for 99.99% color removal when the catalyst weight is increased from 0.7g/L to 1 g/L. So, relatively small amount of cobalt oxide is needed to enhance the degradation of RB5 dye. The removal of COD is also shown in Fig. 6. As shown in figure removal of COD is increases from 50 to 80% as with the increase of cobalt oxide dosage from 0.2 to 1 g/L for the same time period, the further increase in catalyst quantity have no significant increase in COD removal.

3.3. The Influence of Initial Dye Concentration

It's essential to see the effect of initial dye concentration on color and COD removal in catalytic ozonation of RB5 dye. As shown in Fig. 7 the time required for 99% color removal is increased by increasing the dye concentration from 100 to 500 ppm. The COD removal efficiency for 100, 200 and 500 mg/L was 89%, 75% and 57% respectively. The rate of COD removal is more noticeable compared to color and it infers that excess ozone is required to oxidize the intermediates. Hence with increase in initial dye concentration, there seems reducing trend in degradation efficiency of color and COD [12], [2].

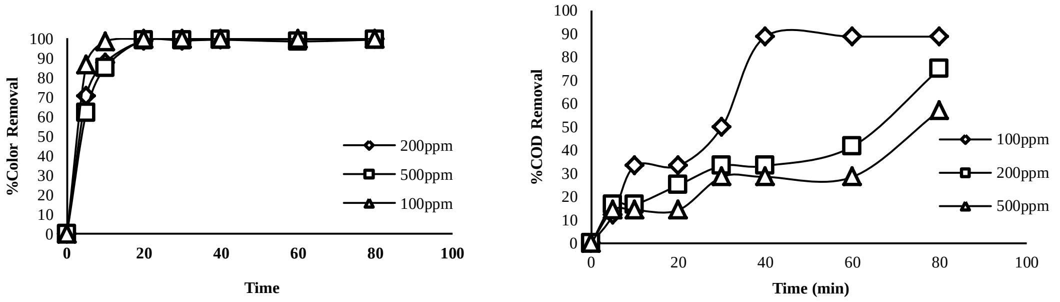

Fig 7. Influence of initial dye concentration

3.4. Effect of Initial pH

In aqueous ozone chemistry, it is essential to check the effect of pH. It influences the kinetics as well as the pathway of ozone reaction. At lower pH, the ozone molecules predominantly degrade the organic molecule and in the alkaline condition, ozone decomposition results in the formation of hydroxyl radicals, which reacts with organic as well as inorganic compounds in water. Even the pH of the solution also influences the surface properties of catalyst[13], [14], [5]. To check the effect of pH,theRB5 dye was tested in a range between 2, 7 and 10. Fig. 8 illustrates the effect of pH on color removal and COD removal on RB5 dye solution.

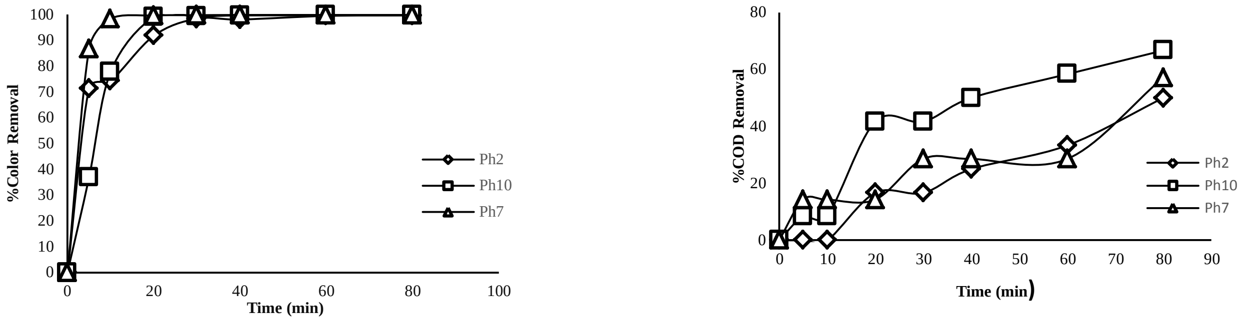

Fig. 8 Effect of initial pH on color and COD removal of RB5 solution

As seen in above figure the percentage of color removal at an acidic, neutral and basic pH is almost same near 99% after 30 min which shows that the ozonation was fast and efficient in color removal [2].J. Wu et al [J. Wu et al., 2015] observed that the decolourisation rate increased with increase in pH.It is observed that in first 15 min of the reaction, the color removal increased as an increase in solution pH. But after 30 min the color removal efficiencies were almost the same which shows that the catalytic ozonation was effective. Figure 8 also shows the trends of COD removal as a function of solution pH. The COD removal efficiency also increases as the pH increases from 2 to 12. The COD removal is maximum in alkaline medium compare to acidic and neutral pH. This reveals that the dual act of ozone on recalcitrant compounds. At low pH, the ozone molecule directly attack the targeted organic compounds and at high pH, there occurs the decomposition of ozone at first, which generates hydroxyl radicals, that have tendency to react with any targeted organic compound in a non-selectively way [12], [15], [16].

3.5 Kinetic Study& Reaction Mechanism

The prepared cobalt oxide catalyst was used in ozonation of aqueous RB5. The kinetic data of the catalytic ozonation of RB5 in the presence of catalyst were shown in Fig. 9.

The overall color removal can be expressed by pseudo-first order reaction[12].

$$-\frac{dc_{RB5}}{dt} = k_1 c_{O3}\, c_{RB5} + k_2 c_{OH\cdot}\, c_{RB5}(2)$$

Where k_1 and $k_2$were the reaction rate constant of the reaction of the RB5 with molecular ozone and hydroxyl radical respectively.

Then equation (2) can be expressed as:

$$kt = \ln\left(\frac{c_{RB5}}{c_{RB50}}\right) \qquad (3)$$

Where c_{RB50}denotes the initial concentration of RB5 and k represented as $k_1 c_{O3} + k_2 c_{OH}$.

The plot ofln $\left(\frac{c_{RB50}}{c_{RB5}}\right)$with time gives a straight line fits (R^2=0.97). The value of the rate constant is 0.1123 min^{-1}.

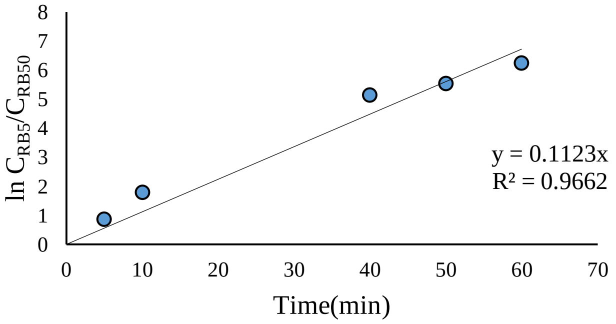

Fig. 9 Pseudo first order plot of RB5 by catalytic ozonation (Dye Concentration 300m/L, gas flow rate 30 LPH, catalyst dosage 0.5 g/L)

There are different reaction mechanisms discussed in the literature for the ozonation process. There are basically two approaches which are well accepted one direct reaction of molecular ozone and second by means of a radical mechanism which involves the formation of OH radical. In a heterogeneous system, it is predominantly assumed that both surface and the liquid bulk reaction can take place which involves molecular ozone, OH radical and surface oxygenated radical species. The proposed mechanism of catalytic ozonation on metal oxides as a catalyst is shown in Fig.10. Here it is assumed that ozone and organic molecule both adsorbed on the surface of the catalyst. As an outcome ozone adsorption and its transformation will help in the formation of hydroxyl radical. Free radicals initiate the radical chain reaction on the surface of the catalyst as well as in bulk liquid. Oxidation goes on stepwise through several oxidized intermediates meanwhile there is a continuous generation of radicals by the dissolved ozone that is passed to the catalyst surface. The affinity of oxidation products on the catalyst surface decreases and final products are desorbed from the catalyst surface [5], [14], [17].

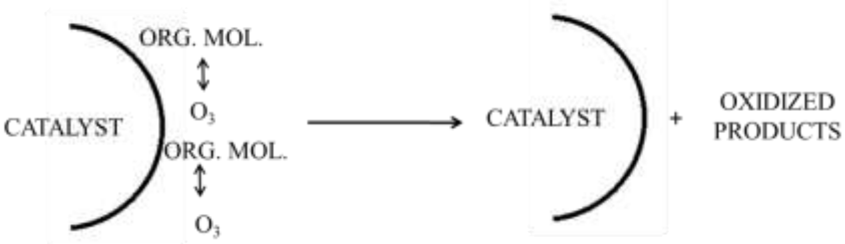

Fig. 10 Reaction mechanism for metal oxides as a catalyst in ozonation process[4]

On the part of cobalt oxide catalysts, many researchers have reported the effectiveness in mineralization of organic pollutants. Beltran et al. reported the use of $Co_3O_4/\gamma - Al_2O_3$ enhanced the results of ozonation of oxalic acid in an acidic environment. They mentioned that as a solid oxide, these catalysts are p-type oxides characterized by their capacity to adsorb oxygen and yield electron rich adsorbed species [18]. Faria et. Al suggested that the multivalence oxidation state of cobalt Co (II) and Co (III) was responsible for the catalytic activity of the catalyst.

4. Conclusion

The Co_3O_4catalyst prepared by direct calcination method has been seen to remarkably improve the ozonation rate of RB5. As the pH changes the COD removal efficiency increase. In basic pH, maximum COD removal efficiency was observed 66.66%. The experimental results suggest that the both ozone and RB5 are adsorbed on the surface of the catalyst and $HO^{\cdot}$ radicals generated by indirect oxidation. The kinetics of the color removal of RB5 was conforming to pseudo-first order rate equation.

References:

1. P. Colindres, H. Yee-Madeira, and E. Reguera, “Removal of Reactive Black 5 from aqueous solution by ozone for water reuse in textile dyeing processes,” *Desalination*, vol. 258, no. 1–3, pp. 154–158, 2010.
2. R. Zhang, D.-X. Yuan, and B.-M. Liu, “Kinetics and products of ozonation of C.I. Reactive Red 195 in a semi-batch reactor,” *Chinese Chem. Lett.*, vol. 26, no. 1, pp. 93–99, 2015.
3. C. Bradu, L. Frunza, N. Mihalche, S. M. Avramescu, M. Neaţă, and I. Udrea, “Removal of Reactive Black 5 azo dye from aqueous solutions by catalytic oxidation using CuO/Al2O3 and NiO/Al2O3,” *Appl. Catal. B Environ.*, vol. 96, no. 3–4, pp. 548–556, 2010.
4. J. Nawrocki, “Applied Catalysis B : Environmental Catalytic ozonation in water : Controversies and questions . Discussion paper,” *"Applied Catal. B, Environ.*, vol. 142–143, pp. 465–471, 2013.
5. B. Kasprzyk-hordern, M. Ziółek, and J. Nawrocki, “Catalytic ozonation and methods of enhancing molecular ozone reactions in water treatment,” vol. 46, pp. 639–669, 2003.
6. F. Qi, B. Xu, L. Zhao, Z. Chen, L. Zhang, D. Sun, and J. Ma, “Comparison of the efficiency and mechanism of catalytic ozonation of 2,4,6-trichloroanisole by iron and manganese modified bauxite,” *Appl. Catal. B Environ.*, vol. 121–122, pp. 171–181, 2012.
7. A. Gonçalves, J. Silvestre-Albero, E. V. Ramos-Fernández, J. C. Serrano-Ruiz, J. J. M. Órfão, A. Sepúlveda-Escribano, and M. F. R. Pereira, “Highly dispersed ceria on activated carbon for the catalyzed ozonation of organic pollutants,” *Appl. Catal. B Environ.*, vol. 113–114, pp. 308–317, 2012.
8. P. C. C. Faria, D. C. M. Monteiro, J. J. M. Órfão, and M. F. R. Pereira, “Cerium, manganese and cobalt oxides as catalysts for the ozonation of selected organic compounds,” *Chemosphere*, vol. 74, no. 6, pp. 818–824, 2009.
9. A. Dejoz, S. H. Taylor, B. Solsona, T. E. Davies, T. Garcia, and I. Va, “Applied Catalysis B : Environmental Total oxidation of propane using nanocrystalline cobalt oxide and supported cobalt oxide catalysts,” vol. 84, pp. 176–184, 2008.
10. J. Wu, H. Gao, S. Yao, L. Chen, Y. Gao, and H. Zhang, “Degradation of Crystal Violet by catalytic ozonation using Fe / activated carbon catalyst,” *Sep. Purif. Technol.*, vol. 147, pp. 179–185, 2015.
11. J. Chen, S. Tian, J. Lu, and Y. Xiong, “Applied Catalysis A : General Catalytic performance of MgO with different exposed crystal facets towards the ozonation of 4-chlorophenol,” *"Applied Catal. A, Gen.*, vol. 506, pp. 118–125, 2015.
12. X. Liu, Z. Zhou, G. Jing, and J. Fang, “Catalytic ozonation of Acid Red B in aqueous solution over a Fe-Cu-O catalyst,” *Sep. Purif. Technol.*, vol. 115, pp. 129–135, 2013.
13. R. C. Martins and R. M. Quinta-Ferreira, “Catalytic ozonation of phenolic acids over a Mn-Ce-O catalyst,” *Appl. Catal. B Environ.*, vol. 90, no. 1–2, pp. 268–277, 2009.
14. J. Nawrocki and B. Kasprzyk-hordern, “Applied Catalysis B : Environmental The efficiency and mechanisms of catalytic ozonation,” *"Applied Catal. B, Environ.*, vol. 99, no. 1–2, pp. 27–42, 2010.
15. G. Moussavi and M. Mahmoudi, “Degradation and biodegradability improvement of the reactive red 198 azo dye using catalytic ozonation with MgO nanocrystals,” *Chem. Eng. J.*, vol. 152, no. 1, pp. 1–7, 2009.
16. C. H. Wu, C. Y. Kuo, and C. L. Chang, “Decolorization of C.I. Reactive Red 2 by catalytic ozonation processes,” *J. Hazard. Mater.*, vol. 153, no. 3, pp. 1052–1058, 2008.
17. C. a. Orge, J. J. M. Órfão, and M. F. R. Pereira, “Catalytic ozonation of organic pollutants in the presence of cerium oxide-carbon composites,” *Appl. Catal. B Environ.*, vol. 102, no. 3–4, pp. 539–546, 2011.
18. F. J. Beltra and F. J. Rivas, “Ozone-Enhanced Oxidation of Oxalic Acid in Water with Cobalt Catalysts . 2 . Heterogeneous Catalytic Ozonation,” pp. 3218–3224, 2003.

*****