



## Catalytic ozonation of Reactive Black 5 in aqueous solution over a La-Co-O catalyst

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Manuscript received online 16 December 2019, revised and accepted 03 January 2020

An attempt has been made in this research for degradation of Reactive Black 5 (RB5) employing catalytic ozonation over the composite catalyst of lanthanum oxide and cobalt oxide (La-Co-O). The catalyst was prepared by co-precipitation method. Synthesized catalyst was characterized by XRD, SEM and BET techniques. The efficiency of catalytic ozonation was compared with ozonation and with adsorption alone. The COD removal efficiency using the La-Co-O catalyst was 68% which is higher than the single ozonation process. The different parameters like the effect of catalyst dose, initial dye concentration, and initial pH of the solution were studied. It was concluded that the degradation efficiency for RB5 was improved by almost three fold in the presence of the catalyst compared to only ozonation.

Keywords: Dye wastewater, catalytic ozonation, composite catalyst, lanthanum-cobalt oxide.

### Introduction

Gujarat is known as the "Textile state of India" since decades. Gujarat is a leader in textile industries with more than 1500 medium and large scale textile units and day by day the growth of textile industries in Gujarat increases. The different processing units of textile industries use a large amount of fresh water and generate the huge quantity of wastewater. The textile effluent mainly contains the dye as a pollutant which is recalcitrant in nature and also imparts the color in water bodies. Improper disposal of textile wastewater creates a serious environmental issue. Therefore several treatments are reported to treat the waste. Among them advanced oxidation processes (AOPs) gain the interest due to their effectiveness for removing recalcitrant pollutants<sup>1</sup>. AOPs are innovative, cost-effective, catalyzed chemical oxidation process to resolve the environmental issues<sup>2</sup>. Among the various AOPs used to treat wastewater ozonation is the most promising method. Ozone is considered as an extremely strong oxidant ( $E^\circ = 2.07$  V) and reacts quickly with organic pollutants. Ozone molecule is selective and so color removal is fast but the mineralization of pollutant is slow<sup>3</sup>. So an improvement in ozonation process is catalytic ozonation process, which allows a more rapid removal of organic pollutants and reduces the economic cost<sup>4</sup>. In catalytic ozonation process, the metal or metal oxides used as a catalyst along

with ozone in homogeneously or heterogeneously. As reported in the literature, homogeneous catalysis is not much in practice because of the recovery of metal ions is difficult and it has a great impact on the aquatic life<sup>2</sup>.

Heterogeneous catalytic ozonation gain the attention due to its effectiveness for mineralisation of recalcitrant compounds effectively. Various studies have been reported that the metal oxides can be effective for a wide range of organic pollutants in the catalytic ozonation. The combination of ozone with transition metal oxides, with supported metal oxides have shown the acceptable results in catalytic ozonation<sup>5</sup>. Maddila *et al.*<sup>6</sup> reported the use of cerium-vanadium oxide loaded on supports alumina and silica catalyst for degradation of chloronitrophenol. Maddila *et al.*<sup>7</sup> reported different loading of cerium-zirconium oxide on metal oxides supports for degradation of trichlorophenol. Tang *et al.*<sup>8</sup> also used silver based composite catalyst for toluene decomposition. Seshu Babu *et al.*<sup>9</sup> reported the use of strong basic Mg/La mixed oxide catalyst for efficient synthesis of polyfunctionalized pyrans. Imamura *et al.*<sup>10</sup> reported the used of cobalt-bismuth complex oxides for wet oxidation of acetic acid.

In this paper, the composite catalyst of lanthanum oxide and cobalt oxide (La-Co-O) was prepared via co-precipitation method. However, the composite catalyst of lanthanum

oxide and cobalt oxide has not been studied and reported exhaustively for catalytic ozonation of Reactive Black 5 (RB5). The color removal of RB5 in presence and absence of catalyst was studied. The effect of the different parameters like the effect of catalyst dosage, initial dye concentration, ozone flow rate, the effect of solution pH was assessed.

*Materials and methods:*

*Materials and preparation of catalyst:*

The RB5 dye was obtained from local industry of Ahmedabad. The lanthanum nitrate, cobalt nitrate, sodium hydroxide were purchased from Piyush Chemicals. The catalyst La-Co-O was synthesized by co-precipitation method<sup>10,11</sup>. The required quantity of lanthanum nitrate and cobalt nitrate was dissolved in water and mixed, and 2 N NaOH was added to an aqueous solution of metal nitrates until the pH of the solution was nearly 10. The resultant precipitates were washed with distilled water for several times and it was dried at 100°C overnight, followed by calcination at 500°C for three hours<sup>12</sup>. Further the catalyst synthesized by changing the ratio of La/Co by 1:2, 1:1 and 2:1. Among them the ratio of

ozone generator, the mixture of oxygen and ozone gas from ozone generator is bubbled into the glass column through the sparger. The catalyst was added from the top. To keep the catalyst in suspension form the magnetic stirrer was used. After certain time intervals, the samples were taken out, filtered through quantitative ashless filter paper and analyzed by UV spectrophotometer at a wavelength of 599 nm. All the experiments were carried out at normal room temperature and pressure only. XRD analysis of catalyst was carried out using XRD with an X-pert MPD system (Philips) Cu-K $\alpha$  radiation ( $\lambda = 1.5406 \text{ \AA}$ ). The catalyst BET surface area and pore volume were determined using nitrogen ( $-195.126^\circ\text{C}$ ) with Micromeritics 3Flex version 4.01. The morphological characteristics and semi-quantitative elemental analysis of catalyst were determined by SEM and energy dispersive of X-ray (EDX).

**Results and discussion**

*Catalyst characteristics:*

In Fig. 2(A) and (B) shows the SEM image of synthesized catalyst. It is used to study about the surface morphol-

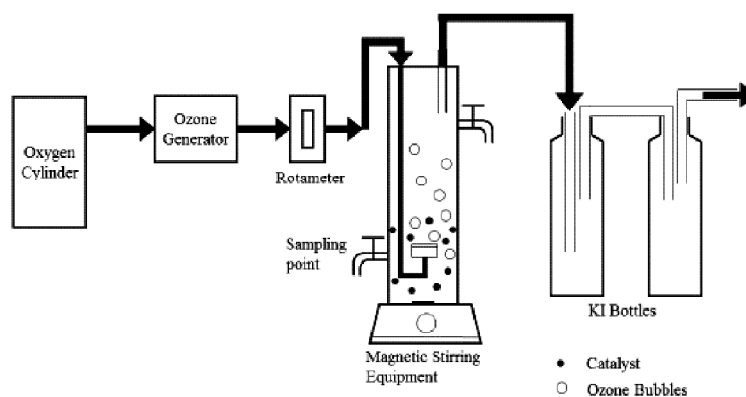


Fig. 1. Experimental setup.

La/Co, 2:1 give the best results so it is used for further experimental work in this paper.

**Experimental**

All the experiments of ozonation and catalytic ozonation were performed in a semi-batch mode apparatus as shown in Fig. 1. The experimental set up having the oxygen cylinder, an ozone generator, glass column reactor and KI bottles. Firstly, the pure oxygen from oxygen cylinder is passed into

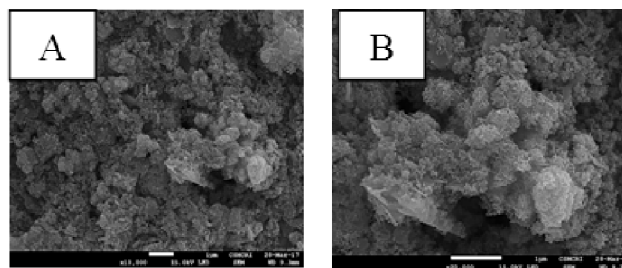


Fig. 2. SEM analysis of La-Co-O catalyst.

ogy of the prepared composite catalyst. The images shows the porous, three-dimensional flower like structure composed of nanosheets. The nanosheets of synthesized catalyst are smooth and regular<sup>13</sup>.

The EDX analysis of the synthesized catalyst is shown in Fig. 3. The results shows the weight percentage of La and Co were 55.25% and 14.51% respectively. The actual percentage of La and Co were 56.84% and 24.47% respectively. The synthesized catalyst having the BET surface area 76.8269 m<sup>2</sup>/g which is large surface area to boost catalytic activity. Pore volume and pore size of the catalyst are 0.543995 cm<sup>3</sup>/g and 249.543 Å respectively. Liu *et al.* had synthesized composite catalyst Fe-Cu-O, reported BET surface area of 4.6 m<sup>2</sup>/g<sup>5</sup>. Orge *et al.* had synthesized the composite catalyst of Ce<sub>0.75</sub>La<sub>0.25</sub>O<sub>2</sub> and Ce<sub>0.75</sub>Sm<sub>0.25</sub>O<sub>2</sub> having surface area 66 m<sup>2</sup>/g and 64 m<sup>2</sup>/g respectively<sup>14</sup>.

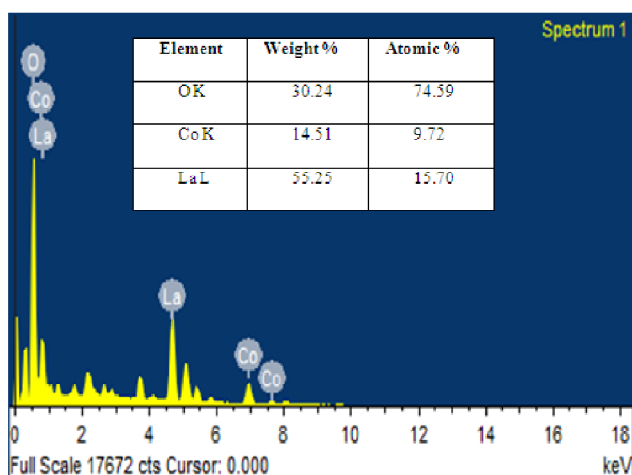


Fig. 3. EDX analysis of synthesized catalyst.

The XRD analysis of prepared composite catalyst is shown in Fig. 4. As shown in Fig. 4, the peaks of lanthanum oxide and cobalt oxide are not detectable. There are weak peaks of lanthanum oxide carbonate and cobalt oxide were present but as it is non-detectable which suggest the prepared catalyst having low crystallinity<sup>15</sup>.

*La-Co-O catalytic ozonation of RB5:*

The catalytic activity of the synthesized La-Co-O, La<sub>2</sub>O<sub>3</sub> and Co<sub>3</sub>O<sub>4</sub> were evaluated and results were shown in Fig. 5. First of all, 0.5 g of each catalyst were added to 1000 mL, 100 ppm RB5 solutions, respectively. Then the ozone flow of 30 LPH was fed to the glass column for 80 min.

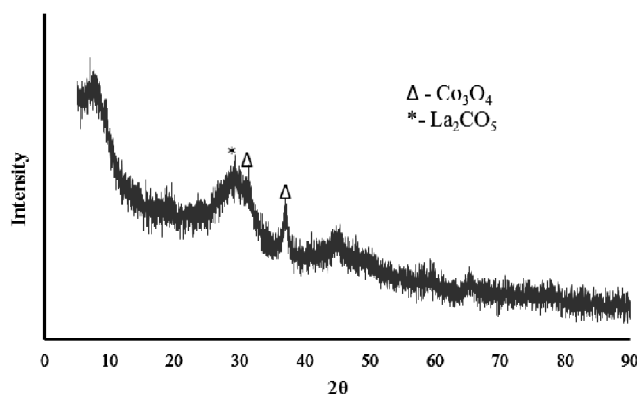


Fig. 4. XRD of La-Co-O composite catalyst.

From the Fig. 5, it can be found that the after 10 min of the experiment the La-Co-O removes color faster than that of ozonation, La<sub>2</sub>O<sub>3</sub> and Co<sub>3</sub>O<sub>4</sub> respectively. The COD removal efficiency was 25% (ozonation), 50% (La<sub>2</sub>O<sub>3</sub>), 57% (Co<sub>3</sub>O<sub>4</sub>) and 68% (La-Co-O) respectively.

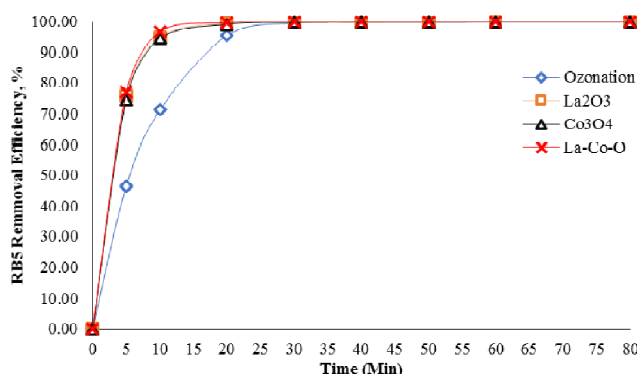
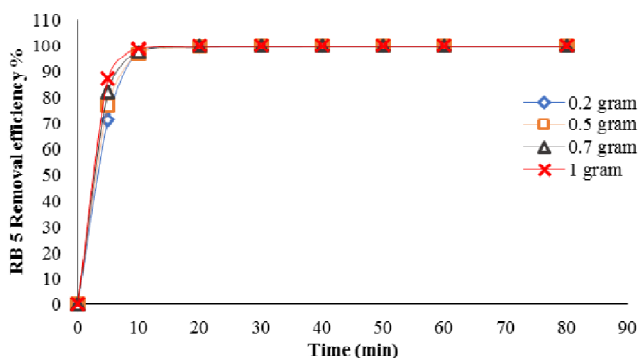


Fig. 5. Comparison of RB5 removal efficiency (concentration of RB5 = 100 ppm, catalyst weight = 0.5 g, ozone flow rate = 30 LPH).

*The influence of catalyst dosage:*

In heterogeneous catalysis, solid catalyst was played the vital role and affect the efficiency of the process. Here in this experiments, the amount of catalyst was varied from 0.2 g/L to 1 g/L. The results were shown in Fig. 6. As the dosage of catalyst increases from 0.2 g/L to 1 g/L the RB5 removal efficiency increases from 71% to 87% after 5 min of the experiment. The similar trend can be observed in COD removal efficiency as shown in Table 1. The COD removal efficiency after 80 min of the experiment was about 58% (0.2 g/L), 68%



**Fig. 6.** Catalytic ozonation of RB5 with different catalyst dosage (concentration of RB5 = 100 ppm, ozone flow rate = 30 LPH).

**Table 1.** Influence of catalyst dosage

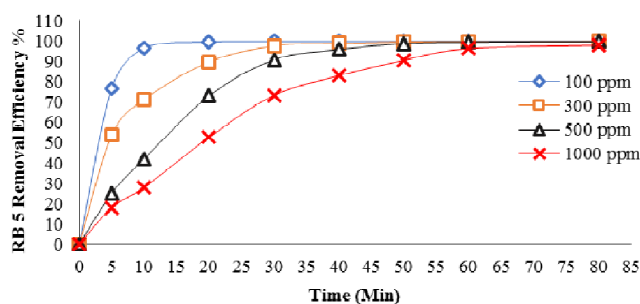
Dosage of catalyst (g/L)	Color removal efficiency (%)		COD removal efficiency (%) after 80 min of the experiment
	After 5 min of the experiment	After 80 min of the experiment	
0.2	71	100	58
0.5	77	100	68
0.7	82	100	70
1	87	100	76
1.2	86	100	75

(0.5 g/L), 70% (0.7 g/L), and 76% (1 g/L) respectively and further increase in dosage the performance was decreased.

The degradation increases as the amount increases until about 1 g; and then decreases when it is increased to 1.2 g. The better performance is due to the more surface area and more active sites for adsorption of ozone and organic pollutants<sup>16</sup>. But, the reduced performance later is due to agglomeration of particles which decreases the available surface area and active sites.

*Effect of initial dye concentration:*

Industrial effluent contains the higher concentration of dye so it is necessary to study the effect of initial dye concentration on the performance of color removal and COD removal efficiency. Here in this work, the RB5 concentration of 100 ppm, 300 ppm, 500 ppm and 1000 ppm were studied. As shown in Fig. 7 the color removal efficiency gradually decreases from 96.67%, 71.31%, 42.18% and 28.05% after 10 min, respectively. The same trend was observed in COD removal efficiency as well. The COD removal efficiency after 80 min of the experiment was 85% (100 ppm), 73% (300



**Fig. 7.** Effect of initial dye concentration (catalyst weight = 0.5 g, ozone flow rate = 30LPH).

ppm), 63% (500 ppm) and 48% (1000 ppm) respectively.

This study suggests that as the initial dye concentration increase from 100 ppm to 1000 ppm, more by-products will form in the solution and ozone is consumed for degradation of original dye as well as for these by-products. So that the reducing trend is observed in degradation of RB5 as we increase the initial dye concentration<sup>5</sup>.

*Effect of initial pH and reaction mechanism:*

To study the effect of pH in aqueous ozone chemistry is mandatory. Because it is reported in the literature that ozone decomposition is strongly pH dependent. pH of the solution also change the surface properties of the catalyst, which can have a direct effect on the adsorption capacity of metal oxides towards the organic pollutants<sup>17</sup>. pH also affect the reaction pathway of ozonation reaction. Generally at low pH ozone molecules directly react with organic pollutants while in another case, at alkaline pH, ozone decomposes and generating hydroxyl radicals, which are a highly oxidizing agent that react with any organic pollutant in a non-selectively way<sup>18</sup>. So to study the effect of pH for both catalytic and non-catalytic ozonation at different values was tested and shown in Fig. 8. The color removal efficiency is more in acidic medium compare to neutral and alkaline medium in non-catalytic ozonation. In catalytic ozonation, the color removal efficiency is faster in alkaline medium compare to the acidic and neutral condition. Even in the alkaline medium the COD removal efficiency is 85% (pH 12) which is higher than the acidic medium (57%) and neutral medium (45%). The COD removal efficiency is higher than the non-catalytic ozonation as well. These suggest that in the alkaline medium the formation of hydroxyl radical takes place and it reacts non-selectively with organic pollutants. The effect of adsorption was

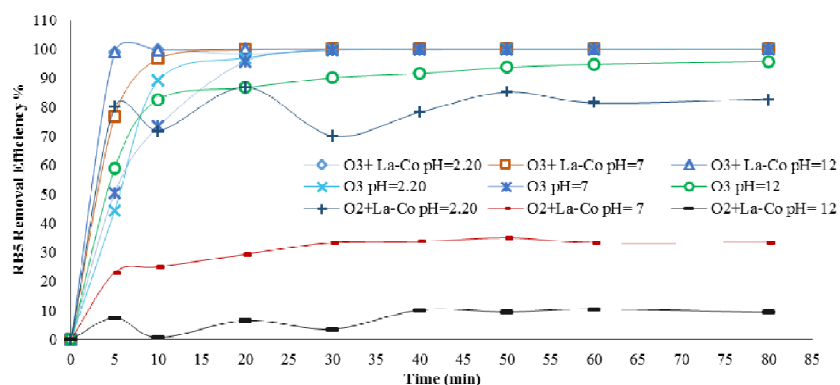


Fig. 8. Effect of solution pH on RB5 removal efficiency (dye concentration = 100 ppm, ozone flow rate = 30 LPH, catalyst weight = 0.5 g).

also studied at different pH conditions. The color removal efficiency is near 82% at acidic pH, 33.22% at neutral pH and 9% at alkaline pH. The COD removal efficiency in case of adsorption is 44% (pH 2.20), 32% (pH 7) and 25% (pH 12) respectively. These results proved that the pH of the solution affects the surface properties of catalyst and hence, the adsorption capacity of organic pollutants<sup>16,18,13</sup>.

There are the different mechanism for ozonation of organic compounds have been presented in the literature. As proposed by Beltran *et al.*, there is no formation of radicals at pH value ranges from 2 to 6 (near neutral) however at basic pH, ozonide and atomic oxygen adsorbed on the surface of the catalyst and hydroxyl radicals are formed<sup>19</sup>. Generally, the proposed mechanism of ozonation catalyzed by metal oxides assumes that both ozone and organic molecules adsorbed on the surface of the catalyst simultaneously. Ozone decomposition on the surface of the catalyst generates free radicals that can initiate the radical chain reaction both on the surface as well as in the bulk liquid phase and finally produce the hydroxyl radicals<sup>20,21</sup>. As described in literature dissolved ozone first adsorbed on the surface of the catalyst and decomposed into radicals due to the hydroxyl group present on the catalyst. The produced radicals would promote ozone molecule to decompose into hydroxyl radical. Then the targeted pollutant adsorbed on the surface of the catalyst would be oxidized by ozone molecule and hydroxyl radical<sup>5</sup>.

## Conclusions

The synthesized catalyst La-Co-O was remarkably increase the degradation of RB5 compared to ozonation alone

and adsorption only. The COD removal efficiency is 25% and 68% in ozonation alone and catalytic ozonation using La-Co-O respectively. The optimum value of catalyst dosage was 1 g/L, then after there was not remarkable change in degradation efficiency of RB5. The increase in pH improved the COD removal efficiency in catalytic ozonation while contrarily, an inhibitory effect was observed in ozonation and adsorption alone. So, the results indicate that the in catalytic ozonation the indirect oxidation reaction by hydroxyl radical and it increases degradation of RB5.

## Acknowledgements

The authors are greatly thankful to Nirma University for providing all the financial help to carry out the experimental work.

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