Catalytic Ozonation: Promising and Effective Method for Dye Wastewater

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***Abstract*-Treatment of wastewater which comes from the various industries is an become crucial problem because they contain different dye types and harmful compounds which reduced self-purification process in the environment and caused carcinogenic effect on human health. Now a day's Advance Oxidation Processes has gain attraction for treatment of dye wastewater. The effectiveness of an Advance Oxidation Process is proportional to its ability to generate hydroxyl radicals. Catalytic ozonation allows a quicker removal of organic pollutants, because catalysts improve the oxidizing power of ozone, markedly reducing the economic cost. Catalytic activity of Titanium dioxide, Zink oxide, Nickel supported on γ-Al_2O_3 catalysts towards the ozonation of RB-5 dye wastewater was investigated.**

Keywords: Advance Oxidation Processes, Ozonation, Catalytic ozonation, Azo dyes, Wet impregnation.

I. INTRODUCTION

Azo dyes are the most widely used dyes and are normally major pollutants in dye effluents. The textile and dyestuff industries are the main sources of dyes that are released to the environment. Conventional treatment cannot efficiently remove dyes from textile wastewater, because they are stable against light and biological degradation. Such treatments as adsorption, flotation and coagulation only alter the phases of pollutants but do not destroy them. Advanced oxidation processes (AOPs) are alternative methods for decolorizingand reducing recalcitrant wastewater loads that are generated by textile companies. Considerable progress has been made in the development of AOPs for textile effluent in recent years, especiallyin ozone-related processes. Ozonation has excellentpotential in decolourization for the following reasons. (i) Decolourization and degradation occur in one step; (ii) danger to humans is minimal; (iii) no sludge remains; (iv) all residual ozone can be decomposed easily into oxygen and water; (v) little space is required and (vi) ozonation is easily performed [1,11]

The term advanced oxidation process is defined asthe oxidation process, which generate hydroxyl radicalsin sufficient quantity to affect water treatment. These processes generally use a combination of oxidationagents (ozone, hydrogen peroxide), irradiation (UV, ultrasound) and catalysts as a means of generatinghydroxyl radicals.[2, 3]

In recent years, ozonation has emerged as a process for removing the colour of dyes, since the chromophore groups with conjugated double bonds, which are responsible for colour, can be broken down by ozone either by direct oxidation by ozone molecules or by indirect radical oxidation . Ozone has a great advantage over other oxidants because of its strong oxidizing property. The oxidation potential of hydroxyl radicalssignificantly exceeds that of ozone molecules; therefore, radical oxidation is faster and more efficient than direct oxidation. A disadvantage of using only ozonation for treating wastewateris the large amount of energy that is required for itsgeneration, such that any improvement that reduces the requiredreaction time would be welcomed from a practical perspective.Metal-catalysed homogeneous ozonation of organic substratesis currently attracting considerable interest, because of the intentto improve ozonation efficiency and optimize economic efficiency.Catalytic ozonation allows a quicker removal of organicpollutants, because catalysts improve the oxidizing power ofozone, markedly reducing the economic cost. [4].

Catalytic ozonation processes utilise several phenomena can be divided into the following sub-techniques, which ozone decomposition and hydroxyl radicals' formation:

(1) Homogeneous catalytic ozonation :
Homogeneous catalytic ozonation utilises ozone decompositionby transition metal ions. There are two major mechanisms of Homogeneous catalytic ozonation:

- Decomposition of ozone by metal ions leading to the generationof free radicals.
  Complexes formation between organic molecule and the catalyst and subsequent oxidation of the complex.

(2) Heterogeneous catalytic ozonation:
Among the most widely used catalysts in heterogeneous catalytic ozonation are: (1) Metal oxides (MnO_2, TiO_2, Al_2O_3, FeOOH and CeO_2). (2) Metals (Cu, Ru, Pt, Co) on supports (SiO_2, Al_2O_3, TiO_2 and activated carbon). (3) Activated carbon [3]

Catalyticozonationisexpectedto:

1. Generate hydroxyl radicals particularly at lower pHs,
2. Control the radical generation to increase the efficiency of ozonation,
3. Lead to higher efficiency of ozone consumption,
4. Avoid bromate formation. [5-10]

II. MATERIALS AND METHOD

2.1 Materials and reagents

Reactive black-5 was obtained from piyush chemicals and used without further purification. The wave length of RB-5 was 599 nm. TiO_2 and ZnO powder with purity of

99.9% was obtained from piyush chemicals where Nickel supported on Al_2O_3 was obtained by wet impregnation method [12]. Here Al_2O_3 was in pellet form and obtained from piyush chemicals. Ozone was produced by ozone generator from pure oxygen. Potassium Iodide was obtained from piyush chemicals.

2.2 Catalyst preparation

Nickel supported on Al_2O_3 was prepared by wet impregnation method. The precursor salt was dissolved in a volume of solvent equal to the catalyst pore volume and this solution was added slowly (drop wise) to the support. Then there was a two hour shaking for better mixing. After that there was overnight drying at 110^0C for moisture removal. Then calcination at 450 ^{0}C at 3 hour. [14, 15]

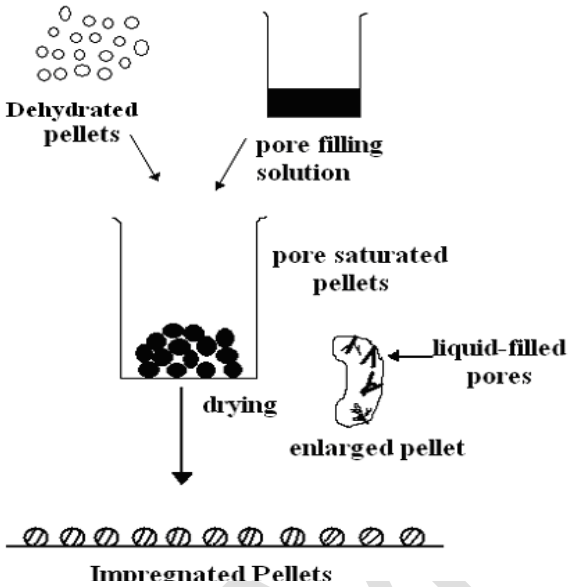

Fig. 1 Process of Impregnation

2.3 Experimental procedure

The catalytic ozonation experiments of RB-5 dye in thepresence of ozone were performed in a semi batch flow mode at 25^0C. Ozone was generated in a laboratory ozonegenerator using pure oxygen as gas source. The flow rate of ozone was 30 LPH. The simulative waste water was RB-5 dye solution (the initial concentration of RB-5 dye solution was 100 mg L^{-1}), and the initial pH was 6.8 without any adjustment. In a typical catalytic ozonation procedure, 0.05gm catalyst and 500 mL of simulative waste water were mixed in a reactor under stirring and thermostatic control. Thenozone was fed into the bottom of the reactor by sparger with continuous stirring.After certain intervals, samples (10.0 mL) were taken from thereactor, and the clear solutions after separation were used foranalytical determination. The control experiments of singleozonation (without catalyst) were also carried out under the same condition. Experiments were carried for 25 minute.

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Fig. 2 Experimental set-up

III. RESULT AND DISCUSSION

3.1 The UV-vis spectra of reactive black-5

The UV-vis absorption spectro photometer (Shimadzu UV-1800) was used to analyse the RB-5 degradation. Here concentration of the RB-5 dye wastewater was 100 ppm. The removal efficiency of catalytic ozonation and simple ozonation was compared by using three different catalysts. The removal efficiency of RB-5 with simple ozonation was nearly 40-45% in 25 minute for 100 ppm dye solution where by using 0.05 gm. Of catalysts TiO_2, ZnO, and Ni supported on γ-Al_2O_3, the efficiency observed was 84%, 91% and 67% respectively. Among these TiO_2catalyst was selected for further experiment because it gives best result and also has low price compare to other catalysts. Fig. 3 shows the initial and final result of the catalytic ozonation of RB-5 dye solution of 100 ppm. The calibration curve of standard RB-5 solution was used to estimate the degradation efficiency of dye. The degradation percentage was calculated based on the following equation:

Degradation % = $Co - C/Co \ * 100$

Where C_0 is the initial concentration of RB-5 and C is the concentration of RB-5 at time t.

Fig. 3 Initial and final product

3.2 Effect of TiO_2 catalyst dosage

Fig. 4 shows the decomposition rates of RB-5 dye due to the different amount of TiO_2catalyst. It illustrate that the degradation efficiency increases gradually with the increase of TiO_2in the catalytic ozonation. It was owing to the increase of catalytic surface and leading to the increase of •OH radical which can improve the degradation efficiency. It can be seen that the decomposition efficiency increased when the catalyst amount increase from 0.05 gm. To 0.2 gm. The degradation increases rapidly but at the high dose there was no change. [17, 18].

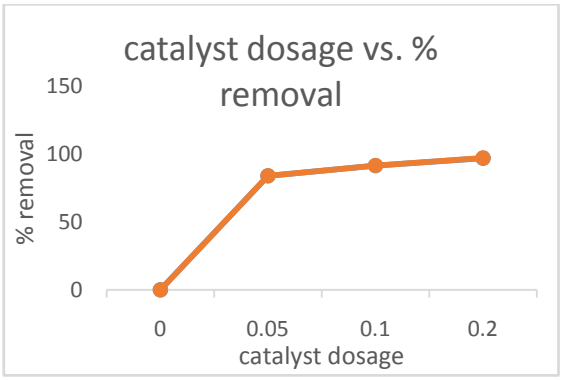

Fig. 4 Effect of amount of catalyst on the decomposition of RB-5 dye solution (pH=7, 100 ppm)

3.3 Effect of RB-5 dye concentration

Fig. 5 shows the decomposition of RB-5 dye solution of different concentration with same amount of catalyst (0.05 gm.) It illustrates that degradation efficiency gradually decrease with the increase of concentration of dye. It can be seen that the decomposition efficiency decreased when concentration of RB-5 dye increases from 0 ppm to 150 ppm

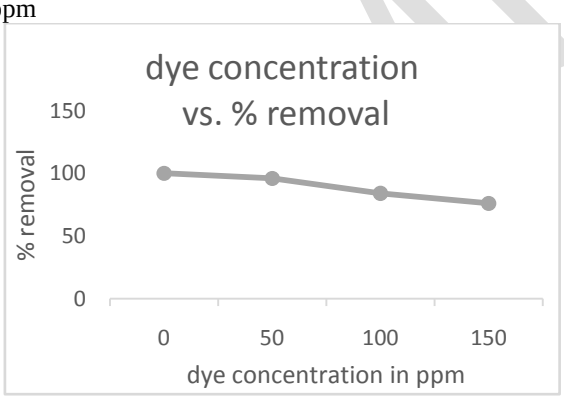

Fig. 5 Effect of dye concentration at same amount of catalyst dosage (0.05 gm., pH=7)

3.4 Effect of pH

Optimised pH value for degradation of RB-5 were in the 7 where around 90-98% degradation efficiency was found. The advantage of pH 7 is that the discharge of wastewater to the environment needs to be neutral and compare to other catalyst the degradation of dye using TiO_2 catalyst can be done in neutral pH value [13].

IV. CONCLUSION

Catalytic ozonation notably enhanced the efficiency of color removal of dye solution. The present study showed the degradation percentage of RB-5 could reach up to 98%. Here experiments were carried out with three different catalysts (TiO_2, ZnO,Nickel supported on γ-Al_2O_3) the result showed that TiO_2 catalyst gives better result compared to other two catalysts. The results with the RB-5 dye showed that decolourization were achieved at neutral pH. A large amounts of bubbles was formed at high inlet gas flow rate. It was conclude that at low dose (0.05, 0.1, 0.2 gm.) the degradation increases rapidly but at the high dose (>0.4) there was no change. It is thus concluded that the catalytic ozonation process is a promising andeconomically viable technology for the treatment of dye wastewater.

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