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Combined catalytic ozonation and UV treatment for removal of reactive red 120 dye from water

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ABSTRACT: Treatment of effluents from textile and tannery industries containing dyes has not been very successful using conventional methods like biological treatments. To overcome this problem various Advanced Oxidation Processes (AOPs) are being suggested in literature. In this paper an attempt has been made with the focus on the degradation of reactive red 120 dye in water by catalytic ozonation in the presence of titanium oxide catalyst and UV light. The removal of dye was monitored by the removal of TOC and color employing all the three processes, ozonation, ozonation/catalyst, ozonation/catalyst/UV have been investigated, and degradation efficiency order observed as ozonation/catalyst/UV > ozonation/catalyst > ozonation. The results proved that the catalyst may be activated by UV + ozone and increases the dye degradation efficiency.

1 INTRODUCTION

Dye and textile industries are major producers of wastewater. Dyes are an important class of pollutants, even if they are present in trace quantities. Dye and textile industries discharges large amount of synthetic wastewater containing dyes (Robinsion 2001). A loss of 1–2% in production and 1–10% in use are estimated. Due to their large-scale production and extensive application, synthetic dyes can cause considerable non-aesthetic pollution and pose a serious health risk factor (Martinez-Huitle 2009). Conventional methods are not effective for degradation of dye in textile effluents because they contain high concentration of toxic pollutants. Chemical oxidation with ozone is a current technology for the removal of organic pollutants and disinfection (Beltrain et al. 2002, Moussavi et al. 2009, Sui et al. 2012, Ikhlaq et al. 2012, Moussavi et al. 2012). Advanced oxidation processes can provide effective technological solution for such effluents.

Ozonation generates hydroxyl radical (•OH), a powerful oxidizing agent, which can completely degrade or mineralize the pollutants into harmless products. Ozone is a very powerful oxidizing agent and it has highly unstable molecules. Ozone degrades pollutants by two mechanism, either by direct reaction in which pollutants react with dissolved molecular ozone or indirect reaction in which pollutants react with hydroxyl radical (•OH) (Baig et al. 2001). Catalyst is also used in the ozonation process to improve the efficiency of the process and to reduce the ozone consumption. The combination of catalytic ozonation process along with UV light further enhances the efficiency of the process and considerably reduces the ozone consumption rate.

For the simple ozonation process, ozone reacts with water and it gives difficult chemical reaction and mechanism like the direct or indirect reaction with ozone.

Direct reaction of ozone with dye molecule occurs as follows (Hordem et al. 2003):

$$O_{3+}\ \text{dye} \rightarrow \text{dye}_{\text{oxid}}\ \text{(oxidation product of dye)} \tag{1}$$

Indirect reaction occurs with the reaction:

$$O_3 + H_2O \xrightarrow{OH\bullet} \bullet OH + O_2 \tag{2}$$

O_3/UV process is an advanced water treatment method for the effective oxidation and destruction of toxic and refractory organics in wastewater. Basically, aqueous systems saturated with ozone are irradiated with UV light of 254 nm in a reactor convenient for such heterogeneous media.

O_3/UV oxidation process is more complex than the other ones, since •OH radicals are produced through different reaction pathways. There is a general agreement about involved reactions (Galindo et al. 1999).

$$O_3 + H_2O + hv \rightarrow H_2O_2 + O_2 \tag{3}$$

$$H_2O_2 + hv \rightarrow 2HO\bullet \tag{4}$$

Photocatalytic processes make use of a semiconductor metal oxide as a catalyst and of oxygen as an oxidizing agent (Konsawa 2003). Many catalysts have been so far tested, although, only TiO_2 in the anatase form seems to have the most interesting attributes such as high stability, good performance, and low cost (Kiwi 1993).

$$TiO_2 + hv \rightarrow e^- + h^+ \tag{5}$$

$$TiO_2^{(h+)} + H_2O^{ad} \rightarrow TiO_2 + HOad\bullet + H^+ \tag{6}$$

$$TiO_2^{(h+)} + HO^{ad} \rightarrow TiO_2 + HOad \tag{7}$$

$$TiO_2^{(h+)} + RX^{ad} \rightarrow TiO_2 + RXad^+ \tag{8}$$

2 EXPERIMENTAL INVESTIGATIONS

2.1 *Material*

In the present study, dye sample of reactive red 120 was taken from the local vendor and used without any further purification. The molecular formula of reactive red 120 dye is $C_{44}C_{12}H_{24}N_{14}Na_6O_{20}S_6$. These dyes are called azo dye as the—N = N—group is present. Distilled water was used for the preparation of the synthetic wastewater for all the experiments.

Ozone was generated from the oxygen by using corona–discharge method. The applied ozone dose was controlled by using flow meter which had the capacity of 0–60 LPH. The semi batch pyrex glass bubble column reactor was used for conducting all the experiments. The unreacted ozone gas was trapped into the two impinger bottles which was filled with the 2% KI solution.

2.2 *Method (preparation of titanium dioxide catalyst)*

The Titanium Tetra Isopropoxide (TTIP) solution (97% synthesis) is directly purchased from the local vendor. TTIP solution is mixed with the 8 ml of the deionized or demineralized water. The solution is stirred up to 1 h for the proper mixing. 1 M of HNO_3 acid was added to maintain the pH of the solution upto 3 pH. The preparation of 1 M of HNO_3 is done by taking 3.2 ml solution of the concentrated HNO_3 and by adding 46.8 ml of deionized water. After mixing the solution mixture is then calcined at 400°C for 6 h in muffle furnace. The calcined mixture is then converted into the anatase phase TiO_2 catalyst, which is used for the degradation of the synthetic wastewater.

3 EXPERIMENTAL SET-UP

Ozonation studies were done using an experimental setup consisting of an ozonator, oxygen cylinder, bubble column reactor, two impinge bottles, and circular sintered glass gas

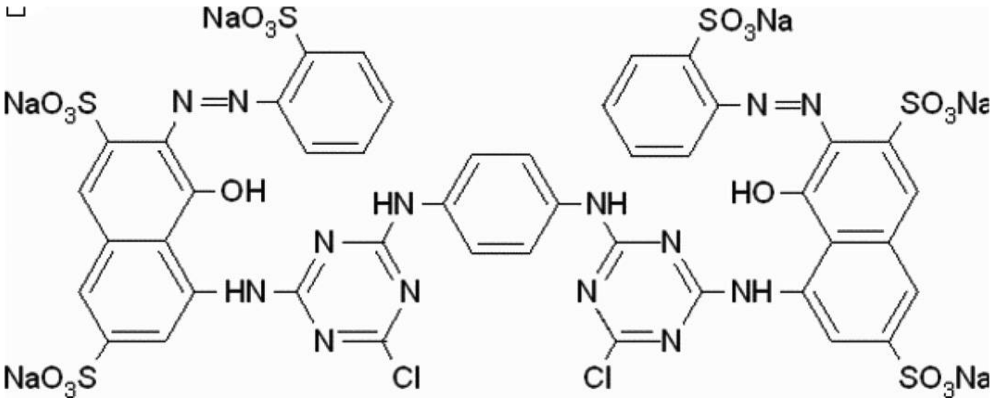

Figure 1. Structure of RR 120.

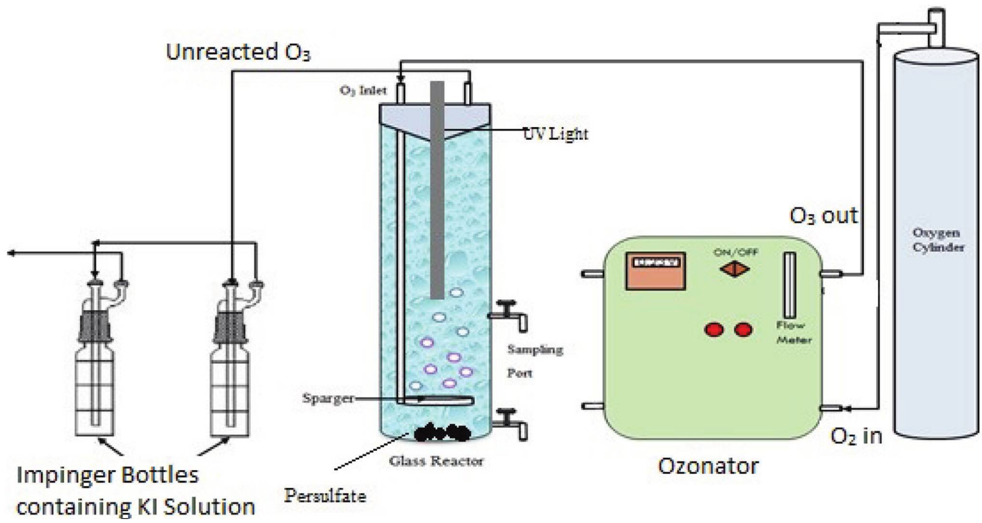

Figure 2. Schematic diagram.

distribution tube as depicted in Figure 1. Silicon tubing was used for the connection between ozone generators, reactor column, and impinge bottle.

The UV light was kept in the reactor, and the catalyst was stirred by using the magnetic stirrer, which was located at the bottom of the reactor.

4 RESULTS AND DISCUSSION

4.1 *Decolorization of reactive red 120*

The synthetic dye waste water was prepared at two different concentrations of 500 and 1000 ppm, and ozone gas flow-rate of 40 LPH. There are three different operating conditions namely, ozonation, ozone/UV, and Ozone/UV/TiO_2 catalyst. The color intensity of the dye is measured in the UV spectrophotometer. After the completion of the process, complete color removal from the wastewater was observed.

The complete decolorization of reactive red 120 dye at 1000 ppm and 500 ppm takes 120 min and 80 min for the simple ozonation process, and for the catalytic ozonation process it requires 110 and 75 min, respectively, for color removal. For the catalytic ozonation process 3 g/2 L of the catalyst is used for the reaction. Whereas in case of ozonation/catalyst/UV process it requires 80 min and 60 min for the complete color removal of reactive red 120 having a dye concentration of 1000 ppm and 500 ppm, respectively.

4.2 *Effect on TOC*

The experiments were also done to see the effect of the ozone concentration in the gas. Unfortunately the ozonation apparatus does not allow one to change the concentration easily without the flow-rate. Three initial ozone concentrations 30, 40, and 50 LPH were used to decolorize the dye and to remove the total organic carbon from the RR 120 dye, respectively.

4.3 *Effect on pH*

The experiments were carried out at the different pH values of 2, 4, 6, 8, and 10 for the single dye RR 120. The concentration of the dye is 500 ppm and the ozone dosage is 40 LPH. The obtained experimental data is shown in the Figure 3. The Figure 3 indicates that the pH value is the most important factor in the ozonation process since pH determines the dissociation of the organic compounds.

As mentioned above, ozone decomposes partly in •OH-radicals. When the pH value increases, the formation of •OH radicals increases. In a solution with a high pH value, there are more hydroxide ions present, see formulas below. These hydroxide ions act as an initiator for the decay of ozone (Song 2007):

$$O_3 + OH^- \rightarrow HO_2^- + O_2 \tag{9}$$
$$O_3 + HO_2\text{-} \rightarrow \bullet OH + O_2^{\bullet -} + O_2 \tag{10}$$

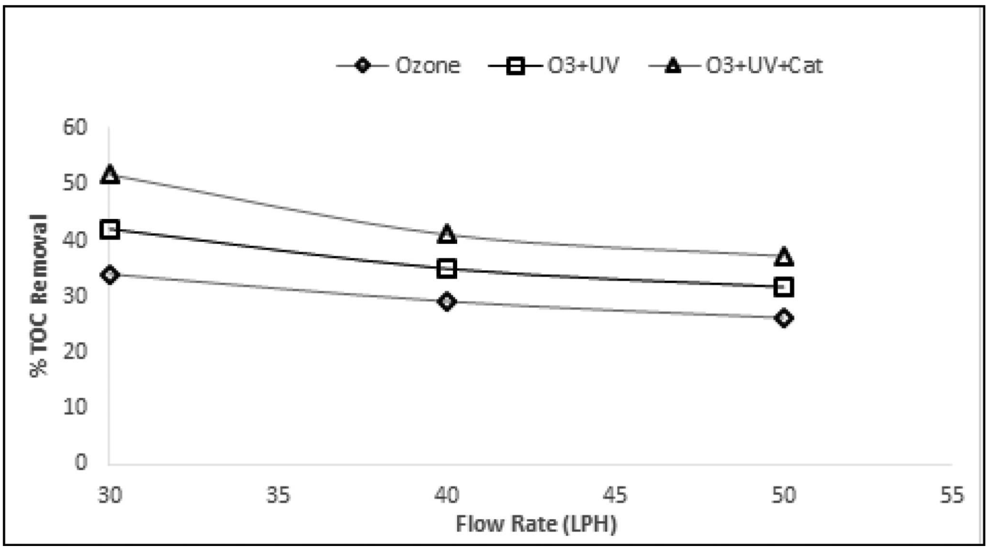

Figure 3. % TOC reduction on RR 120 at different operating condition [ozone dose: 30, 40, and 50 LPH, and UV light range: 8 watt, TiO_2 anatase catalyst dose: 2 g/L and dye concentration: 500 mg/L].

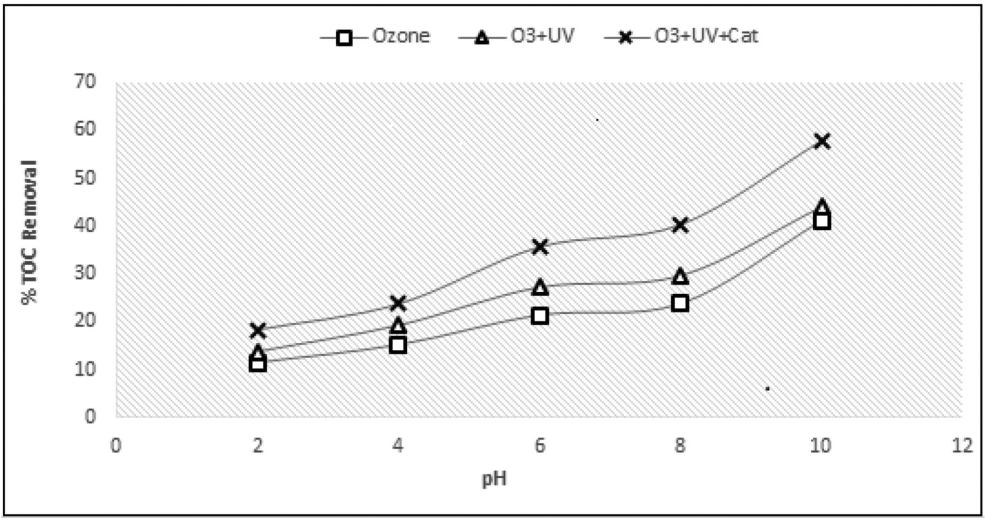

Figure 4. Effect of pH on decolorization and TOC [ozone dose: 40 LPH, pH dose: 2, 4, 6, 8, and 10, and dye concentration: 500 mg/L].

5 CONCLUSION

This experimental work reveals that TOC removal for O_3/UV/TiO_2 catalyst process was almost double as compared with the ozonation process and 10% higher than that of the ozone/UV process. It also provides a valuable comparison between O_3, O_3/UV, and O_3/UV/TiO_2. The UV light and TiO_2 anatase phase catalyst is more effective for wastewater treatment since it generates •OH radicals, which help to degrade the recalcitrant organic matter. It can also be concluded from the given result at higher pH, O_3/UV/TiO_2 gives almost 60% TOC reduction.

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