

## Feasibility study on degradation of RR120 dye from water by $O_3$ , $O_3/UV$ and $O_3/UV/Persulfate$

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**ABSTRACT:** An attempt has been made, in the present study, to do a comparative investigation of the efficiency of ozone based oxidation processes viz.,  $O_3$ ,  $O_3/UV$ ,  $O_3/UV/Persulfate$ , for the removal of Reactive Red 120 dye in synthetic wastewater. All the adopted ozone based oxidation processes for the study were tested for the most appropriate conditions concerning varied parameters like initial pH, ozone flow rate, persulfate concentration. Removal of the dye was observed to be dependent on the type of ozone based oxidation process and their process parameters as well. The maximum TOC removal was 75% and was achieved by  $O_3/UV/Persulfate$  process.

### 1 INTRODUCTION

The available water resources in the world are decreasing whereas the industrial wastewater volume is constantly increasing. Wastewater generated from textile industries possesses high potential to pollute environment, which could have execrable effects on the ecology (Shu 2006). Textile wastewater is considered to be very tricky to treat, since it contains significant amount of recalcitrant substances such as sizing agents, dyeing agents, surfactants, volatile organic compounds, wetting agents, and bleaching agents, etc., and thus troublesome to treat using conventional methods (Arslan & Balcioglu, 2000; Sundarajan et al. 2007). Advanced Oxidation Processes (AOPs) are emerging as a substitute to conventional methods and it holds high potential to be the best option in the near future. AOPs oxidize the dye and organic pollutants which are present in the wastewater. Various researches have been carried out to determine the effect of the ozone based oxidation technology for treating the effluents of textile and dyes & dye intermediate industries, and they have revealed that it leads to considerable color removal, degrades organic compounds, increases biodegradability, and provides effective disinfection without any residuals (Arslan & Balcioglu, 2000). In addition to ozone to be employed alone as oxidizing agent, persulfate ( $S_2O_8^{2-}$ ) is used as an alternative oxidant in the oxidation of contaminants (Tan et al. 2013). Persulfate has drawn attention as it has several advantages such as high oxidizing potential ( $E_0 = 2.01$  V), non-selectively reactive, ease of storage and transportation, pH independence, reasonably stable at room temperature and low cost. It was reported that, performance of persulfate can further be improved by homolysis of the peroxide bond using heat (Ghauch et al. 2012), transition metal ions ( $Me^{n+}$ ) such as  $Fe^{2+}$ , microwave (Qi, Liu, Lin, Zhang, Ma, Tan, & Ye, 2014) and UV light (Fang & Shang, 2012) to form sulfate radical ( $SO_4^{\cdot-}$ ), a stronger oxidant ( $E_0 = 2.60$  V) than persulfate, to significantly enhance the oxidation of contaminants. Research shows that sulfate radicals are more efficient than hydroxyl radicals for the degradation of compounds like 2, 4-dichlorophenol, atrazine, and naphthalene (Rao et al. 2014).

The foremost objective of this study was to determine the degradability of Reactive Red 120 using ozone based AOPs in a lab scale glass reactor to analyze various parameters like decolorization, COD and TOC removal with different operating conditions.

## 2 MATERIAL AND METHODS

### 2.1 Chemicals

In the present study, RR120 bearing solution was used as simulated wastewater in the ozone-assisted AO process. The RR120 was taken from local supplier and used to prepare synthetic wastewater without further purification process. Chemicals like Potassium Iodide (LR grade, Ranbaxy Laboratory Limited), Sodium Thiosulphate ( $\text{Na}_2\text{S}_2\text{O}_3$ ) (LR grade, High Purity Laboratory Chemical), Sodium persulfate ( $\text{Na}_2\text{S}_2\text{O}_8$ ), NaOH and  $\text{H}_2\text{SO}_4$  (LR grade, S.D. Fine Chem. Limited) were purchased and used without further purification. Phillips (TUV G5 T5 8 W  $\lambda = 254$  nm) UV Light was used as UV light source.

### 2.2 Instruments and analytical procedures

The experiments were carried out in a semi batch mode. 3.0 Lit. of  $500 \text{ mgL}^{-1}$  dye solution was taken into the reactor. The reactor configuration is as shown in Figure 1. Ozone flow rate was set in the range of 30 to 60 LPH. Initial pH was adjusted using 1 N NaOH and 1 N  $\text{H}_2\text{SO}_4$  solution. COD to persulfate(PS) ratio was set in the range of 1:5 to 1:12. The excess ozone was trapped in 2% KI solution, and was measured by idometric method (Clesceri et al. 1998).

In this study, the effectiveness of the ozone based AOPs were determined by analyzing various performance indicators like Total Organic Carbon (TOC) ( $\text{mg L}^{-1}$ ), Chemical Oxygen Demand (COD) ( $\text{mg L}^{-1}$ ), and color at different process operating conditions. TOC was measured by TOC Analyzer (TOC-VCPH/CPN, Shimadzu Corporation, Japan). COD of the samples were determined by using HACH DRB 200 reactor. The UV scans of the samples were done using UV-visible spectrophotometer (UV-1800 Shimadzu, Japan) at 200 nm to 800 nm. The Ozone gas concentration was measured using ozone analyzer (ELTECH 200, Eltech Engineers, Mumbai). However, appropriate standard methods for the examination of water and wastewater (APHA) were used to analyze raw and treated wastewater samples.

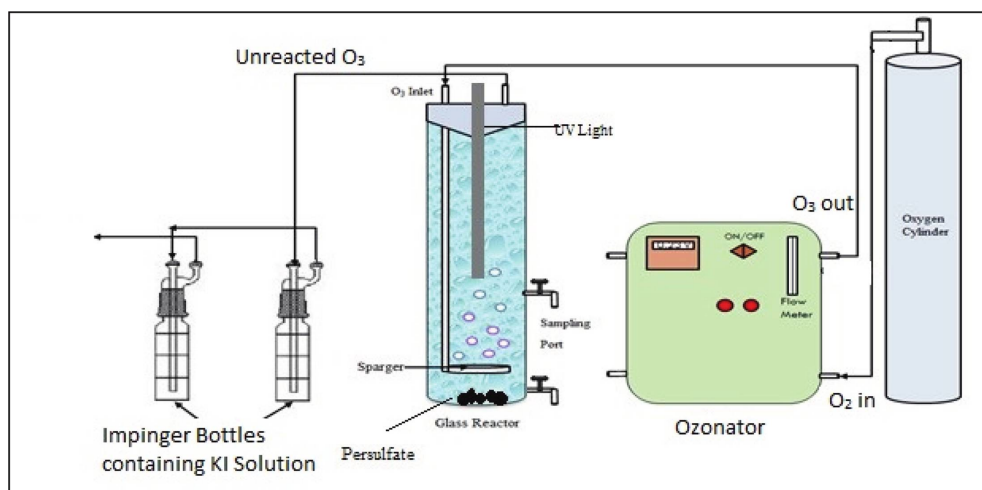


Figure 1. Reactor system.

### 3 RESULTS AND DISCUSSION

#### 3.1 Effect of ozone flowrate

The experiments were conducted to observe the effect of the ozone concentration on dye degradation under fixed initial dye concentration, pH and temperature. The ozone flowrate was maintained at 30, 40, 50 & 60 LPH to study its effect on decolorization, total organic carbon and chemical oxygen demand removal from the RR 120 dye respectively.

Figure 2 depicts that the percentage removal of TOC was increased with increasing the ozone flow rates with match with the previous research (Matheswaran et al. 2009). The percentage of TOC removal efficiency was achieved from up to 70% at 1.25 h by the ozone flow rate of 60 LPH.

It was also observed that O<sub>3</sub>/UV/Persulfate gives better results for removal of TOC as compared to other two processes.

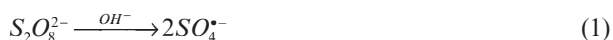
#### 3.2 Effect of initial pH

As it was reported that O<sub>3</sub> is a strong chemical oxidant and it can directly react with the unsaturated compounds. Further, in alkaline pH, Ozone (O<sub>3</sub>) can be decomposed by producing •OH (Wei et al. 2011). Therefore, O<sub>3</sub> and •OH both could react and decompose RR120 into simpler end products. However, the direct reaction of O<sub>3</sub> is selective and is slow (Singh 2008).

TOC removal efficiency of RR120 solution varied from 32% to 76% depending upon type of treatment given as shown in Figure 3. At higher pH, destruction showed better dye degradation and TOC removal efficiency.

In O<sub>3</sub>/UV/Persulfate system, result reveals that RR120 was decomposed more rapidly at a high pH due to two reasons.

It was reported that persulfate activated under under alkaline condition as well as in UV. Thus, chemical reaction representing the phenomena may be given by (Tan et al. 2013, Lin et al. 2013).



In addition, it may also be proposed that, part of SO<sub>4</sub><sup>•-</sup> was transformed to OH• in alkaline condition and reaction showing the phenomena may be given by:

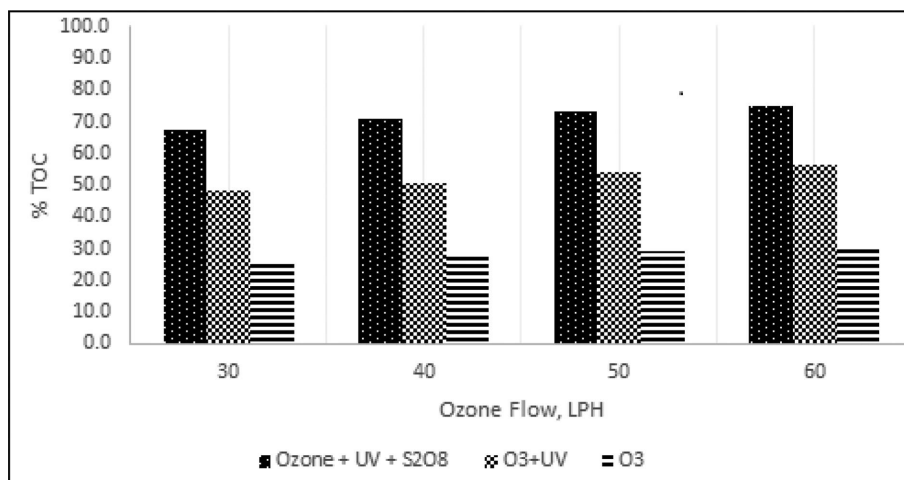


Figure 2. Effect of ozone flowrate on TOC removal of TOC. (500 ppm; pH:10).

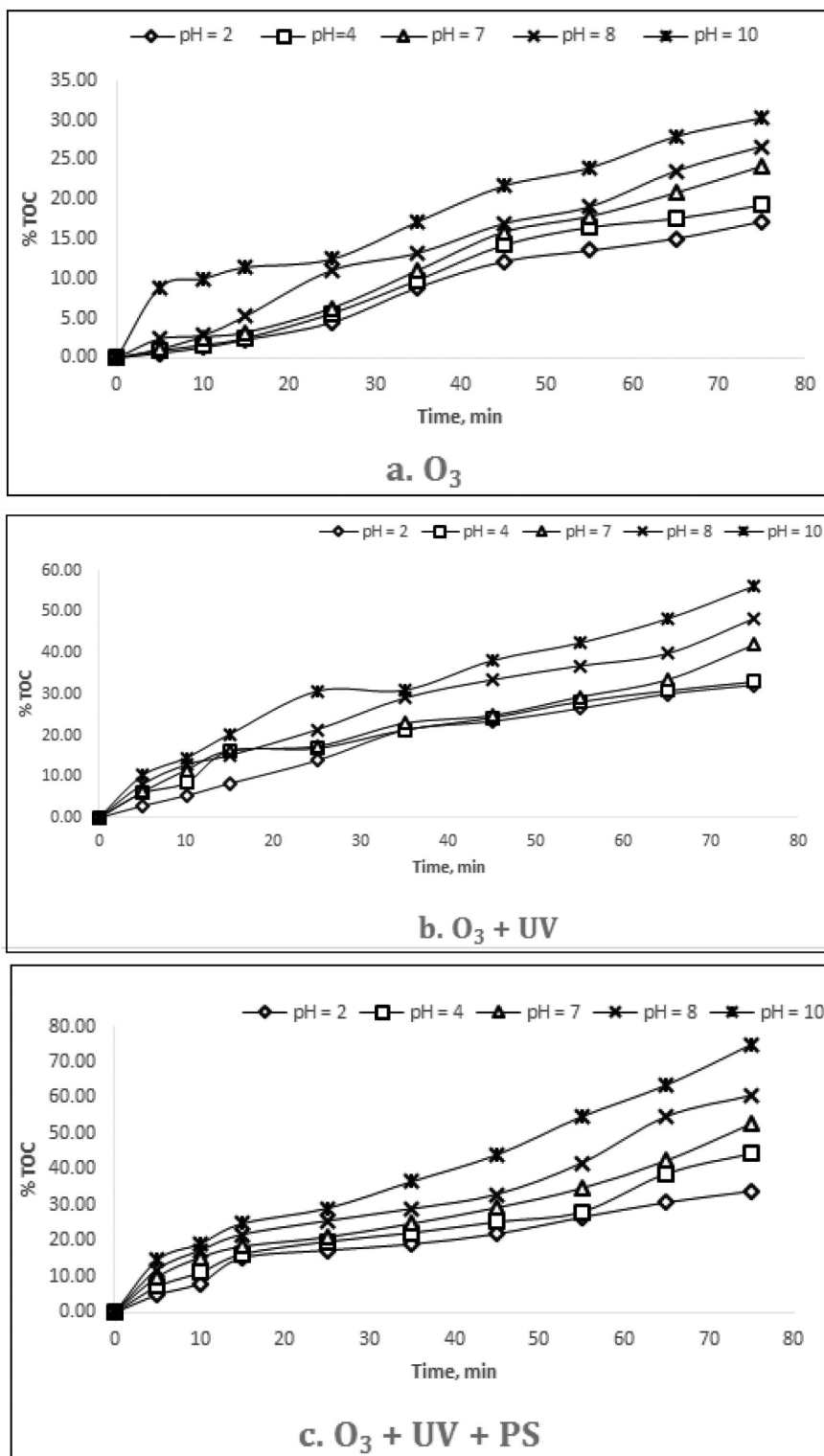


Figure 3. TOC removal efficiency as a function of initial pH and ozone based AOP's.

### 3.3 Effect of persulfate concentration

It is very essential to decide optimum persulfate dosage. Thus, Persulfate dosage was decided by COD to persulfate ratio and it was set in the range of 1:5 to 1:12. Different concentrations of persulfate were investigated in this study and the results are displayed in Figure 4. The initial dye concentration was fixed at 500 mg L<sup>-1</sup> and initial pH value was 10.

It can be observed from Figure 4 that TOC reduction of RR120 increased from 67% to 75% by changing COD to persulfate ratio in the said range. It was observed that after 1:10 ratio TOC removal was marginally around 0.3%.

### 3.4 Effect on ozone consumption

Further quantity of ozone consumed by all the three processes for removal a gram of TOC was calculated. As shown in Figure 5, it was found that, in O<sub>3</sub>/UV/Persulfate process quantity of ozone consumed for per gram removal of TOC was 15.8 mg which is less by 51.46% and 44.56% as compared to O<sub>3</sub> and O<sub>3</sub>/UV process respectively.

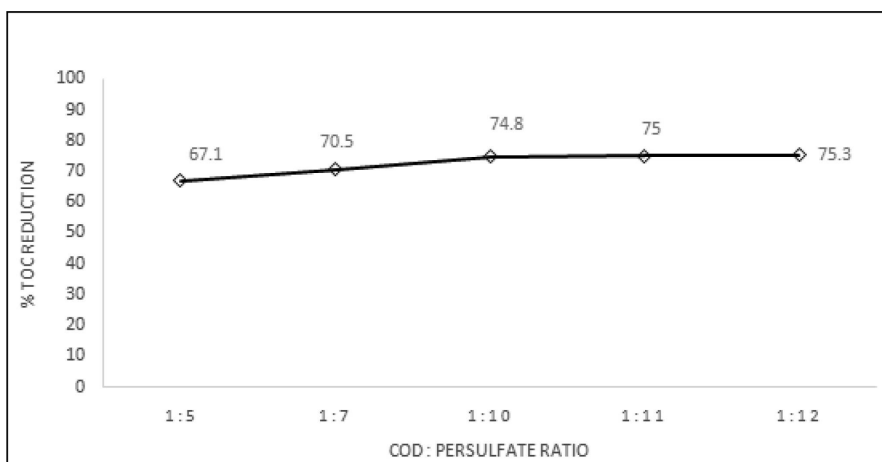


Figure 4. Effect of persulfate dosage on TOC reduction.

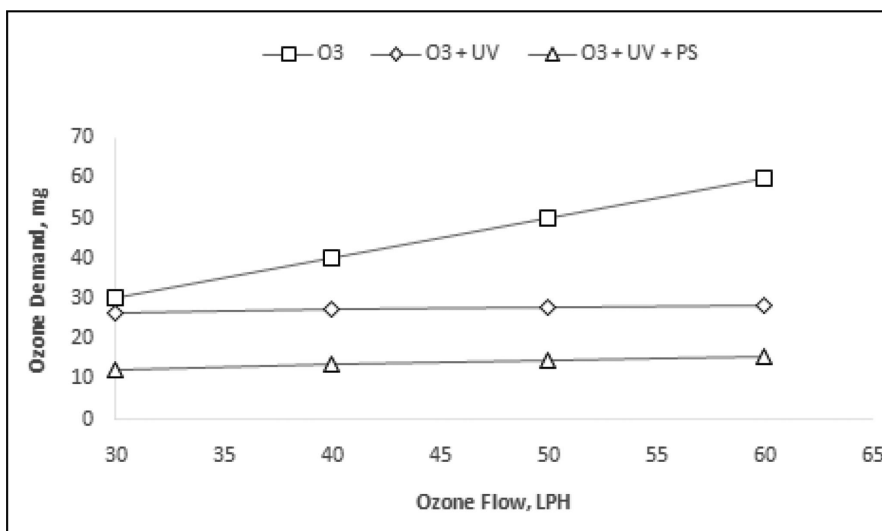


Figure 5. Effect of ozone based AOP's on ozone demand.

## 4 CONCLUSION

This study explores a reliable and promising way to use  $O_3$ /UV/Persulfate for efficient removal of recalcitrant compounds such as dyes and intermediates. Higher efficiency of TOC removal also suggests that the treatment technique provide mineralization of dyes. It also provides valuable information regarding comparison of  $O_3$ ,  $O_3$ /UV, and  $O_3$ /UV/Persulfate treatments for organic compound. In addition, the removal of RR120 dye in wastewater, the removal rate observed for  $O_3$ /UV/Persulfate,  $O_3$ /UV and  $O_3$  was 75%, 52% & 30% respectively at 60 LPH of flow of ozone and 10 pH. It was also observed that COD to persulfate ratio was optimum around 1:10, further increase in persulfate concentration has shown negligible effect on the removal of TOC. Thus, the study proved the importance of various key factors in RR120 dye removal rate. Therefore, to maximize the treatment efficiency, key factors should be further carefully optimized, such as pH, ozone flowrate and persulfate concentration for the targeted compounds. The result demonstrates that  $O_3$ /UV/Persulfate has potential to replace conventional treatment methods when recalcitrant organic compounds in wastewater creates the issues of treatability.

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