Comparative study of ozone-based AOPs for degradation of Reactive Red 120

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Abstract

The present work focuses on the comparative study of ozone-based advanced oxidation processes (AOPs): O_3, O_3/UV and O_3/UV/PS to degrade synthetic wastewater containing Reactive Red 120 (RR120) dye. The effect of various parameters: pH, ozone flow rate, initial concentration of dye, persulfate dosage and UV light intensity was analyzed to assess the performance efficiency of AOPs. All three AOPs' performance was evaluated on decolorization, %TOC removal and ozone consumption.

The highest degradation rate of 86.83% was achieved for O_3/UV/PS, followed by 71.53% and 66.82% for O_3/UV and O_3 respectively. This better efficiency of O_3/UV/PS is attributed to the fact that persulfate ions ($S_2O_8^{2-}$) upon activation produce sulfate radical (SO_4^{-}•), which is a powerful oxidant capable of degrading a wide variety of recalcitrant organic compounds. The study reveals that the efficiency of degradation of RR120 follows the order: O_3/UV/PS > O_3/UV > O_3.

Keywords: Advanced Oxidation Processes (AOPs), Recalcitrant organic compounds, Degradation.

Introduction

Rapid industrialization and the increased population are significant issues related to environmental degradation worldwide. Among various industry sectors, textile industries are significant water polluters. Textile effluents are considered problematic to treat not only due to volume but also due to varying composition[6,10]. The Government has made strict legislation regarding the treatment of industrial effluent and therefore, it is mandatory to treat textile effluents before final disposal. So, to overcome this issue, several techniques are being employed.

The textile industry in India including both domestic and export markets, is expected to grow at 9% CAGR with an estimation to achieve around USD 210 billion by 2021[16]. However, textile effluents are tricky to treat due to their varying composition[6]. In addition, textile effluents are highly colored, toxic recalcitrant organic compounds. They also show high resistance towards treatment by conventional treatment methods[10]. The literature has reported that ozonation is emerging as one of the potential techniques for treating wastewater containing dye[10]. Ozone's better efficiency is attributed to the fact that the oxidation potential of ozone is high (2.07V)[11] and it can react with a wide range of organic compounds through direct or indirect reactions[2,18].

In context to this, ozonation is applied to remove organic pollutants. Therefore, the foremost aim of the present study is to mineralize and treat synthetic wastewater containing Reactive Red 120 (RR120) as a model pollutant. However, it is worth mentioning that ozonation alone cannot degrade dye wastewater[2,5,8]. During ozonation of dye molecule, some by-products are generated such as organic compounds, aldehydes and ketones which cannot be further oxidized with ozone molecule due to high selectivity of ozone molecules[3,8].

Present work is focused on the treatment of synthetic wastewater with ozonation and integrated ozonation process combined with UV and persulfate. Additionally, the effect of various operating parameters such as pH, UV intensity, persulfate dosage, initial dye concentration and ozone flow rate has been analyzed and degradation efficiencies of all three processes based on those parameters have also been compared.

Material and Methods

The commercially available dye Reactive Red 120 was obtained from a local vendor situated at Vatva, Ahmedabad and used without further purification. The physico-chemical properties of Reactive Red 120 are shown in table 1. Potassium iodide was purchased from Ranbaxy Laboratories Limited. Sodium hydroxide (NaOH) and Sulphuric acid (H_2SO_4) were obtained from S.D. Fine Chemicals Limited and diluted to the desired concentration with distilled water. Sodium thiosulphate ($Na_2S_2O_3$) and sodium persulfate ($Na_2S_2O_8$) were purchased from High Purity Laboratory Chemicals. All chemicals used for research work were of analytical grade.

All AOP experiments were carried out in a glass reactor with 70 mm diameter and 60 cm length with a 2-liter reaction volume. The aqueous sample of wastewater containing RR120 dye was taken as model wastewater. Initial pH was adjusted using 1N NaOH and 0.1N H_2SO_4. An 11 W low-pressure Hg lamp (Phillips TUV 11W) was used as the UV Light source. For all AOP experiments, ozone was produced by an ozone generator (Aquazone Solutions, Gujarat, India.) by feeding oxygen. Ozone in the gas phase was measured using an ozone analyzer (model Eltech 200, Eltech engineers, Mumbai, India).

Impinger bottles containing 2% KI were arranged in series to absorb excess ozone from the reactor outlet. All experiments at different initial conditions were carried out at least in triplicate, sometimes in more numbers depending on reproducibility.

Results and Discussion

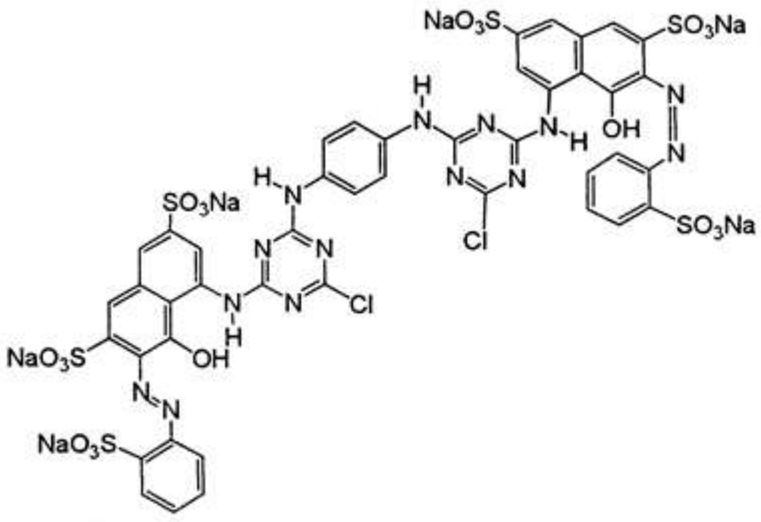
Effect of pH: pH is one of the most critical parameters, the slight change in the initial pH of the aqueous solution will lead to considerable variation in the efficiency of AOPs. Decomposition of ozone in the ozonation process highly depends on the generation of hydroxyl radical which in turn depends on the pH of a solution. At higher pH values, generation of hydroxyl radical will lead to ozone decomposition[4,11,14,18].

Additionally, it is noteworthy to mention that the combination of ozonation with UV and persulfate will promote generation of hydroxyl radical as well as it will generate sulfate radical, which is a more powerful oxidizing agent[12].

As presented in figure 1, the degradation efficiency of the ozonation process increases by increasing pH from 4 to 12 for all three processes. For example, in the O_3/UV/Persulfate process, % TOC removal was increased from 40% at pH 4 to 69% at pH 12. Similar observations were obtained for O_3/UV and O_3 processes with an increasing trend of TOC removal with increasing pH. However, by integrating the ozonation process with UV and persulfate, TOC removal was enhanced with 68.81% removal by O_3/UV/Persulfate process followed by O_3/UV (60.01%) O_3(40.32%) process respectively.

Effect of Ozone Flowrate: Figure 2 depicts the effect on %TOC removal.

Table 1
The characteristics of RR 120 dye studied in this work[1]

Chemical structure	
Dye class	Reactive Dye
Molecular Formula	$C_{44}H_{24}Cl_2N_{14}Na_6O_{20}S_6$
Molecular weight (g mol⁻¹)	1469.98
CAS number	61951-82-4

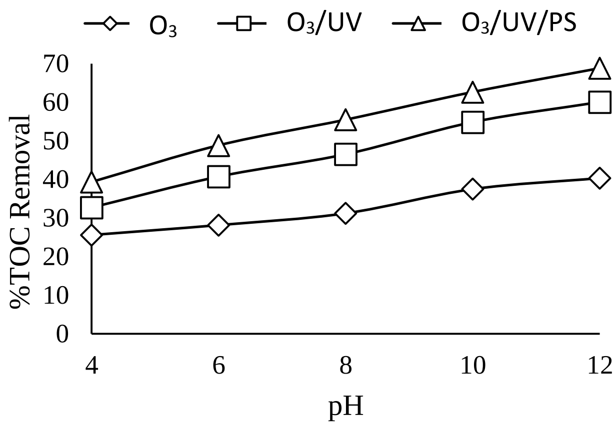


Figure 1: Effect of pH on TOC Removal
(Initial Concentration of Dye: 500 mgl⁻¹; O_3 Flow: 30 LPH; UV Intensity: 11 W; TOC:PS Ratio: 1:10)

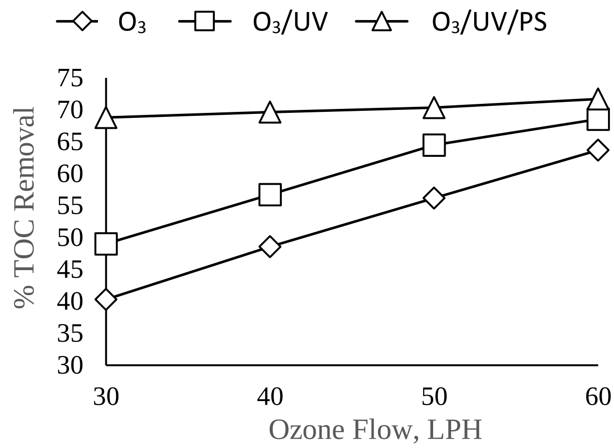


Figure 2: Effect of Ozone Flowrate on TOC Removal
(Initial Concentration of Dye: 500mgl^{-1}; pH:12; UV Intensity: 11 W; TOC:PS Ratio: 1:10)

Several researchers also studied the effects of flowrate on the ozonation and combined ozonation process revealing that as ozone flowrate was increased, the efficiency of the process increases[11,13]. However, it will have a positive effect on color and TOC removal[15].

The results obtained during the present study for TOC removal for ozone flow rate during ozonation and integrated ozonation process are shown in figure 2. TOC removal was observed to show an increasing trend with an increase in ozone flow rate. Additionally, it is worthy to note that an integrated ozonation process gives higher degradation than an ozonation process.

Effect of Persulfate dosage: The literature revealed the effect of persulfate dosage on the integrated ozonation process. It is noteworthy to mention that increasing persulfate dosage will increase sulfate radical, ultimately resulting in an increased amount of sulfate radical and resulting in the degradation of recalcitrant compounds present in synthetic wastewater. However, it should also be mentioned that the optimum value of persulfate has to be obtained because above the optimum value of persulfate dosage, efficiency of the process is decreased as sulfate radical will behave as scavenger[17].

$$SO_4^{-\bullet} + S_2O_8^{2-} \rightarrow SO_4^{2-} + S_2O_8^{-\bullet}$$
$$SO_4^{-\bullet} + SO_4^{-\bullet} \rightarrow S_2O_8^{2-}$$

Six different initial dosages of persulfate were taken for conducting experiments to study the effect of initial persulfate dosage on the degradation of synthetic wastewater. It was observed that % TOC removal was increased with increasing initial persulfate dosage; however, increasing persulfate beyond its optimum dosage will reduce the process's degradation efficiency.

This result may be attributed to the fact that sulfate radical behaves as a scavenger beyond a specific dosage. For example, in figure 3, it is apparent that 1:40 is the optimum dosage of persulfate which gives 88.63% TOC removal.

Effect of UV intensity: The literature revealed that UV intensity would positively influence the degradation and degradation of synthetic wastewater. It is attributed to the fact that UV light will enhance the activation energy of hydroxyl radical and hence more amount of hydroxyl radical is generated[9]. Figure 4 depicts that increasing UV irradiation will enhance the efficiency of the process.

However, it should also be mentioned that the degradation efficiency of the O_3/UV/PS process was higher than that of the O_3/UV process for the same UV irradiation. For example, the UV intensity of the 66W O_3/UV/PS process gives 77.47% TOC removal whereas the O_3/UV process gives 71.53% TOC removal.

Effect of Initial Dye Concentration: It is pretty evident from the literature that the efficiency of the process for degradation of recalcitrant organic compounds present in wastewater depends on initial dye concentration. As dye concentration increases, the effectiveness of the process decreases due to a decline in the ratio of O_3 molecule to dye molecule[3]. Figure 5 shows the effect of the initial dye concentration on the degradation of synthetic wastewater by all three processes.

It was observed that increasing initial concentration will lead to decreased efficiency for all three processes. It is attributed to the fact that as the initial concentration of dye increases, the ratio of dye molecule to oxidizing agent decreases, leading to decreased degradation efficiency. From figure 5, it can be seen that as the initial concentration was increased from 500 mg/L to 1500 mg/L %, TOC removal was almost halved for all three processes.

Effect of Ozone Consumption: From past studies by various researchers, it is evident that ozone consumption varies from process to process. Furthermore, ozone demand for per gram removal of TOC versus flow rate is also reported in various research works and it shows that demand for ozone decreases in integrated ozonation process than that of simple ozone process.

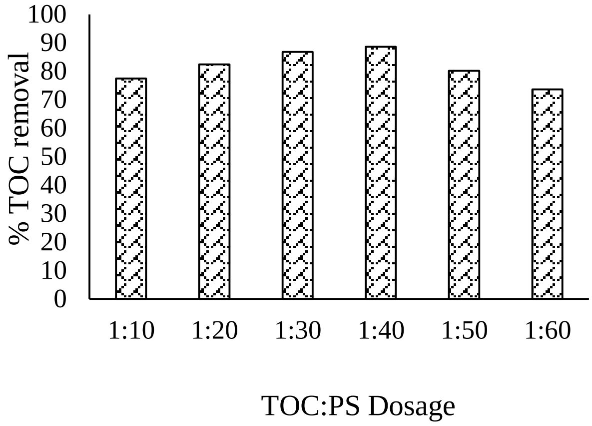


Figure 3: Effect of PS Dosage on TOC Removal
(Initial Concentration of Dye: 500mgl^{-1}; O_3 Flow: 60 LPH; pH:12; UV Intensity: 66 W)

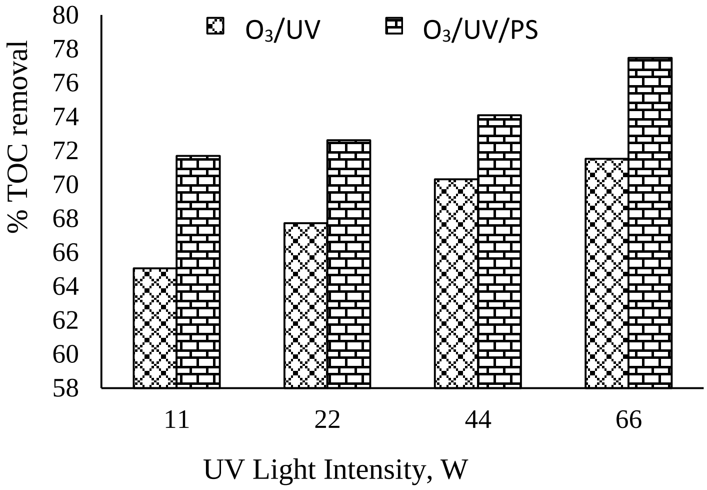


Figure 4: Effect of UV Intensity on TOC Removal
(Initial Concentration of Dye: 500mgl^{-1}; O_3 Flow: 60 LPH; pH:12; TOC:PS Ratio: 1:10)

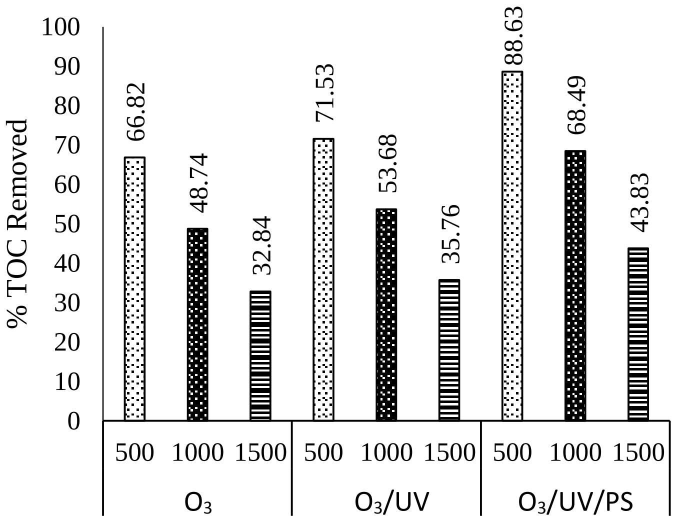


Figure 5: Effect of initial Dye Concentration on TOC Removal
(O_3 Flow: 60 LPH; pH:12; UV Intensity: 66w; TOC:PS Ratio: 1:40)

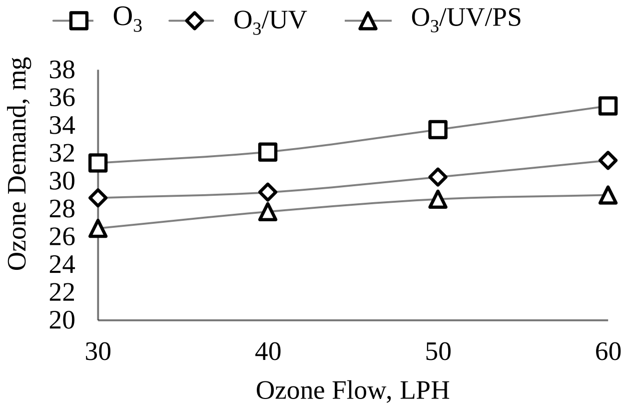


Figure 6: Effect of ozone-based AOP's on ozone consumption

The results shown in figure 6 are similar to that of findings in the literature. Ozone demand for per gm TOC removal was least in the O_3/UV/PS process followed by O_3/UV process and maximum ozone demand was observed in the case of the O_3 process. At 60 LPH, the O_3/UV/PS process consumes 29 mg of ozone per gm of TOC removal, whereas the O_3/UV and O_3 process consumes 31g and 36g of ozone respectively for per gm TOC removal. Similar results were obtained for all other ozone flowrates.

Conclusion

This comparative study analyzed ozonation and ozone-based AOPs to degrade RR120 as a model pollutant. The study was conducted using various operating parameters for the degradation of RR120. TOC removal was used as a critical parameter and all analysis was based only on the TOC removal rate. It was worth noticing that higher pH gives better degradation with TOC removal of almost 69%, 60% and 43% achieved by O_3/UV/PS, O_3/UV and O_3 process respectively at pH 12. Additionally, enhancement of ozone flowrate will positively affect TOC removal. However, it is worthy of mentioning that further increase in persulfate dosage above its optimum dosage will negatively affect the degradation efficiency of RR120.

On the other hand, increasing UV intensity will positively affect TOC removal with almost 78% and 72% TOC removal by O_3/UV/PS and O_3/UV respectively at 66W of UV intensity. TOC removal rate by ozonation and integrated ozonation process follows O_3/UV/PS > O_3/UV > O_3 under all operating parameters. However, ozone demand decreases in the integrated ozonation process and it shows the following pattern: O_3/UV/PS < O_3/UV < O_3.

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References

1. Abidin C.Z.A., Fahmi M.R., Ong Soon-An, Makhtar S.N.N.M. and Nazzery Rosmady Rahmat, Decolourization of an azo dye in aqueous solution by ozonation in a semi-batch bubble column reactor, *Science Asia*, **41**, 49–54 **(2015)**

2. Andreozzi R., Caprio V., Insola A. and Marotta R., Advanced oxidation processes (AOP) for water purification and recovery, *Catalysis Today*, **53**, 51–59 **(1999)**

3. Arslan I. and Balcioglu I., Degradation of commercial reactive dyestu€s by heterogenous and homogenous advanced oxidation processes: a comparative study, *Dyes and Pigments*, **43**, 95-108 **(1999)**

4. Duyar A. and Cirik, K., Textile wastewater treatment with Ozone/Fenton process: Effect of pH KSU, *Journal of Engineering Sciences*, **19(3),** 76-81 **(2016)**

5. Gogate P.R. and Pandit A.B., A review of imperative technologies for wastewater treatment II: hybrid methods, *Advances in Environmental Research*, **8**, 553–597 **(2004)**

6. Hossain M., Uddin M., Molla A.H., Afrad M., Rahman M.M. and Rahman G.M., Impact of Industrial Effluents Discharges on Degradation of Natural Resources and Threat to Food Security, *The Agriculturists*, **8(2)**, 80-87 **(2010)**

7. Kang S.F., Liao C.H. and Po S.T., Decolorization of textile wastewater by photo-fenton oxidation technology, *Chemosphere*, 4**1**, 1287-1294 **(2000)**

8. Ledakowicz S., Solecka M. and Zylla R., Biodegradation, decolourisation and detoxification of textile wastewater enhanced by advanced oxidation processes, *Journal of Biotechnology*, **89**, 175–184 **(2001)**

9. Modirshahla N. and Behnajady M.A., Photooxidative degradation of Malachite Green (MG) by UV/H2O2: Influence of operational parameters and kinetic modeling, *Dyes and Pigments*, 54-59 **(2006)**

10. Pereira L. and Alves M., Dyes—Environmental Impact and Remediation, In Pereira L., Alves M., Malik A. and Grohmann E., eds., Environmental Protection Strategies for Sustainable Development, Heidelberg, Springer, 111-162 **(2012)**

11. Rekhate C.V. and Srivastava J.K., Recent advances in ozone-based advanced oxidation processes for treatment of wastewater-

A review, *Chemical Engineering Journal Advances*, **3**, 100031 **(2020)**

12. Saien J., Soleymani A. and Sun J., Parametric optimization of individual and hybridized AOPs of Fe^{2+}/H_2O_2 and UV/S_2O_8, *Desalination*, **279**, 298–305 **(2011)**

13. Saranya D. and Shanthakumar S., An integrated approach for tannery effluent treatment with ozonation and phycoremediation: A feasibility study, *Environmental Research*, **183**, 109163 **(2020)**

14. Sarayu K., Swaminathan K. and Sandhya S., Assessment of degradation of eight commercial reactive azo dyes individually and in mixture in aqueous solution by ozonation, *Dyes and Pigments*, **75**, 362- 368 **(2007)**

15. Soares O.P., Orfao J.M., Portela D., Vieira A. and Pereira M.R., Ozonation of textile effluents and dye solutions under continuous operation: Influence of operating parameters, *Journal of Hazardeous Materials*, **137(3)**, 1664-1673 **(2006)**

16. Textile Industry and Market Growth in India, https://www.ibef.org/industry/textiles.aspx, 19/04/2021 **(2021)**

17. Wang C.W. and Liang C., Oxidative degradation of TMAH solution with UV persulfate activation, *Chemical Engineering Journal*, **254**, 472–478 **(2014)**

18. Wang J. and Chen H., Catalytic ozonation for water and wastewater treatment: Recent advances and perspective, *Science of the Total Environment*, **704**, 135249 **(2019)**.

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