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$O_3/S_2O_8^{2-}$ OXIDATION OF REACTIVE RED 120: EFFECT OF OPERATIONAL PARAMETERS

(Pengoksidaan $O_3/S_2O_8^{2-}$ Terhadap Reactive Red 120: Kesan Parameter Operasi)

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Abstract

In this research, the decolourisation performance of Reactive Red 120 (RR120) in aqueous solution using $O_3/S_2O_8^{2-}$ was evaluated. RR120 was selected due to high solubility in the aquatic environment. Ozonation (O_3) experiments were conducted as a control, to compare the treatment performance after addition of sodium persulphate. The aim of this research is to identify the effect of operational parameters of $O_3/S_2O_8^{2-}$ treatment on colour and COD removal. All experiments were carried out under continuous operation in a bubble column reactor. Operational parameters, namely initial dye concentration, $S_2O_8^{2-}$ dosage, initial pH, and contact time, were manipulated to optimize the performance of $O_3/S_2O_8^{2-}$. The effect of parameters on decolourisation performance was identified based on colour and COD removal. The performance of colour and COD removal in the O_3 was also compared with $O_3/S_2O_8^{2-}$ treatment processes. The intermediates were characterized based on its spectra evolution via UV-Vis spectrophotometer. The findings showed on increases in $S_2O_8^{2-}$ dosage that leads to an increase in the decolourisation efficiency. In addition, when the initial concentration increased to 300 mg/L, the decolourisation efficiency decreases as high concentration of azo bond cause the deficiency of the oxidation process. The $O_3/S_2O_8^{2-}$ performance also improved in alkaline pH, in the presence of hydroxyl radical. By comparing these two treatments, $O_3/S_2O_8^{2-}$ obtained better removal efficiency in colour than O_3.

Keywords: $O_3/S_2O_8^{2-}$, ozonation, decolourisation, Reactive Red 120, persulphate

Abstrak

Dalam kajian ini, prestasi penyingkiran warna $O_3/S_2O_8^{2-}$ dinilai terhadap Reactive Red 120 (RR120) dalam larutan akues. RR120 telah dipilih kerana keterlarutan tinggi dalam persekitaran akuatik. Eksperimen pengozonan (O_3) telah dijalankan sebagai kawalan, untuk membandingkan prestasi rawatan selepas penambahan natrium persulfat. Tujuan kajian ini adalah untuk mengenal pasti kesan parameter operasi rawatan $O_3/S_2O_8^{2-}$ terhadap penyingkiran warna dan COD. Eksperimen ini telah dijalankan di bawah operasi yang berterusan dalam reaktor turus panjang. Parameter operasi, iaitu kepekatan awal pewarna, dos $S_2O_8^{2-}$, pH awal, dan masa sentuhan, telah dimanipulasikan untuk mengoptimumkan prestasi $O_3/S_2O_8^{2-}$. Kesan parameter terhadap prestasi penyingkiran telah dikenal pasti berdasarkan penyingkiran warna dan COD. Prestasi penyingkiran warna dan COD dalam O_3 juga telah dibandingkan dengan proses rawatan $O_3/S_2O_8^{2-}$. Perantaraan daripada RR120 telah dicirikan berdasarkan perubahan spektrum menerusi spektrofotometer UV-Vis. Hasil kajian menunjukkan peningkatan dos $O_3/S_2O_8^{2-}$ membawa kepada peningkatan kecekapan penyingkiran warna. Di samping itu, apabila kepekatan awal RR120 meningkat kepada 300 mg/L, kecekapan peyingkiran warna turut berkurangan, kerana kepekatan ikatan azo meningkat menyebabkan proses pengoksidaan berkurangan. Prestasi $O_3/S_2O_8^{2-}$ juga bertambah baik pada pH alkali, dengan kehadiran radikal hidroksil. Dengan membandingkan kedua-dua perawatan, didapati $O_3/S_2O_8^{2-}$ mempunyai kecekapan penyingkiran warna yang lebih baik daripada O_3.

Kata kunci: $O_3/S_2O_8^{2-}$, pengozonan, penyingkiran warna, Reactive Red 120, persulfat

Introduction

Textile industry is one of the largest industries in the world in terms of its production and employment [1]. Dyes are widely used in the textile industries due to favourable characteristics, such as intense colour, water fastness, and uncomplicated application techniques. In the industries, the azo are among the most common synthetic dyes both in terms of the number and amount produced with azo bond groups [2]. Besides, azo dyes account for approximately 60 – 70% of all dyes used in food and textile manufacture [3]. Normally industrial effluent is not treated completely before discharging it into the water bodies such as rivers or lakes. There are many industries come out with their own wastewater treatment plant. But the discharge effluents still do not follow the standard that can discharge to water bodies. Dye wastewater is mainly generated from the wet-processing originates from washing and bleaching in textile industry [4,5]. Dye is a colorant used to dye textile fibres; in other words, it has an affinity to the material to which it is applied to. The colour of dyes is due to the presence of chromophore group, which is also known as auxochoromes and conjugated bond [6]. Azo dye wastewater is comprised of high biological oxygen demand (BOD) and chemical oxygen demand (COD) content, which has the impact on visible colour; obstruct light penetration and oxygen transfer into water bodies. The common methods used in dye wastewater treatment are carbon adsorptions and flocculation processes. Though other parameters can be treated by conventional chemical, physical or biological method, colour remained after treatment. Therefore, the colour problem caused by residual dyes requires more effort and time to study and investigate [2].

Advanced oxidation processes (AOPs) have high efficiency in treating dye wastewater in terms of decolourisation and degradation of refractory pollutants compared to other methods. Over years, ozonation and AOPs involving ozone in combination with hydrogen peroxide (O_3/H_2O_2), photolytic H_2O_2 oxidation (UV radiation with H_2O_2) and advanced fenton became the new technology to treat dyes textile and dyestuff industrial effluent. Now, ozone-based concept treatment has extended to the oxidation processes with sulphate radicals ($SO_4^{\bullet-}$), namely ozone persulphate ($O_3/S_2O_8^{2-}$). This treatment has operational advantages over conventional processes such as suitable for wide pH range, low cost of oxidant precursors, no post treatment steps and complete mineralization of pollutants into harmless products [7]. Lastly, the present research is very significant for the development of the efficient and economical treatment for the mineralization of the industrial dye wastewater. Thus, this current study will investigate the efficiency of O_3 and $O_3/S_2O_8^{2-}$ on industrial dye wastewater treatment.

Materials and Methods

Materials

The analytical grade diazo RR120 was selected as model due to its common application in industries obtained from Sigma-Aldrich. Its molecular weight and molecular formula is 1,469.98g and $C_{44}H_{24}Cl_2N_{14}O_{20}S_6Na_6$, respectively. The appropriate weight of dye will be dissolve to ultrapure water for the preparation of stock solution. Figure 1 present the chemical structure of the studied dye.

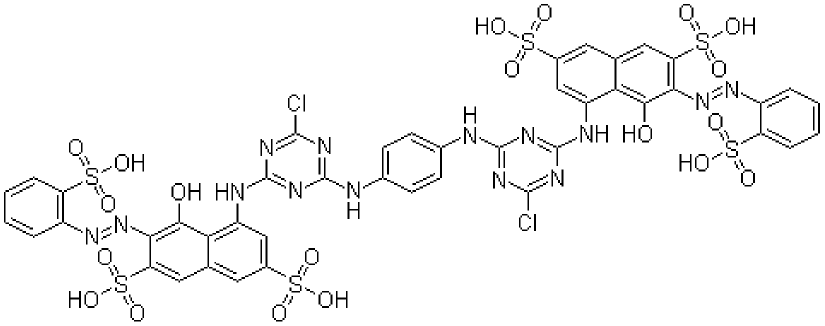

Figure 1. Chemical Structure of RR120 [8]

Experimental set-up

O_3 gas was generated in laboratory and supplied to a 2 L of cylindrical glass reactor connected to 2% of potassium iodide trap which act as O_3 destructor. The O_3 gas was generated using A2Z (model Z-3G) Ozone Generator which continuously supplied with purified O_2. During experiments, O_3 gas constantly flow through a diffuser to produce fine bubbles into 2 L dye sample. For the $O_3/S_2O_8^{2-}$, predetermined $S_2O_8^{2-}$ dosage was added to the dye sample before O_3 entered the reactor.

2 L/min O_2 flow rate was applied to generate O_3 throughout the experiments. Different dosage of 1, 3, and 5 g $S_2O_8^{2-}$/g dye at pH 7. The O_3 and optimum $S_2O_8^{2-}$ dosage were applied to the study of the effects of pH (3, 5, 7, 9, 11), together with the initial concentration of 100 and 300 mg/L. The experiments were conducted at room temperature with different contact time of 0, 1, 2, 3, 4, 5, 10, 15, and 20 minutes. Finally, the samples were withdrawn at definite intervals for analyses.

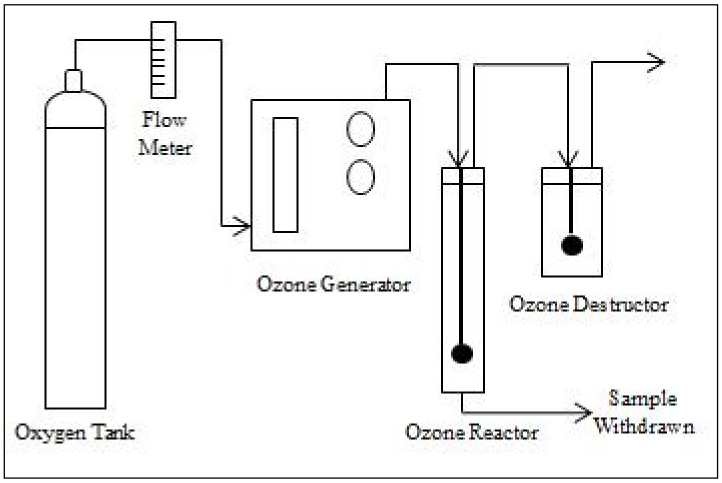

Figure 2. Schematic diagram of experimental set-up for O_3 and $O_3/S_2O_8^{2-}$

Analytical method

The potassium iodide titration will use to determine the O_3 flow rate dye samples. UV-Vis spectrophotometer will be used to analyse the absorbance colour change and dye concentration of the dye samples. The pH value before and after the treatment will be tested by using pH meter (Hannah Instruments H1223). The value of COD will be tested before and after treatment by $O_3/S_2O_8^{2-}$ oxidation with the standard APHA method. HACH DR200 COD reactor and DR2800 spectrophotometer will be used to react and take the COD reading in terms of mg/L, respectively [9]. The COD analysis will repeat for 3 times and the average is calculate. The removal efficiency of COD and colour was determined using Eq. 1.

$$\text{Removal (\%)} = [\, C_i - C_f/C_i \,] \times 100 \tag{1}$$

where C_i and C_f were respectively refer to the initial and final colour and COD concentration.

Results and Discussion

The comparison of colour and COD removal of RR120 for both treatment methods are based on the optimum operating parameter, where the most favourable condition to achieve highest removal efficiency are at pH 7, 100 mg/L of initial dye concentration and dosage of 5 g $S_2O_8^{2-}$/g dye for $O_3/S_2O_8^{2-}$system. In addition, ozone flow rate was maintained at 2 L/min.

Effect of initial pH

The effect of initial pH on the UV-Vis spectra obtained is given in the Figure 3. The visible region reduces rapidly in alkaline condition, might be due to the dissociation of the N=N bonds. The decreasing of the visible region means that there is cleavage of chromophore, which is azo bond that give colour to RR120.

The pH value was known as the important parameters that affect the colour and COD removal. For the initial concentration of 100 mg/L and initial dosage of 5 g S_2O_8/g dye, the dye has completely decolourize after 5 minutes of treatments as shown in Figure 4. Various studies showed that solution of pH is directly effect the decomposition of ozone [10]. The ozone molecular remain as the main oxidant at low pH values, while at high pH hydroxyl radicals are formed from ozone decomposition [11]. Since the decolourization of dye can be at different pH in colour effluents, the effects of pH value in the pH range 3 to 11 was studied. The solution of dyes were adjusted by addition of H_2SO_4 or NaOH in order to get desired pH. The complete decolourization was observed from pH 3 to 5 and the further to 11. This condition may be explained by the radical way reactions predominated at higher pH values which is efficient in colour removal by equal cleavage of two electron bond [12].

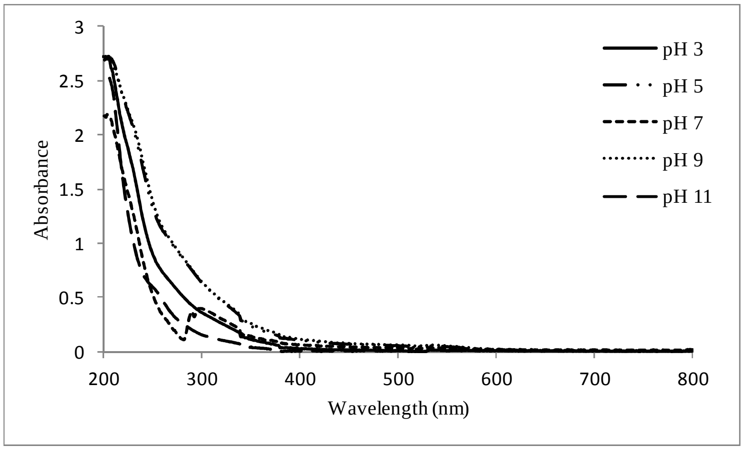

Figure 3. Effect of pH on the UV-Vis spectra

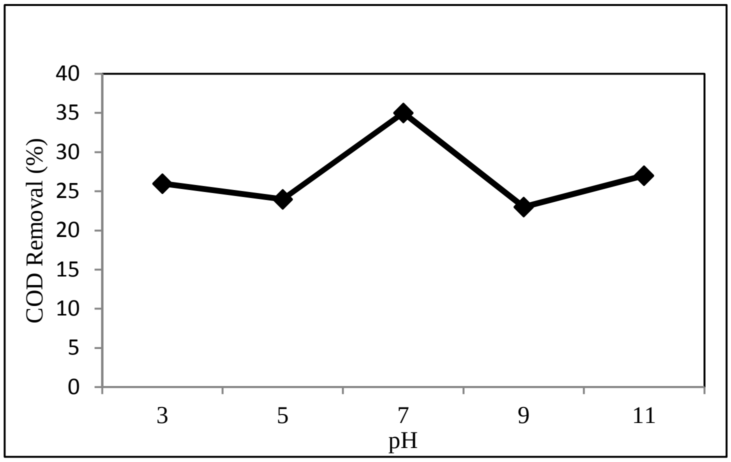

Figure 4. Effect of pH on the COD removal

Figure 4 also presented the COD results obtained for the COD analysis of dye solution after the $O_3/S_2O_8^{2-}$ treatment. COD removal was decreased from pH 3 to 5 and sharply rose to 7. This can explained by reaction between molecular ozone and organic polltant is the predominat mechanism at low pH and took over by hydroxyl radicals at high pH [13]. Therefore, the COD concentration is decreased as pH value increase due to stronger oxidizing power of hydroxyl radicals.

Effect of initial dosage

The changes of UV-Vis spectra obtained from the different intial $S_2O_8^{2-}$ dosage are presented in Figure 5. Figure below represented two different trends of wavelength spectrum; the first is before the treatment and the second is after the treatment. After 20 minutes treatment, the peaks of absorbance in the visible region gradually declined resulting the decolourization. Therefore, the decrease of visible region indicate that azo bonds cleavage, while in UV region indicates aromatic such as benzene and naphthalene cleavage.

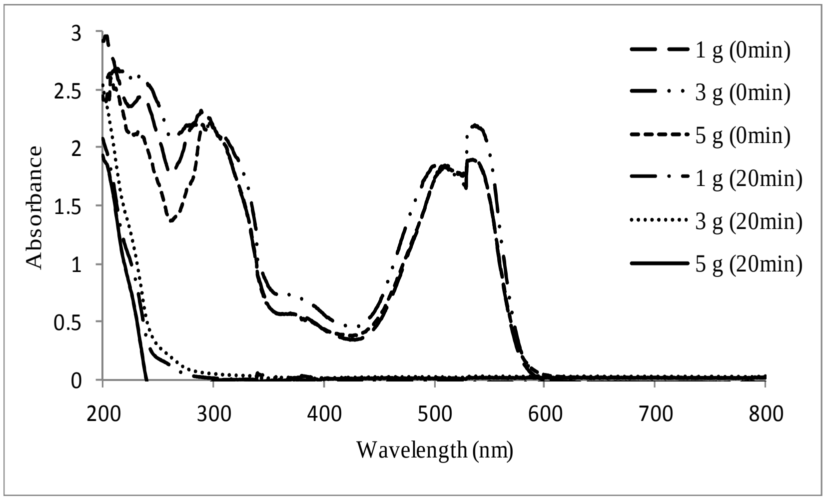

Figure 5. Effect of $S_2O_8^{2-}$ dosage on the UV-Vis spectra

Figure 6 showed that at dosage 5 and 3 g $S_2O_8^{2-}$/g dye, the percentage of colour removal for RR120 almost similar. An amount 5 g $S_2O_8^{2-}$/g dye has 25% COD concentration at 10 min, and 3 g $S_2O_8^{2-}$/g dye achieved after 15 minutes, while dosage 1 g $S_2O_8^{2-}$/g dye only achieved after 20 min of reaction time. Hence, it is necessary to further increase the dosage to various levels in order to investigate the relationship of dosage with colour and COD removal. The initial $S_2O_8^{2-}$ dosage gives a very important effect in the generation of hydroxyl and sulphate radicals for the dye degradation. In general, higher hydroxyl radical concentrations produced from the higher initial dosage which able to decomposes more target compound such as dyes resulting colour and COD removal. In this research, the degradation of dye was evaluate for several initial $S_2O_8^{2-}$ dosage (1, 3, 5 g $S_2O_8^{2-}$/g dye) at constant initial dye concentration and pH. The results indicate that, higher dosage of $S_2O_8^{2-}$ produces higher colour and COD removal. Generally, when $S_2O_8^{2-}$ is added into the ozonation system, the decomposition of O_3 into hydroxyl radical accelerated the process and shift the process entirely to an AOPs [14]. Therefore, with the more number of hydroxyl radicals and the presence of sulphate radical, they can attack the azo bond faster than breaking down the sulphonate group and naphthalene ring in dye [15].

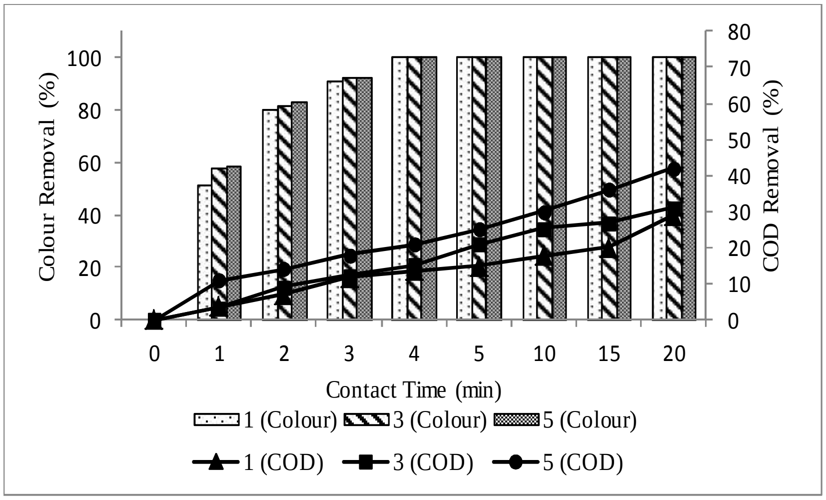

Figure 6. Effect of $S_2O_8^{2-}$ dosage on the colour and COD removal

Effect of initial dye concentration

Figure 7 shows the effect of initial dye concentration on the UV-Vis spectra during $O_3/S_2O_8^{2-}$. It can be seen that the intensity of absorbance was reduced sharply after 20 minutes of treatment time for $O_3/S_2O_8^{2-}$, which represents the cleavage of azo bond and resulting in decolourisation. On the other hand, the benzene and naphthalene ring are connected to the azo bond at 212 and 298 nm, respectively in the UV region also showed greatly reduced with $O_3/S_2O_8^{2-}$ treatment. Azo bond will be attacked first before the degradation on the benzene ring or naphthalene. This is because the absorption bands intensities for UV region is degraded more slowly than visible band. Therefore, the colour of RR120 has been disappeared first by breaking azo bond and the followed by oxidation of benzene ring and naphthalene that cannot been see by eyes, but only detected with UV-Vis [16].

In this study, the dye degradation was investigated for several initial concentrations of dye (100 and 300 mg/L) at a constant initial dosage of 5 g $S_2O_8^{2-}$/g dye. Figure 8 illustrated the effect of initial dye concentration on the colour and COD removal during $O_3/S_2O_8^{2-}$ at constant pH which is pH 7. The colour removal efficiency decrease as the concentration of dye increase due to less production of persistent intermediates [12]. The initial dye concentration of 100 mg/L achieved more that 80% of colour removal after 2 minutes, whereas 300 mg/L obtained after 10 minutes. On the other hand, completely decolourisation was presented after 4 and 15 minutes for 100 and 300 mg/L dye concentration, respectively. The initial dye concentration give an important role in the determination of economical use of ozone for decolourisation [10]. Therefore, longer reaction time is needed to completely decolourise higher concentration of dye. Various researches have obtained that the time required for decolourisation of the dye solution is dependent on the initial dye concentration [17]. The COD removal has the same result as colour reduction efficiency. It can be seen that 100 mg/L achieved better COD reduction compared to 300 mg/L dye concentration. The 100 mg/L dye concentration reduced 10% of the COD concentration after 1 min of treatment, whereas 300 mg/L concentration achieved after 3 minutes. In fact, increasing the dye concentration will decreased the pollutant ration of ozone molecules to dye molecules. Therefore, more oxidants needed to be consumed in order to completely degrade the refractory pollutants. The removal rate of COD will increase as the increasing of the treatment contact time. This condition can be explained by the amount of hydroxyl free radicals in dye solutions increase with the reaction time [18].

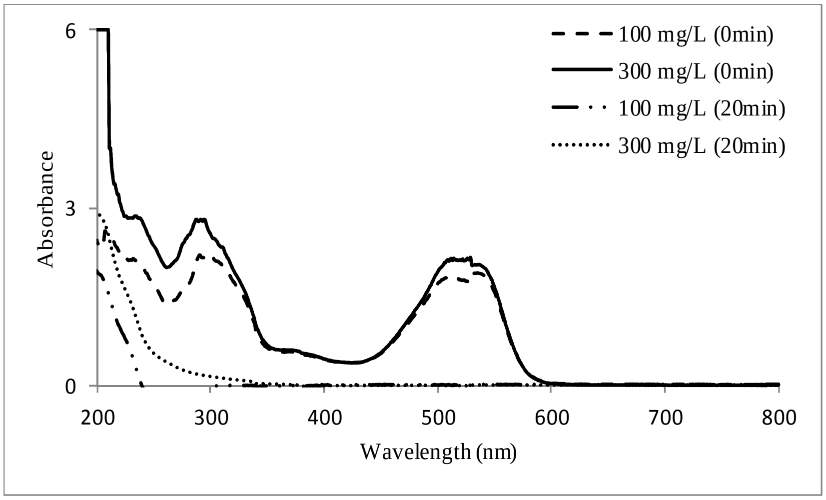

Figure 7. Effect of initial dye concentration on the UV-Vis spectra

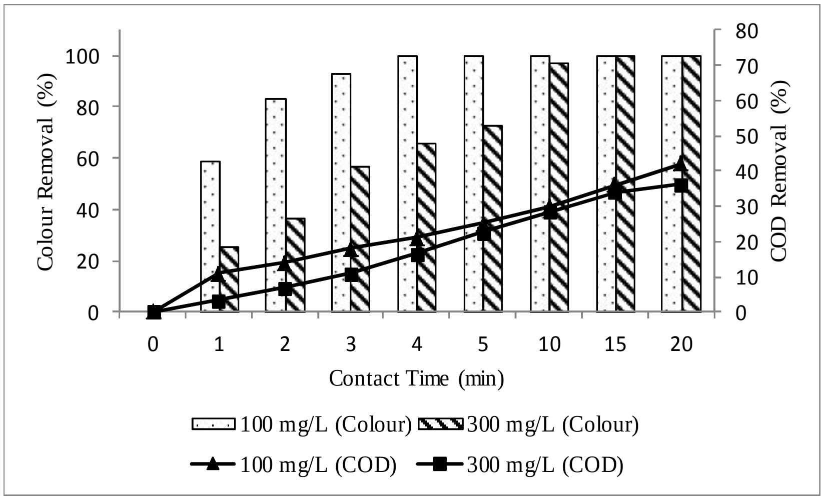

Figure 8. Effect of initial dye concentration on the colour and COD removal

Comparison of O_3 and $O_3/S_2O_8^{2-}$

Figure 9 showed the colour, and COD removal percentages of RR120 at initial dye concentration 100 mg/L for a different method which are O_3 and $O_3/S_2O_8^{2-}$. This graph indicates increasing in reaction time has caused in an increasing in colour and COD removal. The decolourisation of dye occurred faster than the COD removal. This situation may be explained that chromophore may destroyed during treatment and partially mineralized to a smaller fragments [19]. The $O_3/S_2O_8^{2-}$ oxidation achieved completely decolourisation after 4 min, while this condition happened to O_3 after 5 min. The results proved that $O_3/S_2O_8^{2-}$ more capability to breakdown the azo bond from the dye structure than the O_3 alone. This is because the $O_3/S_2O_8^{2-}$ is involving the generation of two type reactive free radicals, which are hydroxyl radicals and sulphate radical at neutral or basic pH. Both radicals played an important role in this processes in terms of decolourisation. On the other hand, O_3 is only able to produce the hydroxyl radicals through the process.

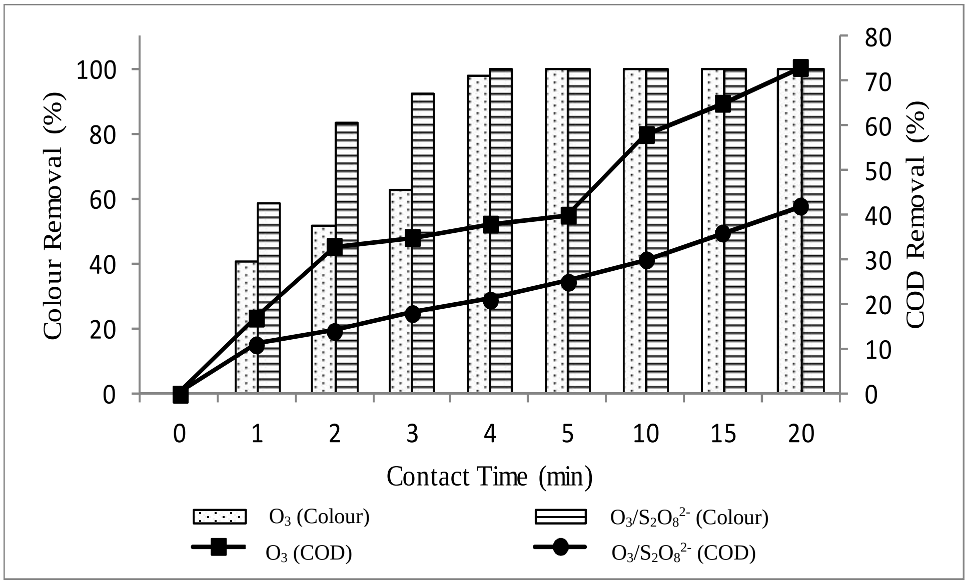

Figure 9. Effect of O_3 and $O_3/S_2O_8^{2-}$ on the colour and COD removal

Conclusion

This study has found that generally, the $O_3/S_2O_8^{2-}$ advanced oxidation treatment provides good performances in the colour removal of the RR120 in water. The initial $S_2O_8^{2-}$ dosage, dye concentration and pH give a very important role in the generation of hydroxyl and sulphate radicals for the dye generations. The results of this investigation show that, the decolourisation was strongly depending on initial $S_2O_8^{2}$ dosage. The decolourisation efficiency increased with increasing $S_2O_8^{2-}$ dosage and reaction time. While, decolourisation efficiency decreased with raising the initial dye concentration.

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References

1. Wang, Z., Xue, M., Huang, K. and Liu, Z. (2010). Textile dyeing wastewater treatment. Intech Open Acess Publisher: pp. 91 – 116.
2. Muqing, Q., Shou, J., Ren, P. and Jiang, K. (2014). A comparative study of the azo dye reactive Black 5 degradation by UV/TiO_2 and photo-fenton processes. *Journal of Chemical and Pharmaceutical Research*, 6(7): 2046 – 2051.
3. Rauf, M. A. and Ashraf, S. S. (2009). Application of advanced oxidation processes (AOP) to dye degradation- an overview. In Dyes and Pigments : New Research. Nova Science Publishers. United Arab Emirates: pp. 260 – 290.
4. Lokesh, K. N. and Kiran, S. R. (2013). Biological methods of dye removal from textile effluents A review. *Journal of Biochemical Technology*, 3(5): 177 – 180
5. Smita, V., Quaff, A. R., Pandey, N. D. and Venkatesh, K. (2014). Decolorization and mineralization of C.I. direct Red 28 Azo dye by ozonation. *Desalination and Water Treatment*, 57(9): 4135 – 4145.
6. Zhang, F., Yediler, A., Liang, X. and Kettrup, A. (2004). Effects of dye additives on the ozonation process and oxidation by-products: A comparative study using hydrolyzed C.I. Reactive Red 120. *Dyes and Pigments*, 60(1): 1–7.

7. Abu Amr, S. S., Aziz, H. A., Adlan, M. N. and Alkasseh, J. M. A. (2014). Effect of ozone and ozone/persulfate processes on biodegradable and soluble characteristics of semiaerobic stabilized leachate. *Environmental Progress & Sustainable Energy*, 33(1): 184 – 191.
8. Sigma Aldrich – Reactive Red 120 (2016). Acess online from http://www.sigmaaldrich.com/catalog/product/sigma/r0378?lang=en&region=MY&gclid=CjwKEAiArfDBRDeyOybg8jd2U4SJAAoE5XqFW4bmf4Mym2M6_ToAcObcO0TA2yKdAJKJkWtwnxoCybrw_wcB
9. American Protect Health Agency (2005). Standard methods for the examination of water and wastewater, 21st edition, Washington DC.
10. Chu, W. and Ma, C. W. (2000). Quantitative prediction of direct and indirect dye ozonation kinetics. *Water Research*, 34(12): 3153 – 3160.
11. Soares, O. S. G. P., Orfao, J. J. M., Portela, D., Vieira, A. and Pereira, M. F. R. (2006). Ozonation of textile effluents and dye solutions under continuous operation: Influence of operating parameters. *Journal of Hazardous Materials*, 137(3): 1664 – 1673.
12. Kazemi, M., Jafar, S. S. M., Ali, B. K. and Mohammad, A. K. (2004). Decolourisation of RR-120 dye using ozone and ozone/UV in a semi-batch reactor. *The Canadian Journal of Chemical Engineering*, 82(6): 1284 – 1288.
13. Poznyak, T., Tapia, R. and Chairez, I. (2006). Effect of pH to the decomposition of aqueous phenols mixture by ozone. *Journal of the Mexican Chemical Society*, 50(1): 28 – 35.
14. Griffini, O. and Iozzelli, P. (1996). The influence of H_2O_2 in ozonation treatment: experience of the water supply service of Florence, Italy in Ozone Science Engineering. Taylor and Francis: pp. 117 – 126.
15. Pachhade, K., Sandhaya, S. and Swaminathan, K. (2009). Ozonation of reactive dye, Procion red MX-5B catalyzed by metal ions. *Journal of Hazardous Materials*, 167(1): 313 – 318.
16. Feng, W., Nansheng, D. and Helin, H. (2000). Degradation mechanism of azo dye C. I. RG2 by iron powder reduction and photooxidation in aqueos solutions. *Chemosphere*, 41(8): 1233 – 1238.
17. Sevimli, M. F. and Sarikaya, H. Z. (2002). Ozone treatment of textile effluents and dyes: Effect of applied ozone dose, pH and dye concentration. *Journal of Chemical Technology and Biotechnology*, 77(7): 842 –850.
18. Yang, D. M., Wang, B., Ren, H. Y. and Yuan, J. M. (2012). Effects and mechanism of ozonation for degradation of sodium acetate in aqueous solution. *Water Science and Engineering*, 5(2): 155 – 163.
19. Abidin, C. Z. A., Muhammad Ridwan, F. and Ong, S. A. (2015). Decolourization of an azo dye in aqueous solution by ozonation in a semi-batch bubble column reactor. *ScienceAsia*, 41: 49 – 54.