

Degradation Characteristics of Monoazo and Diazo Dye by Using Ozone Oxidation

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ABSTRACT

The degradation characteristics of monoazo Acid Orange 7 (AO7) and diazo Reactive Green 19 (RG19) were investigated using ozone oxidation. It was evaluated based on colour, chemical oxygen demand (COD) and total organic carbon (TOC) removal. The effect of operational parameters such as initial dye concentration, contact time and pH were also being studied. The results demonstrated that the ozone oxidation was efficient in decolourization and good in mineralization, based on the reduction of COD and TOC. The mineralization performance for AO7 is better, but the decolourization of RG19 is advantageously. Additionally, an instantaneous drop of pH through the ozone oxidation process indicated the formation of acidic intermediate products. This evidence was supported by the findings of carboxylic acids, sulfite and ketones in Fourier Transform Infrared Spectroscopy (FT-IR).

Keywords: AOPs, COD, Coagulation-Flocculation, Coagulation-Fenton, Colour, Leachate.

1. INTRODUCTION

Textile, printing, and leather industries are the main industries that discharges large amount of wastewater. The textile, printing, and paint industries are familiar to have dye wastewater which contain high total suspended solid (TSS), chemical oxygen demand (COD), biological oxygen demand (BOD) and also high colour content (Zhang *et al.*, 2007). Dyes especially azo dyes and its intermediate products can cause mutagenic and carcinogenic (de Souza *et al.*, 2010). However, due to the dye complexity and diversity of structure, dye wastewater resist degradation to light, water, and some chemicals (Saratale *et al.*, 2011). Currently, there are more than 10,000 dyes used in industries, azo dyes are the oldest synthetic organic compounds and the most widely used dyes (60-70%) among them (Brás *et al.*, 2005).

Adsorption on sludge, living plants and activated carbon are example of physical methods, and research found that these methods are suitable to treat acid dyes (Tee *et al.*, 2015; Wang, 2012; Chu and Chen, 2002). However, the regeneration of adsorbent cause increases of the cost and time. Biological treatment such as aerobic and anaerobic processes are used as alternative to treat dyes, but the environmental conditions like pH and temperature is hard to control and the reaction period was long (Anjaneyulu *et al.*, 2005).

Recently, Advanced Oxidation Processes (AOPs) becomes the most promising technique to decolourize and removal of dye wastewater (Hsing *et al.*, 2007). The versatility of AOPs is enhancing by the different possible ways of hydroxyl radical generation under different conditions. The generation of hydroxyl radical is commonly accelerated by combination of

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oxidants such as UV radiation plus hydrogen peroxide, Fenton's reagent or ozone (Covinich *et al.*, 2014).

The ozone oxidation is one of AOPs that used to treat wastewater contained dyes due to the ability in reduce colour, chemical oxygen demand (COD), and increase the biodegradability of wastewater (Lackey *et al.*, 2006). Moreover, the latest research also show that ozone oxidation can break down the double bonds that attached with the groups which are control for colour to smaller molecules, and hence reduce the colour of the discharge effluents (Sarayu *et al.*, 2007). In this study, the performance of ozone oxidation process for the degradation characteristics of azo dyes based on colour, COD and TOC removal. The evaluation on the ozone oxidation with different dye structures are less being found in the literature. Therefore, the monoazo and diazo dye were used to compare the effectiveness of ozone oxidation. Finally, functional group and pH were used to evaluate the intermediate byproducts through the ozone oxidation process.

2. MATERIALS AND METHODS

2.1 Synthetic Dye Preparation

Monoazo, Acid Orange 7 (A07) and diazo dye, Reactive Green 19 (RG19) were used in this experiment. The analytical grade dyes were obtained from Acros Organics and Sigma-Aldrich. Stock solution of 5000 mg/L concentration was prepared for each dye. The stock solution was then diluted into the desired concentration of 100, 300 and 500 mg/L. The pH of the solution was adjusted by using 1N of HCl and NaOH until reach the desired pH. All solutions were prepared using ultrapure water.

2.2 Experimental Procedure

Ozone is generated in a laboratory scale cylindrical glass reactor from pure oxygen. The reactor is also equipped with ozone destructor that operated in semi-batch. Pure oxygen with flow rate 2 L/min will continue introduced into A2ZZ-3G ozone generator to produce ozone with 4.98 mg/min of flow rate into the ozone reactor. The ozone gas is continue flow through a diffuser and produce fine bubbles at constant rate, supplying to 2 L dye samples. The leftover ozone is trap to 2 % (KI) solution (Sarayu *et al.* 2007). The schematic diagram is shown as below (Figure 1).

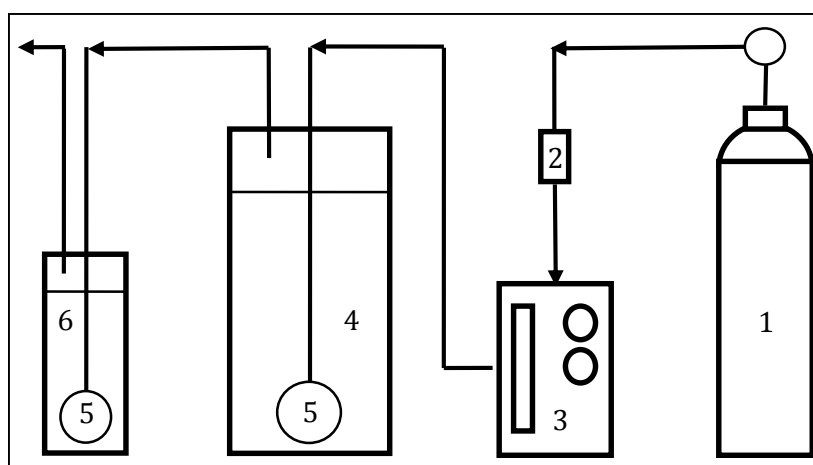


Figure. 1. Schematic diagram of ozonation reactor: 1) O₂ cylinder, 2) flow meter, 3) O₃ generator, 4) glass reactor, 5) diffuser, 6) KI trap.

2.3 Analytical Methods

The decolourization of dyes was analysed using HITACHI U-2800 spectrophotometer. The λ_{\max} of colour was determined at 484 and 626 nm for AO7 and RG19, respectively. The COD was tested by using the standard (APHA-AWWA-WEF) method with the use of HACH DR200 COD reactor and DR2800 spectrophotometer. TOC was measured using commercially available test kits (HACH Direct Method, 10173) (midrange 15 to 150 mg/L). The pH was measured by using Hanna Instruments HI223 pH meter. Finally, Spectrum 400 FT-IR/ FT-NIR PerkinElmer Spectrometer was to determine the evaluation of functional groups. 250 mL of sample solution was heated in oven at temperature of 65 to 70°C for 3 days to ensure all the sample solution is dried out and become powder for FT-IR analysis.

3. RESULTS AND DISCUSSION

3.1 Initial pH

As mention earlier, most of the azo dyes degrade into small fragment molecules such as ketones, aldehydes and carboxylic acids (Khadhraoui *et al.*, 2009). This transformation will also lead to changes in pH value of the treated dye solution. In Figure 2, the pH is decreasing from contact time of 0 to 20 mins especially at the reaction time interval of 0 to 5 mins. This phenomenon can be clarified by the formation of small intermediates fragment such as ketones, aldehydes and especially carboxylic acids that contributes to the acidic pH value. The finding show that the effluent pH for AO7 and RG19 is almost reached a steady pH which is around pH 3 after 5 mins of contact time. Experiments with different initial pH were carried out as to see the effect of initial pH towards the effluent pH. The results obtained were surprisingly as the dye solution of AO7 and RG19 with initial pH of 3, 5, 7, and 9 were around pH 3. This finding is same with Tehrani-Bangha *et al.* (2010).

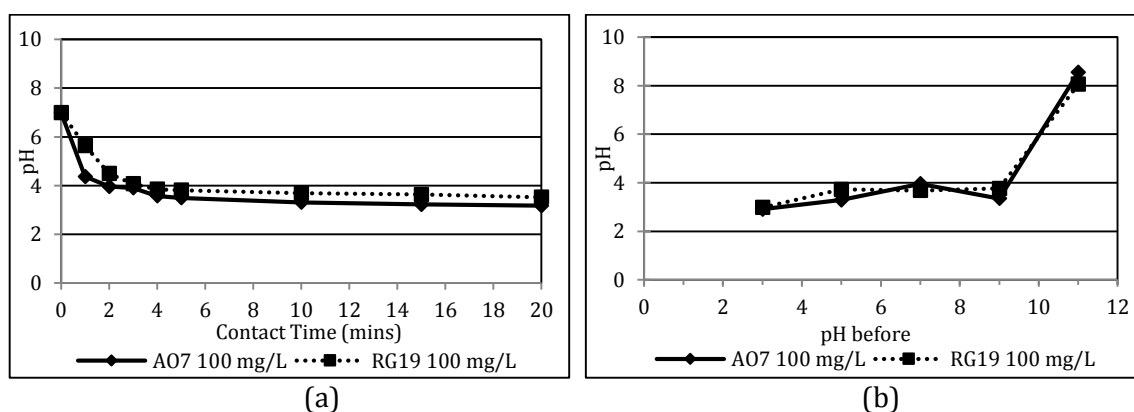


Figure 2. pH of AO7 and RG19 with different (a) contact time; (b) pH.

3.2 UV-Vis Absorption Spectra

Figure 3 shows the UV-Vis spectra with parameter of different contact time. In Figure 3(a), the peak of AO7 at 483 nm is dissipated significantly from 0 to 4 mins. After 5 mins, the azo bond of AO7 can said to be completely broken down. However, the benzene ring at 240 nm degrades slower than naphthalene ring at 320 nm. As mention by Muthukumar *et al.* (2005), this pattern of degradation is cause by the higher reaction rate of ozone toward naphthalene than benzene. From Figure 3(b), the peak decline rapidly and the azo bond is fully broken down at contact time of 4 mins. RG19 consist of one naphthalene ring and 4 benzene rings. Hence, the absorption peak at benzene ring (240 nm) is much higher than the naphthalene ring (320 nm). At contact time of

20 mins, naphthalene ring can be assumed as fully oxidized. This result also enhance by the help of lessen number of naphthalene ring than the benzene ring.

AO7 is not easily degradation compare to RG19 although it is a monoazo dye. In addition, the cleavage of naphthalene ring is faster in RG19 although both azo dyes consist of one naphthalene ring. Hence, it can be conclude that the colour and naphthalene ring degraded quickly in RG19 than AO7 due to the present of 6 sulphonate groups. Sulphonate groups will increase the solubility of the azo dye and therefore increase the interaction between hydroxyl radicals or ozone and the dye molecules

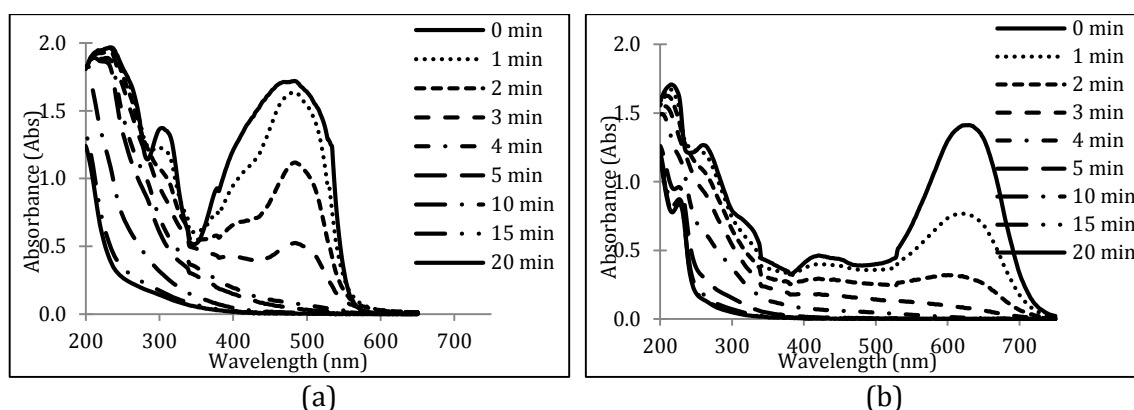


Figure 3. UV-vis spectra of (a) AO7; (b) RG19 with initial concentration of 100 mg/L at different contact time.

3.3 Colour Removal

The percentage colour removal of AO7 and RG19 with different initial concentration and contact time is shown in Figure 4(a). Initially, as the concentration increase, the percentage colour removal decreases. But after certain period of contact time, the colour removal can be achieved up to 100%. Turhan *et al.* (2012) found that with the increasing of the initial concentration, the decolourization time and ozone dissipation also increased. This is because under this condition, the proportional of ozone and dye molecules decreases. Hence, more ozone is needed if the concentration of dye is higher. The percentage colour removal of AO7 and RG19 at various pH with same initial concentration represent in Figure 4(b). At contact time of 10 mins, AO7 and RG19 decolourized completely no matter the initial pH value.

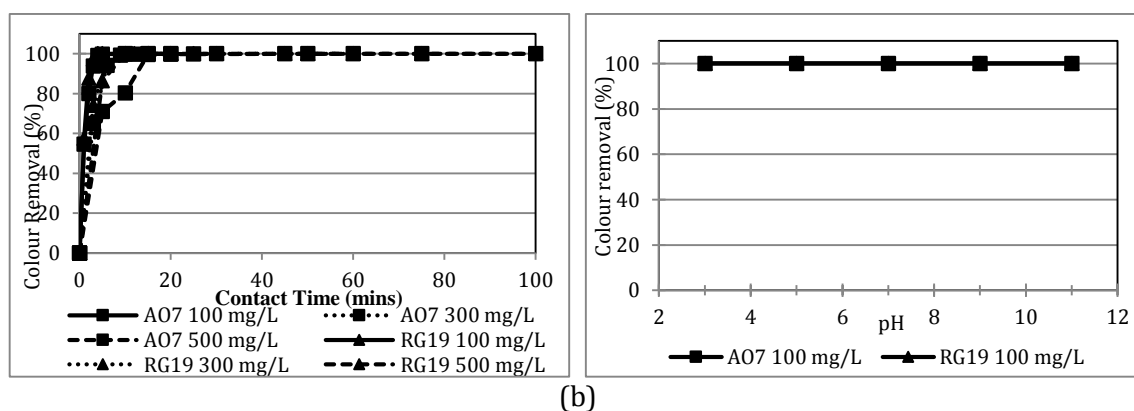


Figure 4. Colour removal of AO7 and RG19 with different (a) contact time; (b) pH.

3.4 COD Removal

The effectiveness of COD removal of AO7 and RG19 as displayed in Figure 5. At contact time of 15 mins, the COD removal efficiencies of AO7 are 56.1, 39.9 and 26.4% for 100, 300 and 500 mg/L, respectively. While for RG19 the percentage COD removal are 52.2, 30.7 and 22.2% with initial concentration of 100, 300, and 500 mg/L respectively. This indicates that the COD removal efficiency at higher concentration is lower at the same contact time. Thus, the higher the concentration, the longer contact time is needed to achieved the similar COD removal efficiency. The COD removal efficiency of AO7 is slightly better than RG19. Ozone oxidation of dyes break the bond of the dye structure and form smaller organic molecular fragments like aldehydes, ketones and acetic acids that contribute to the residual COD (Khadhraoui *et al.*, 2009). The smaller organic fragments formed after the ozone oxidation of AO7 is less than the RG19 since the molecular structure of AO7 is less complex than RG19 and the percentage COD removal is higher.

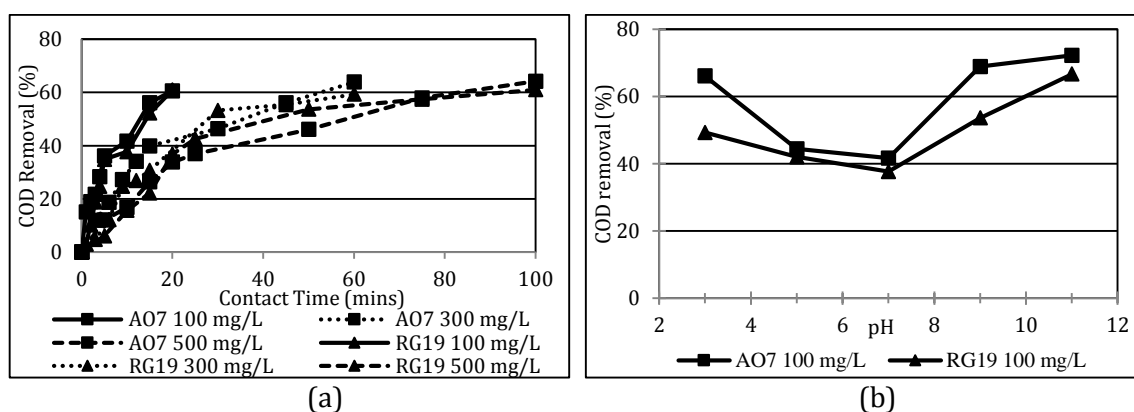


Figure 5. COD removal of AO7 and RG19 with different (a) contact time; (b) pH.

The percentage colour removal with initial concentration 100 mg/L of AO7 and RG19 is 100% after 10 and 4 mins respectively. However, the percentage COD removal only achieved 60.6 and 58.3% after 20 mins of contact time. The lower percentage of COD removal compare to colour removal is described as a result of unfinished oxidation of organic molecules. de Souza *et al.* (2010) detailed out there is significant COD value contribute by the unfinished oxidation small molecules and these molecules cannot be fully oxidized into carbon dioxide and water even though excess ozone oxidation is done. The percentage COD removal for AO7 is slightly more than RG19 at all the pH range. AO7 consist of one azo groups but RG19 consist of two azo groups. Hence, the RG19 COD removal efficiency is not as good as AO7 at acidic condition. RG19 consist of four benzene rings and one naphthalene ring is hardly to undergo oxidation than AO7 which consist of one benzene ring and one naphthalene ring. Hence, the removal percentage of COD in AO7 is more than RG19 in basic conditions.

3.5 TOC Removal

The percentage TOC removal for AO7 and RG19 with initial concentration of 100 mg/L at different contact time is shown in Figure 6(a). The TOC removal of AO7 is slightly more than RG19. Nevertheless, the TOC removal achieved only 33.3 and 32.2% for AO7 and RG19 at 20 mins of ozone oxidation. The low percentage TOC removal perhaps can be describe by the resistance of aromatic compounds to oxidize and small organic molecules is produced and not being fully mineralized under the existing oxidative environment (Tehrani-Bagha *et al.*, 2010, Koch *et al.*, 2002). The percentage TOC removal helps to determine the rate of mineralization. However, the TOC values obtained may not present the total TOC concentrations as some of it depletion as volatile organic compounds such as formaldehyde, acetaldehyde into gaseous stream during ozone oxidation (Parsa *et al.*, 2014, Wu *et al.*, 2008).

The COD removal was more effective than TOC removal as represent in Figure 6(b). For A07, the COD removal at 20 mins contact time is 60.6% while for TOC removal is 33.3%. This ratio is almost similar to RG19 as the COD and TOC removal at 20 mins contact time is 60.9 and 32.2%, respectively. The removal efficiency for COD and TOC is relatively low compare to colour removal. At first 5 mins, the TOC removal is rapidly which is 18.1% for A07 and 17.0% for RG19. This changes point out that carbon dioxide is formed at the extremely early oxidation stage. Furthermore, the COD removal is instantaneous than TOC which specified the initial step of ozone oxidation induce the formation of intermediate organic products with little carbon dioxide produced (Faouzi Elahmadi *et al.*, 2009).

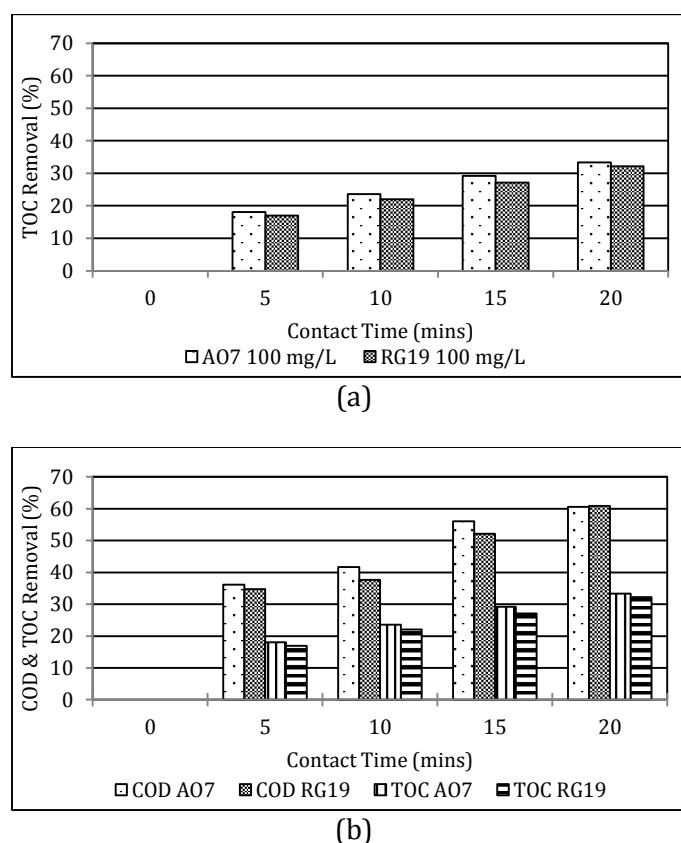
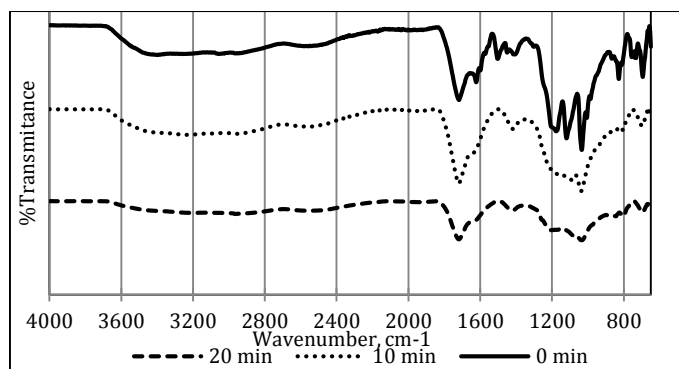


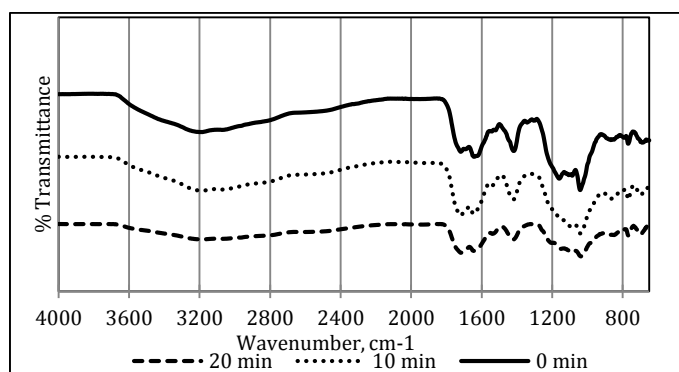
Figure 6. (a) TOC removal; (b) COD and TOC removal of A07; and RG19 with different contact time.

3.6 Functional Group Evolution

The FT-IR spectra for A07 and RG19 are shown in figure 7. The aromatic rings at interval of 870 to 670 cm^{-1} are progressively disappeared after 20 mins indicated that the ring structures in A07 and RG19 are obviously degraded. The cleavage of sulfonate groups can be seen with the peak at range 1,250 to 1,000 cm^{-1} is become weaker. The peak of hydroxyl groups, 3,664 to 3,400 cm^{-1} is become lower due to the decreased of pH (Liu *et al.*, 2007; Liu *et al.*, 2007). At contact time of 10 mins, the azo groups in region 1,630 and 1,575 cm^{-1} disappeared which imply decolourization occur as revealed in percentage colour removal and UV-Vis absorbance spectra. In the end, the intermediate products left behind mostly consist of alkene (1,680 - 1,620 cm^{-1}), ketones (1,725 - 1,705 cm^{-1}), carboxylic acids (1,725 - 1,700 cm^{-1}), amines (3,130 - 3,030 cm^{-1}) and sulfite (1,430 - 1,350 cm^{-1}).



(a)



(b)

Figure 7. FT-IR spectra for AO7 and RG19.

4. CONCLUSION

Based on the results discussed, coagulation-Fenton treatment have higher removal efficiency for SS, COD, $\text{NH}_3\text{-N}$ and turbidity by 82, 13, 54 and 86% respectively, compared with coagulation-flocculation treatment that have only COD (6%) and $\text{NH}_3\text{-N}$ (53%) while others shown negative results. The most suitable pH for coagulation Fenton and H_2O_2 concentration was 3 and 0.5 M respectively. Higher concentration produced hydroxyl radical's scavenger that caused in sludge problems. The most suitable FeCl_3 dosage was 1,000 mg/L. Enough amount of iron ions (Fe^{2+} and Fe^{3+}) were needed to produce hydroxyl radicals for degradation of organic pollutants.

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