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Influence of pH and FeSO₄ to H₂O₂ Ratio in Degradation of p-Cresol by Fenton's Reagent

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Abstract. In this study, the influence of pH and FeSO₄:H₂O₂ ratio in degradation of p-Cresol by Fenton's Reagent was evaluated. Initially, the optimum treatment conditions of p-Cresol which include pH, time and dosage ratio were examined. Subsequently, wastewater containing p-Cresol was treated with the optimum condition. Results from this study were interpreted through spectra overlay, removal percentage of p-Cresol and COD removal percentage. The experiments show that degradation of p-Cresol is more efficient when in weak acid environment. The optimum pH for p-Cresol to degrade is at pH 3.5. In this state, concentration reduction and COD reduction percentage achieved 39.44% and 58.04% respectively. The optimum time for degradation of p-Cresol was found to be 60 minutes. Beyond this time, the concentration reduction only experienced insignificant increase. As for ratio of Fenton's reagent, dosages 1:5 FeSO₄:H₂O₂ has the best reduction efficiency. Excessive of FeSO₄ will induce H₂O₂ to act as the scavenger. The COD removal efficiency of p-Cresol was affected when background wastewater matrix. The COD reduction of p-Cresol solution was 56.03% while 48.16% in rubber manufacturing wastewater. As for leachate, only 28.05% COD was reduced.

INTRODUCTION

Industrial wastewater that containing persistent organic compound (POC) will bring significant impact to the environment when untreated properly prior release to water body [1]. P-Cresol also known as 4-Methylphenol is one of POC that commonly found in landfill leachate [2]. The presence of p-Cresol in environment brought threat not only human but also to aquatic life. Its refractory nature causes it to be persistent and difficult for treatment. As for aquatic life, p-Cresols effect the water quality causing the water not suitable for aquatic life. Hence, it is necessary to treat p-Cresols in wastewater [3].

With current technology, landfill leachate can be treated biologically, physically and chemically. Among these, biological treatment may not be able to treat toxic chemicals and POC such as p-Cresol, while physical treatment can only transfer the compound to other media and not handling the real problem of POC [4]. Chemical treatment in other hands shows effective result by degrading the POC in the wastewater. Amongst chemical methods, advanced oxidation process (AOP) is proposed to be the most effective [5]. By using the concept of oxidizing with hydroxyl radical (OH•), AOP has been promising in terms of times and cost in treating p-Cresol. Fenton's Process is one of the most frequent used techniques among the AOPs [6]. Fe²⁺ is used as the catalyst while H₂O₂ is used as the oxidant. Ferrous ions will then causes dissociation of oxidation agent, forming the hydroxyl radicals which happen

to be active. The hydroxyl radical is then reacting non-selectively with most organic compound by degrading them into carbon dioxide, water and inorganic salt [7].

Fenton's process has been implemented in different type of wastewater from different industries, such as olive-oil mill wastewater, cosmetic wastewater, textile wastewater and dye wastewater, due to their high removing efficiency, simplicity and produce less residue at the end of treatment [5,6]. However, the efficiency of Fenton's process on p-Cresol decomposition that may depend on the $[\text{Fe}^{2+}]/[\text{H}_2\text{O}_2]$ ratio, pH and H_2O_2 concentration are remain unclear. Further, the organic carbon ratio, organic matter content and temperature of effluent may effect the efficiency of Fenton's Process. Hence, in this study, the performance of Fenton reagent in treating p-Cresol contained wastewater was evaluated.

METHODOLOGY

Analytical grade p-Cresol was supplied by Sigma-Aldrich. Potassium dichromate was from R&M Chemicals, while sulphuric acid was from Bendosen Laboratory Chemicals. Two types of wastewater were used in this study, raw leachate and wastewater from rubber manufacturing industry. The raw leachate was obtained from Padang Siding landfill, Perlis (Malaysia) in dark brown color and poor clarity, with initial concentration of COD was ranged between 2800-4700 mg/L. As for wastewater from rubber manufacturing industry was obtained from Sho-rubber Glove Industry, Perlis (Malaysia). Both of the wastewaters obtained were stored in a refrigerator in order to prevent reaction and raised to room temperature before used. The COD of the wastewaters was adjusted to 300 mg/L before adding in with 50 mg/L of p-Cresol.

Experimental Procedure

In this study, WISESHAKE SHO-2D Digital Orbital Shaker was used as the batch reactor to carry out Fenton reaction. The experiment was carried out in two phases, at the first phase, sample was collected every 1 minute from the reactor to study the reaction rate of Fenton's reagent. Second phase will be conducted by retrieving the sample at 10 minutes interval until 80th minute. To determine the optimum pH for p-Cresol degradation, samples were adjusted to different pH (pH 3, 5, 7, 9 and 11) by sodium hydroxide and sulphuric acid. Similar amount of Fenton's reagent was then added into the samples, and the oxidation process was conducted for similar reaction time. To evaluate the efficiency of p-Cresol degradation by Fenton's Reagent under influence of wastewater. 50 mg/L of p-Cresol was added into the wastewater sample. The p-Cresol is added into wastewater with different COD concentration and the Fenton process was conducted at the optimum time periods. The samples were then tested for p-Cresol concentration and COD reduction, and degradation spectrum via UV-Vis wavelength scan.

Analytical Methods

The concentration of p-Cresol reduction was determined via photometry scan using the calibration curve. The intermediate product was identified by using UV-Vis spectrophotometer wavelength scan and FT-NIR Perkin Elmer Spectrometer.

RESULTS AND DISCUSSION

Effect of pH

Figure 1 depict the UV-Vis Spectra overlay of p-Cresol degradation in different pH for 60 min reaction time. The peak at 295 nm indicates the presence of p-Cresol while the flattening of the curve indicates the degradation of it. The absorbance of untreated p-Cresol is at 0.93. For samples of acidic pH there is degradation of p-Cresol, since the maximum peak is lower than 0.93. At pH 3.5 the absorbance has the lowest among the samples. As for sample at weak acid, pH 5 has 0.501 maximum peak. Both samples for strong acid and weak acid have shown sign of degradation of p-Cresol. However, in neutral condition and alkaline state, there is no sign of degradation or the degradation is small. For pH 7 the maximum wavelength of p-Cresol is 0.969. Yet pH 9 sample shows a slight decrease of concentration, 0.916 while pH 11 has a 0.952 wavelength, no degradation occurred. The result shows

that degradation of p-Cresol only occurs in acidic condition while there is no reaction in neutral state and alkaline states. This may due to the characteristics of Fenton's Reaction which it can only react under acidic condition.

Figure 2 shows percentage of p-Cresol removal in different pH. Overall the reduction of p-Cresol only occurs at acidic environment, while in alkaline state there is no reaction or the reduction is rather insignificant. Among the acidic condition, pH 3.5 has the highest reduction percentage, total of 48.05%. Then follow by 44.20% from sample pH 5.0. Sample pH 3 and pH 4 has lesser concentration percent degradation compared to pH 3.5 and pH 5, 39.44% and 36.62% respectively. No reduction of p-Cresol by Fenton's reaction in alkaline state except in weak alkaline state, pH 9. The reduction is insignificant with only 1.35%. This situation may happen when iron oxide composite was applied near to slightly alkaline conditions, pH 9.

Figure 3 indicated the percentage removal of COD during Fenton oxidation of p-Cresol solution. The result showed that pH 5 has the highest COD reduction with total of 64.29% while follow by 58.04% from sample pH 3.5. There are still COD reduction for sample pH 3 and also pH 4, even though the percent reduction is not as high as the other two samples, with 43.75% and 52.68% respectively. Meanwhile there is no reduction of COD observed in neutral and alkaline state.

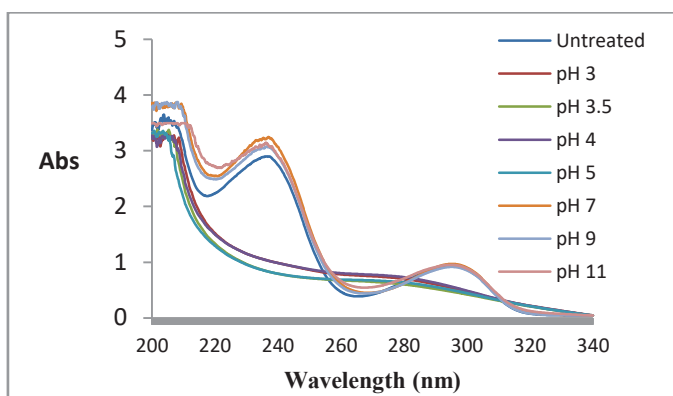


FIGURE 1. UV-Vis Spectra overlay of p-Cresol degradation in different pH (reaction time 60 min)

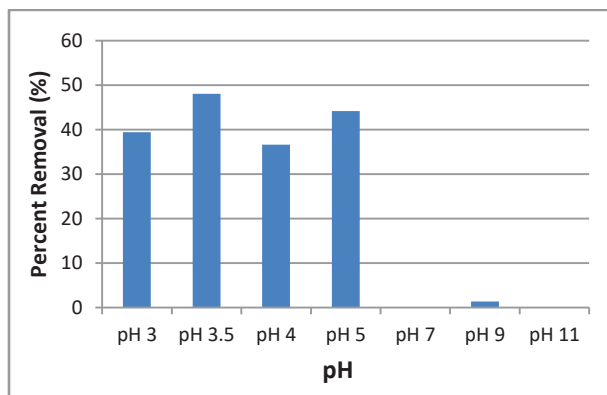


FIGURE 2. Concentration reduction percentage of p-Cresol in different pH

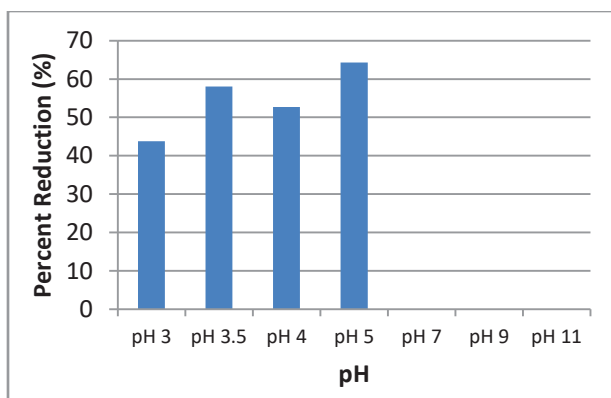
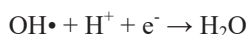


FIGURE 3. COD removal percentage of p-Cresol in different pH

Based on result shown above, pH 3.5 has better concentration reduction efficiency while pH 5 has higher efficiency in terms of COD reduction. However sample pH 5 containing a higher COD reduction efficiency may cause by the precipitation of $\text{Fe}(\text{OH})_3$ in the process. This reaction is important and may have a better treatment result in treating other types of pollutant. As for sample reaction higher than pH 5, the reduction efficiency experienced decreases not only due to the decomposition of hydrogen peroxide but also due to formation of Fe^{3+} , causing the efficiency to decrease. Meanwhile sample less than pH 3.5 experienced efficiency decreased in terms of COD can be explained the excessive amount of hydrogen oxygen, H^+ became the dominant radical scavenger of $\text{OH}\bullet$ as explain as the reaction below:



Thus it can be concluded that pH 3.5 is the optimum pH for the degradation of p-Cresol by Fenton reagent.

Effect of $\text{FeSO}_4:\text{H}_2\text{O}_2$ Ratio

Figure 4 depict the UV-Vis Spectra overlay of p-Cresol degradation in different Fe^{2+} to H_2O_2 ratio for 20 min reaction time. In overall the higher the dosage of H_2O_2 the lower the absorbance at the peak. For dosage 0:1, 1:1 and 1:2 there is no reduction at the peak from the wavelength. Furthermore, when the dosage increase to 1:5 the absorbance started to reduce. The absorbance peak decreases as the dosage increased. Besides, the reduction in absorbance of the peak increases as the Fe^{2+} to H_2O_2 ratio increased. The absorbance peak for the sample 1:15 and 1:20 reached 0.421 and 0.296 abs respectively.

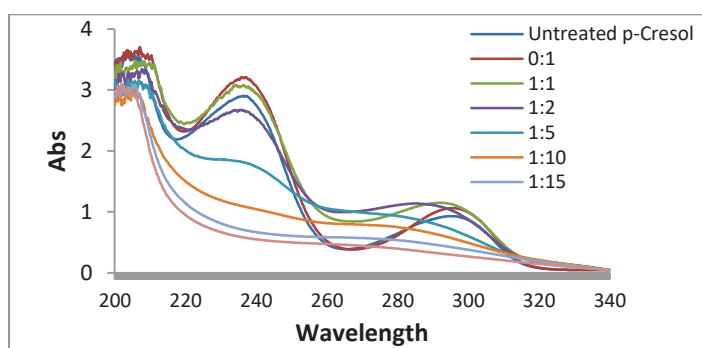


FIGURE 4. UV-Vis spectra overlay of p-Cresol at different dosage

Figure 5 shows percentage of p-Cresol removal in different Fe^{2+} to H_2O_2 ratio for 20 min reaction time. The degradation of p-Cresol improved with higher ratios of Fenton reagent. No degradation was observed when only H_2O_2 was added into the sample. Dosage 1:20 has the highest concentration reduction percentage, with total

reduction of 69.68%. It is followed by 1:15 dosage with 54.49%, and 1:10 with 35.46%. When 1:5 dosage of Fenton reagent was used for treatments, 20.78% of p-Cresol was reduced. The degradation only occurred when ratio of 1:5 Fenton reagent was added, meanwhile there was no reduction occur when the dosage is less than 1:5.

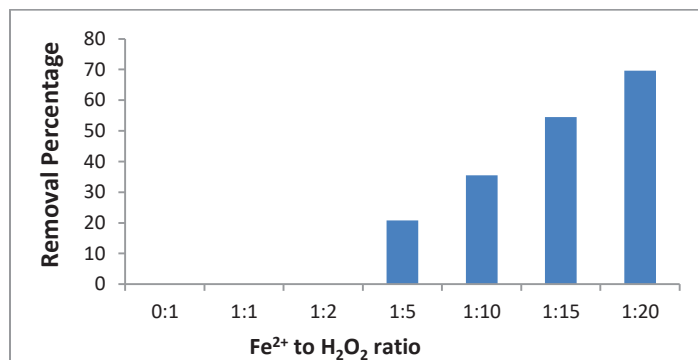


FIGURE 5. Removal percentage of p-Cresol under different dosage of Fenton's reagent.

Figure 6 indicated the percentage removal of COD during Fenton oxidation of p-Cresol in different Fe²⁺ to H₂O₂ ratio. Refer to Fig. 6, 0:1 dosage has the lowest COD reduction with only 12.83% and the reduction efficiency increased as the dosage increased. At the ratio of 1:1 and 1:2 the COD reduction was 36.90% and 39.04% respectively. The COD reduction achieved a higher state, 53.48% when the molar ratio is 1:5. However the COD reduction decreases to 48.13% and 33.16% when the dosage increased to 1:10 and 1:15 respectively.

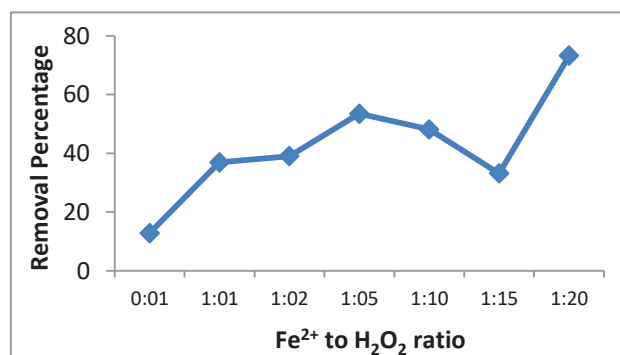


FIGURE 6. COD reduction percentage of p-Cresol at different dosage of Fenton's reagent

In terms of concentration and also COD reduction the 1:20 dosage sample showed better efficiency (69.68% and 73.26%). However, 1:5 dosage sample has the second highest COD reduction efficiency although its concentration reduction efficiency is merely 20.78%. In a Fenton's process H₂O₂ is the main source of OH•, insufficient of H₂O₂ will decrease the treatment efficiency. On the other hand, excessive H₂O₂ will cause the scavenging effect of H₂O₂ on OH•. In addition, excessive of H₂O₂ will also increase the COD of the treated sample. As shown in Fig. 6, COD reduction efficiencies have relative decrease in sample 1:10 and 1:15, this indicates that the amount of H₂O₂ was in excess.

Influence of Wastewater Matrix on p-Cresol

Figure 7 shows the percentage of p-Cresol removal in under influence of wastewater matrix. The result indicated that the COD reduction efficiency was decreased when wastewater was added into the p-Cresol. Among three different samples, p-Cresol containing distilled water has the highest reduction percentage, which is 56.03%. Rubber manufacturing wastewater achieved 48.16% of COD reduction. As for the leachate containing p-Cresol, there is only 28.05% of COD reduction.

The poor COD reduction of p-Cresol in wastewater is due to the existence other organic matters or contaminants which interfered the oxidation process during treatment. Moreover, the reaction of oxidant or free radical and the organic matters or contaminants will form other by-products. These by-products might be more resistant to oxidation, resulting in the lower overall COD reduction. However, detail experimental study such as the feeding method of H₂O₂ [8] and treatment time for the wastewater [9] can be conducted to study the optimum treatment condition for each wastewater.

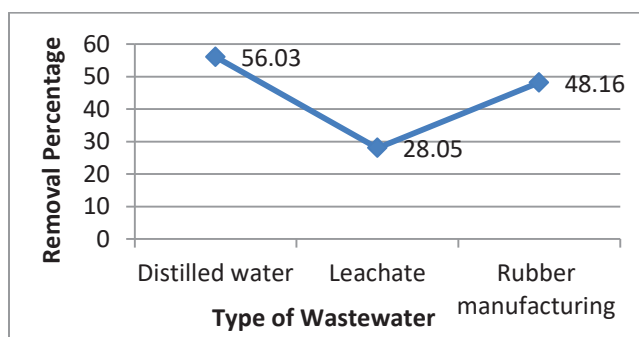


FIGURE 7. Percentage of COD removal of p-Cresol under influence of wastewater matrix

SUMMARY AND CONCLUSIONS

In this study, the influence of pH and FeSO₄:H₂O₂ ratio in degradation of p-Cresol by Fenton's Reagent was evaluated. The conclusions that can be derived from this study are as follows:

- The experiments show that degradation of p-Cresol is more efficient when in the state of weak acid. The optimum pH for p-Cresol to degrade is at pH 3.5. In this state, concentration reduction and COD reduction percentage achieved 39.44% and 58.04% respectively. The optimum time for degradation of p-Cresol was found to be 60 minutes. Beyond this time, the concentration reduction only experienced insignificant increase. As for ratio of Fenton's reagent, dosages 1:5 FeSO₄:H₂O₂ has the best reduction efficiency. Excessive of FeSO₄ will induce H₂O₂ to act as the scavenger.
- The COD removal efficiency of p-Cresol was affected when background wastewater matrix. The COD reduction of p-Cresol solution was 56.03% while 48.16% in rubber manufacturing wastewater. As for leachate, only 28.05% COD was reduced.

REFERENCES

1. S-H. Kow, M. R. Fahmi, C. Z. A. Abidin, S-A. Ong, A. H. Ibrahim, S. N. Sabri and N. A. Razali, *Sains Malaysiana* **47**(6), 1085-1091 (2018).
2. S-H. Kow, M. R. Fahmi, C. Z. A. Abidin, S-A. Ong and S. N. Sabri, *Australian Journal of Basic and Applied Sciences* **11**(3), 71-78 (2017).
3. V. Kavitha and K. Palanivelu, *Water Research* **39**(13), 3062-3072 (2005).
4. S-H. Kow, M. R. Fahmi, C. Z. A. Abidin and S-A. Ong, *Water Environment Research* **88**(11), 2047-2058 (2016).
5. B. Bianco, I. D. Michelis and F. Veglio, *Journal of Hazardous Materials* **186**(2-3), 1733-1738 (2011).
6. N. Wang, T. Zheng, G. Zhang and P. Wang, *Journal of Environmental Chemical Engineering* **4**(1), 762-787 (2016).
7. E. Neyens and J. Baeyens, *Journal of Hazardous Materials* **98**(1-3), 33-50 (2003).
8. A. Mashal, J. A. Daherieh, M. Ahmad, F. Aiouache and D. Rooney, "Fenton's Catalytic Oxidation Process to Treat Landfill Leachate", in *The Sixth Jordan International Chemical Engineering Conference 2012*, (Amman, Jordan, 2012), Vol 1.
9. L. Wang, Q. Yang, D. Wang, X. Li, G. Zeng, Z. Li, Y. Deng, J. Liu and K. Yi, *Journal of Hazardous Materials* **318**, 460-467 (2016).