Enhancement of activated sludge disintegration and dewaterability by Fenton process

G C Heng¹ and M H Isa
Department of Civil and Environmental Engineering,
Universiti Teknologi PETRONAS, 32610 Bandar Seri Iskandar, Perak, Malaysia

E-mail: chgan26@gmail.com, hasnain_isa@petronas.com.my

Abstract. Municipal and industrial wastewater treatment plants produce large amounts of sludge. This excess sludge is an inevitable drawback inherent to the activated sludge process. In this study, the waste activated sludge was obtained from the campus wastewater treatment plant at Universiti Teknologi PETRONAS (UTP), Malaysia. Fenton pretreatment was optimized by using the response surface methodology (RSM) to study the effects of three operating conditions including the dosage of \( \text{H}_2\text{O}_2 \) (g \( \text{H}_2\text{O}_2 \)/kg TS), the molar ratio of \( \text{H}_2\text{O}_2/\text{Fe}^{2+} \) and reaction time. The optimum operating variables to achieve MLVSS removal 65%, CST reduction 28%, sCOD 11000 mg/L and EPS 500 mg/L were: 10 000 g \( \text{H}_2\text{O}_2 \)/kg TS, \( \text{H}_2\text{O}_2/\text{Fe}^{2+} \) molar ratio 70 and reaction time 45 min. Fenton process was proved to be able to enhance the sludge disintegration and dewaterability.

1. Introduction
Sludge production in the industrialized world has steadily been increasing during the last decades due to biological processes for treating wastewater [1]. Though these processes are effective in treating wastewater to ensure minimum residual impact on the aquatic environment, they have the serious drawback of producing huge amounts of excess sludge. With more stringent disposal regulations, this has caused a demand for more efficient sludge conditioning and dewatering techniques to reduce the volume of sludge in order to lower cost of processing as well as transport and disposal of sludge.

Pretreatment methods are attracting much attention for their suitability to alter the structure and composition of the biomass and hence enhance sludge stabilization. These methods disrupt cell walls which result in lysis or disintegration of sludge cells. Organic materials are converted to low molecular weight and readily biodegradable compounds, thus bypassing the rate-limiting hydrolysis stage. Different sludge disintegration methods have been tested such as acid/alkaline treatment [2–4], chemical oxidation [5,6], sonication [4], thermal treatment [4,7] and electrical treatment [8]. Fenton process is an advanced oxidation process (AOP) that utilizes activation of ferrous (Fe\(^{2+}\)) ion and hydrogen peroxide (\( \text{H}_2\text{O}_2 \)) to catalyze the formation of hydroxyl radicals (•OH) in acidic condition according to Reaction [9]. Past studies showed pH 3 to be optimum pH for Fenton treatment [10,11].

\[
\text{Fe}^{2+} + \text{H}_2\text{O}_2 \rightarrow \text{Fe}^{3+} + \cdot \text{OH} + \text{OH}^- 
\]

¹ To whom any correspondence should be addressed.
Fenton process has been applied on activated sludge [11–14]. In Fenton process, the microbial cells in sludge burst and the bound water is released; hence improving sludge dewaterability. A common characteristic of different sludges is the very high water content. Consequently, a reduction of sludge volume is generally required before handling and disposal. Due to their relatively low energy consumption, mechanical processes such as filter presses or centrifuges are often used for dewatering, albeit with low efficiency. Sludge dewatering is difficult mainly because of the colloidal nature of particles and the gel-like structure of the flocculated system known as extracellular polymeric substances (EPS) [15]. Proteins and polysaccharides are two of the predominant organic components of EPS; the total mass has been found to represent up to 80% of the mass of activated sludge [16]. Considering the high water binding properties of EPS, it is concluded that the dewatering efficiency of activated sludge can be increased by degrading the EPS. The objective of this paper was to investigate the effectiveness of Fenton process in enhancement of sludge disintegration and dewaterability.

2. Materials and methods
In this study, waste activated sludge (WAS) was obtained at the return pipe from secondary clarifier sludge hopper of a municipal wastewater treatment plant in Universiti Teknologi PETRONAS. The sludge samples were thickened to the required solids concentration and stored in the cold room prior to use. The characteristics (range from triplicate samples) of the raw samples are presented in Table 1.

| Parameter                              | Unit  | Value (mean) |
|----------------------------------------|-------|--------------|
| pH                                     | -     | 6.27         |
| Total solids (TS)                      | mg/L  | 29470        |
| Volatile solids (VS)                   | mg/L  | 18270        |
| Mixed liquor suspended solids (MLSS)   | mg/L  | 25391.3      |
| Mixed liquor volatile suspended solids (MLVSS) | mg/L  | 16000        |
| Soluble chemical oxygen demand (sCOD) | mg/L  | 1154.4       |
| Capillary suction time (CST)           | s     | 120          |
| Extracellular polymeric substances (EPS)| mg/L | 395.2        |

2.1. Experimental procedures and data analysis
The Fenton process was performed in a 500-mL Pyrex reactor using 250 mL of the activated sludge at pH 3. Ferrous sulfate (FeSO₄•7H₂O) and hydrogen peroxide (H₂O₂) were added according to the selected dosage of H₂O₂ (g H₂O₂/kg TS) and the molar ratio of H₂O₂/Fe²⁺ simultaneously. The mixture was stirred continuously to ensure complete homogeneity during reaction. Aliquots were taken at selected reaction time, adjusted to pH above 10 with sodium hydroxide and mixed for 10 min to avoid interference by H₂O₂ in COD determination [17]. Design expert software (version 6.0.7) was used for statistical design of experiment and data analysis. Central composite design (CCD) and response surface methodology (RSM) were applied to optimize the three important operating variables of the Fenton process: dosage of H₂O₂ (g H₂O₂/kg TS), molar ratio of H₂O₂/Fe²⁺ and reaction time. A total of 20 experimental runs were set and the experimental data were fitted to the empirical second order polynomial model of a suitable degree for the optimum conditions of sludge treatment by the Fenton process. The study ranges were chosen as 464-1136 g H₂O₂/kg TS, 26-94 molar ratio of H₂O₂/Fe²⁺ and reaction time 34.8-85.2 min based on the preliminary tests. In order to obtain the optimum operating conditions, four parameters were analyzed as responses: MLVSS removal (%), CST reduction (%), sCOD concentration and EPS (total protein and polysaccharides) concentration. Regression analyses, graphical analyses and analyses of variance (ANOVA) were conducted using the design expert software. The optimum region was identified based on the main parameters in the overlay plot.
2.2. Analytical methods
Solids analysis was made according to Standard Methods [18]. sCOD was measured by the Reactor Digestion HACH Method No. 8000 [19]. Capillary suction time (CST) was measured using Triton type 319 Multi-CST (Triton Electronics Ltd.). Protein and polysaccharide concentrations were measured by Bicinchoninic acid (BCA) method [20] and sulfuric acid-UV method [21], respectively.

3. Results and Discussion
The effect of Fenton treatment was studied to evaluate the optimum operating conditions in terms of organic matter solubilization and hence to improve the disintegration and dewaterability of sludge.

3.1. Statistical analysis
ANOVA results for the response surface quadratic model are shown in Table 2. Adequate precision (AP) compares the range of the predicted values at the design points with the average prediction error. Ratios greater than 4 indicate adequate model discrimination and justify navigation of the design space defined by the CCD. AP for all the responses was greater than 4 in this study. The coefficient of variance (CV) is the ratio of the standard error of estimate to the mean value of the observed response and defines reproducibility of the model. A model normally can be considered reproducible if its CV is not greater than 10% [22]. All of the responses are less than 10% except CST reduction. The $R^2$ value gives the proportion of the total variation in the response predicted by the model. The $R^2$ value was found to be close to 1 indicating that the regression model explained the prediction well [23].

3.2. Process analysis
The response surface plots for MLVSS removal, CST reduction, sCOD and EPS are shown as two-dimensional contour plots on the dosage of $H_2O_2$/kg TS and $H_2O_2$/Fe$^{2+}$ molar ratio at reaction time 1 h (Figure 1). The maximum MLVSS removal, maximum CST reduction, maximum sCOD and minimum EPS were 70.2%, 34.7%, 11627.4 mg/L and 423.2 mg/L at about 600-1000 g $H_2O_2$/kg TS and $H_2O_2$/Fe$^{2+}$ molar ratio 60-80 at 1 h reaction time. Figure 1(a) shows MLVSS removal was increasing with the increase in $H_2O_2$ dose and $H_2O_2$/Fe$^{2+}$ molar ratio. This was presumably due to the fact that increased $H_2O_2$ dose produced more hydroxyl radicals leading to higher substrate degradation [24]. On the other hand, higher molar ratio of $H_2O_2$/Fe$^{2+}$ consumes lesser ferrous salts and hence contributes lesser iron sludge. Figure 1(b) shows the CST reduction reached the maximum value of about 35% at 800-900 g $H_2O_2$/kg TS and $H_2O_2$/Fe$^{2+}$ molar ratio 60-70 and reaction time 1h. Further increase of $H_2O_2$ dose or Fe$^{2+}$ did not improve the removal efficiency. This was due to scavenging of •OH radicals (Reaction 2) [17]. This leads to the production of hydroperoxyl radical, a species with much weaker oxidizing power compared to hydroxyl radical [25]. On the other hand, excess Fe$^{2+}$ and organic compounds compete to react with hydroxyl radicals and thus affect the efficiency in terms of MLVSS removal and sCOD concentration as in Reaction 3 [26].

•OH + $H_2O_2$ $\rightarrow$ HO•$_2$ + $H_2O$  \hspace{1cm} (2)
Fe$^{2+}$ + •OH $\rightarrow$ Fe$^{3+}$ + OH$^-$ \hspace{1cm} (3)

| Table 2. ANOVA for response surface quadratic model |
|-----------------------------------------------|
| Response                      | AP      | CV     | $R^2$ |
|---------------------------------|---------|--------|-------|
| Response                       | 11.529  | 6.65   | 0.8854 |
| MLVSS removal (%)              | 10.757  | 34.86  | 0.9194 |
| CST reduction (%)              | 9.658   | 5.67   | 0.8864 |
| sCOD                           | 10.903  | 8.87   | 0.9162 |
| EPS                            | 11.529  | 6.65   | 0.8854 |
Figures 1(c) and 1(d) show that sCOD and EPS concentrations increased with increase of H$_2$O$_2$ dose due to release of cellular substances and EPS from activated sludge into the aqueous phase. Sludge dewaterability deteriorates with the increase of the EPS concentration. Higher dosages not only disrupt floc structures and cell membranes but also reduce floc size and increase the concentration of EPS [8]. While lower dosages would only destroy the sludge surface and some organic substance would be degraded. The effect of reaction time (results not shown) shows that the MLVSS removal and EPS concentration increased when the reaction time increased. However, CST reduction and sCOD decreased with the increase of reaction time. Soluble organic matters (mainly protein and polysaccharides) in the inner fraction of sludge flocs could become soluble and released to the slime owing to the pretreatment, resulting in deterioration of sludge dewaterability [8]. It could be that soluble EPS had strong water binding capability and affect sludge dewaterability. Increase of reaction time above 1 h did not reduce sCOD significantly due to rapid breakdown of organics within 1 h.

3.3. Process optimization

With multiple responses, the optimum operating variables where all parameters simultaneously meet the desirable response criteria could be visualized graphically by superimposing the contours of the response surfaces in an overlay plot. Graphical optimization displays the area of feasible response value in the factor space and the regions that do fit the optimization criteria would be shaded. In order to obtain a moderately precise optimum zone, response limits as the minimum permissible values were chosen for each parameter close to their acquired levels – MLVSS removal 65%, CST reduction 28%, sCOD 11000 mg/L and EPS 500 mg/L (Figure 2). The shaded region shows the optimum parameters – 1000 g H$_2$O$_2$/kg TS, H$_2$O$_2$/Fe$^{2+}$ molar ratio 70 and reaction time 45 min and constitute the optimum operating variables (conditions). The results agreed well with literature; optimum dosage of H$_2$O$_2$/kg
TS in the range 400-1000 \([11,12,14]\) and optimum \(\text{H}_2\text{O}_2/\text{Fe}^{3+}\) molar ratio at 40 [14] reported for Fenton treatment of activated sludge.

Figure 2. Overlay plot for optimal region at reaction time 45 min

4. Conclusions
CCD and RSM were used with three operating variables viz. dosage of \(\text{H}_2\text{O}_2\) (g \(\text{H}_2\text{O}_2/\text{kg TS}\)), molar ratio of \(\text{H}_2\text{O}_2/\text{Fe}^{3+}\) and reaction time to investigate their interactive effects on the MLVSS removal, CST reduction, sCOD and EPS concentration from activated sludge samples by the Fenton process. The optimum operating variables to achieve MLVSS removal 65%, CST reduction 28%, sCOD 11000 mg/L and EPS 500 mg/L were: 1000 g \(\text{H}_2\text{O}_2/\text{kg TS}\), \(\text{H}_2\text{O}_2/\text{Fe}^{3+}\) molar ratio 70 and reaction time 45 min. The study has revealed that RSM is a useful tool to optimize the treatment process and Fenton is an effective pretreatment of activated sludge for sludge disintegration and dewaterability.

References
[1] Feng X, Deng J, Lei H, Bai T, Fan Q and Li Z 2009 Bioresour. Technol. 100 1074–81
[2] Liao B Q, Allen D G, Leppard G G, Droppo I G and Liss S N 2002 J. Colloid Interface Sci. 249 372–380
[3] Chen Y, Yang H and Gu G 2001 Water Res. 35 2615–20
[4] Apul O G, Atalar I, Zorba G T and Sanin F D 2010 Dry. Technol. 28 901–909
[5] Neyens E, Baeyens J, Dewil R and De heyder B 2004 J. Hazard. Mater. 106 83–92
[6] Kwon J H, Ryu S H, Park K-Y, Yeom I-T and Ahn K-H 2001 J. Chin. Inst. Chem. Eng. 32 555–558
[7] Neyens E and Baeyens J 2003 J. Hazard. Mater. 98 51–67
[8] Yuan H, Zhu N and Song F 2011 Bioresour. Technol. 102 2308–15
[9] Yoon J, Lee Y and Kim S 2001 Water Sci. Technol. J. Int. Assoc. Water Pollut. Res. 44 15–21
[10] Mohajeri S, Aziz H A, Isa M H, Zahed M A and Adlan M N 2010 J. Hazard. Mater. 176 749–758
[11] Şahinkaya S, Kalîpcî E and Aras S 2015 Process Saf. Environ. Prot. 93 274–281
[12] Dewil R, Baeyens J and Neyens E 2005 J. Hazard. Mater. 117 161–170
[13] Erden G and Filibeli A 2010 Desalination 251 58–63
[14] He M and Wei C 2010 P J. Hazard. Mater. 176 597–601
[15] Dursun D and Denel S K 2009 Water Sci. Technol. J. Int. Assoc. Water Pollut. Res. 59 1679–85
[16] Frølund B, Palmgren R, Keiding K and Nielsen P H 1996 Water Res. 30 1749–58
[17] Andreozzi R, Canterino M, Marotta R and Paxeus N 2005 J. Hazard. Mater. 122 243–250
[18] APHA 2005 Standard methods for the examination of water and wastewater. (Washington D.C., USA: American Public Health Association)
[19] HACH 2003 Water analysis handbook (Loveland, CO, USA: Hach Company)
[20] Zuriaga-Agustí E, Bes-Piá A, Mendoza-Roca J A and Alonso-Molina J L 2013 Sep. Purif. Technol. 112 1–10
[21] Albalasmeh A A, Berhe A A and Ghezzehei T A 2013 Carbohydr. Polym. 97 253–261
[22] Beg Q K, Sahai V and Gupta R 2003 Process Biochem. 39 203–209
[23] Ölmez T 2009 J. Hazard. Mater. 162 1371–78
[24] Deng Y and Englehardt J D 2006 Water Res. 40 3683–94
[25] Ting W-P, Lu M-C and Huang Y-H 2009 J. Hazard. Mater. 161 1484–90
[26] Mohajeri S, Aziz H A, Isa M H, Bashir M J K, Mohajeri L and Adlan M N 2010 J. Environ. Sci. Health Part A Tox. Hazard. Subst. Environ. Eng. 45 692–698