Effect of H$_2$O$_2$ Oxidation/Alkaline Hydrolysis on Waste Activated Sludge Disintegration and Dewaterability

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Abstract. In the present study, the effect of hydrogen peroxide oxidation/alkaline hydrolysis was investigated on waste activated sludge (WAS), to enhance its disintegration and dewaterability. The effects of three operating parameters viz., pH, H$_2$O$_2$ dose and reaction time, on the degree of WAS disintegration and dewaterability were assessed using response surface methodology. The optimum operating variables to achieve VSS removal 20%, CST reduction 20%, sCOD 6100 mg/L and EPS 455 mg/L were: pH 10.5, 1300 g H$_2$O$_2$/kg TS and 40 min reaction time. Results showed that WAS can be efficiently disintegrated and dewatered by H$_2$O$_2$ oxidation/alkaline hydrolysis for subsequent biological digestion.

1 Introduction

In the process of treating wastewater, sludge is generated as a by-product. In general, the production of sludge is relates to the character of the raw wastewater and processing units employed. Satisfactory waste activated sludge (WAS) processing and disposal can be a complex and expensive operation in a municipal wastewater treatment system [1]. The sludge consists of materials settled from the raw wastewater and solids generated in the wastewater treatment processes. The WAS withdrawn from the treatment process is still in high water content. Sludge treatment processes, hence, are essentially concerned with separating the huge amount of water from the solid residues. Efficient sludge management is among the most challenging issues in wastewater treatment today, and biological digestion is considered as a viable solution. Therefore, disintegration and dewaterability of WAS is regarded as a pre-requisite for biological digestion to enhance the reduction of the volume of sludge. Sludge dewatering is challenging due to the existence of extracellular polymeric substances (EPS) which has high affinity for water [2]. Proteins and polysaccharides are the major organic components in EPS and it constitutes 80% of the mass of WAS [3].

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Hydrogen peroxide (H$_2$O$_2$) has been widely applied in water treatment processes as well as in industrial applications. H$_2$O$_2$ may generate a wide range of reactive species (free radicals) that are able to decompose organic matters when catalyzed in water. However, the limitation of H$_2$O$_2$ oxidation was obvious with the absence of catalysts due to the poor reaction rates at a decent amount of H$_2$O$_2$. Nevertheless, improvements can be achieved by using alkaline hydrolysis as suggested by Kim and co-authors [4]. Alkali treatment is normally combined with other treatments [5-7] and found to work well in sludge solubilization, of its efficiency in the sequence of NaOH> KOH> Mg(OH)$_2$ [8]. [4] studied the combined alkaline and H$_2$O$_2$ oxidation to enhance the efficiency of sludge pretreatment by assessing the total solids concentration and particle size distribution. The results showed that total solids can be reduced by 49% whereas sludge particle size decreased from 34.5 µm to 10.8 µm (diameter) at pH 11 and 1800 g H$_2$O$_2$/kg TS dose. Generally, the efficiency of H$_2$O$_2$ oxidation increases with increase in H$_2$O$_2$ concentration. The increased amount of H$_2$O$_2$ reacts and produces more hydroxyl radicals leading to higher sludge disintegration as in advanced oxidation process but in lower rate comparatively. However, excess H$_2$O$_2$ results in auto-decomposition of excessive H$_2$O$_2$ [9] and residual H$_2$O$_2$ may inhibit downstream biological treatment.

We have previously studied the sludge solubilization in terms of disintegration and dewaterability by H$_2$O$_2$ oxidation under different conditions (H$_2$O$_2$ alone, H$_2$O$_2$ with acid/alkaline hydrolysis) [10]. Results showed that H$_2$O$_2$ oxidation/alkaline hydrolysis enhanced the sludge solubilization most significantly. In this study, further studies were applied by optimizing the H$_2$O$_2$ oxidation/alkaline hydrolysis using response surface methodology (RSM). The regression model and analysis of variance (ANOVA) was applied to identify the parametric significance statistically. The influences of parameters were presented in response surface plots. Finally, three additional experiments were performed to verify the model prediction.

### 2 Materials and methods

#### 2.1 Material and analytical methods

The WAS was obtained from Universiti Teknologi PETRONAS municipal wastewater treatment plant. The sludge samples were settled and dewatered to a desired concentration at about 3% total solids (TS) and kept at 4°C prior to use. Table 1 shows the characteristics (based on triplicate samples) of the raw sludge.

| Parameter                           | Unit   | Value (mean) |
|-------------------------------------|--------|--------------|
| pH                                  |        | 5.81         |
| Total solids (TS)                   | mg/L   | 29268        |
| Volatile suspended solids (VSS)     | mg/L   | 18146        |
| Soluble chemical oxygen demand (sCOD) | mg/L   | 1127.2       |
| Capillary suction time (CST)        | s      | 109          |
| Extracellular polymeric substances (EPS) | mg/L   | 410.2        |

The pH was measured using a pH meter (HACH sension 4). Solids tests were analyzed according to Standard Methods [11]. sCOD was measured by a HACH spectrophotometer (DR2800) [12]. CST measurement was performed using Triton type 319 Multi-CST (Triton Electronics Ltd.). EPS concentrations were measured by Bicinchoninic acid (BCA) method [13] and sulfuric acid-UV method [14] for protein and polysaccharide, respectively.
2.2 Experimental procedures and data analysis

The H\textsubscript{2}O\textsubscript{2} oxidation/alkaline hydrolysis process was performed using 250 mL WAS. The pH of WAS was pre-adjusted using 1 N sodium hydroxide followed by adding a pre-selected dosage of H\textsubscript{2}O\textsubscript{2}. The mixture was stirred at a constant rate and the aliquots were taken for the measurement of solids (TS and VSS), sCOD, CST and EPS after the pre-selected reaction time.

Response surface methodology (RSM) and central composite design (CCD) were applied to optimize the three operating variables of the H\textsubscript{2}O\textsubscript{2} oxidation/alkaline hydrolysis process: pH, dosage of H\textsubscript{2}O\textsubscript{2} (g H\textsubscript{2}O\textsubscript{2}/kg TS) and reaction time. Twenty experimental runs were generated by the Design Expert software for the optimum conditions to be achieved (Table 2). The ranges were studied at pH 9.32-12.68, 829.6-1670.4 g H\textsubscript{2}O\textsubscript{2}/kg TS and reaction time 23.18-56.82 min based on our previous study [10]. VSS removal (%), CST reduction (%), sCOD concentration and EPS (total protein and polysaccharides) concentration were analyzed as responses to acquire the optimum operating conditions. The optimum operating conditions of the process was determined from the overlay plot by superimposing the contour plots.

| Run no. | A: pH | B: H\textsubscript{2}O\textsubscript{2} dosage (g H\textsubscript{2}O\textsubscript{2}/kg TS) | C: Reaction Time (min) |
|---------|-------|---------------------------------|-----------------------|
| 1       | 10    | 1500                            | 50                    |
| 2       | 11    | 1250                            | 40                    |
| 3       | 11    | 1250                            | 40                    |
| 4       | 10    | 1000                            | 50                    |
| 5       | 9.32  | 1250                            | 40                    |
| 6       | 11    | 829.55                          | 40                    |
| 7       | 11    | 1250                            | 40                    |
| 8       | 12    | 1500                            | 50                    |
| 9       | 10    | 1500                            | 30                    |
| 10      | 12    | 1000                            | 30                    |
| 11      | 11    | 1250                            | 23.18                 |
| 12      | 11    | 1670.45                         | 40                    |
| 13      | 10    | 1000                            | 30                    |
| 14      | 12    | 1500                            | 30                    |
| 15      | 11    | 1250                            | 56.82                 |
| 16      | 12    | 1000                            | 50                    |
| 17      | 11    | 1250                            | 40                    |
| 18      | 11    | 1250                            | 40                    |
| 19      | 11    | 1250                            | 40                    |
| 20      | 12.68 | 1250                            | 40                    |

3 Results and discussion

3.1 Statistical analysis

Table 3 shows the ANOVA results of each response. The model is statistically significant (p < 0.05) for the four responses in this process. For ratio of adequate precision (AP) greater than 4, it indicates acceptable value for model discrimination [15]. All of the
responses’ AP were exceeding 4. R² value gives the quality of the polynomial fitting model. The R² values for all the responses were closed to 1 showed that the model data agreed well with the experimental results [16].

| Response      | Model  | Adequate Precision (>4) | R²  |
|---------------|--------|--------------------------|-----|
| VSS removal   | 0.0001 | 14.045                   | 0.9273 |
| sCOD          | 0.0004 | 11.867                   | 0.9104 |
| CST reduction | 0.0045 | 9.229                    | 0.8464 |
| EPS           | 0.0019 | 10.269                   | 0.8734 |

### 3.2 Process analysis

The three-dimensional response surface plots represent the responses as function of pH and dosage of H₂O₂/kg TS at reaction time 40 min (Fig. 1). The highest VSS removal, sCOD, CST reduction and lowest EPS were 24%, 9333 mg/L, 29.2% and 392 mg/L, respectively at pH 11-12.5. The figure shows VSS removal, sCOD, CST reduction and EPS increased with the increase in pH. When alkali is added to a sludge sample, the cell undergoes disruption followed by cell lysis [17]. The hydrolysis rate of WAS was accelerated at pH > 7, which was in good agreement with other researchers [18, 19]. Past researchers [20] revealed that desorption occurred in EPS due to high electrostatic repulsion on bacteria surfaces with the addition of alkali. However, sCOD and CST reduction were not enhanced appreciably at pH > 12. One possible reason is that the soluble EPS deteriorated the sludge dewaterability because of its high water affinity [21]. The highest VSS removal, sCOD, CST reduction and lowest EPS were 24%, 9333.3 mg/L, 32.5% and 422.1 mg/L, respectively at 1200–1500 g H₂O₂/kg TS, in good agreement with Kim et al. [4] who have found the most effective H₂O₂ dose at ≈1800 g H₂O₂/kg TS. With the increase in dosage of H₂O₂, VSS removal, sCOD, CST reduction and EPS increased significantly. With the increased of H₂O₂ dose, there is a higher chance to produce more hydroxyl radicals (•OH), subsequently causing a higher substrate degradation [22]. The •OH oxidize organics (RH) by abstraction of protons producing organic radicals (R•), which are highly reactive and can be further oxidized [23-24]. This was due to scavenging of •OH that enhances the production of hydroperoxyl radical (HO•₂), which has lower oxidizing power as compared to •OH [25]. Besides, excessive amount of H₂O₂ can cause the recombination of •OH radicals and auto decomposition of H₂O₂ to H₂O and O₂ [26], which can reduced the degradation efficiency.
The $R^2$ value gives the quality of the polynomial fitting model. The $R^2$ values for all the responses were close to 1 showed that the model data agreed well with the experimental results. 

Table 3. ANOVA for response surface quadratic model.

| Response | Model | Adequate Precision (>4) | $R^2$ | VSS removal | sCOD | CST reduction | EPS |
|----------|-------|--------------------------|-------|-------------|------|--------------|-----|
| VSS removal | 0.0001 | 14.045 | 0.9273 |
| sCOD      | 0.0004 | 11.867 | 0.9104 |
| CST reduction | 0.0045 | 9.229 | 0.8464 |
| EPS       | 0.0019 | 10.269 | 0.8734 |

3.3 Process optimization

The optimum operating conditions could be identified by superimposing the contour plots of various responses which is known as an overlay plot. The range of response limits (minimum permissible values) were set for each parameter close to their obtained efficiencies: VSS removal 20%, sCOD 6100 mg/L, CST reduction 20% and EPS 455 mg/L as shown in Fig. 2.

**Fig. 1.** Response surface plots of (a) VSS removal, (b) sCOD, (c) CST reduction and (d) EPS as a function of pH and dosage of H$_2$O$_2$/kg TS at reaction time 40 min.
Verification test were examined by conducting three experiments in the optimum region (pH 10.5, 1300 g H$_2$O$_2$/kg TS and 40 min reaction time) achieved from the model. The treatment efficiency obtained from the experiments and model were agreed well with less than 15% error (Table 4).

| Response          | Model response | Experimental values (mean) | Error (%) |
|-------------------|----------------|---------------------------|-----------|
| VSS removal (%)   | 20             | 22.6-24.8 (23.5)          | 14.9      |
| sCOD (mg/L)       | 6100           | 5500-5800 (5666.7)        | 7.6       |
| CST reduction (%) | 20             | 21.6-22.8 (22.1)          | 9.5       |
| EPS (mg/L)        | 455            | 402-438 (420.7)           | 8.2       |

4 Conclusions

H$_2$O$_2$ oxidation/alkaline hydrolysis was observed to be optimum at 10.5 pH, 1300 g H$_2$O$_2$/kg TS and 40 min reaction time for 20% VSS removal, sCOD 6100 mg/L, 20% CST reduction and 455 mg/L EPS. RSM performed exceptionally well in optimizing treatment process with more than two interfering parameters which is required to meet the objective of the study while satisfying different constraints. For instance, EPS was maintained at low concentration to improve the sludge dewaterability because CST is highly correlated with EPS. H$_2$O$_2$ oxidation/alkaline hydrolysis was found to be an adequate pretreatment of WAS to enhance its disintegration and dewaterability.

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Table 4. Experimental removal efficiency and model prediction.

| Response        | Model response | Experimental values (mean) | Error (%) |
|-----------------|----------------|---------------------------|-----------|
| VSS removal (%) | 22.6           | 24.8 (23.5)               | 14.9      |
| sCOD (mg/L)     | 5500           | 5800 (5666.7)             | 7.6       |
| CST reduction (%)| 21.6          | 22.8 (22.1)               | 9.5       |
| EPS (mg/L)      | 402            | 438 (420.7)               | 8.2       |

Conclusions

H2O2 oxidation/alkaline hydrolysis was observed to be optimum at 10.5 pH, 1300 g H2O2/kg TS and 40 min reaction time for 20% VSS removal, sCOD 6100 mg/L, 20% CST reduction and 455 mg/L EPS. RSM performed exceptionally well in optimizing treatment process with more than two interfering parameters which is required to meet the objective of the study while satisfying different constraints. For instance, EPS was maintained at low concentration to improve the sludge dewaterability because CST is highly correlated with EPS.

H2O2 oxidation/alkaline hydrolysis was found to be an adequate pretreatment of WAS to enhance its disintegration and dewaterability.

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