Effect of H_2O_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_2O_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_2O_2/kg TS and 40 min reaction time. Results showed that WAS can be efficiently disintegrated and dewatered by H_2O_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 The WAS withdrawn from the treatment process is still in high water content.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_2O_2) has been widely applied in water treatment processes as well as in industrial applications. H_2O_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_2O_2 oxidation was obvious with the absence of catalysts due to the poor reaction rates at a decent amount of H_2O_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_2O_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_2O_2/kg TS dose. Generally, the efficiency of H_2O_2 oxidation increases with increase in H_2O_2 concentration. The increased amount of H_2O_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_2O_2 results in auto-decomposition of excessive H_2O_2 [9] and residual H_2O_2 may inhibit downstream biological treatment.

We have previously studied the sludge solubilization in terms of disintegration and dewaterability by H_2O_2 oxidation under different conditions (H_2O_2 alone, H_2O_2 with acid/alkaline hydrolysis) [10]. Results showed that H_2O_2 oxidation/alkaline hydrolysis enhanced the sludge solubilization most significantly. In this study, further studies were applied by optimizing the H_2O_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.

Table 1. Characteristics of raw waste activated 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_2O_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_2O_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_2O_2 oxidation/alkaline hydrolysis process: pH, dosage of H_2O_2 (g H_2O_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_2O_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.

Table 2. CCD for study of operating conditions of hydrogen peroxide oxidation.

Run no.	Experimental Design		
	A: pH	B: H_2O_2 dosage (g H_2O_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. R^2 value gives the quality of the polynomial fitting model. The R^2 values for all the responses were closed to 1 showed that the model data agreed well with the experimental results [16].

Table 3. ANOVA for response surface quadratic model.

Response	Model	Adequate Precision (>4)	R^2
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 H_2O_2/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 occured in EPS due to high electrostatic repulsion on bacteria surfaces with the addition of alkali. However, sCOD and CST reduction were not enhanced appreaciably 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 H_2O_2/kg TS, in good agreement with Kim et al. [4] who have found the most effective H_2O_2 dose at ≈1800 g H_2O_2/kg TS. With the increase in dosage of H_2O_2, VSS removal, sCOD, CST reduction and EPS increased significantly. With the increased of H_2O_2 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 H_2O_2 can cause the recombination of •OH radicals and auto decomposition of H_2O_2 to H_2O and O_2 [26], which can reduced the degradation efficiency.

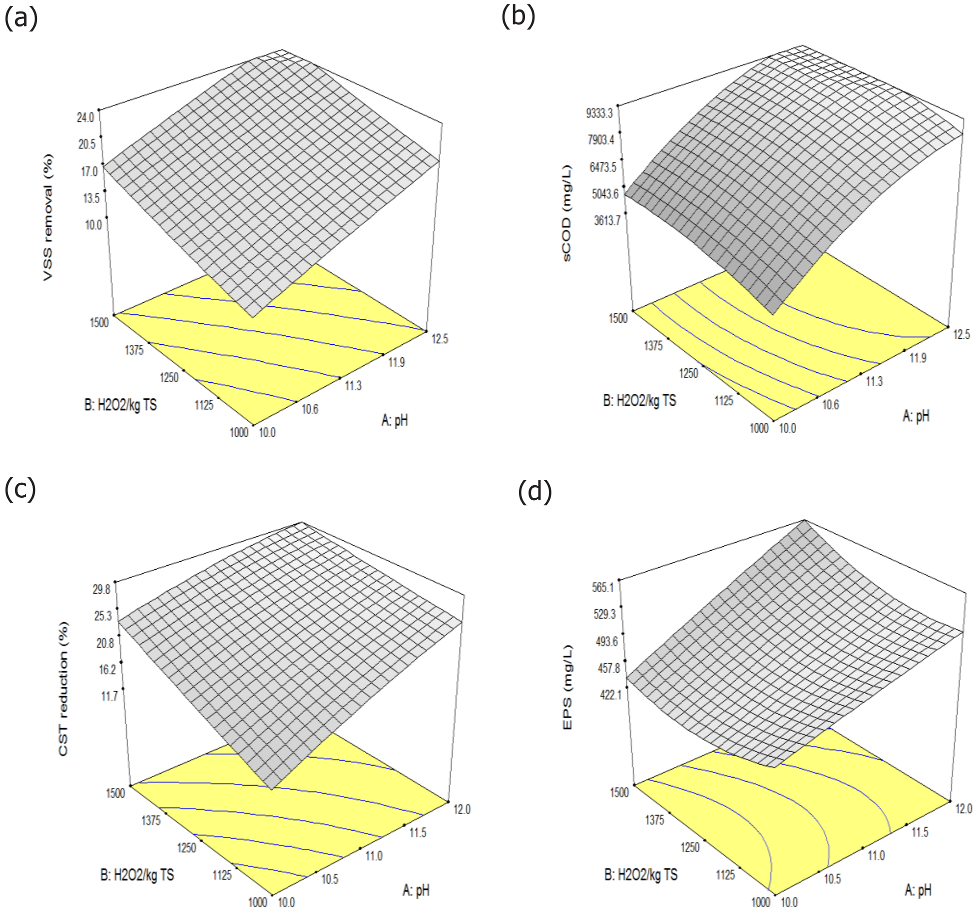

Fig. 1. Response surface plots of (a) VSS removal, (b) sCOD, (c) CST reduction and (d) EPS as a function of pH and dosage of H_2O_2/kg TS at reaction time 40 min

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.

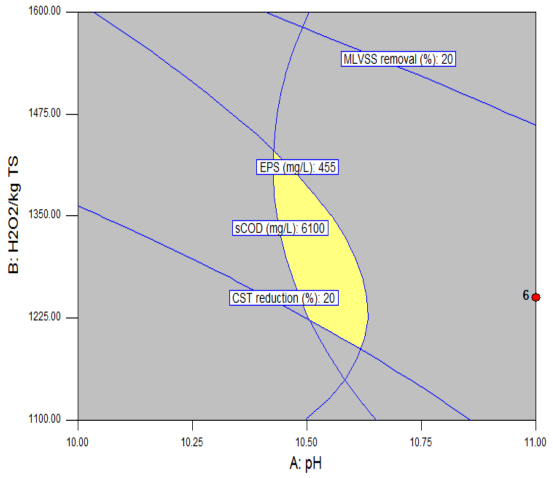

Fig. 2. Overlay plot at reaction time 40 min

Verification test were examined by conducting three experiments in the optimum region (pH 10.5, 1300 g H_2O_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).

Table 4. Experimental removal efficiency and model prediction.

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_2O_2 oxidation/alkaline hydrolysis was observed to be optimum at 10.5 pH, 1300 g H_2O_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_2O_2 oxidation/alkaline hydrolysis was found to be an adequate pretreatment of WAS to enhance its disintegration and dewaterability.

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