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Application of oxidation–reduction potential as a controlling parameter in waste activated sludge hydrolysis

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Abstract

In order to destroy the refractory structure of waste activated sludge (WAS) and increase its biodegradability, chemical pretreatment by adding NaOH was used in this study to enhance the hydrolysis of the WAS collected from the Taipei Min-Sheng Sewage Municipal Wastewater Treatment Plant located in northern Taiwan. Experiments were conducted with four total suspended solids (TSS) concentrations (0.5–2.0%) and four NaOH dosages (20–80 meq/l) at 25 °C. It was found that the optimal condition for WAS hydrolysis was TSS of 1% and NaOH dosage of 40 meq/l; 45% of soluble chemical oxygen demand (SCOD) was solubilized in the pretreatment time of 10 h. When the WAS was hydrolyzed by adding NaOH, profiles of oxidation–reduction potential (ORP) values were monitored on-line; also, a model covering the relationship between the change of ORP value and increase in SCOD was developed. This verified that the ORP monitoring technique is not only useful to investigate the solubilization rate but also suitable for the determination of optimal solubilization in WAS treatment. Considering the release of nitrogen by alkaline pretreatment, profiles of total Kjeldahl nitrogen, ammonia-nitrogen and amino acids were investigated.

Keywords: Waste activated sludge; Biodegradability; Alkaline hydrolysis; Oxidation–reduction potential

1. Introduction

It is well known that the activated sludge treatment process is one of the most common methods used in a sewage wastewater treatment plant to remove organic contaminants. The large amount of waste sludge, constituting of refractory and non-biodegradable cellulose compounds, which is produced by this process leads to the difficulty of sludge disposal. In order to destroy the refractory structure of waste activated sludge (WAS) and increase its biodegradability, a physio-chemical pretreatment method is commonly carried out to transform the particulate compounds contained in WAS into soluble compounds [1,16–20]. While a thermal or a thermochemical pretreatment of sludge results in an increase in biodegradability, a thermal process consumes substantial amounts of energy in addition to chemical consumption. Lin et al. [16] used a chemical pretreatment method by dosing NaOH to hydrolyze the WAS collected from a municipal sewage wastewater treatment plant. The authors proposed that an alkaline pretreatment method was significantly effective for the solubilization of WAS, represented by the increase in soluble chemical oxygen demand (SCOD) concentration, and the increase in biodegradability. Lin et al. [18] also used the alkaline pretreatment method to hydrolyze the WAS collected from an industrial wastewater treatment plant. A comparable result was obtained. When the alkaline pretreatment was carried out for 24 h, it was found that the solubilization of WAS was 24.7% and the release of nitrogen was 46%. In addition, a biochemical methane potential (BMP) test was developed to study the effect of NaOH dosage on the increase in solubilization and biodegradability of a chemically pretreated WAS [15]. Results of BMP tests showed that carbon and nitrogen had 94–105% recoveries and the methane produced was 349 ml for 1 g of COD removal. Hence the BMP test was shown to be a valuable tool for studying the kinetics and efficiency of an anaerobic digestion process. Also, chemical pretreatment such as alkaline hydrolysis of municipal WAS to convert the particulate fraction into soluble materials was shown to be effective in enhancing the digestibility of the WAS. Based on above description, alkaline hydrolysis could be applied in pretreating the WAS to destroy the complex structures and recover the organic matters contained in supernatant; also, alkaline hydrolysis could reduce the amount of WAS to save the cost for final sludge disposal.

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The oxidation–reduction reaction is known to take place by an electron transfer from substrate to oxidant. This reaction plays a very important role in drinking water and wastewater treatments such as chemical oxidation, aerobic and anaerobic biological processes [7,8,10,24] applied an on-line oxidation–reduction potential (ORP) monitoring technique in textile wastewater decoloring. They proposed that the change in ORP value significantly related to the removal of color. As noted above, it is estimated that the ORP values can be applied as a good indicator during the treatment of wastewater. Peddie et al. [21] applied alkali with different alkaline dosages to pretreat and hydrolyze the WAS prior to anaerobic sludge digestion. The authors found that the ORP value could be used as a valuable parameter to monitor and control the anaerobic sludge digestion process. The ORP can obviously be used for on-line monitoring of physico-chemical reactions, and therefore it could be applied as a parameter in controlling the alkaline dosages used in the reaction. This finding accords with results reported by other investigators. Lin et al. [17] examined the performance of on-line ORP and pH value for chemical pretreatment at ambient temperature using alkali to treat WAS. The authors used a modified-Nernst equation to indicate the optimal solubilization of WAS, based on the profiles of pH and ORP values. It was found that monitoring the profiles of ORP value could be used as the control strategy instead of time control strategy to find out the optimal solubilization of WAS in anaerobic hydrolysis. The modified-Nernst equation is shown as Eq. (1).

$$\mathrm{ORP}_0 - \mathrm{ORP} = -\left(\frac{RT}{nF}\right)\ln\left(\frac{[\mathrm{pH}_0]}{[\mathrm{pH}]}\right) \qquad (1)$$

where $\mathrm{ORP}_0 =$ ORP value of WAS before the addition of NaOH, mV; ORP = ORP value of WAS after the addition of NaOH, mV; $\mathrm{pH}_0 =$ pH value of WAS before the addition of NaOH; pH = pH value of WAS after the addition of NaOH; R the gas constant, 8.314 kJ/(mol K); T the absolute temperature, K; n the number of moles of electrons transferred per mole during the redox reaction; F the Faraday's constant, 96,500 C.

The term RT/nF in the above equation is a constant value under the consistent conditions within which the oxidation test is performed. Varying addition of NaOH affects the pH value so that the ORP value is affected, based on the previous discussion. Many researchers suggest that the addition of NaOH affects the solubilization rate represented by the increase in SCOD concentration of a chemically pretreated WAS [16,22]. It is estimated that a relationship between the profiles of ORP and solubilization of WAS could be observed. In this regard, it is interesting to study the relationship between the change of ORP value and increment of SCOD and thus verify the above estimation. Hence in this study, a chemical pretreatment method involving NaOH dosing was used to hydrolyze the municipal sewage WAS. Generally, ORP has been used as the monitoring and controlling parameter in many wastewater treatment plants, especially in chemical treatment and biological treatment units in Taiwan. For example, as the denitrification process was carried out at anoxic condition, ORP value could be used as the set-point to lead the operator to understand how much time was needed to reach the optimal denitrification condition. Other examples were electroplating wastewater treatment. To reduce the toxicity of heavy metals contained in electroplating wastewater, some reductants such as $Na_2S_2O_3$ were needed to add into the reactor. ORP value was a good tool to indicate the suitable addition of reductant. In this work, our objective is to identify possible correlations between NaOH concentration and ORP value, based on a modified-Nernst equation. Additional objectives are to develop a relationship between the change in ORP value and SCOD concentration and to study the effect of NaOH dosage and total suspended solid (TSS) concentration on the release of nitrogenous compounds.

2. Materials and methods

2.1. Materials

In this study, the WAS was collected from a municipal sewage wastewater treatment plant located in northern Taiwan. This plant had the capacity for wastewater treatment of 15,500 m^3 per day. Since the WAS was collected from a recirculation sludge tank, it was found that the initial concentration of TSS ranged from 1500 to 2000 mg/l; this was below an acceptable level than the substrate introduced into the reactor. Therefore the original WAS was needed to be concentrated by four to six times in the field to produce the WAS with TSS concentration of 3800–6000 mg/l. In this study, we collected the original WAS in the field five times; its general characteristics are shown in Table 1. In this table, it is found that the total chemical oxygen demand (TCOD) and SCOD of WAS was 2237 ± 1162 and 82 ± 77 mg/l, respectively. The BOD_5 concentration was 368 ± 198 mg/l.

Table 1
Characteristics of the original WAS collected from a municipal sewage wastewater treatment plant

Item	Average	Standard deviation[a]	Unit
pH	6.9	0.1	–
Dissolved oxygen	1.6	0.2	mg/l
Capillary suction time	9.5	2.1	s
Alkalinity	266	53	mg/l as $CaCO_3$
SCOD	82	77	mg/l
TCOD	2237	1162	mg/l
SCOD/TCOD	0.03	–	–
BOD_5	368	198	mg/l
BOD_5/TCOD	0.16	–	–
$A_{420\,\mathrm{nm}}$	0.04	0.01	Abs
TKN	154	44	mg/l
TSS	1531	210	mg/l

[a] WAS was collected five times and every WAS sample was analyzed three times.

This indicates that this WAS mainly consisted of particulate compounds and was non-biodegradable due to a very low observed SCOD/TCOD ratio of 0.03 and BOD_5/TCOD of 0.16.

2.2. *Experimental setting*

To understand the effect of TSS concentration and NaOH dosage on WAS solubilization, the increase in SCOD appears to be a useful method to study the performance of WAS hydrolysis by the alkaline pretreatment method. TSS content was concentrated to 0.5, 1.0, 1.5 and 2.0% prior to alkaline hydrolysis; the NaOH dosage used in this study was 20, 40, 60 and 80 meq/l, respectively. All the chemicals used in this study were reagent-grade without further purification. Prior to experiment, the NaOH was dissolved in distilled water with the concentration of 12 mmol. After this, the needed NaOH solution was introduced into the reactor and the mixer was run on for 2 min to lead the WAS and NaOH mixing completely. Design of the reactor is shown in Fig. 1. A 1 l reactor made of Pyrex glass was used in the hydrolysis experiment. To mix the chemicals and WAS completely, a magnetic stirrer equipped with a hotplate of 25 °C was employed. In order to understand the profiles of ORP and pH values during the reaction, a Suntex pH/ORP controller (PC-310) equipped with an ORP sensor (Mettler Toledo InLab® 501 REDOX, Electrolyte 9811) and a pH sensor (P14805-60-P-PA-k19/120 combination pH) was used to measure the results and were recorded by a printer.

2.3. *Analysis*

Most of the analyses performed on the WAS followed the procedures recommended in the 19th edition of Standard Methods for the Examination of Water and Wastewater [2]. TSS was measured by filtration through a 0.45 μm membrane and drying at 103 °C. SCOD was determined by a closed reflux-colorimetric method (heater: Hach model 45,600; colorimeter: Hach DR/2000 Box 389, Loveland, CO, USA). Ammonia-nitrogen (NH_3-N) content was determined by the titrimetric method; total Kjeldahl nitrogen (TKN) content was determined by the semi-micro-Kjeldahl method. Analysis of amino acids was conducted with a HPLC (Jasco International, Tokyo, Japan) equipped with an UV detector.

3. Results and discussion

3.1. *Development of relationship between pH and ORP values by dosing NaOH into pure water*

Monitoring of ORP value is an available technique for investigating the performance in aerobic, anoxic and anaerobic biological systems. Eq. (2) shows the general chemical reaction, where A and B are the reactants and C and D are the oxidants. If we added NaOH into pure water, the reactants were H_2O molecule and OH^- (which were dissociated from NaOH) then Eq. (2) could be written as Eq. (3). As noted in Eq. (3), the difference of ORP value between time t (term E) and initiation (term E^0) is correlated to the molar concentration of OH^-.

$$aA + bB \rightarrow cC + dD \tag{2}$$

$$E = E^0 - \frac{RT}{-nF}\ln\frac{1}{[OH^-]^b} \tag{3}$$

The term RT/nF has been described in the introduction. Because the reaction was carried out at constant temperature, the term $[RT/nF]$ was a constant. In addition, the concentration of OH^- equals $10^{-14}/[H^+]$, and the term $[H^+]$ could be represented as the pH. Based on this, Eq. (3) can be written as Eq. (4); therefore a linear relationship is observed.

$$\text{ORP} = a - b \times \text{pH} \tag{4}$$

where "a" is a constant and "b" is the slope of the regression line developed by the ORP vs. pH value.

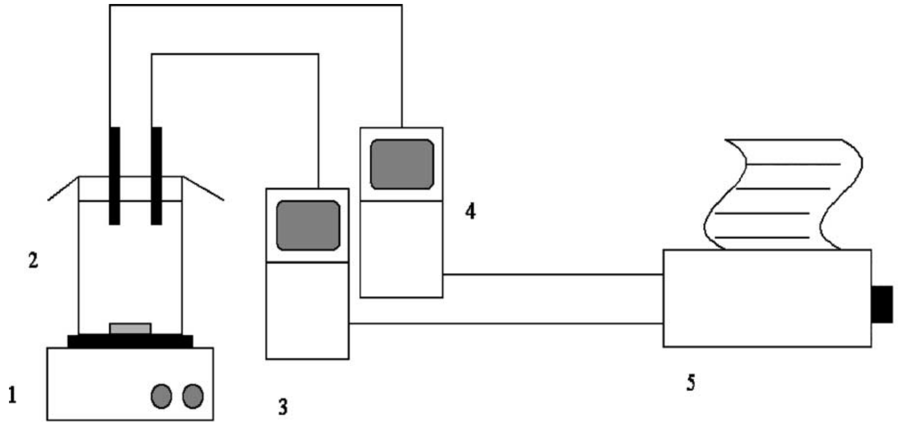

Fig. 1. Schematic diagram of experimental setup. (1) Magnetic stirrer equipped with a hot plate and a spinbar; (2) Pyrex glass reactor; (3) pH meter equipped with a pH sensor; (4) ORP meter equipped with an ORP sensor; (5) printer.

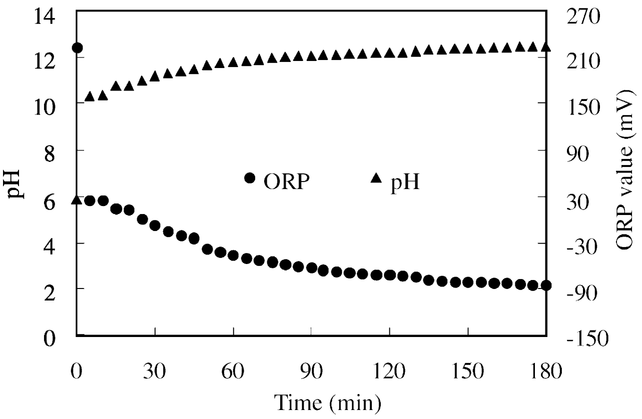

Fig. 2. Profiles of pH and ORP when NaOH was added into pure water continuously. (Rate of NaOH dosing: 1 ml/min of 1 N NaOH solution.)

To verify the above estimation, the deionized and distilled water manufactured from a millipore purification system was introduced into a 1 l reactor; when a 1 NaOH solution was added into the reactor, profiles of pH and ORP values were monitored on-line and recorded by a printer. These results are plotted in Fig. 2. The initial pH and ORP value of water was 5.9 and 223 mV, respectively. After adding NaOH, it is apparent that the pH value increases first remarkably fast and then slowly with time. Profiles of the ORP value reveal an opposite trend to the pH value. It is interesting to understand the relationship between pH and ORP values; hence the data shown in Fig. 2 are re-plotted in Fig. 3. In this figure, according to a high R^2-value of 0.98, the equation of the regression line is ORP $= -47.06 \times \text{pH} + 506.11$. This confirms the validity of Eq. (4).

3.2. Effect of alkaline dosage on solubilization

As noted above, it was understood that alkaline pretreatment was useful to enhance the efficiency of WAS hydrolysis. When NaOH or lime was used to hydrolyze a municipal WAS at 0.5 and 1.0% TSS, it was found that 40 meq/l NaOH led to the best performance [16]. The quantity of COD solubilized during the initial 24 h constitutes 60% of the total. In this study, the initial TSS concentration of WAS was only 0.15%; too low for a solubilization test. Therefore the raw WAS was concentrated to the TSS concentration of 1%. After this procedure, 1 l of the adjusted WAS was introduced into the reactor and NaOH stock solution was diluted and introduced to test the effect of alkaline dosages on the solubilization of WAS. The NaOH concentrations were 20, 40, 60 and 80 meq/l, respectively. Solubilization of WAS, represented as the increase in SCOD concentration, by alkaline pretreatment is shown in Fig. 4. It can be seen in Fig. 4 that the concentration of SCOD increased with increasing alkaline dosage (from 20 to 60 meq/l) and time. However, since the dosage of NaOH increased to 80 meq/l, the concentration of SCOD was lower than the result of 60 meq/l of NaOH, which could be explained by the phenomenon of a browning reaction. Lin et al. [16] also proposed that an additional dosage of NaOH led to the browning reaction taking place so that the solubilization of sludge by alkaline pretreatment was reduced. In Fig. 4, the increase in SCOD after the pretreatment time of 2 h was insignificant; i.e., solubilization of WAS in the initial 2 h constituted 64.5–82.9% of the total solubilization. A similar phenomenon was observed by Chiu et al. [9]. When the alkaline pretreatment process was performed in the hydrolysis of WAS, it was found that the SCOD concentration was significantly enhanced during the initial 2–4 h.

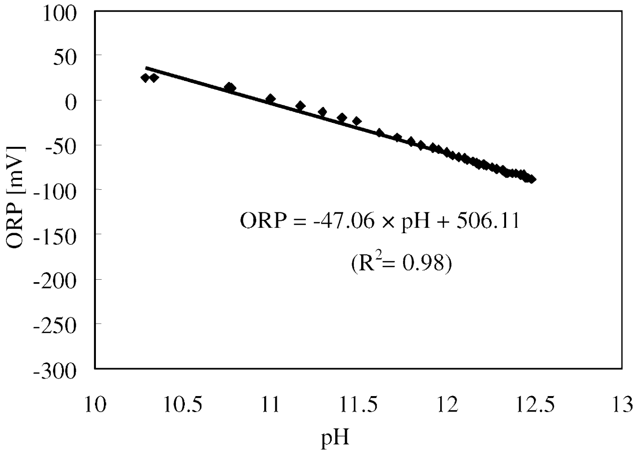

Fig. 3. Relationship between pH and ORP values (data obtained from Fig. 2).

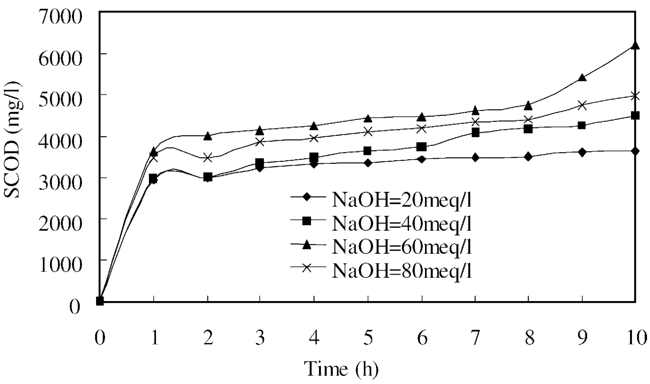

Fig. 4. Profiles of SCOD solubilized from WAS (1% TSS) by added 20, 40, 60 and 80 meq/l of NaOH.

To study the effect of alkaline dosage on the solubilization of WAS, Table 2 summarizes the results shown in this work and other studies. For these studies, the TSS concentration was adjusted to 1%. It can be seen in Table 2 that the higher the temperature the higher the rate of SCOD generation [5,22]. Rajan et al. [22] used the alkaline pretreatment method to hydrolyze WAS collected from a municipal wastewater treatment plant. It was found that the solubilization increased from 18 to 45% when the reaction temperature increased from 20 to 38 °C. Beccari et al. [5]

Table 2
Results of COD solubilization in several sludge treatment studies

Item	Method	Temperature (°C)	Time (h)	Results	References
Municipal WAS	NaOH	20	24	COD 18% solubilized	[2]
		38		COD 45% solubilized	
MSWOF[a]	NaOH	20	24	COD 24% solubilized	[5]
		100		COD 30% solubilized	
Domestic WAS	NaOH	25	24	COD 37% solubilized	[6]
	NaOH/sonication			COD 89% solubilized	
Municipal WAS	NaOH	25	24	COD 30% solubilized	[18]
Industrial WAS	NaOH	25	24	COD 25% solubilized	[17]
Municipal WAS	NaOH	Ambient	24	COD 55% solubilized	[19]
Municipal WAS	NaOH	Ambient	10	COD 31% solubilized	This study

[a] MSWOF: organic fraction of municipal solid wastes.

also found a comparable result. However, the increase in SCOD concentration with increasing temperature shown in [5] was insignificant. In this study, solubilization of 31% was observed after 10 h pretreatment by dosing NaOH. The WAS used in the report of Lin et al. [19] was collected from the same municipal wastewater treatment plant presented in this study. Hence it is found that the result of COD solubilization shown in [19] and this study is very close.

3.3. Effect of alkaline dosage on ORP profiles

As noted above, it is clear that the dosage of NaOH introduced into the solution affects the concentration of OH^- and profiles of ORP values. Also, in Fig. 4, dosage of NaOH affects the solubilization of WAS. Hence it is interesting to study the relationship between the solubilization of WAS and profiles of ORP values. Fig. 5 shows the profiles of ORP values when the WAS was pretreated at various concentrations of NaOH and 1% TSS. The initial ORP value of these four runs before NaOH introduction was 101 mV. After introducing NaOH, the ORP value declined remarkably, i.e., after the reaction time of 5 min, the ORP value was in the range −287 to −483 mV, and then it increased slowly due to the consumption of OH^-. In fact, the profiles of ORP values (Fig. 5) and SCOD concentrations (Fig. 4) are similar. Based on this, a relationship between ORP and SCOD can be developed. The results are illustrated in Fig. 6. The vertical axis is the concentration of SCOD; the horizontal axis is the difference between the ORP value at 5 min and at time t ($[\mathrm{ORP}]_t - [\mathrm{ORP}]_{5\,\mathrm{min}}$), designated as ΔORP). The results shown in Fig. 6 indicate that the solubilization of WAS represented by the concentration of SCOD increases with increasing difference of ORP values. For example, when the hydrolysis test was performed with 40 meq/l of NaOH, it was found that the concentration of SCOD increased from 2976 to 4504 mg/l and the ORP value increased from −293 to −203 mV or the term ΔORP increased from 101 to 191 mV. The results shown in Fig. 6 also indicate that if the initial SCOD value was very low, addition of NaOH might not make much difference in WAS solubilization. To explain this, the authors suppose if the sampling interval of ORP values and SCOD concentration could be reduced to less than 5 min, we could discuss them at smaller ΔORP. Hence, the ΔSCOD against ΔORP would make more sense in Fig. 6. In

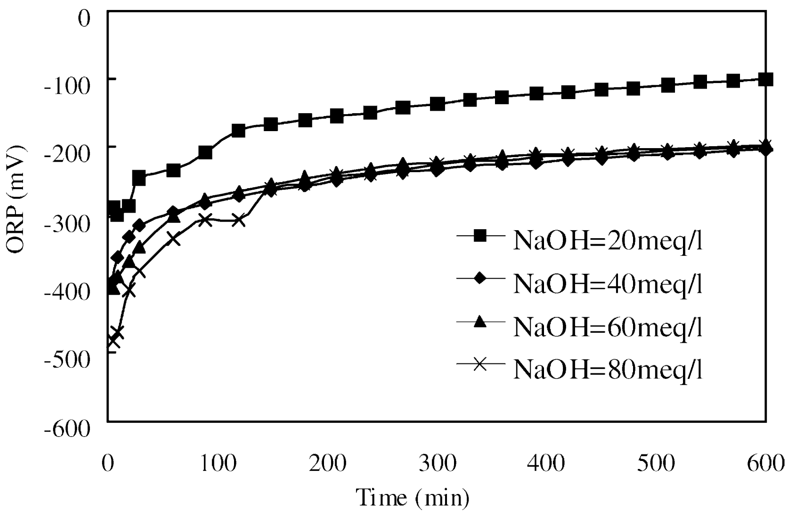

Fig. 5. ORP profiles when 1% WAS was pretreated by various NaOH concentrations (20, 40, 60 and 80 meq/l).

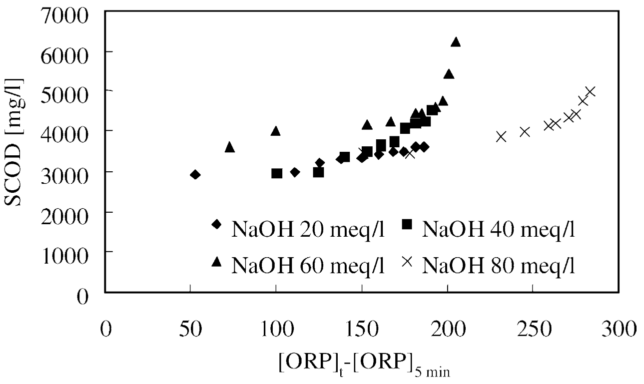

Fig. 6. Relationship between ΔORP ($[\mathrm{ORP}]_t - [\mathrm{ORP}]_{5\,\mathrm{min}}$) and SCOD when 1% WAS was pretreated by various NaOH concentrations.

fact, the initial SCOD of untreated WAS was on an average of 82 mg/l, which was significantly lower than treated WAS. Hence, Fig. 6 still gives us the information that the increase in ORP value lead to the increase in SCOD concentration.

The relationship between SCOD and ΔORP at various NaOH dosages is shown in Table 3. It is found that the SCOD correlates well with ΔORP in several tests. Lin and Ma [15] have assessed the feasibility of an ORP value monitoring technique for estimating the decomposition of *ortho*-chlorophenol (2-cp). Experimental results indicated that a good relationship between the ORP ratio and the percentage of 2-cp decomposition was observed. Also, it is noted that the efficiency can be easily determined by monitoring the ORP values when the industrial wastewater is treated using an ultrasonic/Fenton process. In this study, even though the R^2-value of the regression line developed with 60 meq/l of NaOH was below the accepted level, yet in the other three tests, the R^2-values were greater than 0.8. This phenomenon verifies that the profile of ORP is valuable for determining the solubilization of WAS. In Table 3, it is also found that the slope of the regression line for 40 meq/l of NaOH is higher than for the other three tests. This reveals that an optimal NaOH dosage is obtained, due to an effective increase in SCOD by dosing NaOH, which may produce an increase in ORP value.

3.4. *Effect of TSS concentration on solubilization*

Even though an optimal NaOH dosage has been obtained from previous discussions, it is interesting to study the effect of TSS concentration on WAS hydrolysis by alkaline pretreatment. The TSS concentration of the WAS produced from a real wastewater treatment plant varies each day, therefore, if a relationship between the increase in SCOD and ΔORP value for various TSS concentrations can be developed, it is useful for later studies on WAS hydrolysis. Fig. 7 shows that TSS concentration affects the profiles of SCOD concentration. When the hydrolysis of WAS was performed at TSS of 0.5% and NaOH content of 40 meq/l, more than 2900 mg/l of SCOD increase was observed after a reaction time of 10 h. With the same reaction conditions but the TSS concentration adjusted to 2%, more than 6600 mg/l of SCOD increase was observed. However, considering the TCOD concentration, it is found that 40, 31, 28 and 23% of TCOD was solubilized from WAS by adding NaOH at a TSS concentration of 0.5, 1.0, 1.5 and 2.0%, respectively. This indicates that the rate of solubilization decreases with an increase in TSS concentration when the dosage of NaOH in the pretreatment of WAS is constant. Lin et al. [18] used NaOH to pretreat an industrial WAS collected from southern Taiwan. When the hydrolysis reaction was carried out with NaOH content of 30 meq/l, solubilization of WAS or SCOD value increased with increasing TSS concentration. Lin et al. [18] also proposed that if the ratio of SCOD/TCOD was considered, TSS of 1% showed the best solubilization ratio, which was higher than at TSS concentration of 0.5 and 2%.

Table 3
Summary of regression lines of 1% TSS between SCOD and ΔORP developed for various NaOH dosages

NaOH dosages (meq/l)	Regression line	R^2-value
20	SCOD = 5.6 × ΔORP + 2542.3	0.92
40	SCOD = 17.4 × ΔORP + 972.8	0.92
60	SCOD = 12.4 × ΔORP + 2535.4	0.56
80	SCOD = 9.8 × ΔORP + 1780.2	0.80

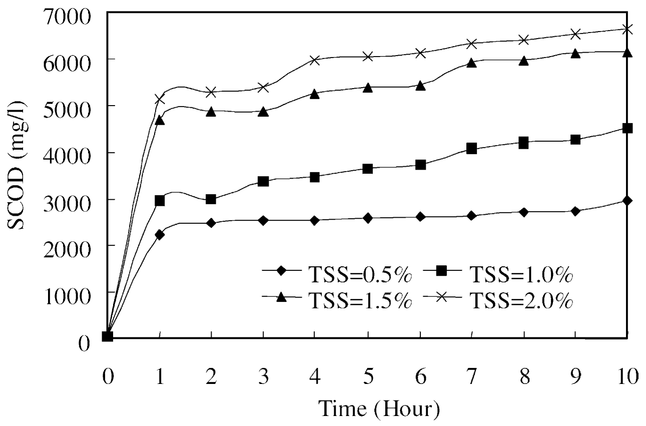

Fig. 7. Profiles of SCOD solubilized from various TSS concentrations of WAS treated by alkaline process (40 meq/l of NaOH).

3.5. *Effect of TSS concentration on ORP profiles*

The initial ORP values at different TSS concentrations are in the range −227 to −498 mV, due to the addition of 40 meq/l of NaOH. After that, the ORP value increases significantly. The final ORP value for four TSS concentrations is similar, from −101 to −112 mV. In the previous discussion, it is understood that the profiles of ORP value and SCOD concentration are similar. In this section, it is apparent that the increase in SCOD concentration and ORP value is very close. For example, at a TSS concentration of 0.5%,

Table 4
Summary of regression lines between SCOD and ΔORP developed for various TSS concentrations with the NaOH dosage of 40 meq/l

TSS concentration (%)	Regression line	R^2-value
0.5	SCOD = 7.3 × ΔORP + 1970.4	0.84
1.0	SCOD = 11.9 × ΔORP + 2003.9	0.83
1.5	SCOD = 12.9 × ΔORP + 1221.1	0.86
2.0	SCOD = 10.3 × ΔORP + 2514.2	0.90
0.5–2.0	SCOD = 11.9 × ΔORP + 1762.7	0.96

the ORP value increases from −227 to −112 mV; at a TSS of 2.0%, the ORP value increases from −498 to −111 mV. That is, the difference between initial and final ORP values was 115 and 387 mV at TSS concentrations of 0.5 and 2.0%, respectively. In Fig. 7, increases in SCOD concentration for TSS values of 0.5 and 2.0% were 744 and 1511 mg/l, respectively. Based on this, it is predicted that the profiles of ORP value and SCOD concentration are affected by TSS concentrations. Hence the relationship between ΔORP and SCOD is discussed and plotted in Fig. 8. It can be seen that there is a good relationship between ΔORP and SCOD. In addition, it is apparent that a linear regression line can be derived when the TSS concentration of WAS is in the range 0.5–2.0%. Equations of the regression lines are listed in Table 4. A very high R^2-value of 0.96 is observed in Table 4 for a general relationship between SCOD and ΔORP, if the effect of TSS concentration is not considered. In this regard, this information is very valuable for an alkaline pretreatment of WAS; i.e., even though the concentration of TSS affects the solubilization of WAS and profiles of ORP, an increase in SCOD concentration can be predicted based on the profiles of ORP values.

3.6. Release of nitrogen

A minor objective for the hydrolysis of WAS by adding NaOH is that an alkaline pretreatment method causes the supernatant of chemically pretreated WAS to be biodegradable; hence it can be used as a carbon source for the denitrification processes. Releases of nitrogen in the supernatant from chemically pretreated WAS should be noticed, because it will lead to an increase in nitrogen loading for biological processes. In Table 5, the releases of TKN and NH_3-N in the supernatant when the municipal WAS was pretreated by NaOH at different reaction conditions is summarized. It is obvious in Table 5 that releases of TKN and NH_3-N increase with increasing TSS concentrations. Also, releases of TKN and NH_3-N at the pretreatment time of 1 h contribute more than 73 and 20% of the total release, respectively.

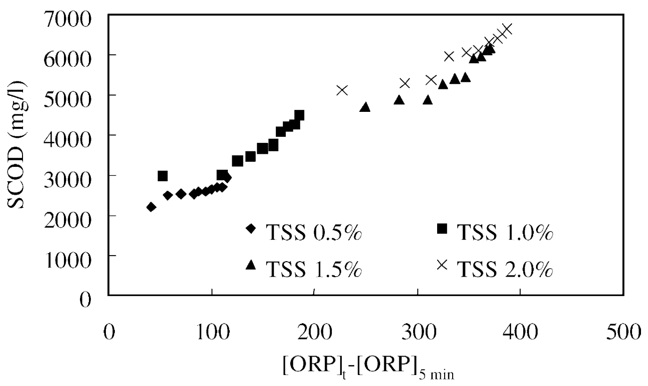

Fig. 8. Relationship between ΔORP ([ORP]$_t$−[ORP]$_{5\,min}$) and SCOD when various TSS concentrations of WAS were pretreated by 40 meq/l of NaOH.

Table 5
Release of TKN and NH_3-N when municipal WAS was pretreated by NaOH under different reaction conditions

	TKN (mg/l)			NH_3-N (mg/l)		
	Pretreatment (h)			Pretreatment (h)		
	0	1	10	0	1	10
NaOH (TSS 1.0%)						
20 meq/l	95.2	215.6	672.0	30.1	35.0	115.0
40 meq/l	145.6	655.2	896.0	30.1	33.0	22.5
60 meq/l	95.2	588.0	551.6	30.1	22.5	165.0
80 meq/l	95.2	131.6	305.2	30.1	42.5	52.5
TSS (NaOH 40 meq/l)						
0.5%	145.6	366.8	490.0	30.1	26.0	20.5
1.0%	145.6	655.2	896.0	30.1	33.0	22.5
1.5%	145.6	938.0	1038.8	30.1	71.0	197.0
2.0%	145.6	1142.0	1318.8	30.1	77.0	256.0

Barlindhaug and Ødegaard [4] pretreated the mixed sludge with a thermal process, showing that 85% of nitrogen was solubilized after a 30 min reaction time. Smith and Göransson [23] also pretreated the mixed sludge but using a thermal/H_2SO_4 process; experimental results showed that 80% of nitrogen was released from WAS. Kristensen et al. [13] used a biological method to hydrolyze primary sludge, and only 22% nitrogen release was observed. Lin et al. [18] pretreated 1% TSS industrial WAS with 30 meq/l of NaOH for 24 h, and it was found that 46% of nitrogen was released into the supernatant. In this study, the TKN contained in the original WAS (MLSS of 1531 mg/l) was 154 mg/l. Prior to hydrolysis, the WAS was concentrated to 0.5, 1.0, 1.5 and 2.0% MLSS values, hence the total TKN contained in concentrated WAS were ranging from 502 to 2008 mg/l. In Table 5, releases of TKN are ranging from 490 to 1319 mg/l, hence it is understood that 65.6–97.4% of nitrogen was released from WAS, when the WAS was pretreated with 40 meq/l of NaOH and TSS concentration 0.5–2.0%. Based on this, it is found that the ratio of nitrogen release shown in this study is remarkably higher than in other studies. The types of WAS used in other studies were industrial or mixed (industrial/municipal) sludge, hence the solubilization ratio of WAS was lower than in this study, due to the stronger structures of WAS composition which were observed. In this study, the nitrogen content of WAS was contributed by human activity. As contrasted with an industrial WAS, a

Table 6
Composition of amino acids obtained in the effluent of WAS chemically pretreated by NaOH at TSS concentration of 1% of this study and other reports

	Type of WAS				
	Municipal (this study, 0 h)	Municipal (this study, 10 h)	Municipal (Liaw [14][a])	Municipal (Huang [12][a])	Industrial (Huang [11][a])
Amino acids (mg/l)					
Asparagine	0.18	2.45	1.26	0.24	3.05
Theronine	ND[b]	1.17	ND	1.47	1.63
Serine	ND	2.02	0.67	2.57	1.77
Glutamine	0.28	2.98	3.37	1.80	2.47
Proline	ND	1.23	ND	1.24	1.70
Glycine	0.51	4.36	5.10	4.07	3.73
Alanine	0.48	3.86	2.63	2.93	4.40
Valine	0.24	1.79	1.35	2.13	2.15
Isoleucine	ND	0.86	3.21	0.86	1.07
Leucine	0.02	1.35	1.53	1.50	1.92
Tyrosine	ND	0.27	ND	1.31	0.54
Phenylalanine	ND	4.33	1.74	0.80	1.10
Histidine	0.04	0.32	ND	13.87	0.84
Lysine	0.13	1.59	2.72	1.20	2.68
Arginine	ND	0.58	ND	5.09	0.17
Total	1.88	29.16	23.25	41.08	29.22

[a] Hydrolysis time period of these three experiments were 24 h.
[b] Not detected.

municipal WAS can be decomposed or hydrolyzed readily by adding NaOH hence the solubilization of nitrogen is higher than that of an industrial WAS.

3.7. Release of amino acids

The amount of amino acids in the soluble portion of WAS appears to indicate the efficiency of pretreatment in solubilizing nitrogen-containing organic substances. Concentrations of amino acids before and after alkaline pretreatment measured in this and other studies are listed in Table 6. Prior to alkaline hydrolysis, it is found that the concentration of amino acids is 1.88 mg/l; after alkaline hydrolysis, 29.16 mg/l of amino acids is observed. Alanine and glutamic acid mainly constitute the cell wall of bacteria. If dosing with NaOH can destroy the cell wall of sludge, it is predicted that the concentrations of alanine and glutamic acid increase. By adding NaOH for 10 h, it can be seen in Table 6 that the concentrations of alanine and glutamic acid increase from 0.48 and 0.28 mg/l to 3.86 and 2.98 mg/l, respectively. This confirms the previous prediction. Comparing with other research, the concentration of total amino acids present in the reports of Huang [11] and Liaw [14] are comparable to this study. Huang [12] found that the concentration of histidine was significantly higher than other amino acids. Based on the results shown by Ashoor and Zent [3], it is understood that histamine belongs to the group of low browning reactions. Hence it is proved that the alkaline pretreatment is valuable for WAS hydrolysis, even though a very high concentration of histidine was observed. In this study, 52% of amino acids consisted of the medium browning reaction group such as proline, leucine, alanine and so on; the low browning reaction group such as histidine, aspartic acid and glutamic acid contributed 26.3% and the high browning reaction group such as lysine and glycine contributed 21.7% of the total production of amino acids.

4. Conclusions

In this study, a WAS collected from the Taipei Min-Sheng Municipal Sewage Wastewater Treatment Plant located in northern Taiwan was pretreated by NaOH dosing. The increase of SCOD and release of nitrogen at different pretreatment conditions were determined. Experimental results indicate that amount of SCOD increases with increasing NaOH dosages and TSS concentrations. Also, increase of SCOD for the reaction time of 2 h contributes 64.5–82.9% of total solubilization. With respect to nitrogen release, a comparable result to SCOD increase was observed. During the reaction, profiles of ORP value were monitored on-line to study the relationship between SCOD and ORP. There is a satisfactory relationship with a R^2-value of 0.96 between the profiles of SCOD and ORP developed. It is estimated that the increase of SCOD could be predicted from ORP values, based on the relationship developed in this study.

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