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ALKALINE HYDROLYSIS OF THE SLUDGE GENERATED FROM A HIGH-STRENGTH, NITROGENOUS-WASTEWATER BIOLOGICAL-TREATMENT PROCESS

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Abstract
The production of acrylonitrile butadiene styrene (ABS, a petrochemical product) in Taiwan is one of the biggest manufactoring processes in the world. The large amount of ABS sludge generated in the wastewater treatment plant from the highly nitrogenous-wastewater contains significant amount of complex and biorefractory organic substances. Resource recovery is the optimal conception of the traditional sludge treatment for the purpose of organic matters removal. An alkaline pretreatment method is used to enhance the efficiency of biological hydrolysis of industrial wastewater sludge in the present study. The operating conditions for the alkaline pretreatment of the ABS sludge were maintained at room temperature (25 ± 3°C), reaction time of 24 h, total solids in the feed of 0.5–2%, and NaOH dosages of 10–50 mg l^{-1}. Considering the increasing concentrations of soluble chemical oxygen demand and biochemical oxygen demand, the experimental results indicated that the alkaline pretreatment method was useful in biodegradability enhancement. © 1998 Elsevier Science Ltd. All rights reserved.

Key words: alkaline pretreatment, carbon source, nitrogenous wastewater, resource recovery, sludge.

INTRODUCTION

The nitrogenous compounds in municipal sewage or industrial wastewaters include ammonia, nitrite, nitrate, soluble organic nitrogen (org-N) and particulate org-N. Nitrification and denitrification are the major reactions for the reduction of nitrogenous compounds. From the literature, the organic carbon source plays an important role in biological nitrification and denitrification processes (Abufayed and Schroeder, 1986; Henze *et al.*, 1994; Artan *et al.*, 1995). Battistoni and Fava (1995) proposed that the denitrification rate could be increased in the activated sludge treatment-system by adding an external carbon source generated from the fermentation of primary sludge. Therefore, how to transform the complex and biorefractory organic material in industrial wastewater sludge into an available carbon source is an important step in biological treatment technology.

Traditional chemical technologies such as thermal pyrolysis, alkaline hydrolysis and acid hydrolysis are often applied as the pretreatment method for the waste activated sludge (WAS). These technologies can enhance the soluble organic matter in the hydrolysate which can then be used as the carbon source (Mason *et al.*, 1992; Sawayama *et al.*, 1995). Recently, several authors have found that the alkaline pretreatment method can enhance biodegradability of sludge (Rajan *et al.*, 1989; Lin *et al.*, 1997). Alleman *et al.* (1994) demonstrated that alkaline treatment is effective in solubilizing munitions-grade nitrocellulose into soluble organics. Woodard and Wukasch (1994) conducted a laboratory-scale study in the development of a hydrolysis/thickening/filtration technology to improve the efficiency of solid digestion of WAS generated in the biological treatment of pharmaceutical wastewater. Substantial solubilization (50–60%) of activated sludge suspended solids was achieved at room temperature, with a relatively short time of hydrolysis. Rajan *et al.* (1989) showed that low-level alkaline pretreatment of waste activated sludge with NaOH could increase levels of solubilization up to 46%. Furthermore, Ray *et al.* (1990) examined the ability of the single-stage high-rate anaerobic digester to stabilize the alkaline-treated WAS with digesters operated at 35°C and different hydraulic retention times. Pretreatment with sodium hydroxide improved the volatile solid reduction by 25–35% and increased gas production by 29–112% over the

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control sludge samples undergoing no alkaline pretreatment.

In this study, the characteristics of original and pretreated sludge were examined and compared. The ratio of soluble chemical oxygen demand (COD) SCOD/total chemical oxygen demand (TCOD) and the concentration of biochemical oxygen demand (BOD_5) were applied as an indicator to evaluate the changing of biodegradability. The objectives of the present study were to investigate the effect of alkaline pretreatment on the enhancement of biodegradability of sludge hydrolysate.

METHODS

Sludge collection and characterization

The waste biological sludge (WBS) was collected from a wastewater-treatment plant of an ABS manufactory in Taiwan. The original wastewater was treated with preliminary processes, including air flotation, denitrification, nitrification and final sedimentation. Sludge sample were collected from the final sedimentary tank, and immediately transported to the laboratory. Initial analyses, including pH, total solids (TS), volatile solids (VS), SCOD, TCOD, dissolved organic carbon (DOC), total organic carbon (TOC), total phosphorus (TP), total Kjeldahl nitrogen (TKN), ammonia nitrogen (NH_3–N), org-N, nitrite (NO_2–N) and nitrate (NO_3–N) measurements were performed and the sludge was stored at 4°C.

Hydrolysis

The process of sludge hydrolysis was carried out in a 3 l, closed, Pyrex glass, cylindrical reactor. A mechanical stirrer was used ensure sufficient mixing of the sludge. The mixing speed was maintained at 250 rpm, which dispersed the NaOH and prevented sludge from settling. Alkali (NaOH) concentrations ranging from 10 to 50 m-equiv l^{-1} (1–40 g-NaOH/100 g-TS) were employed, while the sludge concentrations ranged from 0.5 to 2% TS. The experiment was operated under anoxic condition, that is, no air or oxygen was introduced into the reactor. The reaction temperature was maintained in the range of 25 ± 3°C. The total reaction duration was 24 h. Samples were taken from time to time and filtered through a 0.45 μm glass fiber to obtain the filtrate as hydrolysate. At the end of each batch test, TS, VS, SCOD, DOC, BOD5, NO_2–N, NO_3–N, NH_3–N, org-N and TP of the hydrolysate were determined and the solubilization of carbonous, nitrogenous and thus phosphorous compounds by alkaline pretreatment could then be calculated.

Analysis

Most of the analyses performed on the filtrate followed the procedures recommended in the 18th edition of *Standard Methods* (APHA, AWWA, WPCF, 1992). The pH value was determined using a pH metre (Schott CG841 Schott-Geräte, GmbH., West Germany). TS and VS were measured by drying and ashing at 103 and 550°C, respectively. SCOD and TCOD were determined by a closed reflux-colorimetric method (heater: Hach model 45600; colorimeter: Hach DR/2000 Box 389, LOVELAND, Colo., USA). Organic carbon, including TOC and DOC, was determined by combustion-infrared and persulfate-ultraviolet oxidation methods (Astro 2001 TOC analyzer Astro International Co., League, Texas, USA). Potassium hydrogen phthalate (KHP) was used as the standard for TOC analysis. Ammonia nitrogen (NH_3–N) was determined by the titrimetric method; and org-N was determined by the semi-micro-Kjeldahl method. Nitrate and nitrite were determined by ion chromatograph (Dionex 4500i Dionex Corp., Sunnyvale, California, USA) and phosphorus by the vanadomolybdophosphoric acid colorimetric method (ultraviolet colorimeter, Hitachi U-3210 Hitachi Ltd., Tokyo, Japan).

RESULTS AND DISCUSSION

To verify the effectiveness of the alkaline pretreatment process, the concentrations of SCOD, BOD_5 and DOC were used as the indicator of the biodegradability enhancement.

Characteristics of waste biological sludge

Table 1 describes characteristics of the original WBS generated from the high-strength nitrogenous-wastewater treatment process. The SCOD of the original sludge was only 3% of the TCOD. This result indicated that the sludge had the potential for converting particulate COD into SCOD. The DOC was *ca* 2% of TOC. Nitrate, NH_3–N and org-N were

Table 1. The fundamental characteristics of the original WBS

Item	Value	STD	*n**
pH	7.32	0.12	8
TS (mg l^{-1})	14272	3994	8
VS (mg l^{-1})	8825	2759	8
VS/TS	0.59	0.09	8
TCOD (mg l^{-1})	11439	4034	8
SCOD (mg l^{-1})	313	157	8
TOC (mg l^{-1})	5756	806	5
DOC (mg l^{-1})	96.5	29.6	4
NH_3-N(mg l^{-1})	15	7.7	8
org-N (mg l^{-1})	394	212	8
TKN-N (mg l^{-1})	409	212	8
NO_2^- (mg l^{-1})	ND[†]	—	6
NO_3^- (mg l^{-1})	36.7	14	7
TKN/COD	0.04	0.01	8
TP(mg $- PO_4^{3-}$ l^{-1})	5.6	2.3	7

*Frequency of the sampling and analysis.
[†]Not detected.

the predominant nitrogenous species. The TKN of the original sludge was only 4% of the TCOD. The amount of nitrogen in the sludge was low. The concentration of soluble phosphorus was only 2% of TP.

Effect of TS concentration on SCOD profiles

Figure 1 demonstrates the profiles of SCOD during the WBS pretreated by the alkaline hydrolysis. The initial SCOD concentrations of 0.5, 1.0 and 2.0% TS were 356, 432 and 554 mg l^{-1}, respectively. In Fig. 1, the concentration of SCOD was increasing with the pretreatment time. Within the first hour, the sludge was solubilized intensively, and thus the concentration of SCOD was increased quickly. After 12 h reaction duration, the change in SCOD concentration was insignificant. The concentration of SCOD was also affected by the sludge concentration at the same alkali level. In general, the greater the sludge concentration, the greater the SCOD generated. When the sludge concentration was adjusted at 0.5% TS, the concentration of SCOD after 24 h was 1200 mg l^{-1} at a NaOH dosage of m-equiv l^{-1}. When the sludge concentration was increased to 2% TS, the concentration of SCOD was increased to 3570 mg l^{-1}. Therefore, this result showed that a long-term reaction and a high solid concentration was significant to the increment of SCOD.

Effect of TS and alkaline dosage on COD solubilization

Figure 2 distinguishes the relationship between the alkaline dosage and the ratio of SCOD/TCOD, that is, solubilization ratio of COD, after 24 h. The yield of SCOD is dependent on the amount of NaOH added. In addition, the ratio of SCOD/TCOD increased with an increasing alkaline dosage. The relationship between the alkaline dosage and the increment of COD solubilization was almost linear. Though the greater sludge concentration could generate a larger amount of SCOD (Fig. 1), the solubilization ratio did not increase with the TS of the sludge. The optimal sludge concentration based upon the greatest SCOD/TCOD ratio was 1% TS. The results showed that an additional NaOH dosage was needed for more COD solubilization with 2% TS.

Apart from the greatest solubilization ratio and the shortest reaction time, the effect of alkaline dosage was also investigated. Three sludge concentrations of 0.5, 1.0 and 2.0% TS were examined. Figure 3 illustrates the relationship between the solubilization rate and the alkaline dosage. In Fig. 1, all the profiles of the concentrations of SCOD vs time fitted well with first-order kinetics. Therefore, the solubilization rate was calculated based on first-order kinetics. The optimal dosage was found to be 30 m-equiv l^{-1} NaOH. When the alkaline dosage was > 30 m-equiv l^{-1}, there was no significant improvement on the solubilization rate. On the basis of above description, 1% TS concentration showed the best performance in the sludge hydrolysis. Therefore, the optimal alkaline pretreatment condition was at 1% TS and 30 m-equiv l^{-1} NaOH in this study.

The results of COD solubilization in several sludge treatment studies are summarized in Table 2. It is certain that a high reaction temperature can increase the rate of SCOD generation (Rajan *et al.*, 1989; Beccari *et al.*, 1993). Rajan *et al.* (1989) reported that when the reaction temperature increased from 20 to 38°C, the solubilization of COD increased from 18 to 45%. In this study, the reaction temperature was maintained at 25°C. After

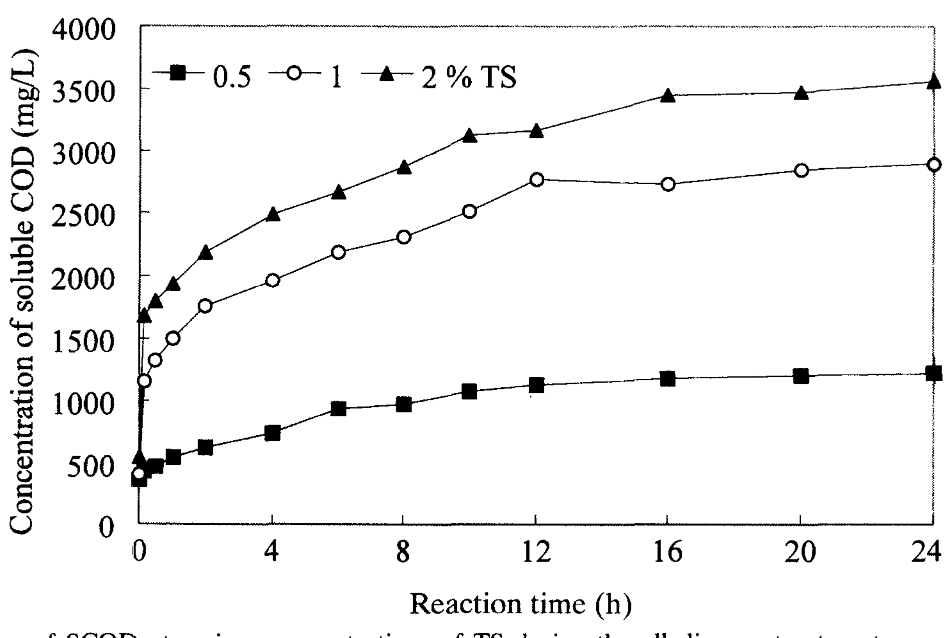

Fig. 1. The profiles of SCOD at various concentrations of TS during the alkaline pretreatment process (NaOH dosage 30 m-equiv l^{-1}, TS range from 0.5 to 2%, initial pH 7.2).

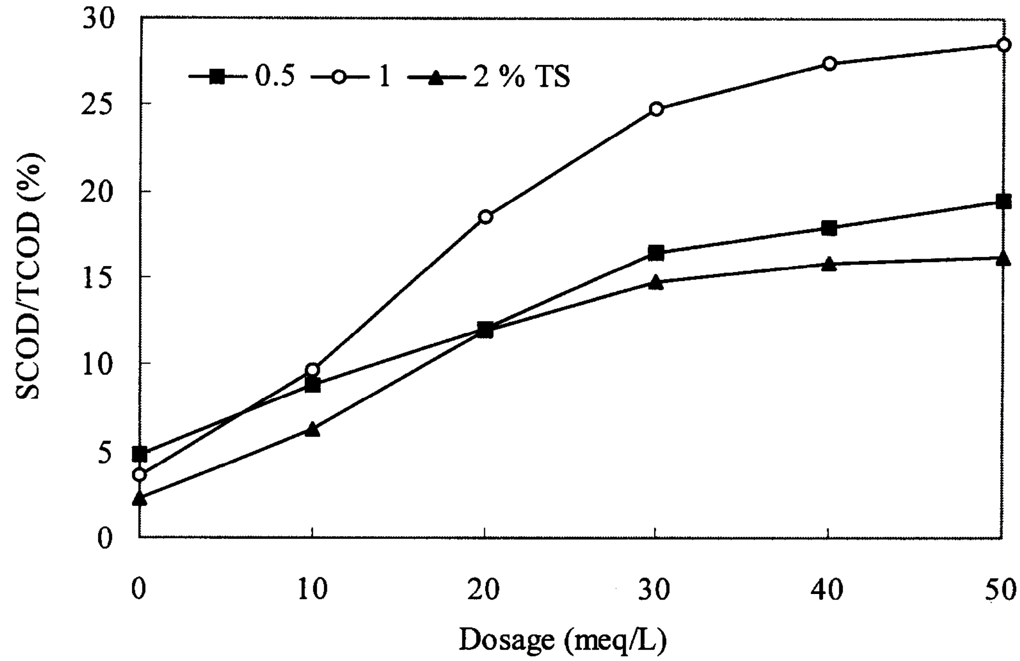

Fig. 2. The solubilization of the COD after 24 h alkaline pretreatment (NaOH dosages ranging of 10–50 m-equiv l^{-1}, TS range from of 0.5 to 2%, initial pH 7.2).

24 h pretreatment, the solubilization was 25%. The result is comparable to those reports. The species of the sludge also affects the amount of SCOD generated by sludge treatment. Table 2 shows that the domestic WAS can generate more soluble organic matters than industrial WAS at the same level of alkaline treatment. Industrial WAS contains significant complex and biorefractory organics. However, if the alkaline sludge hydrolysis is combined with other treatments such as the Fenton process (Mukherjee and Levine, 1992) and sonication (Chang *et al.*, 1997), the amount of SCOD generated will also be increased.

Relationships of DOC, SCOD and BOD_5

Not only the SCOD and DOC but also the BOD_5 can be applied as the indicator of biodegradability enhancement. In this study, we determined the concentrations of DOC, SCOD and BOD_5 in each sample after they have been pretreated by alkali. All the data of alkaline pretreated sludge at various solid concentrations and NaOH dosages are plotted

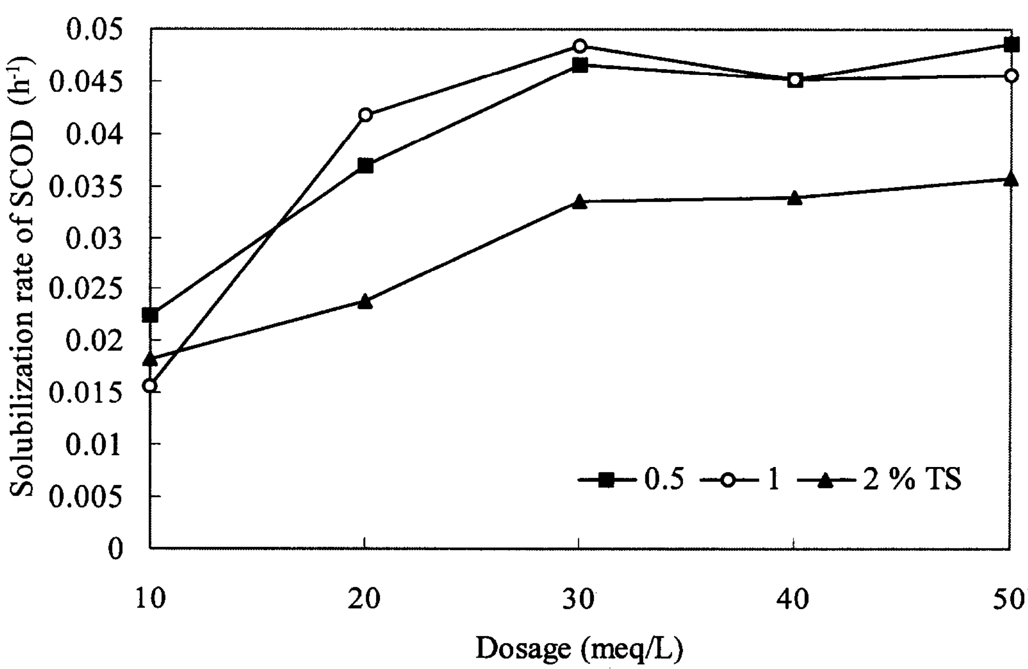

Fig. 3. The rate coefficients of the SCOD solubilization (NaOH dosages ranging of 10–50 m-equiv l^{-1}, TS range from 0.5 to 2%, initial pH 7.2).

Table 2. The results of COD solubilization in several sludge treatment studies

Item	Method	Temp. (°C)	Time (h)	Results	References
Municipal WAS	NaOH	20	24	COD 18% solubilized	Rajan *et al.* (1989)
		38		COD 45% solubilized	
Corn process waste	NaOH	25	24	COD 16% solubilized	Mukherjee and Levine (1992)
	$NaOH/H_2O_2/FeSO_4$			COD 32% solubilized	
MSWOF*	NaOH	20	24	COD 24% solubilized	Beccari *et al.* (1993)
	NaOH	100		COD 30% solubilized	
Domestic WAS	NaOH	25	24	COD 33% solubilized	Lin *et al.* (1996)
Domestic WAS	NaOH	25	24	COD 37% solubilized	Chang *et al.* (1997)
	NaOH/Sonication			COD 89% solubilized	
Industrial WAS	NaOH	25	24	COD 25% solubilized	This study (1997)

*MSWOF, organic fraction of municipal solid wastes.

in Fig. 4. The correlations of SCOD vs DOC and SCOD vs BOD_5 were determined. It is apparent that both the concentrations of DOC and BOD_5 increased with an increasing concentration of SCOD. The increasing BOD_5 concentration could offer a significant verification of the biodegradability enhancement.

From the stoichiometric calculation of the sludge composition, the structural formula of activated sludge is $C_5H_7NO_2$ (Metcalf and Eddy, Inc., 1991). It reveals that each unit of carbon needs 2.67-fold oxygen for oxidizing completely to form carbon dioxide. In this study, a liner relationship between SCOD and DOC was established. The regression line was DOC = 0.30 SCOD − 99.87 and the ratio of SCOD/DOC was 3.33. This result indicated that 30% of SCOD was contributed by the DOC. The other 70% of SCOD was contributed by other compounds, that is, various kinds of nitrogeneous compounds. This value is slightly greater than that from the stoichiometric calculation. This might be due to the background substances, such as organic polymers, which could connect with the particles of the WBS. The DOC could be obtained from both the WBS and the organic polymers.

Release of soluble nitrogen

Several nitrogenous compounds such as ammonium, org-N and ionic-formed nitrogen (NO_2^- and NO_3^-) were solubilized in the supernatant after alkaline pretreatment. Since the WBS was treated under alkaline conditions, nitrogen could be released from the sludge. If the supernatant of hydrolyzed WBS were to be recycled to the nitrification-denitrification process, the additional nitrogen loading should be taken into consideration. Figure 5 shows the correlation between the unit alkaline dosage (g-NaOH/100 g-TS) and total solubilized nitrogen (mg-N l^{-1}) at different solid concentrations. The amounts of total solubilized nitrogen increased with increasing alkali dosage. It was also found to increase with the sludge concentrations if the alkali dosage was kept

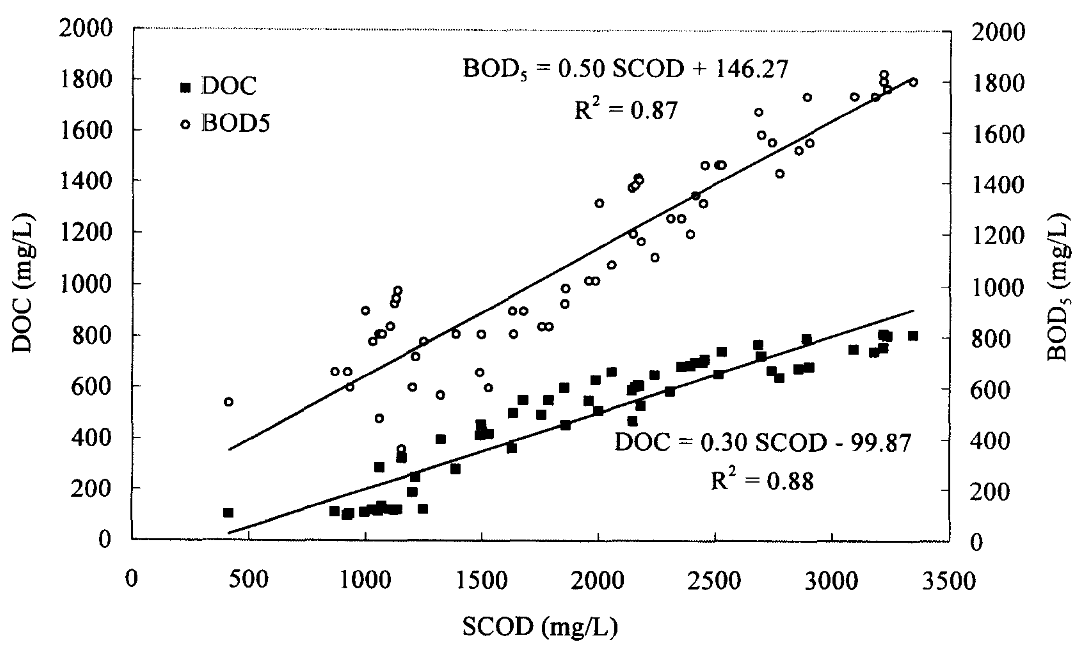

Fig. 4. The correlation of SCOD vs DOC and SCOD vs BOD5 (NaOH dosages range from 10–50 m-equiv l^{-1}, TS range from 0.5 to 2%, initial pH 7.2).

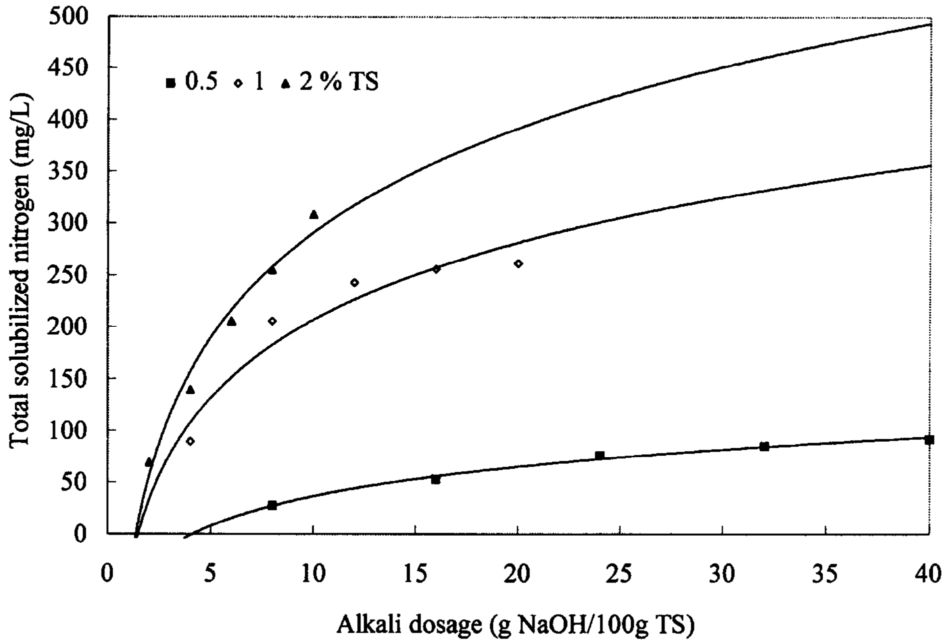

Fig. 5. The correlation between the unit alkali dosage and total solubilized nitrogen.

constant. At the treatment condition of 1% TS and NaOH 30 m-equiv l^{-1} (i.e. the point at 12 g NaOH/100 g TS of the 1% TS curve), the concentration of total nitrogen solubilized was 242.6 mg N l^{-1}. While the experimental condition was changed to 2% TS and 50 m-equiv l^{-1} NaOH (i.e. the point at 10 g NaOH/100 g TS of the 2% TS curve), the concentration of total nitrogen solubilization increased to 304.3 mg N l^{-1}.

Figure 6 illustrates the distribution of various nitrogenous compounds under 1% TS concentration and different NaOH dosages. Org-N was found to be the major product in all six NaOH dosages (0–50 m-equiv l^{-1}). The percentages of org-N distribution ranged from 45–69%. Nitrate was the lowest product, with a percentage <10%.

According to the data obtained from the ABS manufacturing factory, the concentration of total nitrogen of the wastewater was 371 mg l^{-1}, and the amount of the influent wastewater is was 3.84×10^6 l day^{-1}. Therefore, the total amount of nitrogen in the influent is 1 420 kg day^{-1}. The amount of WBS generated from the wastewater treatment plant is was *ca* 10^5 l day^{-1}. If all the WBS

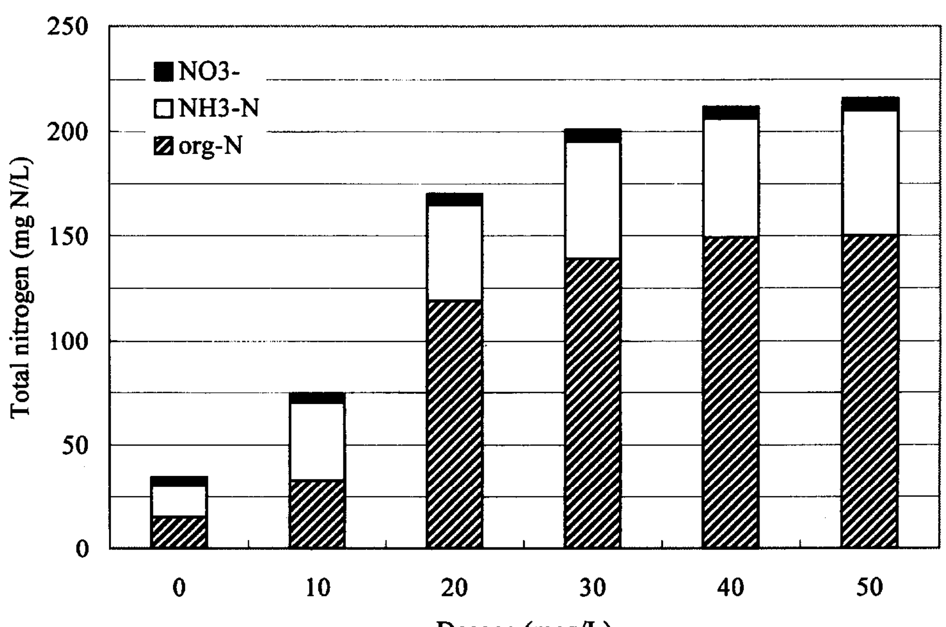

Fig. 6. The distribution of the solubilized nitrogen in the hydrolysate (TS 1%, alkali dosage varied).

Table 3. The nitrogen and phosphorus in different pretreatment methods

References	Type of sludge	Treatment method	Solubility of nitrogen (%)	Soluble P ($mg\ l^{-1}$)
This study, 1997	Industry WAS (1% TS)	30 meq/L NaOH (24 h)	46	11.9
Barlindhaug and Ødegaard (1996)	Mixed sludge	180°C, 30 min	85	20–100
Smith and Göransson (1992)	Mixed sludge	120–160°C, 1 h, H_2SO_4 (pH<2)	80	16.3
Kristensen *et al.* (1992)	Primary sludge	Biological hydrolysis	22	12.0

were hydrolyzed, the production of total soluble nitrogenous matters would be equal to 24.0 kg day^{-1}. However, based upon the experimental result, the total nitrogen of the supernatant was only 1.7% of the total nitrogen of the influent wastewater. Therefore, the additional amount of solubilized nitrogen must have been negligible. The release of phosphorus within the sludge hydrolysate was also remarkably low. The initial concentration of soluble phosphorus at 1% TS was 11.7 mg $PO_4^{3-}\ l^{-1}$. After alkaline treatment (NaOH 30 m-equiv l^{-1}) the concentration of soluble phosphorus was 11.9 mg $PO_4^{3-}\ l^{-1}$.

Table 3 shows the solubilization of nitrogen and phosphorus in several sludge treatment methods. In general, thermal treatment solubilizes more nitrogen than does chemical treatment and biological treatment. Barlindhaug and Ødegaard (1996) pretreated the mixed sludge with a thermal process, 85% of nitrogen was solubilized after 30 min reaction duration. In this study, only 46% of nitrogen was solubilized after 24 h alkaline pretreatment. Apart from the nitrogen released, the solubilization of phosphorus was also low, no matter which treatment process was applied.

CONCLUSIONS

Alkaline pretreatment does significantly enhance the amount of the soluble organic matter from the WBS of a high-strength nitrogenous-wastewater treatment plant. The optimal operating condition were found to be 1% TS and 30 m-equiv l^{-1} NaOH based upon the best solubilization efficiency and rate. Under this condition, the solubilization of COD was *ca* 24.7%, and the solubilization rate was 0.048 h^{-1}. The amount of solubilized nitrogen of the hydrolysate to be recycled to the denitrification step was negligible, and the release of phosphorus was remarkably low. The biodegradability also increased with an increasing pretreatment time, NaOH dosage and TS concentration.

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