Maejo Int. J. Sci. Technol. **2010**, *4*(02), 250-260

Maejo International
Journal of Science and Technology

ISSN 1905-7873
Available online at www.mijst.mju.ac.th

Full Paper

Effects of thermochemical pretreatment on the biodegradability of sludge from a biological wastewater treatment system

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Received: 21 January 2010 / Accepted: 16 July 2010 / Published: 19 July 2010

Abstract: The effects of thermochemical pretreatment on the sludge biodegradability were examined. Two types of tests were conducted: aerobic biodegradation and denitrification using thermochemically pretreated sludge as carbon source. In the aerobic biodegradation tests, the biodegradation efficiency for the sludge pretreated at 60, 70, 80 and 90^{o}C (pH 11) was 1.4-2.2 times higher than that for the untreated sludge. The biodegradation efficiency for the supernatant was also about 1.9 times higher than that for the particulates. The biodegradation enhancement for the thermochemically pretreated sludge was demonstrated in denitrification tests. The supernatant showed its potential as a carbon source for the denitrification process.

Keywords: wastewater treatment, sludge, thermochemical pretreatment, biodegradability, denitrification

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Introduction

Sludge disintegration has been commonly practiced as a pretreatment for sludge digestion [1]. Pretreatment destroys cell walls leading to the solubilisation of extracellular and intracellular materials into the aqueous phase [2]. With pretreatment, not only hydrolysis is accelerated by the increase in dissolved components but improvement of biodegradability, sludge dewatering and reduction of pathogens and foaming can also be achieved as well [3]. There have been several kinds of pretreatment method studied so far, which are either physical, chemical, mechanical or biological in nature, or a combination of any two of these methods [1].

Recently, ozone treatment of sludge followed by recirculation of the treated sludge into the bioreactor was reported to effectively reduce sludge production [4-5]. However, through ozonation at a high ozone dose, e.g. above 1.0 g O_3/g of mixed-liquor suspended solids, a large portion of sludge was mineralised [6-7]—in other words, some organic compounds or released soluble chemical oxygen demand (SCOD) were lost, probably due to complete oxidation to CO_2 since ozone has a strong oxidative power [8-10]. Although this phenomenon is good for the reduction of the sludge, it should be noted that the supernatant from the ozonated sludge also contains some nitrogen [6]. The carbon/nitrogen (C/N) ratio in the supernatant is consequently low and not sufficient for denitrification of released nitrogen in the supernatant [4, 10-12]. External organic compounds such as methanol, ethanol and acetic acid are usually added to the denitrification tank if the wastewater does not contain sufficient reducing power [13]. The use of these external electron donors imposes a financial burden [14]. A thermochemical method for sludge pretreatment may provide a solution for the problem. Organic compounds have not been lost during the pretreatment because the thermochemical process does not oxidise any materials but only promotes hydrolysis and helps split complex polymers into smaller molecules [15-16]. The thermochemical process is simple and cost-effective [1-2], with sodium hydroxide being found to be the most efficient alkali for inducing hydrolysis and cell lysis [17].

Themochemical method has in fact been studied elsewhere [1-2, 17-19]. However, there is still a lack of quantitative information about the enhancement of biodegradability of sludge pretreated thermochemically. Therefore, in the present study, the effects of thermochemical pretreatment on the biodegradability of sludge are evaluated. Two types of tests were first conducted to quantify the enhancement of biodegradability of the thermochemically pretreated sludge: aerobic biodegradation and denitrification. The aerobic biodegradation tests were carried out with the pretreated sludge, particulate and supernatant. The denitrification experiment using the supernatant as a carbon source was also examined.

Materials and Methods

Thermochemical pretreatment of sludge

The sludge used for the experimental work was obtained from the aerobic basin of a bench-scale anoxic-aerobic membrane bioreactor located in a wastewater treatment plant in Sungkyunkwan University, Suwon, Korea. The sludge was passed through a standard sieve (0.5 mm) to remove coarse debris.

In order to study the hydrolysis process of the sludge, a series of experiments were performed at different temperatures (60, 70, 80 and 90°C) while pH and experimental time were fixed at 11 and 7 hours respectively. All determinations were carried out in duplicate. The sludge sample (1.0 L) was put in a 2.0-L glass beaker. A stock solution of sodium hydroxide (>98%, Samchun Pure Chemical Co., Korea) was added to increase the pH of the sample to 11. The beaker was put in a water bath (Model KMC-1205WP, Vision Scientific Co., Korea) to maintain the desired reaction temperature for 7 hours. The sludge in the beaker was kept in suspension by a slow-speed mixer (Model GT-S20, 0-600 rpm, Green Tech Co., Korea). In order to minimise evaporation during the pretreatment, the beaker was covered with aluminum foil. Chemical oxygen demand (COD), soluble chemical oxygen demand (SCOD) and mixed-liquor suspended solids (MLSS) were measured every hour.

The sludge solubilisation efficiency after thermochemical pretreatment was evaluated through SCOD release efficiency and MLSS reduction efficiency as follows:

$$\text{SCOD release efficiency} = \frac{SCOD}{COD} \times 100 \ (\%)$$

where SCOD (mg/L) was measured after thermochemical pretreatment and COD (mg/L) was measured before thermochemical pretreatment.

$$\text{MLSS reduction efficiency} = \frac{MLSS}{MLSS_o} \times 100 \ (\%)$$

where MLSS (mg/L) was measured after thermochemical pretreatment and $MLSS_o$ (mg/L) was mixed liquor suspended solids measured before thermochemical pretreatment.

Aerobic biodegradation experiment

After the thermochemical pretreatment, a part of the pretreated sludge was centrifuged at 5000 rpm for 10 minutes in a centrifuge (Model MF550, Hanil Science Industrial Co., Korea) to afford the supernatant and particulates. The aerobic biodegradation experiments were conducted in a series of 500-mL bioreactors (Comput-OX respirometer, Model AV4R, N-CON Systems Co., USA). The designed sample volume for testing in a bioreactor is 300 mL [20]. Therefore, three sets of testing samples were prepared for each bioreactor: (i) 150 mL of sludge (untreated sludge taken directly from the aerobic basin) and 150 mL of each of the differently pretreated sludge (60, 70, 80 and 90^{o}C at pH 11 for 3 hours); (ii) 150 mL of untreated sludge and 150 mL of supernatant; and (iii) 150 mL of untreated sludge and 150 mL of particulates. Besides, a control test was prepared in another bioreactor which only consisted of 150 mL of untreated sludge and 150 mL of distilled water. Allylthiourea (>98%, Acros Organics, USA) was added to each bioreactor at 1.4 mg/L to inhibit nitrification process which can utilise some oxygen. As respiration takes place, oxygen is depleted and carbon dioxide is released at the same rate [20]. Potassium hydroxide pellets (>85%, Showa Chemical Co., Japan) were used to trap the generated CO_2 as potassium carbonate. As a result, the pressure in the reactor dropped. Oxygen consumption was determined by measuring the change in headspace pressure created by oxygen consumption. The Comput-OX system detected the drop in pressure and delivered pure oxygen to the reactor in measured increments and also recorded the volume of oxygen and the time it was delivered. The oxygen utilisation (in mg/L) was computed automatically by the Comput-OX program and presented both in numeric and graphic displays for each test. Also, COD of the sludge in each bioreactor was measured before and after the aerobic biodegradation tests.

Batch denitrification experiment

The biodegradability of the supernatant (obtained by centrifuging the pretreated sludge as described in the above section) was also evaluated by batch denitrification experiment. A 250-mL flask containing 35 mg NO_3^-N per L (prepared from a stock solution of potassium nitrate (>99%, Yakuri Pure Chemical Co., Japan)) and 50 mL of sludge (taken from the anoxic basin) or the supernatant (diluted to C/N ratio of 5, 10 or 15) was sealed and incubated at 30^{o}C in an incubator (Model DH.WTH0115, Daihan Scientific Co., Korea) with slow agitation (50 rpm, using a magnetic stirrer). Aliquot samples were periodically taken from the flask and analysed for nitrate (NO_3^--N).

Analysis methods

The proper standard methods for the examination of water and wastewater by APHA [21] were used for all the monitoring analyses in this study.

Mixed-liquor suspended solids (MLSS) and mixed-liquor volatile suspended solids (MLVSS) were measured by using the methods 2540D and 2540E respectively. Sample for the measurement of MLSS and MLVSS was filtered through a 0.45-µm glass microfibre filter (GD/X, Whatman, UK). The solids retained by filter were dried in an oven (Memmert UFP600, GmbH, Germany) at 105^{o}C for 2 hours for the MLSS measurement, and then ignited in a furnace (DH.WFH12.27, Daihan Co., Korea) at 550°C for 20 minutes for the MLVSS measurement.

COD was determined by the closed reflux, colorimetric method (Method 8000). Sample was added into the COD vial and heated in a COD heater (Model DRB200, Hach Co., USA) at 150^{o}C for 2 hours, then cooled to room temperature and its absorbance measured at 620 nm by a spectrophotometer (DR/2500, Hach Co., USA) to afford COD (in mg/L). SCOD was similarly determined except the sample was first centrifuged at 5000 rpm for 10 minutes and then filtered through a 0.45-µm glass microfibre filter.

Total nitrogen (TN) was analysed by the persulphate digestion method (Method 10071). Sample was added into the TN vial. A Total Nitrogen Reagent Powder Pillow (Hach Co., USA) was also added to the TN vial, which was then heated at 105^{o}C for 30 minutes (using COD heater, Model DRB200, Hach Co., USA). After the sample was cooled to room temperature, it was measured at 410 nm to obtain TN (in mg/L).

Nitrate (NO_3^--N) was measured by the cadmium reduction method (Method 8039). Sample was filtered through a 0.45-µm glass microfibre filter and added to the NO_3^--N vial. NitraVer 5 Nitrate Reagent Powder Pillow (Hach Co. USA.) was then added to the vial. A 5-minute reaction period was required. Then the sample was analysed spectrometrically at 500 nm to afford NO_3^- -N (in mg/L).

The pH value of each sample was measured using a pH meter (Horiba Navi, Model F-54, Japan).

Results and Discussion

Sludge pretreatment and solubilisation efficiency

The initial MLSS and MLVSS were measured and found to be 7500 and 5540 mg/L respectively. The ratio of MLVSS/MLSS is about 74%. The solubilisation efficiency of sludge after thermochemical pretreatment can be inferred through two aspects, i.e. SCOD release efficiency and MLSS reduction efficiency. The experimental data related to SCOD release and MLSS reduction during thermochemical pretreatment process are given in Figures 1-2.

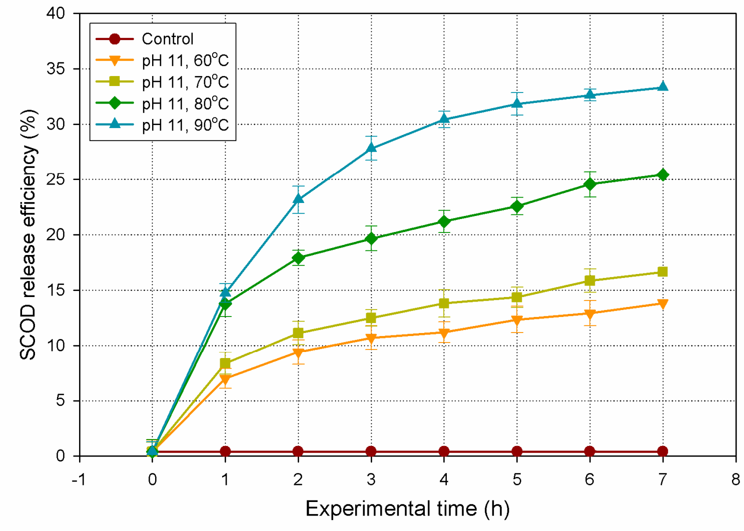

Figure 1. SCOD release efficiency during thermochemical pretreatment

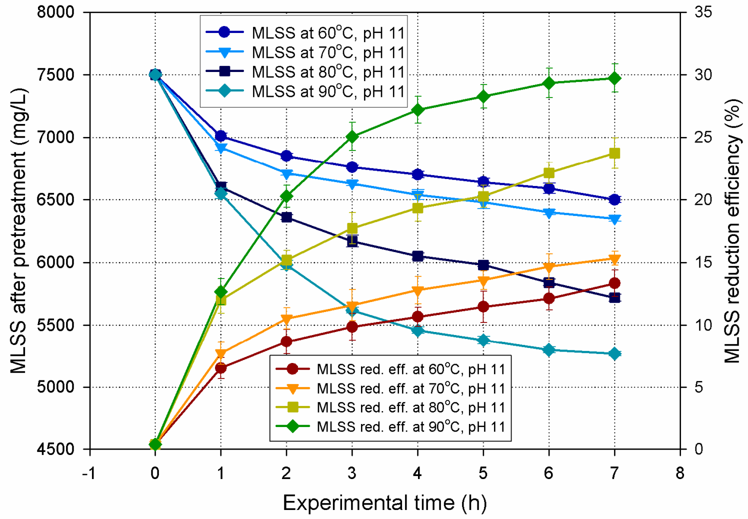

Figure 2. MLSS reduction efficiency during thermochemical pretreatment

An increase in SCOD release efficiency and decrease in MLSS were used to evaluate the hydrolysis process. For all thermochemical pretreatment conditions, a rapid increase in SCOD release was observed during the first hour (Figure 1). Then a decreasing rate of SCOD release was observed until a maximum value was reached. Rocher et al. [18] reported that the cells were completely deactivated by a temperature above 60°C. Their study also showed that alkaline treatment (by using NaOH) combined with thermal treatment was an efficient process to induce cell lysis. With intermediate conditions of pH 10 and 60°C, the released dissolved organic carbon was higher than or equal to that obtained by thermal treatment at 100°C and neutral pH or by alkaline treatment at pH 12 and 30°C [19]. In this study, with intensive hydrolysis conditions (pH 11 and T ≥ 80°C), the COD release efficiency increased significantly during the first 3 hours of the pretreatment process, in which about 75-80% of COD release efficiency was achieved.

The MLSS reduction efficiency is presented in Figure 2. The MLSS reduction efficiency during the first 3 hours was about 60-75% of the final values, obtained after 7 hours of pretreatment.

Increasing the temperature from 60 to 90°C after the third hour of operation at high pH value (pH 11) decreased MLSS concentration significantly from 7500 mg/L down to about 6750 and 5600 mg/L (at the 3rd hour), corresponding to about 10 and 25% of sludge reduction respectively.

Aerobic biodegradation tests

The biodegradability enhancement of sludge after thermochemical pretreatment is demonstrated in the aerobic biodegradation experiment. Figure 3 shows the oxygen consumption by the thermochemically pretreated sludge in the aerobic bioreactor. Two phases of biodegradation—the fast and slow degradation—were observed. The duration of the fast degradation phase increased with temperature. Although it is obvious that biodegradability of sludge was enhanced by thermochemical pretreatment, accurate quantification of the biodegradability of the pretreated sludge is not easy because the initial sludge added in the bioreactor itself consumed oxygen.

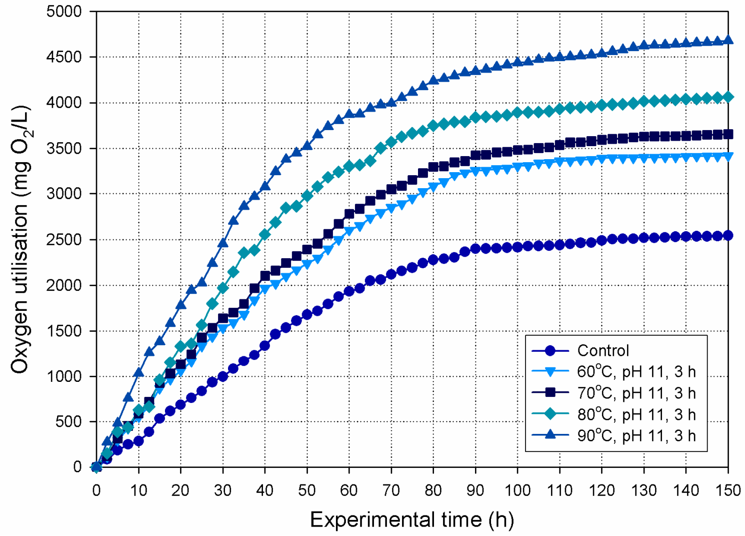

Figure 3. Oxygen consumption during aerobic biodegradation tests for the thermochemically pretreated sludge

As previously mentioned, during the aerobic biodegradation tests the oxygen utilised by nitrification was negligible since allylthiourea was added in the bioreactor to inhibit nitrification process [20]. Considering the volume ratio of the pretreated sludge and the untreated sludge (1:1), the biodegradation efficiency can be regarded as an average value of that for the thermochemically pretreated sludge and the untreated sludge. The biodegradation efficiency for the pretreated sludge is estimated based on the COD before and after aerobic biodegradation tests (after 150 hours) as presented in Figure 4. From the figure, the biodegradation efficiency for the differently pretreated sludge (60, 70, 80 and 90°C at pH 11 for 3 hours) is 41.4, 44.3, 53.1 and 62.4% respectively, compared to 28.7% for the untreated sludge. Thus, the biodegradation efficiency for the thermochemically pretreated sludge was 1.4-2.2 times higher than that for the untreated sludge. In fact, most of the biodegradation of the thermochemically pretreated sludge occurred within 80 hours while that of the untreated sludge was steady after more than 90 hours (Figure 3). One of the interesting observations is the suppression of biodegradation rate at relatively high temperature (> 80°C).

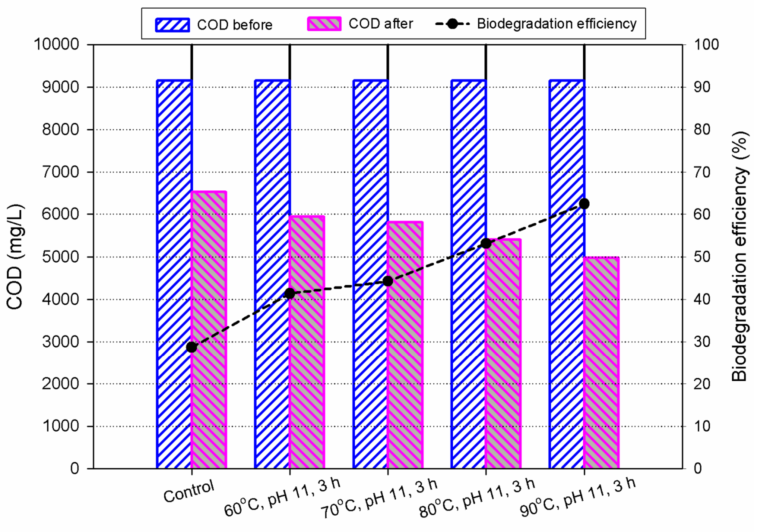

Figure 4. Biodegradation efficiency of thermochemically pretreated sludge prepared by different Conditions

The biodegradation efficiency for the particulates and supernatant obtained from sludge pretreated at 80°C (pH 11) for 3 hours was also determined by the aerobic biodegradation tests, in comparison with the pretreated and the untreated sludge (control). The oxygen consumption during the aerobic biodegradation for these cases is shown in Figure 5. It can be seen that the biodegradation of the supernatant was predominant during the first 40 hours. Also, the biodegradability of the particulates was better than that of the untreated sludge. Most of the biodegradation of the particulates occurred within 100 hours.

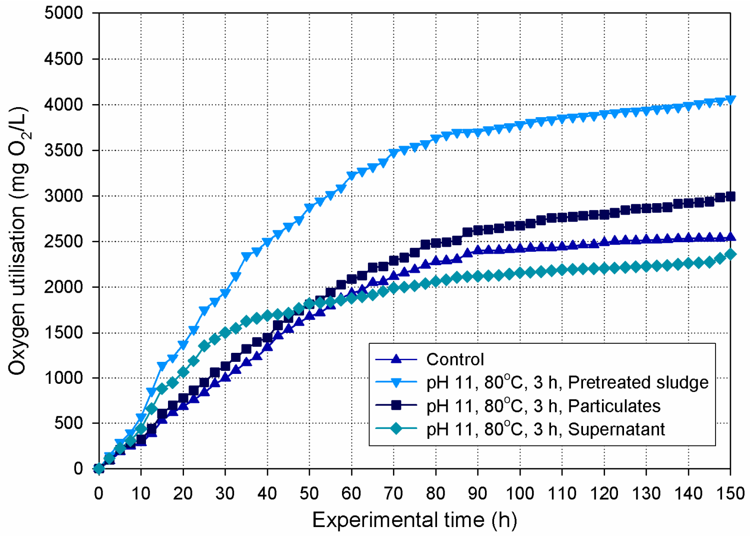

Figure 5. Oxygen consumption during aerobic biodegradation of sludge portions

Figure 6 presents the estimated biodegradation efficiency for the sludge portions. From the figure, the biodegradation efficiency for the supernatant was found to be 84.4% at 150 hours. In contrast, the biodegradation efficiency for the untreated sludge was found to be 28.7%. Thus, the supernatant was much easier to biodegrade, with biodegradation efficiency being enhanced approximately 55.7% more than that for the untreated sludge. The biodegradation efficiency for the particulates was found to be 44.2% after 150 hours of aerobic biodegradation, showing an enhancement of 15.5% more than that for the untreated sludge. From the obtained results it is evident that the biodegradation efficiency for the supernatant was about 1.9 times higher than that for the particulates.

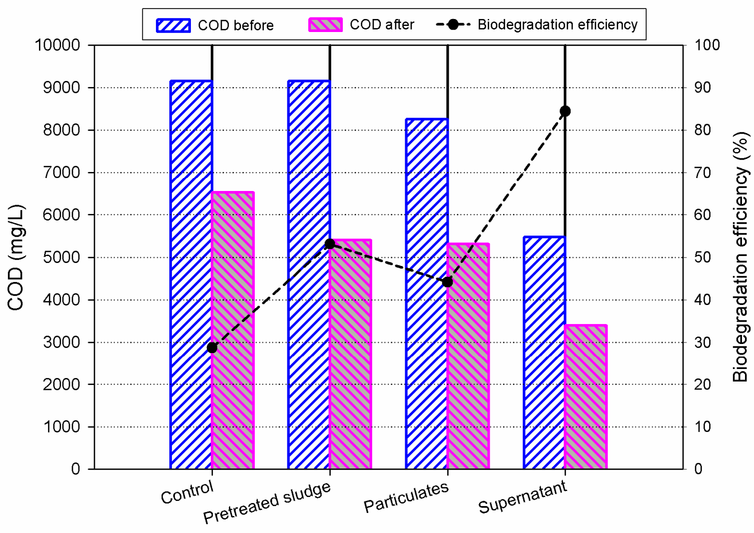

Figure 6. Biodegradation efficiency of sludge portions

Batch denitrification tests

Figure 7 shows the changes in nitrate concentration during denitrification tests using the supernatant (obtained by centrifuging the sludge pretreated at 80°C, pH 11, for 3 h) as carbon source at C/N ratios of 5, 10 and 15. Although the rate of denitrification is affected by the amount of carbon supply, it is known that the supernatant could be utilised as a carbon source for denitrification [19]. Figure 8 shows another denitrification experimental result obtained by using the supernatant pretreated at different temperatures at a fixed C/N ratio of 10.

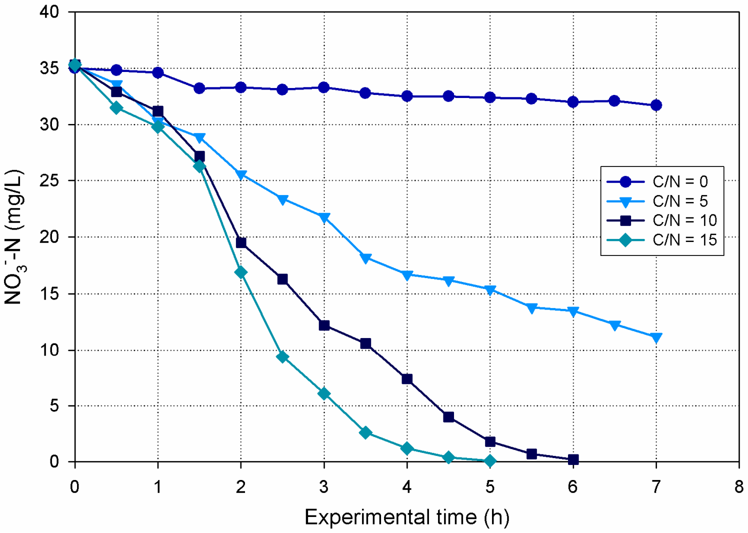

Figure 7. Result of denitrification tests using supernatant at different C/N ratios

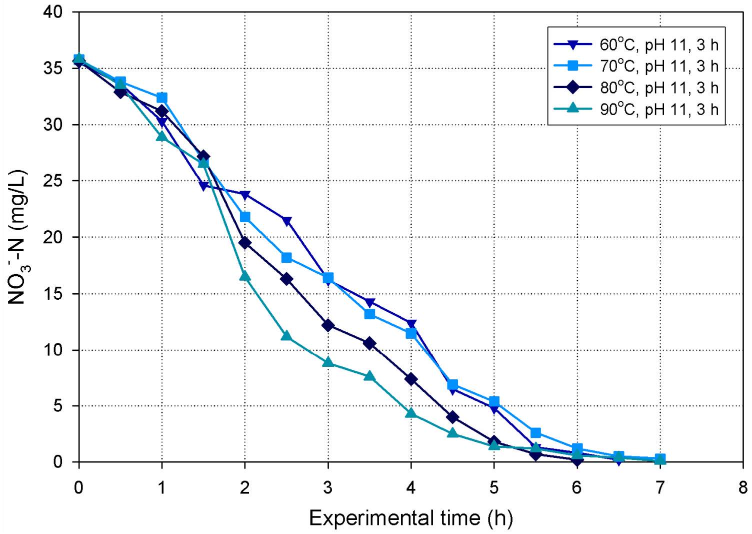

Figure 8. Result of denitrification tests using supernatant pretreated at different temperatures (at fixed C/N ratio of 10)

The result clearly indicates that the supernatant was available for biodegradation as a good carbon source regardless of the different thermal pretreatments. The average specific denitrification rate was found to be about 1.85 g NO_3^--N/g MLVSS/h (grams of nitrate per gram of mixed-liquor volatile suspended solids per hour). In Table 1, the feasibility of the solubilised organics after thermochemical pretreatment as carbon source is compared with that of other carbon sources commonly used for denitrification. It should be noted that the supernatant from the thermochemically pretreated sludge also contained some nitrogen. At 80°C and pH 11 for 3 hours, however, the C/N ratio of the supernatant became larger than 15.6, indicating that the recycling of the supernatant to the influent wastewater stream of the wastewater treatment plant can increase the overall C/N ratio.

Table 1. Comparison of specific denitrification rates by various carbon sources

Carbon source	Specific denitrification rate (g NO_3^--N/g MLVSS/h)		Reference
	Range	Average	
Methanol	2.88-21.6	10.32	[13]
Wastewater	0.72-2.64	1.68	[22]
Supernatant*	1.16-2.18	1.85	This study

*obtained from thermochemically pretreated sludge centrifuged at 5,000 rpm for 10 minutes.

Conclusions

The effects of thermochemical pretreatment on the sludge biodegradability were determined by aerobic biodegradation tests. Thermochemically pretreated sludge at 60, 70, 80 and 90°C (pH 11) showed 1.4-2.2 times greater biodegradation compared to the untreated sludge. The biodegradation of the thermochemically pretreated sludge mostly occurred within 80 hours while that of the untreated sludge was steady and required more than 90 hours. Thus, the biodegradability of sludge was greatly enhanced by thermochemical pretreatment. The biodegradation of the supernatant was about 1.9 times greater than that of the particulates. The biodegradability of the particulates was also somewhat better than that of the untreated sludge.

The biodegradation enhancement of thermochemically pretreated sludge was confirmed by the denitrification tests. The supernatant obtained from the thermochemically pretreated sludge showed its potential as a carbon source for denitrification with an average specific denitrification rate of 1.85 mg NO_3^--N/g MLVSS/h. As a result, the supernatant demonstrated its capability as a carbon source for denitrification.

The sludge was also reduced significantly (up to 25%) after 3 hours of pretreatment. Thus, combining the thermochemical method with the biological wastewater treatment could be a good solution for the overall sludge reduction. Further study will be necessary to compare this pretreatment technique with others such as mechanical and biological pretreatments in terms of biodegradability enhancement.

Acknowledgements

This study was financially supported by the Korean Ministry of Education, Science and Technology through Brain Korea 21 (BK-21) program. The authors would also like to thank the editor and referees for the helpful comments.

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