Songklanakarin J. Sci. Technol.
31 (6), 635-639, Nov. - Dec. 2009

Songklanakarin Journal
of Science and Technology
http://www.sjst.psu.ac.th

Original Article

Weight and volume reduction of organic sludges and enhanced recovery of biomass resources using sonophotocatalysis

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Received 28 September 2007; Accepted 9 March 2009

Abstract

The efficiency of sonophotocatalysis, a pretreatment process involving ultrasonic irradiation and photocatalysis, in decreasing the emission amount of sewage sludge and enhancing the recovery of valuable materials, was investigated experimentally. The results indicated a 50% reduction in the sewage sludge emission after sonophotocatalysis was carried out for 2 h. In addition, the recovery ratio of methane gas by anaerobic digestion and dissolved phosphorus were 1.7 and 2.5 times more than those of methane and phosphorus in the recovery process without pretreatment, respectively.

Keywords: sewage sludge, pretreatment process, sonophotocatalysis, enhanced recovery, methane gas, phosphorus

1. Introduction

Currently, almost 50% of the industrial wastes produced in Japan are waste sludges (~188 million tons) (http://www.env.go.jp/en/recycle/, August 17, 2007). In particular, sewage sludge constitutes the largest portion of these sludge (~75 million tons), and it is generated in the activated sludge system. Recently, the increase in capacity of sewage lines has led to an increase in the emission amount of sewage sludge. Moreover, landfill capacity continues to decrease.

Therefore, some novel experiments have been conducted on the activated sludge system. One such experiment involves the introduction of a pretreatment process to increase the biodegradation ability potential of microorganisms in the sludge before returning the sludge to the aeration tank for treatment with the activated sludge (Yasui and Shibata, 1994). This pretreatment is expected to enhance the recovery of biomass resources such as hydrogen, methane and phosphorous from the sludge, since the cell walls and membranes of the microorganisms are easily disintegrated (Tiehm *et al.*, 2001; Arakane *et al.*, 2005; Goel *et al.*, 2003; Hasegawa, 2001).

The authors propose the use of sonophotocatalysis, which is the combination of ultrasonic irradiation and photocatalysis (Koike *et al.*, 2006), as an efficient pretreatment process. This process has been employed for the degradation of various types of environmental pollutants. This process has been proved to improve reaction efficiency owing to the strong combined effect of ultrasonic irradiation and photocatalysis (Gogate and Pandit, 2004).

In this study, the process of sonophotocatalysis has been tested for degradation of sewage sludge to increase its biodegradability and enhance the recovery of methane gas and phosphorus from it. Experiments were conducted on a batch scale using the necessary equipment. The 5-day BOD_5 (biochemical oxygen demand) of the sludge sample and D-COD (dissolved chemical oxygen demand) of its filtrate were measured to determine the extent of biodegradation. The

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amounts of methane gas generated by anaerobic digestion and dissolved phosphorous in the filtrate were also measured.

2. Experiment

2.1 Equipment

The authors first built a cylindrical batch reactor equipped with a UV lamp (wavelength: 254 nm, power: 25 W) at the centre and an ultrasonic transducer (frequency: 28 kHz, power: 100 W) at the bottom (Koike *et al.*, 2006). From the experiments conducted using the reactor, it was observed that the intensity of the ultrasonic standing wave inside the reactor was weak and the penetration ratio of UV light was very small (Hayashi, 2006). Therefore, for the present study, a new reaction chamber was built to improve the reaction efficiency.

Figure 1 shows the schematic drawing of the experimental equipment. The reactor is rectangular in shape and is made of stainless steel. Its length, width and height are 85, 61 and 66 mm, respectively. The wavelength range of the UV light is between 254 and 579 nm, and the power of the lamp is increased to 400 W from 25 W. The sonicator and ultrasonic transducer are the same as those in the previously used equipment.

2.2 Sample

For the experiments, mixed sewage sludge, which was a mixture of the excess sludge and crude sludge, was obtained from the sewage treatment plant in Sendai City, Japan. The concentration of solids in the sludge sample was adjusted to 1.0% by adding distilled water. Then, TiO_2 powder (anatase type, average particle size: 6.4 μm) was added to the sample until the concentration of TiO_2 was 0.15 g/L. The elemental composition of the solids is shown in Table 1.

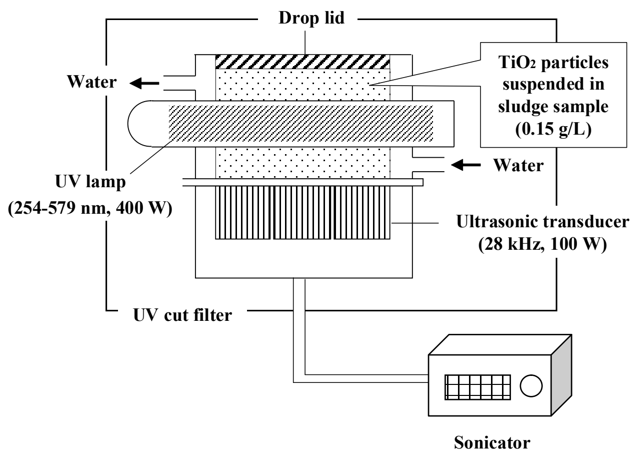

Figure 1. Experimental equipment

Table 1. Elemental composition of sample

Element	Rate [%]
C	41.1
H	6.30
N	6.83
P	1.92
Cl	0.37
S	0.98
Ash	14.9

2.3 Method

Three hundred millilitres of the sludge sample in which the TiO_2 particles were suspended was placed in the reactor. The drop lid was brought down on the sample so that no air space was present. Then, the experiment was commenced under the given ultrasonic and photocatalytic conditions and continued for 2-4 h. All experiments were triplicated or repeated 3 times. In addition to sonophotocatalysis, ultrasonic irradiation and photocatalysis were also individually used as pretreatment processes.

2.4 Analyses

2.4.1 Biodegradability

After the experiment, BOD_5 of the sample and D-COD of its filtrate were measured using BODTrak (CB-5, Hach Lange Gmbh) and a COD meter (HC-607, Central Kagaku Corp.), respectively (Japan Sewage Works Association, 2004). For the COD measurements, potassium permanganate ($KMnO_4$) was used as the oxidant.

2.4.2 Methane gas recovery

After the experiment, anaerobic digestion was carried out at 35°C in a batch anaerobic digester. The schematic of the digestion process is shown in Figure 2.

Three hundred millilitres of the sample of the pretreated sludge and 200 mL of the digestive sludge (concentration of solids: 2.0%), which was added to enhance digestion, were mixed thoroughly using a magnetic stirrer (speed: 300 rpm).

The biogas generated after digestion was collected in an aluminium gas bag and analysed by a gas chromatograph (CP-3800, Varian, Inc.) every day. The volume of gas generated was measured by the underwater substitution method.

2.4.3 Phosphorus recovery

Phosphorus in the sewage sludge is expected to be recovered as MAP (magnesium ammonium phosphate) particles, which can be directly used as fertilizer. The MAP

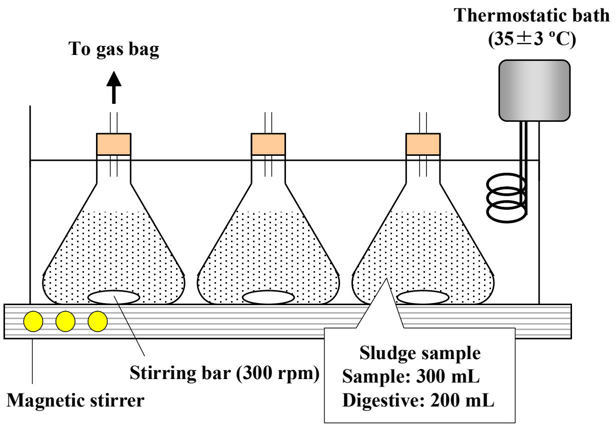

Figure 2. Anaerobic digester

formation under basic conditions occurs as per the following equation (Hagino and Hirashima, 2005):

$$Mg^{2+} + NH^{4+} + PO_4^{3-} \rightarrow MgNH_4PO_4\downarrow + 2H^{+}\ 00\ \ 00 \qquad (1)$$

The equation shows that it is important to investigate the effect of the increase in the total amount of phosphorus (PO_4-P) caused by sonophotocatalysis in the various ionic species, *i.e.*, PO_4^{3-}, HPO_4^{2-}, $H_2PO_4^{-}$ and H_3PO_4. Phosphorus compounds in sewage sludges exist in many forms such as orthophosphoric acid, pyrophoric acid, ester phosphates and organic phosphorus.

In this study, the concentrations of PO_4-P, dissolved phosphorus and total phosphorus in the pretreated sludge were measured by the molybdenum blue method (Japan Sewage Works Association, 2004).

The sample was filtered, and the filtrate was decomposed by nitric and sulphuric acids. Subsequently, the dissolved phosphorus, which included PO_4-P was determined by the molybdenum blue method. The concentration of total phosphorus was determined in a similar manner after decomposition of the entire sample (solid + filtrate).

3. Results and Discussion

3.1 Effect of the pretreatment process on biodegradability

The effect of the pretreatment process on the increase in the BOD_5 and D-COD values of the sludge sample are shown in Figures 3 and 4, respectively. In these figures, the experimental results obtained by the authors (Koike *et al.*, 2006) when using the cylindrical reactor are also included. “SP” represents sonophotocatalysis. The initial values of BOD_5 and D-COD are 2,092 and 46.2 mg/L, respectively.

The degradation time was fixed at 4 h. In the photocatalysis experiments, the magnetic stirrer was operated at a speed of 100 rpm.

Figure 3 shows that the improvements made to the reactor yielded positive results, which is evident from the increase in the reaction rate. When sonophotocatalysis or ultrasonic irradiation alone was used as the pretreatment process, BOD_5 could be increased to ~60% in 1 h, suggesting 50% decrease in the emission amount of sewage sludge (Nawa, 2002).

However, BOD_5 obtained when sonophotocatalysis was carried out for more than 2 h showed a gradual decrease. In this case, CO_2 present in the gas generated during the experiment was not analysed; however, it was thought that complete degradation (mineralization) of the organic materials in the sample might occur owing to the strong oxidizability. Therefore, to achieve a sufficient increase in BOD_5, degradation must be carried out for 1 h.

When photocatalysis was used for pretreatment, BOD_5 increased only slightly despite carrying out the treatment process in the rectangular reactor for 4 h. However, compared with the results of sonophotocatalysis and only ultrasonic irradiation, the combination of ultrasound and

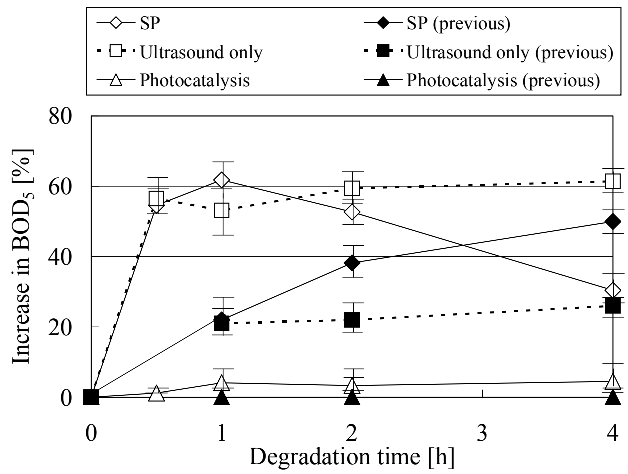

Figure 3. Effect of pretreatment process on BOD_5

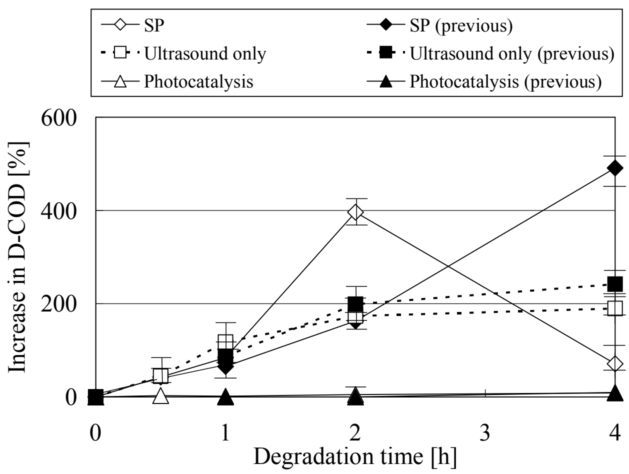

Figure 4. Effect of pretreatment process on D-COD

photocatalysis showed better results. This was because of the difference in BOD_5 in the previous study and the present study, after long-time degradation.

Figure 4 shows a similar trend in the case of D-COD. The reason for the decrease in D-COD after 2 h of sono-photocatalysis appeared to be the same as tha t for the decrease in BOD_5.

When sonophotocatalysis was used for the pretreatment, the increase in D-COD reached 400 mg/L or more. Therefore, the combination of ultrasound irradiation and photocatalysis was found to favour the increase in D-COD.

3.2 Effect of the pretreatment process on methane gas recovery

The effect of the pretreatment process (for 2 h) on methane gas recovered by anaerobic digestion (for 9 days) is shown in Figure 5.

For enhanced recovery of methane gas, it appeared to be sensible to introduce the pretreatment process before anaerobic digestion. After sonophotocatalysis and 9 days of anaerobic digestion, the total amount of methane gas generated was approximately 1.7 times that of methane generated in the untreated process.

Compared with only ultrasonic irradiation, the increase by the combination with photocatalysis was 13%. From the results of increase in BOD_5 and D-COD, this might be because of the increase in D-COD.

Figure 5 shows the increase in the rate of methane gas generation; however, we cannot discern whether or not the total amount of available methane gas would increase. Therefore, it is necessary to increase the time taken for anaerobic digestion by 20 days or more for ascertaining the total amount of methane gas.

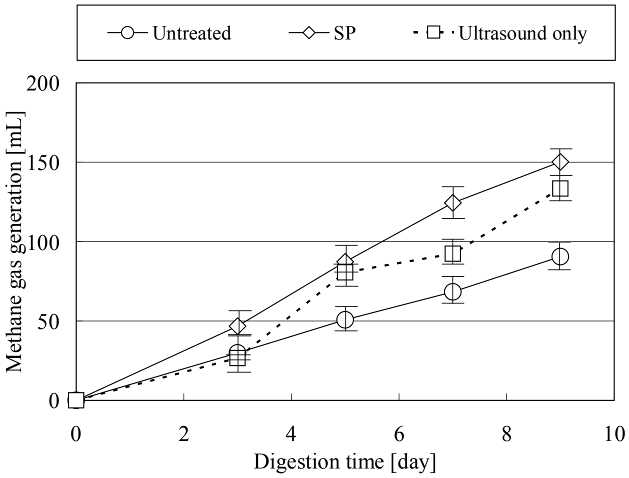

Figure 5. Effect of pretreatment process on methane gas generation

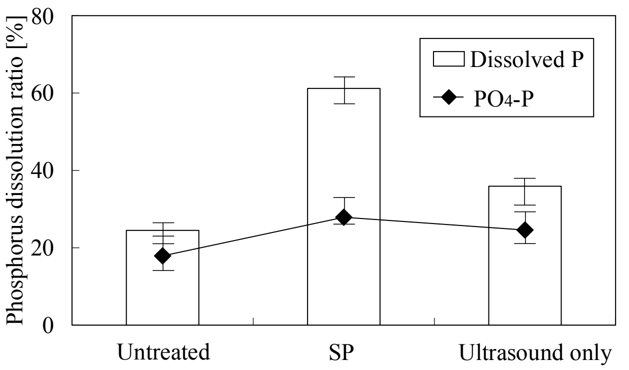

Figure 6. Effect of pretreatment process on phosphorus dissolution

3.3 Effect of the pretreatment process on phosphorus recovery

The effect of the pretreatment process (2 h) on the rates of dissolved phosphorus and PO_4-P is shown in Figure 6. These rates were calculated from the amount of total phosphorus in the sample. In this study, the concentration of total phosphorus was 188 ppm.

From Figure 6, it can be seen that the ratio of the dissolved phosphorus by sonophotocatalysis was 2.5 and 1.7 times that obtained in the cases of untreated and only ultrasonic irradiation, respectively. Therefore, it can be concluded that sonophotocatalysis helps disintegrate the cell wall of microorganisms and dissolve the cytoplasm.

However, after sonophotocatalysis, the increase in the PO_4-P rate was much less. Therefore, in order to recover phosphorus in the form of MAP particles, it is necessary to combine other processes such as thermal treatment with the pretreatment process so as to enhance hydrolysis of the dissolved phosphorus compounds.

4. Conclusions

The efficiency of sonophotocatalysis and other kinds of pretreatment processes in decreasing the emission amount of sewage sludge and to enhance the recovery of methane and phosphorus were investigated experimentally.

From the experiments, the following results were obtained:

1) Improvement in the design of the experimental reactor had a positive effect on the biodegradability of the sewage sludge sample. When sonophotocatalysis or ultrasonic irradiation was used, BOD_5 could be increased to approximately 60% in 1 h, indicating a 50% decrease in the emission amount of sewage sludge.

2) After carrying out sonophotocatalysis for more than 2 h, complete degradation (mineralization) of the organic materials in the sample was thought to occur owing to the strong oxidizability.

3) Compared with the results of sonophotocatalysis, ultrasonic irradiation and photocatalysis, the combination of

ultrasound and photocatalysis showed better results.

4) Methane gas generated by anaerobic digestion for 9 days after sonophotocatalysis was approximately 1.7 times that in the untreated case. This was attributed to the increase in D-COD.

5) It can be seen that the rate of the dissolved phosphorus by sonophotocatalysis was 2.5 and 1.7 times more than the cases of untreated and only ultrasonic irradiation, respectively. However, after sonophotocatalysis, the increase in the PO_4-P rate was much less. Hence, it is necessary to combine other processes such as thermal treatment with sonophotocatalysis so as to enhance hydrolysis of the dissolved phosphorus compounds.

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