J Mater Sci (2008) 43:2431–2436
DOI 10.1007/s10853-007-1957-3

Sewage sludge hydrothermal treatment by microwave irradiation combined with alkali addition

Wei Qiao · Wei Wang · Rui Xun · Wenjing Lu · Keqing Yin

Received: 30 October 2006 / Accepted: 20 June 2007 / Published online: 22 December 2007

Abstract This article focuses on the effects of microwave treatment on sewage sludge with alkali addition. Both the solubilization of organic matters and the settleability of sludge were investigated. It was found that the combined treatment provided a rapid and efficient process to release organics from sludge flocs. Anaerobic digested sludge with low organic content (37%) obtained better results as compared to fresh sludge with high organic content (56%). For digested sludge, 50–70% of VSS was dissolved into a solution at 120–170 °C with a dose 0.2 g NaOH/g-DS within 5 min, and 80% of the total COD was released to supernatants. The liquor soluble COD concentration increased up to 20 g/L. Nearly 60% of nitrogen dissolved at 170 °C. For fresh sludge, solo microwave heating reduced 40% of VSS at 170 °C within 1 min. Adding 0.05 g NaOH/g-DS increased the VSS dissolution ratio to 50% and got 35% of SS reduction. After 1 min microwave treatment with alkali, the treated digested sludge provided a significant settleability improvement. Nevertheless, the high organic content of fresh sludge lessened the improvement of settleability behavior.

Introduction

Wastewater treatment plants produced large amounts of waste primary and secondary sewage sludge, containing organic bacterial microbes and inorganic mineral components. In 2005, there were approximately 11 million tons of dewatered sludge cake (80% moisture content) generated in China [1]. The biological gel structure properties of sludge resulted in the difficulty in dewatering and anaerobic digestion [2]. An effective treatment and disposal method of sludge has been one of the major concerns in wastewater treatment process. Heat treatment has been recognized for many years as a useful aid to sludge conditioning [3–5]. Using heat treatment, liquid sludge is heated to a temperature of about 170 °C for over 30 min. The process is effective to break down sludge gel networks, and reduce the water affinity of sludge solid. As a result, the sludge could be digested and dewatered readily. The hydrolysis of organics is a dominant characteristic to distinguish heat treatment with other pretreatment methods. In the study of Brooks [6], 40–60% of volatile suspended solid (VSS) dissolved from waste activated sludge (WAS) at 170 °C was reported. Using the advantages of heated sludge settling improvement, Wang and Wang [7] combined heat treatment with an anaerobic sequencing batch reactor to increase biogas production. Further efficiency was available by adding acid and alkali called thermo-chemical treatment [8–10]. Researchers found that thermo-chemical treatment gives the best VSS solubilization results as compared to heat treatment with chemical treatment by adding NaOH (0.3 g/g-VSS) [11]. However, the conventional thermal or thermo-chemical treatment is a time-consuming process. With the purpose of heating sludge, microwave irradiation might serve as an alternative method. In recently years, microwave as a novel technique to treat sludge has attracted interests. A uniform microwave field generates energy through the realignment of dipoles with oscillating electric fields to generate heat both internally and at the surface of the treated material. The sludge is a multiphase medium containing water, mineral and organic substances, proteins,

W. Qiao (✉) · W. Wang · R. Xun · W. Lu · K. Yin
Department of Environmental Science and Engineering, Tsinghua University, Beijing 100084, P.R. China
e-mail: qw04@mails.tsinghua.edu.cn

and cells of microorganisms. Due to high water content, sewage sludge absorbs microwave irradiation. Techniques such as microwave drying, pasteurization sterilization, pyrolyzing, gasifying, microwave-hydrothermal synthesis, and organic compound decomposition have been investigated [12–15]. Eskicioglu et al. [16] used microwave heat sludge under 96 °C, a batch anaerobic digestion test which provided a 17% biogas increase over untreated sludge. As compared to conventional heat treatment, microwave resulted in a more soluble protein and volatile fatty acid but less sugar solution. Park and Ahn [17] reported that microwave treated sludge could increase 79% methane production higher than untreated sludge. Wojciechowska [18] used microwave to condition sludge, after 180 s microwave heating specific resistance to filtration (SRF) of mixed sludge (primary and secondary sludge) and anaerobically digested sludge decreased 73 and 84%, respectively. Recent literature report that organics hydrolysis by combing microwave with hydrogen peroxide and acid would be used to recovery sludge nutrients [19]. Therefore, the effectiveness of microwave has been recognized by researchers. However, the exact nature of the sterilization effect and whether it is due solely to thermal effects or to nonthermal effect have continued to be a matter of controversy.

The objective of this study is to investigate sludge microwave hydrothermal reaction behavior combined with alkali addition by investigating solid dissolving at various process. Sludge type, heating temperature, reaction time, and alkaline dose were considered to evaluate their effects in terms of organics solubilization and sludge settling performance.

Materials and methods

A mixture of primary and secondary sludge was collected from a local municipal wastewater treatment plant (Beijing, China). The dry solid (DS) content of sludge was thickened to 4–5% in laboratory and then screened by a 3.2 × 3.2 mm mesh sieve to remove large particles. Such prepared sludge called fresh sludge was stored in a refrigerator at 4 °C for subsequent experiments. In order to evaluate the organic solid content effect, a low organic sludge called digested sludge was obtained by keeping it at room temperature for 25 days. The VSS to SS ratio of digested sludge decreased to 0.37. Table 1 lists the characteristics of fresh and digested sludge. Microwave oven (2,450 MHz, 1,000 W, MSD6, Shanghai Sineo Co., Ltd) with PTFE vessels was used for heating sludge. This frequency of microwave energy has been widely used in scientific research [20, 21]. Sludge hydrothermal treatment was performed by batch tests. An alkali dose of 0–0.2 g NaOH/g-DS (0; 0.03; 0.05; 0.1; 0.2) was mixed by 30 mL sludge with NaOH solution (2 mol/L). About 30 mL sludge with alkali was subjected to a 70 mL PTFE vessel. Temperature and pressure were measured and controlled by microwave oven. Fresh sludge comprised of 38.6% carbon, 5.78% hydrogen and 3.74% nitrogen. The molecular formula of fresh sludge could be described as $C_6H_{11}O_2N_{0.5}$. Meanwhile, digested sludge comprised of 20.4% carbon, 2.18%, and 2.26% nitrogen. All test samples were subjected to microwave heating with temperature settings of 80, 120, 150, and 170 °C. For digested sludge, the microwave heating time was 1, 5, 10, 20, and 30 min with 0.2 g NaOH/g-SS. Further tests for fresh sludge were performed for 1 min with an alkali dose of 0–0.2 g NaOH/g-DS.

The total COD (TCOD) was determined by the potassium dichromate/ferrous ammonium sulfate method. Sludge particles were kept uniformly suspended by a magnetic stirrer when sampling. The supernatants separated from sludge by centrifuging (LG10-2.4A) at 2,775 × *g* for 10 min were used for soluble COD (SCOD) determination. TS and SS were measured by drying sludge slurry at 105 °C for 24 h; VS and VSS were tested by burning it at 600 °C for 2 h. For SS and subsequent VSS analysis, before heating, sludge was centrifuged to remove soluble solids as described in SCOD determination. After the sludge was cooled to room temperature, sludge solid-liquid interfaces movement in a 100 mL graduate was recorded for 25 h. Dry sludge cake elements (carbon, hydrogen and nitrogen) were measured by TOC5000 (SHIMADZU).

Results and discussion

VSS solubilization tendencies

Composition of fresh sludge was 11.6% carbohydrate, 46.3% protein, and 7.4% lipid according for 65.3% of the VSS. The VSS to SS ratio decreased from 0.56 to 0.37 after anaerobic biodegradation. Under conventional heat treatment, the organics hydrolysis pathway was assumed as follows: the lipids hydrolyzed to palmitic acid, stearic acid, and oleic acid; protein to a series of saturated and unsaturated acids, ammonia, and some carbon dioxide; the carbohydrate to polysaccharides with a smaller molecular weight and possibly, even to simple sugars [22]. Although these mechanisms have not been entirely conformed towards so complicated sludge, organic matters solubilization acting as a dominant process, which reduced sludge viscosity and improve dewaterability has been widely approved. VSS dissolution depicted the trend of sludge becoming an inorganic product. The VSS solubilization trend with a dose of 0.2 g NaOH/g-DS of digested sludge is

Table 1 Characteristic of sludge

Digested sludge		Fresh sludge	
TS (g/L)	48.4	TS (g/L)	40.9
VS (g/L)	18.5	VS (g/L)	23.8
SS (g/L)	45.2	SS (g/L)	40.2
VSS (g/L)	16.6	VSS (g/L)	22.5
VSS/SS	0.37	VSS/SS	0.56
SCOD (g/L)	0.20	SCOD (g/L)	0.28
TCOD (g/L)	3.36	TCOD (g/L)	2.79

shown in Fig. 1. Different from conventional heat treatment, VSS hydrolysis took place within a very short holding time. Most of the VSS dissolved within the first 5 min. There were about 50–70% VSS dissolved at 120–170 °C. The increase in temperature from 80 to 120 °C resulted in more than 20% of VSS being dissolved. The change in VSS to SS ratio after microwave heating is shown in Fig. 2. The VSS to SS dropped from 0.37 to 0.16 at 170 °C for 5 min (from 0.37 to 0.2 at 120 °C). Further microwave heating presented a constant VSS to SS ratio, which means that after the rapid organic matter dissolution stage, the residual organics dissolved at the same speed with inorganic solid. In order to evaluate alkali influence on organic solid solubilization, further tests using fresh sludge were performed at an alkali dose of 0–0.2 g NaOH/g-DS. The microwave holding time was then adjusted to 1 min referring to the quick VSS hydrolysis. Figure 2 show that higher alkali dose increased VSS dissolution ratio. While adding base more than 0.05 g NaOH/g-DS only brought a slight increase of hydrolysis efficiency. Temperature was the most influential parameter on VSS solubilization. Approximately 60% VSS dissolved into aqueous phase at 170 °C with 0.2 g NaOH/g-DS. Meanwhile, VSS

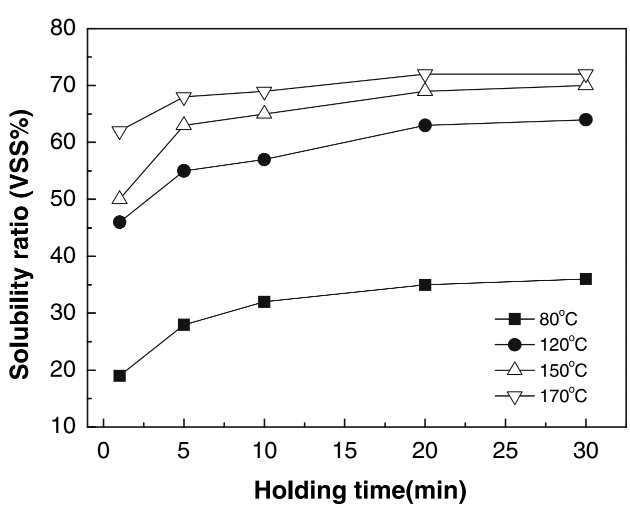

Fig. 1 Digested sludge VSS dissolving curve (0.2 g NaOH/g-DS)

dissolution of above 30% could be achieved at 120 °C for 0.05 g NaOH/g-DS

SS solubilization tendencies

Normally, sludge suspended solid was defined as two categories: organic solid (VSS) and inorganic solid. The release of organic matter from solid sludge reduced SS concentration, which contributed to the need for a sludge amount for final disposal. Generally, the SS dissolving ratio was lower than that of VSS because the inorganic fraction could not be decomposed readily. The SS solubilization of microwave treated digested sludge is plotted in Fig. 3. For only 1 min, the SS dissolving ratio increased from 27 to 32% at 170 °C (from 23 to 27% at 150 °C) (Fig 4). The SS solubilization ratio for fresh sludge provided a clear climbing trend with the increasing of alkali dose. As show in Fig. 5, 35% SS dissolved at 170 °C with 0.05 g NaOH/g-DS, whereas it took more than 30 min at 170 °C without alkali addition. At 120 °C (0.05 g NaOH/g-DS), approximately 25% SS dissolved within 1 min. The alkali dose above 0.05 g NaOH/g-DS gave slight SS reduction increasing. This trend was like the VSS dissolution behavior.

COD and elements solubilization tendencies

Organic matters moving to liquor apparently increased the SCOD of sludge supernatant. Graphic of SCOD at various treatment conditions is shown in Fig. 6. Fast VSS dissolution resulted in a significant increase in SCOD concentration. The liquor SCOD concentration at 170 °C with 0.2 g NaOH/g-DS reached above 20 g/L for 10 min (25.8 g/L for 30 min). It was obvious that SCOD concentration at 80 °C was nearly one a half of that at higher temperature (120, 150, 170 °C). Also, the close of SCOD value at high temperature was obvious. As shown in Fig. 7, the TCOD decreased from 33 g/L to nearly 29 g/L. This was caused by a small part of organic solid decomposed to CO_2. The ratio of SCOD to TCOD could indicate the efficiency of biosolid thermal hydrolysis. As shown in Fig. 8, the ratio of SCOD to TCOD increased as heating progressed. For 30 min, about 80% of SCOD was transformed to liquor. Except at 80 °C, a similar SCOD dissolution trend was observed at 120, 150, and 170 °C. The release of N and P provided a new way to utilize sludge by struvite precipitation, resulting in the production of valuable land fertilizer [23]. Microwave has been used as an effective method to disrupt bacterial cell and release internal N and P [24]. Also, C could be converted to methane. In this paper, C, H, and N of sludge cake were determined. Elements solubilization ratio are illustrated in Fig. 9. At 170 °C, N solubilization ratio was 60%, while

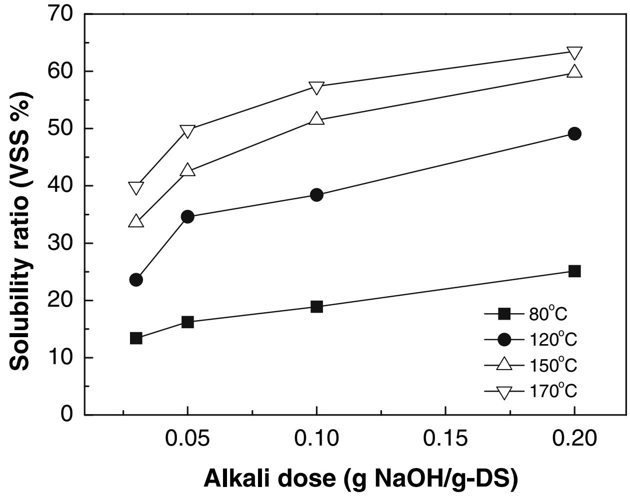

Fig. 2 Fresh sludge VSS dissolving curve (1 min holding time)

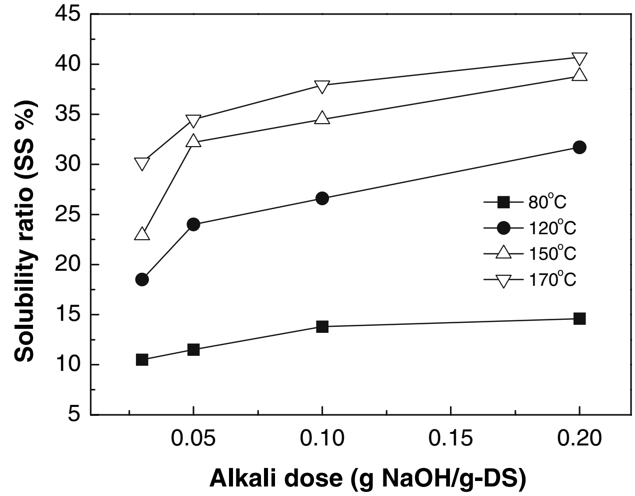

Fig. 5 Fresh sludge SS dissolving curve (1 min treatment)

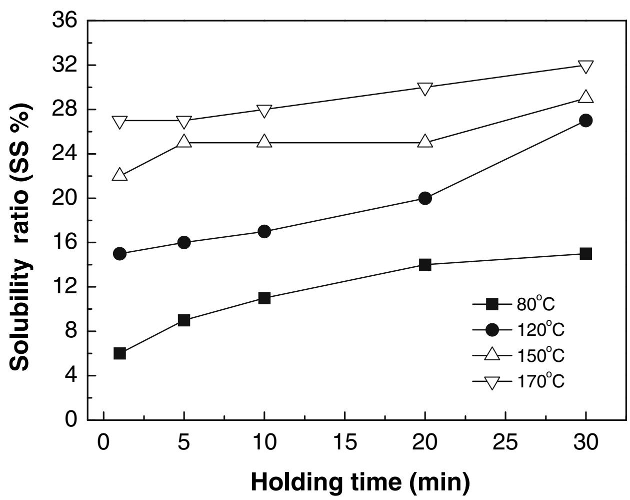

Fig. 3 Digested sludge SS dissolving curve (0.2 g NaOH/g-DS)

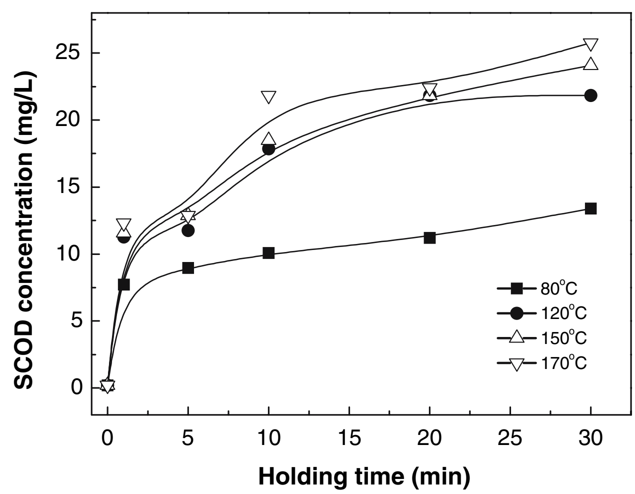

Fig. 6 Digested sludge SCOD under microwave heat treatment (0.2 g NaOH/g-DS)

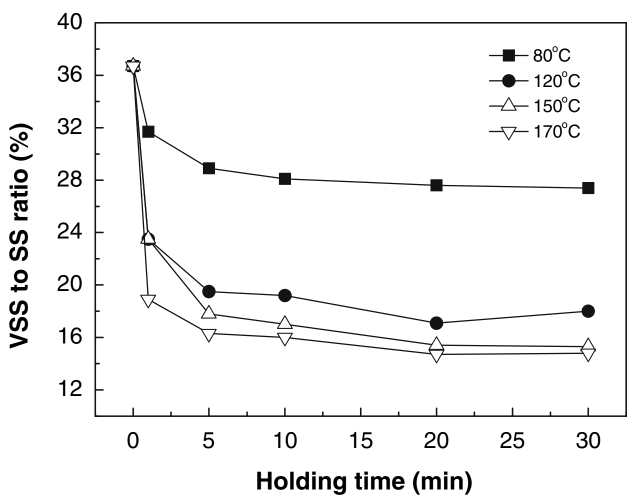

Fig. 4 Digested sludge VSS/SS ratio (0.2 g NaOH/g-DS)

the ratio of C and H was 31 and 47% respectively. Even at 80 °C, there was 26% N solubilization ratio was achieved.

Sludge settling improvement

Sludge microbes cell disruption by heating changed water distribution, and reduce binding water, which could not be removed by conventional dewatering process [25]. Though SRF and capillary suction time (CST) were widely used to describe sludge setting and dewaterability, settling curves could provide more visual description. Furthermore, the settling curves are useful to regular thermal treated sludge thickening design. The image of heated digested sludge settling behaviors is shown in Fig. 10. The fast settlement of heated sludge was obvious as compared to that of untreated sludge. The final solid-liquid interface of heated sludge was much lower than that of untreated sludge.

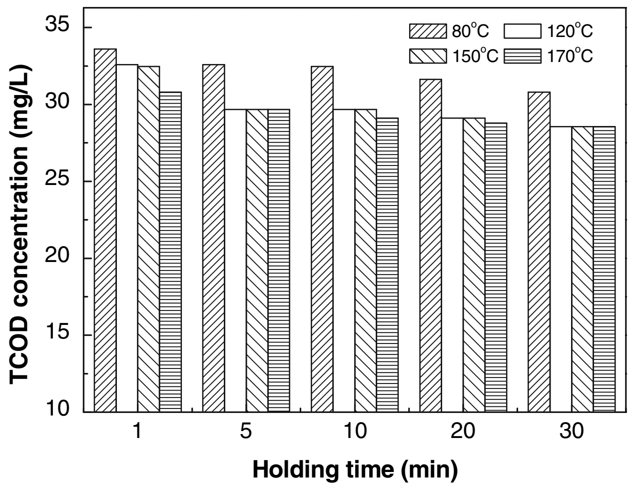

Fig. 7 Digested sludge TCOD under microwave heat treatment (0.2 g NaOH/g-DS)

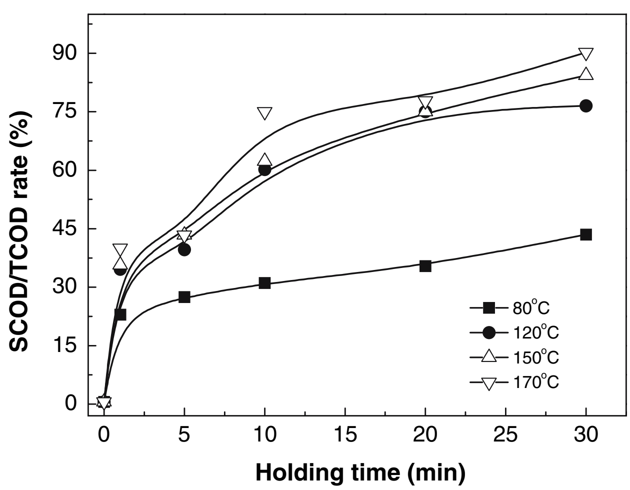

Fig. 8 Digested sludge SCOD/TCOD under microwave heat treatment (0.2 g NaOH/g-DS)

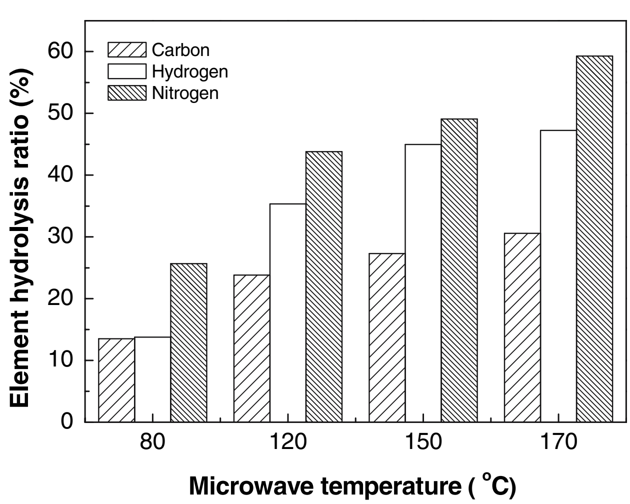

Fig. 9 Elements dissolving curve of digested sludge

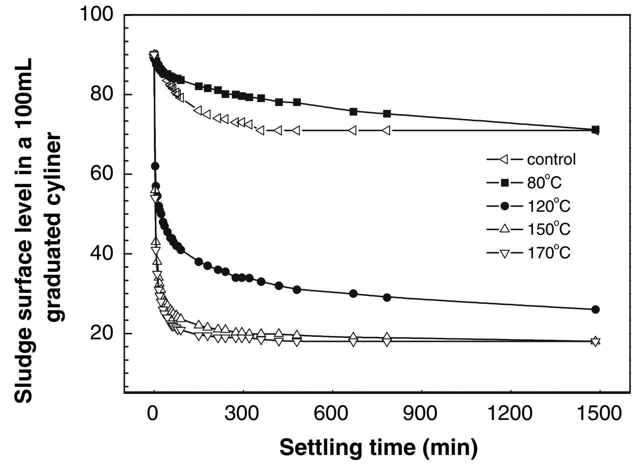

Fig. 10 Settling curve of microwave heated treated digested sludge (1 min; 0.2 g NaOH/g-DS)

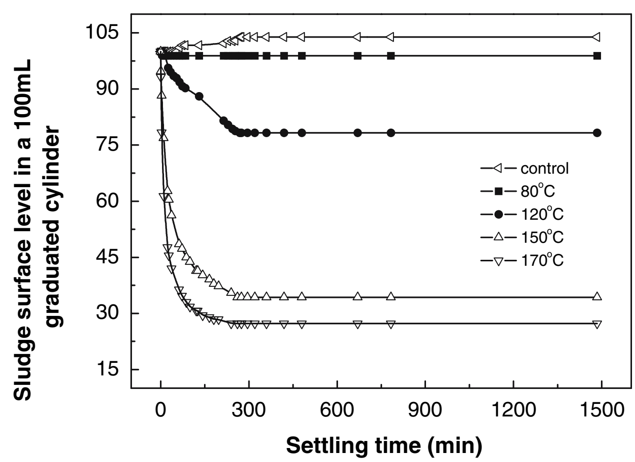

Fig. 11 Settling curve of microwave heated treated fresh sludge (1 min)

Sludge setting improvement could be regarded the same at 150 and 170 °C because the curves were almost overlapped. Gel sludge floc disruption promoted the release of internal organics, and the hydrolysis organic matter could act as flocculation. Therefore, though the particles size was reduced, the settleablity and dewaterability of sludge was improved [26]. As shown in Fig. 11, as compared to digested sludge, fresh sludge settling improvement at 120 °C was lower. This explained that the organic content influenced the dewaterability improvement of microwave-treated sludge.

Conclusions

Microwave heating combined with alkali, which was examined in this article as an alternative method to treat sludge, provided a fast and effective sludge hydrolysis process. In general, most organic fractions could dissolve into a solution within 5 min. Adding NaOH could increase above 20% the VSS dissolution ratio and 10% the SS dissolution ratio. The process resulted in high COD supernatants containing a high level of C, H, and N. Further utilization and treatment such as anaerobic digestion and the recovery of useful materials were determined by those parameters. Moreover, an improved treated sludge settling behavior provided an opportunity to hold more sludge solid in an anaerobic reactor, thereby obtaining greater biogas production.

Sludge used in this work was adjusted to about 4% DS content. Thus, various primary and secondary sludge should be tested to decide how universally applicable the results were there. Also, the microwave used in this work was a domestic frequency microwave oven; the energy efficiency of microwave to heating should be further tested. Intensive tests provided that an airtight (more than 100 °C for water) system was necessary for the process. So, in terms of industrial application microwave for sludge hydrothermal treatment there should be much works to be performed.

Acknowledgements This work was supported by a grant form the National High Technology Research and Development Program of China (863 program) (No. 2006AA06Z384).

References

1. State EPA (2006) China environment yearbook. China environmental science press
2. Carberry JB (1983) Sludge characteristics and behavior. Martinus Nijhoff Publ
3. Neyens E, Baeyens J (2003) J Hazard Mater B98:51
4. Weemaes MPJ, Verstraete WH (1988) J Chem Technol Biotechnol 73:83
5. Bougrier C, Albasi C (2006) Chem Eng Process 45:711
6. Brooks RB (1970) Water Pollut Control 69(2):221
7. Wang ZHJ, Wang W (2006) Environ Sci (in Chinese) 1(26):68
8. Neyens E, Baeyens J (2003) J Hazard Mater B97:295
9. Neyens E, Baeyens J (2003) J Hazard Mater B98:275
10. Li YY, Noike T (1992) Water Sci Technol 26:857
11. Tanaka S, Kyobayashi T (1997) Water Sci Technol 8:209
12. Miles NJ (2002) Resour Conserv Recy 34:75
13. Idris A, Khalid K (2004) Appl Therm Eng 24:905
14. Komarneni S (1995) Ionics 21:95
15. Park M, Komarneni S (2000) Mater Lett 43:259
16. Cigdem E, Kennedy KJ (2006) Water Res 40:3725
17. Park B, Ahn JH (2004) Water Sci Technol 50(9):17
18. Wojciechowska E (2005) Water Res 39:4749
19. Chan W, Wong W (2007) J Environ Sci Health A 42:59
20. Zhu SHD, Wu YX (2005) Process Biochem 40:3082
21. Plazl S (1995) Chem Eng J 59:253
22. Brooks RB (1968) Water Pollut Control 592
23. Miles A, Ellis TG (2001) Water Sci Technol 43(11):259
24. Liao PH, Wong WT (2005) J Environ Eng Sci 4:77
25. Erdincler A, Veslind PA (2000) Water Sci Technol 42(9):119
26. Nomura T, Araki S (2007) J Mater Cycles Waste Manage 9:34