

The influence and mechanism of influent pH on anaerobic co-digestion of sewage sludge and printing and dyeing wastewater

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Abstract

Two pilot-scale activated sludge systems consisting of an anaerobic baffled reactor (ABR) and an aerobic plug flow reactor (PFR) were operated with the aim of minimising excess sludge output of the activated sludge process through coupled alkaline hydrolysis and anaerobic digestion. Variations in the effluent of total chemical oxygen demand (TCOD), $\text{NH}_4^+\text{-N}$ and TP concentration proved that the recirculation ratio of aerobic excess biomass recirculated to ABR could obtain 60% of theoretically total aerobic excess sludge production, under aerobic conditions with effluent TCOD concentration well below the discharge limit of 150 mg/l. After hydrochloric acid addition in the influent to neutralise high influent pH, the solubilisation of alkaline hydrolysis was obviously damaged and the effluent concentrations exceeded the discharging limit. High influent pH could promote the reduction efficiency of excess sludge production during co-digestion of printing and dyeing wastewater and sewage sludge. A possible mechanism of influent pH acting on anaerobic co-digestion was put forward.

Keywords: alkaline hydrolysis, anaerobic co-digestion, influent pH, printing and dyeing wastewater, sludge

Introduction

In developing countries such as China, secondary wastewater treatment plants (WWTPs) are being built rapidly throughout the country (Qian, 2000). Biological treatment, mainly represented by the activated sludge processes has become the major treatment method for both municipal and industrial wastewaters. The biggest problem associated with the growing application of the activated sludge process is the production of huge amounts of sludge generated daily as a by-product of the transformation of dissolved and suspended organic pollutants into biomass and evolved gases (CO_2 , CH_4 , N_2 , SO_2 , etc.). The current sludge disposal methods of require processing, transport and disposal costs amounting up to 65% of the total operating cost of a WWTP (Liu, 2003).

Stakeholders are concerned about reducing sludge output to save on sludge disposal costs. In recent years, a series of strategies for reducing excess biomass production in activated sludge treatment system have been introduced, such as lysis-cryptic growth (Abbassi et al., 2000; Egemen et al., 2001; Roman et al., 2006; Tiehm et al., 2001), uncoupling metabolism (Chen et al., 2003; Liu et al., 1998; Yang et al., 2003), predation on bacteria (Lapinski et al., 2003), and membrane bioreactors (Rosenberger et al., 2002), etc. Some of these methods have considerable potential to reduce sludge production, but the running costs of using such techniques are still high.

Being an economical biotechnology, anaerobic treatment was introduced to increase digestion of waste activated sludge, diverse kinds of industrial wastewater, and even municipal waste-

water in recent years. However, anaerobic digestion has been used as a method to deal with wastewater only or sludge separately, and anaerobic co-digestion to treat sewage sludge and wastewater simultaneously, has been attempted only rarely (Zhu et al., 2005). This is especially true for the municipal wastewater of WWTPs mainly composed of industrial wastewater from printing and dyeing industries. Shaoxing Wastewater Treatment Plant (SWWTP) in Shaoxing County Zhejiang Province, P. R. China is an example comprising municipal and industrial wastewater.

Because waste activated sludge is less subject to decomposition, especially when the operational sludge age is longer (De Souza et al., 1998), alkaline hydrolysis of excess sludge is a promising pretreatment method before anaerobic digestion (Chu et al., 2004; Jean et al., 2000; Watts et al., 2006). However, few researchers have utilised sludge for anaerobic digestion under alkaline conditions. The purpose of this study is to show the performance of the activated sludge process during anaerobic co-digestion of dyeing and printing industry effluents and sewage sludge from SWWTP under alkaline pH to minimise excess sludge output. In order to clarify the main factors affecting co-digestion, two pilot-scale activated sludge systems each comprising aerobic and anaerobic reactors were employed to investigate the influence of influent pH in order to minimise excess sludge production.

Materials and methods

Characteristics of influent

The main characteristics of the influent of SWWTP are shown in Table 1. These data were collected during an actual SWWTP engineering project for the year 2005. SWWTP wastewater is composed of 8% municipal sewage, 90% dyeing and printing wastewater and 2% other industrial wastewater. The main compo-

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ment of SWWTP wastewater originating from the alkali-decomposition processes of dyeing, printing, and terylene artificial silk printing and dyeing (TPD), it was characterised by high pH, COD (chemical oxygen demand), colour, SS (suspended solids) and a low BOD (biochemical oxygen demand)/COD ratio (different from traditional printing and dyeing wastewater and municipal sewage). Terylene artificial silk printing and dyeing which originated in the 1980s and developed in the 1990s, is now very popular in China and TPD wastewater is the main component of SWWTP. Terephthalic acid (TA) accounts for 40% to 60% TCOD of SWWTP wastewater. TA is readily biodegradable under aerobic conditions (Guan et al., 2003) while relatively hard to decompose under anaerobic conditions (Kleerebezem et al., 2005).

Experimental set-up

SWWTP is responsible for treating municipal and industrial wastewater with a total treatment capacity of 700 000 m³/d. The conventional anaerobic-aerobic treatment process is employed in No.1 Stage Project comprising an ABR (comprising 6 similar compartments) and an aerobic plug flow reactor (PFR) also with 6 similar compartments. No.2 Stage Project with a total treatment capacity of 250 000 m³/d applies Orbal anaerobic ditch and Orbal oxidation ditch processes.

Two pilot-scale activated sludge systems each consisting of aerobic and anaerobic reactors were employed during present study. The schematic diagram of reactor systems is shown in Fig. 1. The experimental set-up is a replica of the No.1 Stage Project of SWWTP. The seeding sludge was transferred from the corresponding tanks of the plant. In line with the actual engineering project parameters, pilot-scale ABR and aerobic PFR reactors were both designed for 8.55 m³ reaction volume with an HRT of 20 h, followed by a settling tank with an HRT of 5 h.

Experimental plan and the process

The experiment was divided into two separate stages. Each stage lasted 2 months. The 1st stage in System A operated with-

out sludge recirculation while System B operated with recirculation in to investigate the effects of excess sludge recirculation from aeration tank (PFR) to anaerobic tank (ABR). The 2nd stage comprised System C by adding hydrochloric acid to all the reactors of System A used in the 1st stage; and System D without adding acid, using all the reactors of System B used in the 1st stage, to compare the degradation efficiency in the presence or absence of acid to neutralise the high influent pH and alkalinity. During the entire investigation, the temperature of the reactors was kept fixed at an average 35.2°C suitable for activated sludge systems.

Analytical methods

The pH value was measured using a digital pH meter (PHS-3C, China). *Standard Methods* (1999) were used to analyse the following parameters: mixed liquor suspended solids (MLSS) or suspended solids (SS); MLVSS (g/l); mixed liquor volatile suspended solids in the effluent and sludge samples; TCOD; and NH₄⁺-N and TP. Methane production was measured by a wet-type gas meter. Short-chain fatty acid (SCFA) concentrations were measured by gas chromatography (Shimadzu GC-2010). The DO (dissolved oxygen) was determined by a digital DO meter.

Results and discussion

Reactor performance of the first stage

The first stage investigated the effect of excess sludge recirculation from aeration tank to anaerobic tank. The experimental data were collected after activated sludge Systems A and B had been run steadily for over 1 month without excess sludge recirculation from aeration tank to anaerobic tank to ensure the effluent quality below the discharging limit. Anaerobic and aerobic reactors were both run at an HRT of 20 h while the HRT of the settling tank was kept at 5 h. Due to the results of a previous lab-scale experiment, the recirculation ratio at the start was set at 60% of

TABLE 1
The main characteristics of SWWTP wastewater

Index	pH	TCOD	BOD	Color	SS	Temperature	Alkalinity	TP	NH ₄ ⁺ -N
Unit	\	mg/l	mg/l	times	mg/l	°C	mg/l	mg/l	mg/l
max	10.21	1502	512	350	605	42.1	900	4.0	30.2
min	9.14	1030	408	300	214	25.4	600	2.1	18.4
Average	9.52	1372	452	320	413	35.2	764	3.4	23.6

Notes: These values were obtained from an actual operational SWWTP engineering project over the year 2005. Editorial Board of Environment Protection Bureau of China Standard Methods (2002) were applied for analyses of the above parameters.

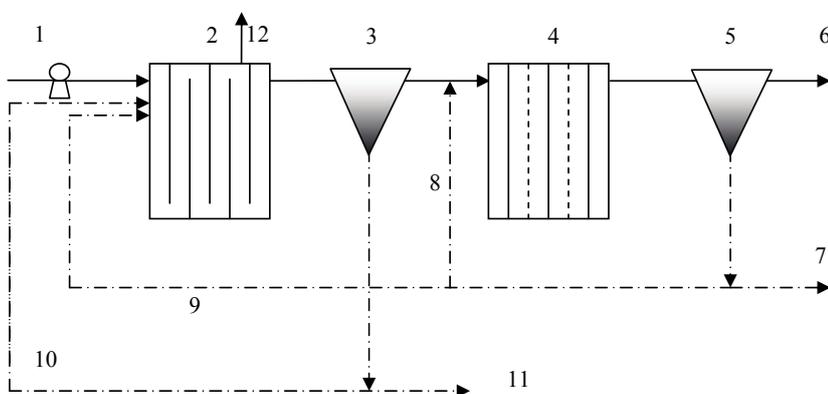


Figure 1
The schematic diagram of pilot-scale reactor system: (1) influent; (2) anaerobic baffled reactor (ABR, composed of Compartment I-VI); (3) settling tank; (4) aerobic plug flow reactor (PFR, composed of Compartment I-VI); (5) settling tank; (6) effluent; (7) discharged aerobic excess sludge; (8) recycle aerobic sludge to PFR; (9) recirculation aerobic sludge to ABR; (10) recycle anaerobic sludge to ABR; (11) discharged anaerobic excess sludge; (12) biogas.

Parameter	Influent	Effluent of System D (without adding acid)		Effluent of System C (adding acid)	
TCOD (mg/l)	1315±61	Settling tank 3		Settling tank 3	Settling tank 5
		862±46	135±12	1185±68	175±21
SS (mg/l)	451±57	194±31	90±4	367±75	121±43
pH	9.81±0.46	Compartment II of ABR: 8.24±0.53 Compartment VI of ABR: 9.11±0.36	7.76±0.38	Compartment I of ABR: neutral Compartment VI of ABR: 8.21±0.49	7.96±0.55
SCFA (mg/l)	184±63	Compartment II of ABR: 247±43 Compartment VI of ABR: 107±28	-	Compartment II of ABR: 169±43 Compartment VI of ABR: 113±29	-
Methane yield (l/d)	-	624±73		415±72	

Notes: Values represent means of all determinations ± SD (standard deviation). – No data

theoretically total aerobic excess sludge production for an ABR of System B; in contrast the aerobic excess biomass of System A was not recirculated. In spite of daily fluctuations in the influent characteristics, the obvious conclusion can be reached by critical comparison of the operation of the two reactor systems.

Figure 2 summarises the variations in the influent and effluent TCOD, $\text{NH}_4^+\text{-N}$ and TP concentrations of the two systems. It can be seen from Fig. 2 that, in Phase I (1-20 d), the TCOD of anaerobic effluent significantly decreased and $\text{NH}_4^+\text{-N}$ obviously increased for System B. This can be attributed to the anaerobic co-digestion product of azo dye (Razo-Flores et al., 1997; Yemashova et al., 2006) of TPD wastewater and protein which is the largest constituent of excess biomass (Yuan et al., 2006). TP decreased a little for System A while it increased significantly for System B because of anaerobic phosphorus release from sludge (Watts et al., 2006). At the same time the aerobic effluent TCOD of Systems A and B both were well below the discharge limit of 150 mg/l. During Phase II (21 to 40 d), all given indices of the effluent increased gradually for System B in contrast to System A showing that the increased excess sludge had exhausted the digestion ability of the anaerobic system when the inverse ratio was 70%. Later in Phase III (41 to 60 d), all given indices of System B slowly became equal to Phase I. A review of the entire stage reveals that the aerobic effluent TCOD of System A had dropped well below the discharge limit of 150 mg/l. However, System B could attain similar effluent quality under the recycled sludge ratio of below 60%. It proved that the process cannot only realise the reduction of excess sludge production but also guarantee the quality of the effluent at a recirculation sludge ratio of below 60%.

Reactor performance of the second stage

Hydrochloric acid was added to System A in order to neutralise influent alkalinity and was run for over a month under neutral conditions without excess sludge recirculation for ABR before reaching steady state, which was then used for System C during the 2nd stage. At the same time, System B was run without excess sludge recirculation to ABR before it was used for System D of the second stage. While adding acid to System C but not to System D, the anaerobic co-digestion efficiency was compared at different influent pH values. During this stage, the ratios of aerobic excess biomass to anaerobic reactor both remained at 60%.

Table 2 shows the experimental results for System C and System D over the run-time of 2 months. After treatment, the mean TCOD of system C was only 175 mg/l, while that of System D decreased to 135 mg/l. It can be seen from Table 2 that the aerobic effluent TCOD of System D was well below the discharge limit (150 mg/l); however, the aerobic effluent TCOD

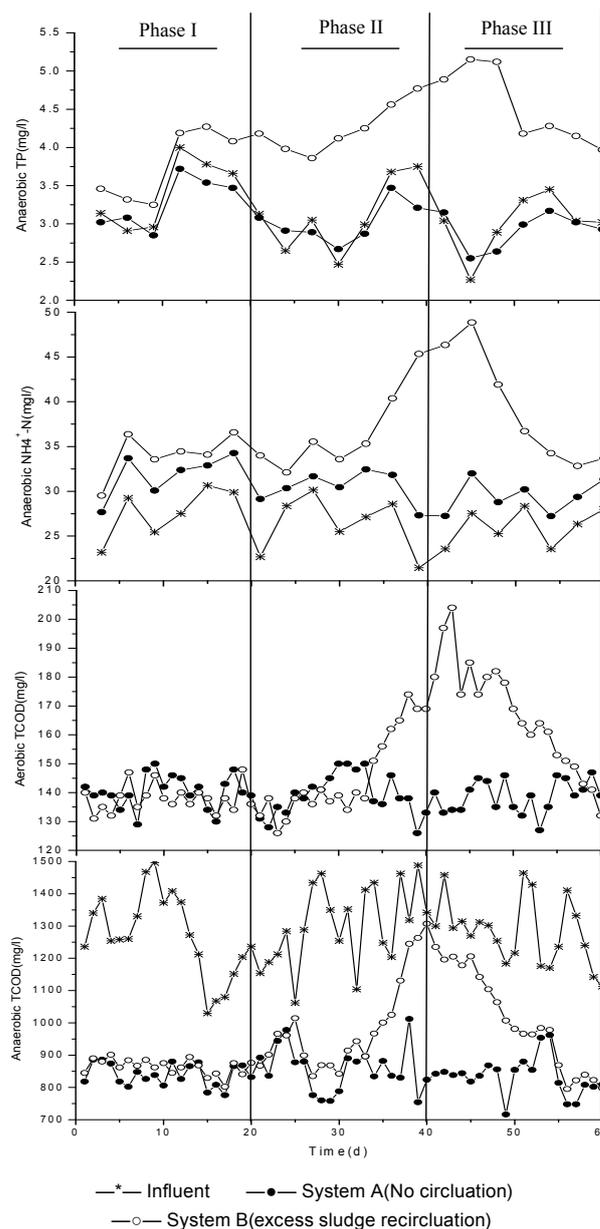


Figure 2
The variations of TCOD, $\text{NH}_4^+\text{-N}$ and TP concentration at the first stage of the experiment.
Notes: Aerobic excess sludge recirculation ratio for System B of Phase I (1-20 d): 60%; Phase II (21-40 d): 70%; Phase III (41-60 d): 60%.

of System C exceeded the discharge limit by far. These results demonstrated that alkaline hydrolysis (with high initial pH) can promote anaerobic digestion effectively to decrease excess sludge production.

As seen in Table 2, the effluent pH for Compartment II of ABR in System D decreased on average from 9.81 to 8.24 while SCFA mean increased from 184 to 247 mg/l. In particular, the effluent SS diminished to 257 mg/l in compartment VI of the ABR. However, the ABR effluents in System C changed very little, consequently implying that alkaline treatment of sludge or high influent pH had least impact on the hydrolytic, acidogenic and acetogenic bacteria even though the growth of methanogenic bacteria had been inhibited (Cai et al., 2004; Yuan et al., 2006). In this study, the anaerobic reactor was of the plug-flow ABR type, its main advantage being its compartmentalised structure (Uyanik et al., 2002). The pre-compartments of the ABR may act as alkaline pretreatment and buffer zones for all toxic and inhibitory materials in the feed thus allowing the latter compartments to be loaded with a relatively harmless, balanced and mostly acidified influent. Alkaline treatment is effective in solubilising organic matter from sewage sludge and provides more bio-available organic matter for hydrolytic and acidogenic bacteria (Cai et al., 2004; Chu et al., 2004; Jean et al., 2000; Neves et al., 2006) in the ABR. In the following ABR compartments, active populations of the relatively sensitive methanogenic bacteria can make use of acidified influent to produce methane.

In former researches, alkaline treatment was used usually for pretreatment of sludge separated from anaerobic system (Cai et al., 2004; Chu et al., 2004; Jean et al., 2000; Neves et al., 2006; Saiki et al., 1999; Watts et al., 2006; Yuan et al., 2006). In our study, the higher excess sludge recirculation ratio was obtained at the high initial pH (average 9.81) compared with the initial pH ranges close to neutral reported in the literature previously (Chu et al., 2004; De Souza Araújo et al., 1998; Jean et al., 2000; Saiki et al., 1999; Watts et al., 2006). This investigation proved that making use of the high initial pH of printing and dyeing wastewater to decrease excess sludge production by coupling alkaline hydrolysis and anaerobic co-digestion in the ABR not only improves excess sludge reduction efficiency but also saves the space and cost for treating excess biomass.

Mechanism of influent pH acting on anaerobic co-digestion

When the aerobic activated sludge was recirculated to anaerobic reactor (i.e. ABR), the aerobic bacteria could not adapt to the high pH and anaerobic environment and had to go into a state of dormancy or die with resulting internal or external decay (Van Loosdrecht and Henze, 1998). Kaprelyants and Kell (1996) indicated that most of the bacteria probably do not die, instead they become dormant. However, self-digestion (decay) generally occurs when the growth environmental factors such as pH, aerobic condition, temperature, etc., are changed (Saiki et al., 1999). With the activated sludge inverted to an anaerobic reactor, especially the system with high influent pH, aerobic bacteria could undergo decay more easily due to alkaline solubilisation. Moreover, protozoa are not active under anaerobic/anoxic conditions (Griffith, 1997) and can also undergo decay. The decay may lead to a reduction in the number, weight and the activity of micro-organisms. At the same time, the decay products of aerobic bacteria and other organic materials are converted into soluble substrates such as SCFA. The substrates are then converted to anoxic or anaerobic biomass again by the growth process

in the latter ABR compartments. An anoxic yield of 0.402 mg particulate COD/mg consumed COD was calculated to be 62% of the corresponding aerobic yield of 0.645 mg particulate COD/mg consumed COD (Copp and Dold, 1998). A sludge yield of 0.040 mgVSS/mgCOD was calculated for anaerobic biomass (Herbert et al., 1995). The obvious difference in sludge yield between aerobic and anaerobic/anoxic processes shows the advantage of anaerobic co-digestion in reducing excess sludge production.

Conclusions

The following conclusions can be drawn from the present study:

- The variations in TCOD, $\text{NH}_4^+\text{-N}$ and TP concentrations of the settling tanks of two contrast systems proved that the process could not only decrease excess sludge production but also guarantee an effluent quality of well below the discharge limit at a recycled sludge ratio of below 60% of theoretically totally aerobic excess sludge production
- Comparing the reduction efficiency achieved by adding hydrochloric acid to the ABR to neutralise initial high influent pH, the effluent TCOD and SS increased prominently which demonstrated the solubilisation of alkaline hydrolysis at high influent pH.
- The high influent pH of printing and dyeing wastewater could promote reduction of excess sludge production by coupling alkaline hydrolysis and anaerobic co-digestion. The reason for influent pH affecting anaerobic co-digestion has been given.

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References

- ABBASSI B, DULLSTEIN S and RABIGER N (2000) Minimization of excess sludge production by increase of oxygen concentration in activated sludge flocs: experimental and theoretical approach. *Water Res.* **34** (1) 139-146.
- CAI M, LIU J and WEI Y (2004) Enhanced biohydrogen production from sewage sludge with alkaline pretreatment. *Environ. Sci. Technol.* **38** (11) 3195-3202.
- CHEN GH, AN KJ, SABY S, BROIS E and DJAFER M (2003) Possible cause of excess sludge reduction in an oxic-settling-anaerobic activated sludge process (OSA process). *Water Res.* **37** (16) 3855-3866.
- CHU CP and LEE DJ (2004) Effect of pre-hydrolysis on floc structure. *J. Environ. Manage.* **71** (3) 285-292.
- COPP JB and DOLD PL (1998) Comparing sludge production under aerobic and anoxic conditions. *Water Sci. Technol.* **38** (1) 285-294.
- DE SOUZA ARAUJO L, CATUNDA PFC and VAN HAANDEL AC (1998) Biological sludge stabilisation Part 2: Influence of the composition of waste activated sludge on anaerobic stabilization. *Water SA* **24** (3) 231-236.
- EDITORIAL BOARD of ENVIRONMENT PROTECTION BUREAU of CHINA (2002) *Monitoring and Determination Methods for Water and Wastewater*. (4th edn.) Beijing: China Environmental Science Press (in Chinese).
- EGEMEN E, CORPENING J, NIRMALAKHANDAN N (2001) Evaluation of an ozonation system for reduced waste sludge generation. *Water Sci. Technol.* **44** (2-3) 445-452.

- GRIFFITH P (1997) The rate of death and predation in activated sludge systems incorporating anoxic zones. *Proc. BNR3 Conf.*, 30 Nov - 4 Dec, IAWQ Brisbane, Australia. 85-93.
- GUAN BH, WU ZB, WU ZC, XU GL and TAN TE (2003) Biodegradability of terephthalic acid in terylene artificial silk printing and dyeing wastewater. *J. Environ. Sci.* **15** (3) 296-301.
- HERBERT HHP, LI YY and CHUI HK (1995) Performance and sludge characteristics of UASB process treating propionate-rich wastewater. *Water Res.* **29** (3) 895-898.
- KAPRELYANTS AS and KELL DB (1996) Do bacteria need to communicate with each other for growth? *Tren. Microbiol.* **4** (6) 237-242.
- KLEEREBEZEM R, BECKERS J, HULSHOFF POL LW and LETTINGA G (2005) High rate treatment of terephthalic acid production wastewater in a two-stage anaerobic bioreactor. *Biotechnol. Bioeng.* **91** (2) 169-179.
- JEAN DS, CHANG BV, LIAO GS, TSOU GW and LEE DJ (2000) Reduction of microbial density level in sewage sludge through pH adjustment and ultrasonic treatment. *Water Sci. Technol.* **42** (9) 97-102.
- LAPINSKI J and TUNNACLIFFE A (2003) Reduction of suspended biomass in municipal wastewater using bdelloid rotifers. *Water Res.* **37** (9) 2027-2034.
- LIU Y, CHEN GH and PAUL E (1998) Effect of the S0/X0 ratio on energy uncoupling in substrate-sufficient batch culture of activated sludge. *Water Res.* **32** (10) 2883-2888.
- LIU Y (2003) Chemically reduced excess sludge production in the activated sludge process. *Chemosphere* **50** (1) 1-7.
- NEVES L, RIBEIRO R, OLIVEIRA R and ALVES MM (2006) Enhancement of methane production from barley waste. *Biomass Bioenergy* **30** (6) 599-603.
- QIAN Y (2000) Appropriate processes and technology for wastewater treatment and reclamation in China. *Water Sci. Technol.* **42** (12) 107-114.
- RAZO-FLORES E, LUIJTEN M, DONLON B, LETTINGA G and FIELD J (1997) Biodegradation of selected azo dyes under methanogenic conditions. *Water Sci. Technol.* **36** (6-7) 65-72.
- ROMAN HJ, Burgess JE, Pletschke BI (2006) Enzyme treatment to decrease solids and improve digestion of primary sewage sludge. *Afr. J. Biotechnol.* **5** (10) 963-967.
- ROSENBERGER S, KRUGER U, WITZIG R, MANZ W, SZEWCZYK U and KRAUME M (2002) Performance of a bioreactor with submerged membranes for aerobic treatment of municipal wastewater. *Water Res.* **36** (2) 413-420.
- SAIKI Y, IMABAYASHI S, IWABUCHI C, KITAGAWA Y, OKUMURA Y and KAWAMURA H (1999) Solubilization of excess activated sludge by self-digestion. *Water Res.* **33** (8) 1864-1870.
- STANDARD METHODS (1999) (1999) *Standard Methods for the Examination of Water and Wastewater* (20th edn.). American Public Health Association (APHA), American Water Works Association (AWWA), and Water Environment Federation (WEF) Washington DC, USA.
- TIEHM A, NICKEL K, ZELLHORN and NEIS U (2001) Ultrasonic waste activated sludge disintegration for improving anaerobic stabilization. *Water Res.* **35**(8) 2003-2009.
- UYANIK S, SALLIS PJ and ANDERSON GK (2002) The effect of polymer addition on granulation in an anaerobic baffled reactor (ABR). Part I: process performance. *Water Res.* **36** (4) 933-943.
- VAN LOOSDRECHT MCM and HENZE M (1998) Maintenance, endogenous respiration, lysis, decay and predation. *Water Sci. Technol.* **39** (1) 107-117.
- WATTS S, HAMILTON G and KELLER J (2006) Two-stage thermophilic-mesophilic anaerobic digestion of waste activated sludge from a biological nutrient removal plant. *Water Sci. Technol.* **53** (8) 149-157.
- YANG XF, XIE ML and LIU Y (2003) Metabolic uncouplers reduce excess sludge production in an activated sludge process. *Proc. Biochem.* **38** (9) 1373-1377.
- YEMASHOVA N and KALYUZHNYI S (2006) Microbial conversion of selected azo dyes and their breakdown products. *Water Sci. Technol.* **53** (11) 163-171.
- YUAN H, CHEN Y, ZHANG H, JIANG S, ZHOU Q and GU G (2006) Improved bioproduction of short-chain fatty acids (SCFAs) from excess sludge under alkaline conditions. *Environ. Sci. Technol.* **40** (6) 2025-2029.
- ZHU H, CHEN JH (2005) Study of hydrolysis and acidification process to minimize excess biomass production. *J. Hazard. Mater.* **127** (1-3) 221-227.

