Asian Journal of Chemistry; Vol. 27, No. 8 (2015), 2786-2790

ASIAN JOURNAL OF CHEMISTRY

http://dx.doi.org/10.14233/ajchem.2015.18047

Effects of Slow-Release Trace Ni^{2+} Ceramsite on the Performance of Anaerobic Treatment of Wastewater

HUIDONG SU* and DONGLING SHI

School of Environmental and Chemical Engineering, Shenyang Ligong University, Shenyang, P.R. China

*Corresponding author: Tel: +86 13940525879; E-mail: suhd1963@sina.com

Received: 20 May 2014; *Accepted*: 1 August 2014; *Published online*: 27 April 2015; AJC-17131

The experimental load of Ni^{2+} to the adsorbent of ceramsite, making it release Ni^{2+} slowly, increasing the biological effective degrees of microscale metals element, improving the microbial treatment efficiency of organic wastewater.Using fly ash, cement, lime, gypsum as main raw material, $CaCl_2$, Na_2SO_4 and NaCl as activating agent, using steam curing method, determine the best proportion of raw material, investigating the technological conditions.Discussing the release process of trace Ni^{2+} metal element of ceramsite. Through contrast test with the control group, homemade common ceramsite group, commodity ceramsite group and slow-release Ni^{2+} ceramsite group in the microbial reactor can obtain: the removal rate of COD is 72.8 %, 81.4 %, 81. 3 % and 91.8 % respectively, removal rate of adding modification ceramsite is the peak, 19 % higher than control group. Slow-release ceramsite can increase the activity of activated sludge,comparing with other ceramsite and adding trace metal element directly,which has more superior process performance.

Keywords: Ceramsite, Trace nickel, Anaerobic biological treatment.

INTRODUCTION

In the process of wastewater anaerobic biological treatment, pH, reactor temperature, toxic substance, carbon sources, constant nutrition (N, P), vitamin, metabolic time, oxidation-reduction potential and the raw material mixed all have effect on the microbial anaerobic treatment[1-3]. At the same time, since the composition of trace metal elements involved in the enzyme[4,5], thus affecting the whole reactor running effect and stability[6]. Studies have shown that Ni^{2+} is the components of coenzyme, hydrogenated enzyme, methane bacteria F430 and carbon monoxide dehydrogenase[7], promoting the growth of methanogens and formation of methane and lacking of it can lead to reduce biological activity. Literature surveyed[8] revealed that addition of an appropriate amount of trace metal elements in reactor can improve substrate biodegradation rate and gas yield, the reaction activate speed and promoting formation of anaerobic granular sludge, but when it contains excessive additive amount, resulting in suppression of the growth of bacteria. Dosing trace metal elements salts can provide directly necessary trace metal elements of microbial, but the hydroxyl in the water and the precipitation and complexation of colloid will reduce its biological effective degrees[9], excessively dosing will produce heavy metal pollution of water. Slow release technology has a series of good characters, such as saving the dosage, extending the valid time of ion release, improving the treatment effect, reducing side effects *etc*. The preparation of steam curing unburned ceramsite is that making the fly ash release the active substance SiO_2, Al_2O_3 and enable to generate hydration calcium silicate by carry out hydration with gypsum, calcium oxide and cement, then producing a lot of C-S-H gel and aluminized hydrates form a certain strength of ceramsite[10-12]. Experimental will load Ni^{2+} to the adsorbent of sawdust, add the sawdust which adsorbing of Ni^{2+} in the process of ceramsite preparation, we prepare unburned ceramsite by the method of steam curing, loading Ni^{2+} into ceramsite and slowly releasing of trace Ni^{2+} in the water, available to microorganisms in wastewater and promoting the growth of microorganisms increasing the biological effective degrees of microscale metals element, improving the microbial treatment efficiency of organic wastewater, reducing the potential environmental pollution risks of heavy metal by dosing metal ions directly to the wastewater.

EXPERIMENTAL

Glucose, potassium dihydrogen phosphate, urea, sodium hydrogen carbonate, potassium bichromate, concentrated sulphuric acid, silver sulphate, nickel chloride, potassium hydrogen phthalate, fly ash, cement, lime, gypsum, sodium sulphate, fused calcium chloride, *etc*. are all of analytical grade.

Preparation of unburned ceramsite

Preparation of ceramsite: Grinding fly ash, cement, lime, gypsum in the mortarbox respectively and mixing thoroughly in beaker of 250 mL, then putting them into 100 ºC in drying box, the condition is 100 ºC and 40 min; putting adequate amount Na_2SO_4, NaCl and $CaCl_2$ into the beaker of 50 mL, dissolving with appropriate water then in certain proportion mixed with the main ingredient, putting in press or extrusion press with manual granulation get spherical granule ceramsite, grain size is 4-6 mm. Aging, natural drying and then steam curing, after make un-burned ceramsite. In the process of preparation of ceramsite, adding sawdust with Ni^{2+}, then obtain ceramsite which can release Ni^{2+} slowly[13].

Release experimental methods of different carrier ceramsite: Putting 20 g ceramsite which loads different trace metals element into 150 mL cone shaped bottle respectively, add water to 100 mL, under 298 K and constant temperature with the oscillations of 80 r/min, take and replenish 50 mL solution to analysis the release quantity of Ni^{2+} everyday.

Application experiment of biological ceramsite: Putting 200 mL sludge in the culture flask, then add 200 mL nutrient solution, take 20 g sample ceramsite in microbial cultures respectively and fully mix into incubator. Heating up 1 ºC everyday, stop it until heated up 33 ºC and then stable for 5 days. Collecting the production of gas through drainage method, sampling solution through sampling mouth every day and each 2 mL, collect the production of gas through drainage method and measuring the COD_{Cr}.

RESULTS AND DISCUSSION

Determination of the ratio of ceramic raw material preparation: Fly ash, cement, lime, plaster, *etc*. used in the preparation of ceramisite, the main reaction is as follows:

$$CaO + H_2O \rightarrow Ca(OH)_2$$

$$2CaO·SiO_2 + nH_2O \rightarrow xCaO·SiO_2·yH_2O + (2-x)Ca(OH)_2$$

$$xCa(OH)_2 + Al_2O_3 + (n-1)H_2O \rightarrow xCaO·Al_2O_3·nH_2O$$

$$xCa(OH)_2 + SiO_2 + (n-1)H_2O \rightarrow xCaO·SiO_2·nH_2O$$

$$Al_2O_3 + Ca^{2+} + OH^- + Cl^- \rightarrow 3CaO·Al_2O_3·CaCl_2·10H_2O$$

Fly ash free SiO_2, while Al_2O_3 content is higher, improve its activity. We must make the fly ash unburned ceramic diving hard to get excited and activated[14], steam curing conditions in the system to generate a greater amount of C-S-H gel, so that a certain strength of ceramic. Because of the fly ash by high temperature melting, the structure is also very tight, thus its hydration speed is slower than the cement. Cement and lime belongs to high alkaline materials, they can provide an effective alkaline environment of fly ash, effective corrosion of vitreous body, stimulate the activity of fly ash, the solution of a trunk SiO_2, Al_2O_3; meanwhile lime generated $Ca(OH)_2$ in a humid environment $Ca(OH)_2$ can stimulate the activity of fly ash to provide break Si-O, Al-O bond of the OH^-, with gypsum and provides the hydration of fly ash generated Ca^{2+} the water rigid gelled material needed, react with the active SiO_2, Al_2O_3 in the fly ash vitreous, generating hydrated calcium silicate and hydrated calcium aluminate, making the ceramic strength increases. Exciting agent NaCl and $CaCl_2$ produce Ca^{2+} and Cl^- diffusion ability is stronger, it can through the hydration layer on the surface of the fly ash particles, react to generate chlorine hydrated calcium aluminate with the internal active Al_2O_3. To further enhance the strength of the ceramsite; Na_2SO_4 is relatively easy to dissolve in water, it can react with the $Ca(OH)_2$ in the system and the $CaCl_2$ in the ceramic systems generated $CaSO_4$ highly dispersion effect, SO_4^{2-} under the effect of Ca^{2+} and inclusion in the fly ash particles on the surface of the gel and dissolved in the liquid phase AlO^{2-} reaction generated more easily than separate plus gypsum hydration ettringite calcium sulphoaluminate (Aft); the expansion of the Aft has certain effect, can fill the porosity of the hydration space, improve the strength of ceramsite[15-17].

Ceramic raw material ratio of orthogonal experiment: According to preparation of unburned ceramsite experimental method, dry 2 h at 100 ºC, steam curing 10 h at 100 ºC, select and confirm 0.1 g Na_2SO_4 and 0.4 g $CaCl_2$ as stimulating agent, choose fly ash, cement, lime, gypsum four raw materials as factors, designing orthogonal test of three level and four factors (Table-1).

TABLE-1
ORTHOGONAL EXPERIMENTAL
FACTOR LEVELS LIST OF L_9 (3^4)

Factors	Level		
	1	2	3
Fly ash (A)	16(1)	17(2)	18(3)
Cement (B)	2.8(1)	3(2)	3.2(3)
Lime (C)	1.6(1)	1.8(2)	2(3)
Gypsum (D)	0.4(1)	0.6(2)	0.8(3)

Through orthogonal experiment, the size of four factors on the influence of the strength of ceramsite is: cement > fly ash> lime> gypsum, the best recipe of main raw material for preparation of ceramsite is $A_1B_3C_1D_1$, namely: fly ash 16 g, cement 6.4 g, lime 3.2 g, gypsum 0.4 g, strength of ceramsite is 47 kg.

Orthogonal experiment of excitation agent: Based on the above orthogonal experiment, keep the amount of fly ash, cement, lime and gypsum, respectively 16, 3.2, 1.6 and 0.4 g, with $CaCl_2$, Na_2SO_4, NaCl three external excitation agent for factors, designing orthogonal test of three level and three factors (Table-2).

TABLE-2
ORTHOGONAL EXPERIMENT TABLE OF ACTIVATOR

Factors	Level		
	1	2	3
$CaCl_2$ (A)	0.1 (1)	0.2 (2)	0.3 (3)
Na_2SO_4 (B)	0.2 (1)	0.4 (2)	0.6 (3)
NaCl (C)	0.05(1)	0.1(2)	0.2(3)

Through orthogonal experiment, the size of four factors on the influence of the strength of ceramsite is: Na_2SO_4 > NaCl > $CaCl_2$, at the same time by factor and level indicators relations obtain the best formula of the ceramsite preparation of exciting agent for $A_1B_2C_2$, namely: 0.4 g Na_2SO_4, 0.1 g NaCl, 0.1 g $CaCl_2$, according to the optimal conditions for verification experiment, measured the strength of ceramsite is 49 kg.

Ceramic preparation conditions determined

Influence of moisture content towards the strength of ceramsite: According to the results, the preparation of unburned ceramsite method, prepared ceramic under the conditions of different water content, measure its strength (Fig. 1).

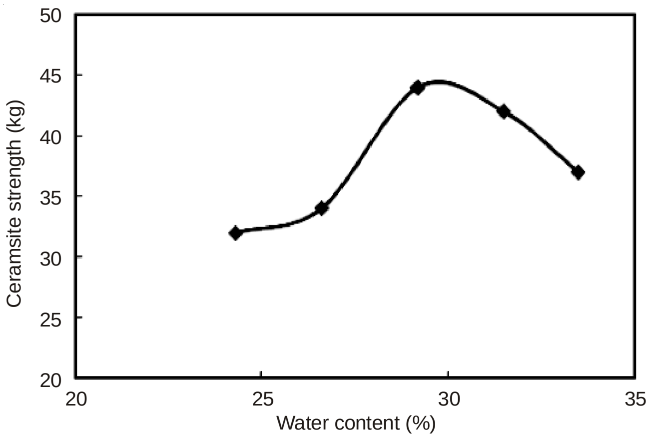

Fig. 1. Effect of water content on the ceramsite strength

Fig. 1 shows that when the moisture content of 29.2 % ceramsite maximum intensity, this is due to the moisture content is below 29.2 %, is because of too little water in the ceramsite, cannot be effective at the beginning of the ceramsite into a ball and adequate hydration reaction, The experiment found that low moisture content of ceramsite not easily into a ball at the beginning and obviously dried; when the moisture content is higher than 29.2 %, because of the ceramsite has too much water, ceramic material can not make full contact with each, affect the hydration reaction effect, ceramsite strength decreased.

Steam curing temperature on the strength of ceramic: In accordance with the method of orthogonal experiment and preparation of unburned ceramsite, drying at different times and at different temperatures, steam curing 10 h, measure its strength (Fig. 2).

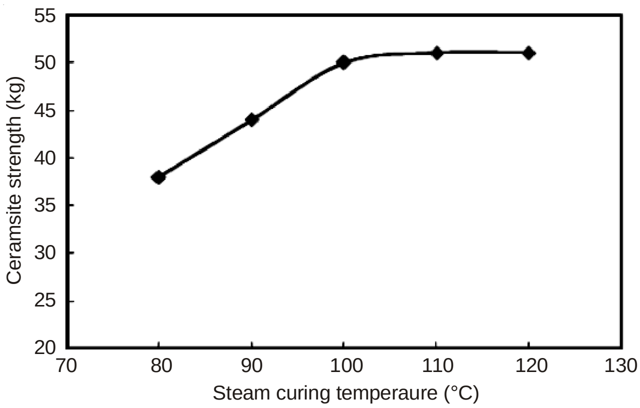

Fig. 2. Effect of steam curing temperature on the ceramsite strength

Fig. 2 shows that with steam curing temperature increased, the strength of ceramic are increasing, from 80-100 ºC, ceramsite strength growth rapidly, starting from 100-120 ºC, ceramsite strength growth is slowing down and tends to balance. This is because in the condition of the steam curing, temperature promoted the vitreous body in the fly ash in the alkaline hydrolysis, active material of fly ash Al_2O_3, SiO_2 is more easily dissolved out, accelerate the hydration reaction of fly ash mineral structure of the transfer and the formation of hydration products, ceramic intensity increases[15]. Considering the pressure and energy consumption factors, select 100 ºC for the steam curing temperatures.

Steam curing time on the strength of ceramic: Accordance with the previous results and the preparation of unburned ceramsite preparation of ceramic, the influence of steam curing time (Fig. 3).

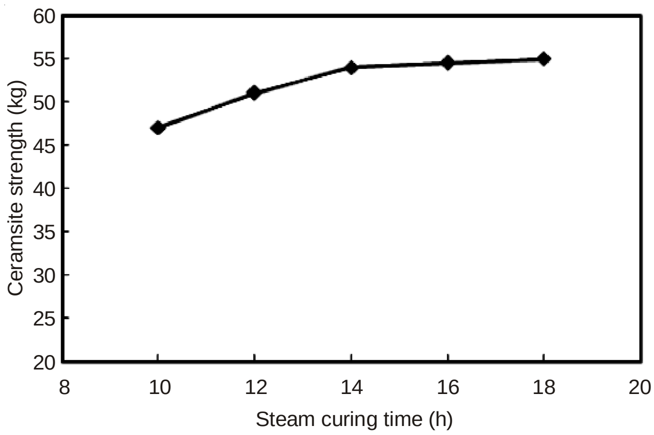

Fig. 3. Effect of steam curing time on the ceramsite strength

As can be seen from Fig. 3, with the extension of steam curing time, the strength of ceramsite increase, start from 14 h, ceramsite strength growth is slowing down. The results show clearly that sustained thermal excitation, can continually make fly ash in the vitreous in alkaline hydrolysis, activation reaction can be better, produce hydration products to rapidly improve the strength of ceramsite[10-12]. Comprehensive energy and other factors to consider, select 14 h for the steaming time.

Determination of dosage of sawdust: Preparation of ceramic raw materials to maintain constant content, adding different amounts of nickel adsorption saturation sawdust, thoroughly mix and prepare ceramsite. Measured the intensity of each sample under the same conditions (Fig. 4).

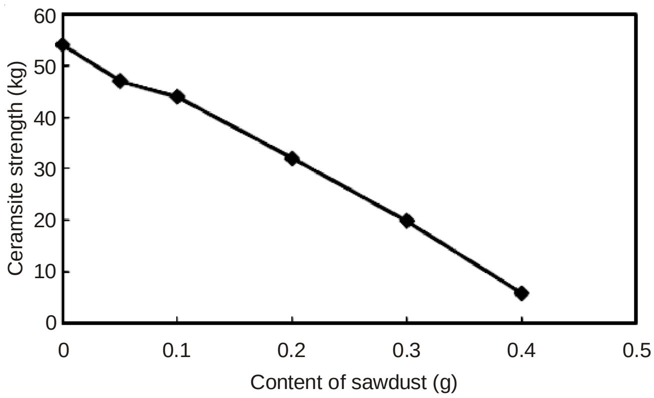

Fig. 4. Effect of content of sawdust on the ceramsite strength

As can be seen from Fig. 4, adding an appropriate amount of sawdust can maintain a certain strength ceramic, however, with the increase of the amount, ceramsite strength fell sharply. This is because the sawdust itself does not participate in the reaction system, excessive adding sawdust fly ash will make fly ash diving rigid cannot be effectively motivate, thereby affecting the activation reaction lytag system, therefore, the content of sawdust should be adequate. When the content of sawdust at 0.1 g, the strength of ceramsite is 47 kg, conform to the standard, select sawdust dosage of 0.1 g.

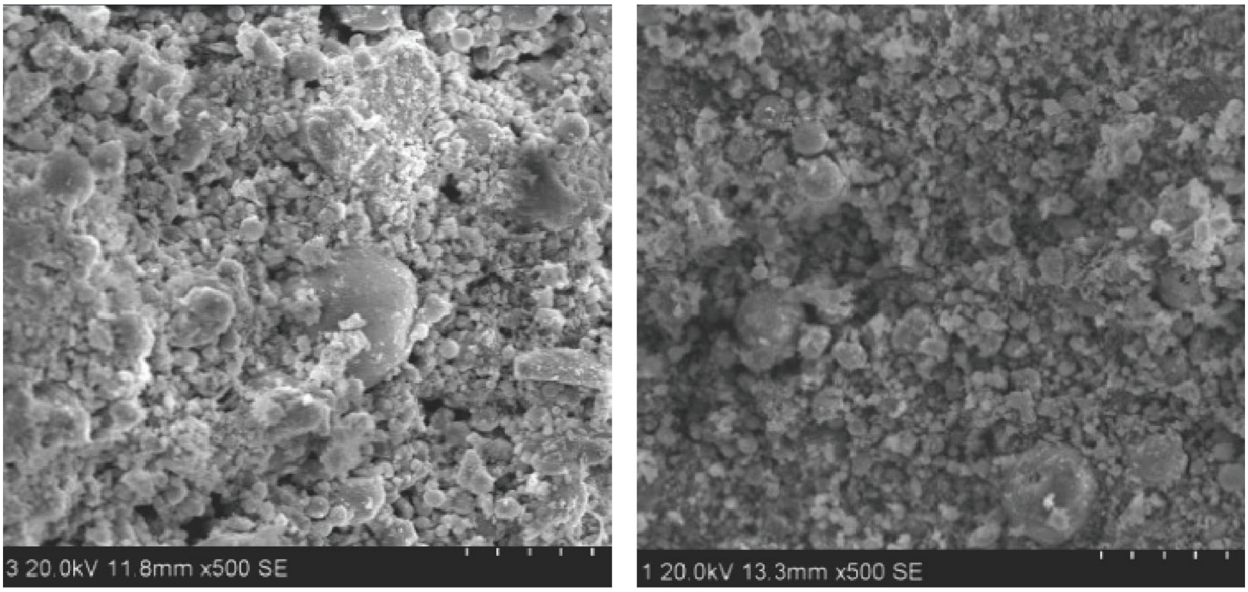

Fig. 5. SEM photograph of normal ceramsites and ceramsites contained sawdust

Performance test of ceramsite and the analysis of microcosmic morphology: Physico-chemical properties test of ceramsite, specific performance parameters are given in Table-3.

It can be seen that from the SEM graph (Fig. 5) shows that ceramsite's surface roughness, and surface distribution has many microporous shape structure, slow-release Ni^{2+} ceramsite's surface has apparent aperture channel; explain that ceramsite has large specific surface area, which is able to provide appropriate environment for the contact, mix between microbial and matrix, thus, can improve the adhesive power of microorganism and hang membrane carrier, promoting the formation of biofilms speed.

Release of haydite for Ni^{2+}: According to the release experimental methods of different carrier ceramsite method for experiment, the results of which shows in Fig. 6.

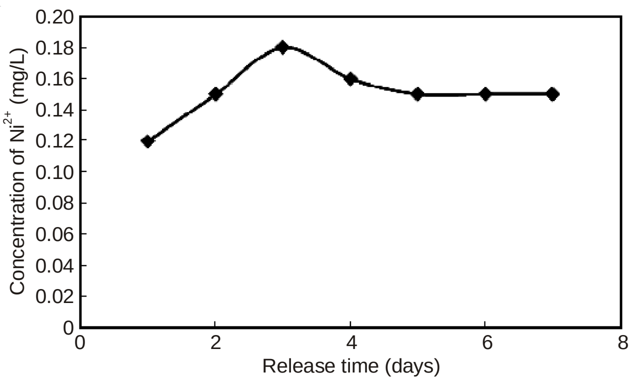

Fig. 6. Relationship between ceramsites slow release Ni^{2+} with time

As can be seen from Fig. 6, initially, slow-relese ceramic increases the release of nickel, in the third day to reach maximum, starting from the fourth day gradually reach equilibrium concentration 0.15 mg/L, has the ability to release and release the concentration is low, will not cause pollution of water bodies.

Release Ni^{2+} ceramic effects on anaerobic biological treatment: The addition of ordinary ceramsite, ceramsite of load Ni^{2+} and commodity ceramsite respectively in incubators, simultaneously adding no ceramsite in another incubators as control group (Fig. 7).

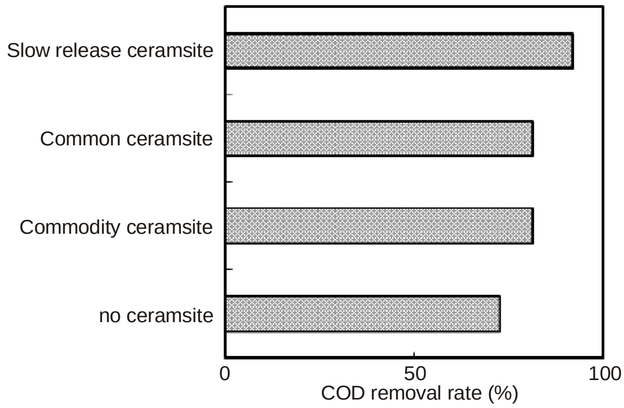

Fig. 7. COD removal rate of different ceramsites

From Fig. 7, the treatment effect of ceramsite which is loaded Ni^{2+} is best, the removal rate of COD with 91.8 %, the control group that doesn't have ceramsite, only amounting to 72.8 %, explaining that the ceramsite which loaded trace metals element enable to slow release trace metal elements and adherent places because it has large specific surface area, which benefits to the hang of membrane formation rate, the treatment effect is significantly higher than the control group. Meanwhile, add pottery making ceramsite and goods ceramsite in the reactor, the removal rate of COD reach to 80 %, which has a

TABLE-3
PERFORMANCE PARAMETERS OF CERAMSITE

Parameter	Strength of ceramsite (kg)	Particle size (min)	Water absorption rate (%)	Bulk density (kg/m^3)	Grain density (kg/m^3)
Numerical value	52	5.1	5.7	825	1357

good film-forming effect. But its treatment effect still exists a certain gap, comparing with the ceramsite which load Ni^{2+}, with the difference of the removal rate of COD amount to 10 % approximately.

Conclusion

Through the orthogonal test, confirming the proportion of ceramsite: the best proportion is 16 g fly ash, 16 g cement, 3.2 g lime, 0.4 g gypsum; the ratio of activator is 0.4 g Na_2SO_4, 0.1 g NaCl, 0.1 g $CaCl_2$; curing conditions is: Moisture, steam curing temperature, steam curing time are 29.2 %, 100 ºC, 14 h. As can be seen from the scanning electron microscopy that ceramsite's surface coarser, gap bigger, benefit to the film-forming of microbial. The strength of ceramsite, average particle size, water absorption, bulk density and particle density respectively 52 kg, 5.1 mm, 5.7 %, 825 and 1357 kg/m^3, which conform to the national standard. The contrast experiment among blank control group, homemade common ceramsite group, commodity ceramsite group and ceramsite of slow-release Ni^{2+} shows that the removal rate of COD respectively is 72.8, 81.4, 81.3 and 91.8 % in those reactor, the highest removal rate of COD is ceramsite of slow-release Ni^{2+}, 18.95 % higher than the control group, ceramsite of slow-release Ni^{2+} has better treatment performance.

ACKNOWLEDGEMENTS

This research has received the financial support by Key Laboratory of Experimental Fundation of ShenYang Ligong University (No. 4771004KFS09) and the Chinese Environmental Protection Foundation, the fourth "Lattice Flat Green Action, Liaoning Environmental Research and Education of '123 project support (CEPF2011-123-2-12)'.

REFERENCES

1. R.E. Speece, G.F. Parkin and D. Gallagher, *J. Water Res.*, **17**, 677 (1983).
2. H. Yong, C. Kong and X. Yin, *China Biogas J.,* **27**, 19 (2009).
3. G. Gonzalez-Gil, R. Kleerebezem and G. Lettinga, *Appl. Environ. Microbiol.*, **65**, 1789 (1999).
4. L. Yaxin, *J. Water Treat.*, **10**, 145 (1995).
5. P.Y. Feng and W.Z. Li, *J. Renew. Energy Sources*, **25**, 51 (2007).
6. R.E. Speece, in eds.: D.P. Chynoweth and R. Isaacson, Nutrient Requirements, In: Anaerobic Digestion of Biomass, Elsevier Applied Science, London, pp. 109-128 (1987).
7. A.E. Dwayne, R.K. Lee and S. Ralph, *Appl. Environ. Microbiol.*,**65**, 5541 (1999).
8. J. Sharma and R. Singh, *J. Bio-Res. Technol.*, **79**, 203 (2001).
9. C. Dong, R. Lv and X. Su, *Environ. Prot. Chem. Indus. J.*, **24**, 190 (2004).
10. B. Pacewska, I. Wiliñska and G. Blonkowski, *J. Therm. Anal. Calorim.*, **93**, 769 (2008).
11. Z. Giergiczny, *J. Therm. Anal. Calorim.*, **83**, 227 (2006).
12. B.G. Ma, Z.T. Luo, X.G. Li, M.X. Zhang and Y.B. Wang, *J. Wuhan Univ. Technol. (Mater. Sci. Ed.)*, **24**, 826 (2009).
13. S. Huidong and Z. Pengfei, The Experimental Study of Preparation of Unburned Ceramsite and its Reaction Mechanism, Proceedings of International Conference on Computer Distributed Control and Intelligent Environmental Monitoring, Wuhan, China, pp. 1874-1878 (2011).
14. B.W. Langan, K. Weng and M.A. Ward, *Cement Concrete Res.*, **32**, 1045 (2002).
15. F.S. Wang, Y.-N. Zhu and L. Zhang, *Bull. Chinese Ceram. Soc.*, **28**, 31 (2009).
16. G. Ke, X. Yang, H. Peng, F. Jia and H. Yue, *Coal*, **30**, 366 (2005).
17. D. Ye, *Flyash*, **2**, 10 (2009).