Aim and Scope

The objective of the *Journal of Residuals Science & Technology* is to provide a forum for technical research on the management and disposal of residuals from pollution control activities. The Journal publishes papers that examine the characteristics, effects, and management principles of various residuals from such sources as wastewater treatment, water treatment, air pollution control, hazardous waste treatment, solid waste, industrial waste treatment, and other pollution control activities. Papers on health and the environmental effects of residuals production, management, and disposal and are also welcome.

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Sludge Disposal and Reuse as Resource

EDITORIAL

Continuation of Selected Papers Presented During the IWA-Sludge Conference Held in Harbin, China on August 8–10, 2009 and Articles Independent of the IWA-Sludge Conference Submitted to the Journal of Residuals Science & Technology (JRS&T)

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PLEASE find articles in this issue that are a continuation of the 2009 IWA-Sludge Conference papers from our last issue in addition to articles independent of the conference. The second part of the conference articles contained in this issue focuses on sludge disposal and its reuse as a resource. The following issue in 2010, Volume I, will contain the final set of conference articles related to land application controversies and solutions. The previous JRS&T issue contained the first set of conference articles from the areas of sludge treatment technologies, innovative technologies in sludge treatment and management, and sludge characteristics and analysis methods.

Regarding the journal, I am keeping with the tradition and history of the JRS&T for its members and to preserve its original ideals and direction. However, I do want to consider the addition of more interdisciplinary articles in 2010 in addition to papers we currently receive. I would like to expand the JRS&T's audience and scope. Topic ideas to be explored in 2010 include:

- Energy from sludge
- Sludge management's carbon footprint
- Energy utilization in sludge management
- Differences among developing and developed countries regarding residuals' handling
- Emerging contaminants
- Technology, environmental issues, and economy of source separated MSW and WM in third world countries
- Renewable energy from biomass
- Sludge treatment liquors
- Energy self-sufficiency
- Ecosystem restoration with biosolids
- Ways to minimize sludge/biosolids production
- Invited topical papers on controversial issues (e.g., regrowth/reactivation of pathogens in biosolids)
- New processes

Finally, I would also like to take this opportunity to introduce myself to everyone. My name is Dr. P. Brent Duncan and I am the new Editor-in-Chief for the JRS&T as of 2009. This has been a great year for me and I would like to especially thank John Novak, former Editor-in-Chief, for his help with the journal. I would also like to thank the Editorial Board that has been a great help in both reviewing manuscripts and providing excellent conference papers to the journal. Therefore, let's make 2010 a very special year and let's keep moving onwards and upwards! Thank you everyone for your contribution and/or attention to the JRS&T!

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Experiment of Gatifloxacin Adsorption by Sludge Activated Carbon

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ABSTRACT: In this paper, sludge activated carbon was made from two kinds of sludge by physical-chemical methods. The sludge was taken from the Gaobeidian municipal wastewater treatment plant in Beijing and $ZnCl_2$ was used as activated reagent. The adsorption mechanism of gatifloxacin, a new 4-quinolones antibiotic, by the two kinds of sludge activated carbon was studied. The Characteristics of sludge and sludge activated carbon, such as specific surface area, ζ-potential, particle size distribution, stereoscan photograph, were tested in order to have a better understanding about the adsorption mechanism. The results show that the sludge activated carbon can adsorb antibiotic effectively. The sludge activated carbon made of the sludge from sedimentation tank has a better adsorption capability than that from dewatering house. Meanwhile, the adsorption can be affected by environmental conditions. Higher temperature can enhance the adsorption. Moreover, a lower $CaCl_2$ concentration can restrain the adsorption, while a higher concentration can promote it. This study shows that it is applicable for sludge activated carbon to be used as an adsorbent to treat antibiotic wastewater or nondegradable wastewater. It also shows a new direction for sludge disposal and sludge reuse as a resource.

1. INTRODUCTION

ACTIVATED sludge process is the most commonly used method in sewage treatment, although it produces a large amount of excess sludge. It is reported that approximately 1.3 million tons (dry weight) sludge was produced per year from all municipal wastewater treatment plants in China and it still increased at a rate of more than 10% annually, especially in those big cities and some areas with high urbanization level. in order to solve this big problem, Yue Qinyan [1] used dewatering sludge from the municipal wastewater treatment plant as raw materials to make activated sludge by using chemical methods. Then the activated sludge was used to adsorb reactive red K-2BP, acid scarlet GR and direct violet N. The adsorption kinetics of these adsorption processed were also investigated in her study. The results showed that activated carbon can effectively adsorb all there kinds of dye. Liu Chunhua etc. [2] used the activated sludge from the municipal wastewater treatment plant as raw material to produce dry sludge and the modified sludge by chemical methods. Those two kinds of adsorbents were used for the adsorption of Hg^{2+} in wastewater. The results showed that the adsorptions of Hg^{2+} by using two kinds of sludge were matched with the Lagergren first-order kinetic equation. Under the experimental conditions, both adsorbents removed Hg^{2+} from the industrial wastewater effectively and the modified sludge showed a higher efficiency for Hg^{2+} adsorption. The preparation of the remaining sludge and its effect on dye adsorption were investigated by Chen Chunyun [3]. The modified sludge was also used as adsorbent in beryllium-containing wastewater treatment by Zhuang Minglong [4] and it showed a high efficiency. The activated sludge carbon modified from sludge has been widely used for adsorption in refractory wastewater treatment and is a hot topic recently. This is a promising way for sludge reuse as resources and also a new method for refractory wastewater treatment. However, the study on antibiotics adsorption by using the activated sludge carbon has not been reported.

This study focused on the mechanism of the gatifloxacin adsorption and the antibiotics adsorption in wastewater by using the activated sludge carbon,

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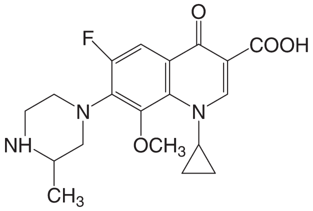
which used the sludge from the secondary settling tank and the dewatered sludge as raw materials and modified with $ZnCl_2$.

2. MATERIALS AND METHODS

2.1. Experimental Materials

Sludge used in this study was collected from the secondary sedimentation tank and the sludge-dewatering room in Beijing Gaobeidian sewage plant.

Antibiotic used in the experiment is gatifloxacin which is used widely as a new generation of quinolone antibiotic. Its chemical structural formula and pharmacological characteristic are shown as follow:



Gatifloxacin; Molecular Formula: $C_{19}H_{22}FN_3O_4$; Molecular Weight: 375.40

2.2. Experimental Instruments

UV-Vis spectrophotometer (USA HACA); analytical balance; SHA-CA oscillator constant temperature water bath oscillator, SHZ-82A gas constant temperature bath oscillator; GT10, such as high-speed centrifuge (Beijing Times centrifuge North Lee Co., Ltd.); SX-4-10 box-type resistance furnace control box (Tianjin Instrument Co., Ltd. Theis); 101-2B-type electric blast drying oven (Shanghai Experimental Instrument Co., Ltd.); Mastersizeer-2000 laser particle size distribution analyzer (Malvern Co., Ltd., the United States); Zetasizet-2000 type Zeta potential analyzer (Malvern Instruments Ltd., UK) scanning electron microscope (S-3000N, Hitachi, Japan).

2.3. Experimental Methods

2.3.1. Preparation of the Activated Sludge Carbon

The sludge activated carbon used in this study was modified by physical-chemical methods. The sludge from the sedimentation tank was washed before settling. After removing the supernatant, the sludge was washed at least twice and dried in oven. Then the dry sludge was grinded in mortar, screened with a 60 head sieve and was ready to use as the dry sludge. For the modified sludge, the dry sludge was mixed with $ZnCl_2$ at a ratio of 5:3, stirred with distilled water and put in water bath at 80°C for 24 hours followed by drying in the oven at 100°C for 24 hours. Then the sample was transferred into a 50 mL the crucible sung and dried in oven at 550°C for 1 hour. After cooling and grinding, the sample was screened with a 60 head sieve and was ready to use as the modified sludge.

2.3.2. Gatifloxacin Standard Curve

A series of *gatifloxacin* solution was prepared, and its absorbance was determined at 292 nm [5]. Then a line equation A = 0.0631C with a correlation coefficient of 0.999 was obtained.

2.3.3. Experimental Methods

When it is Isotherm experiments, respectively, we preparate 10 mg/l, 20 mg/l . . . 100 mg/l series gatifloxacin solution, and according to the pre-test results put 0.05 g of sludge activated carbon in the conical flask by adding 10 ml the above-mentioned series solution, sealing with membrane then placed them in shaker at 25°C for 96 h, so as to achieve a basic balance, after centrifugation take its supernatant to determine the absorbance and calculated the adsorption capacity.

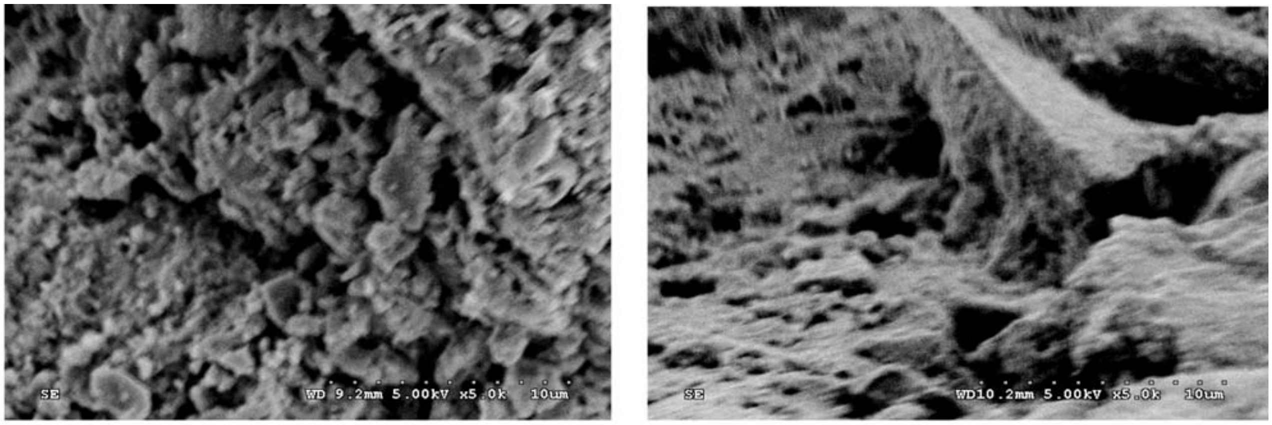
In Kinetic experiments, using 100 mg/g gatifloxacin solution to determine the adsorption capacity of different times There we taken 0.5 h, 1 h, 2 h, 4 h . . . 96 h different points in time, when times reached? quick centrifuged and determine the absorbance of supernatant, thus further calculate the adsorption in the experiments.

3. RESULTS AND DISCUSSION

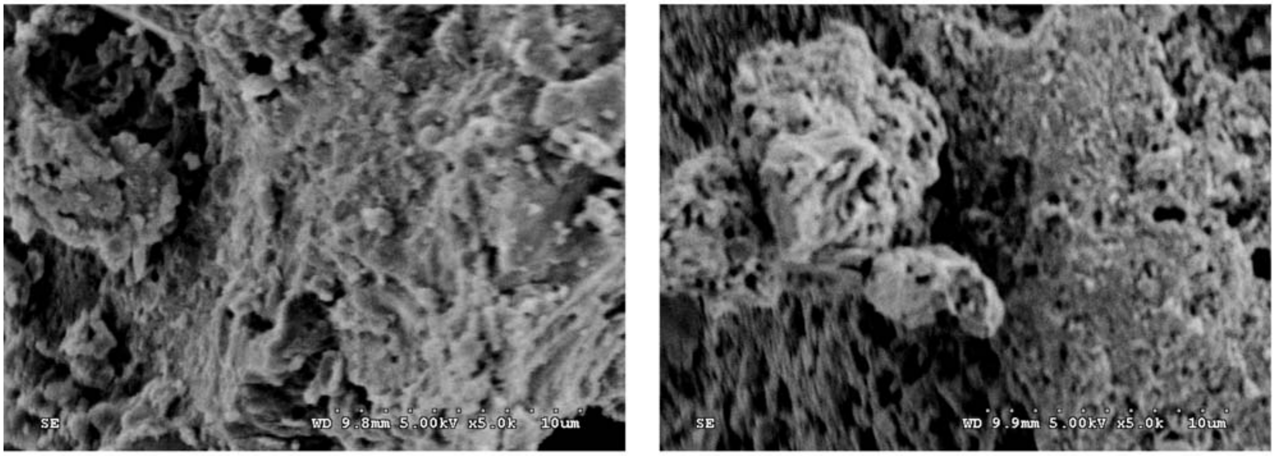
3.1. Characteristic of Activated Sludge

In order to understand better the adsorption mechanism, the physical and chemical characteristics of the sludge before and after modification were tested in this experiment. The SEM images are shown in Figire 1, the particle size and specific surface area were summarized in Table 1 and the zeta potential was listed in Table 2.

Base on the SEM images of the sludge before and after modification shown in Figure 1, it can be seen that after modification, the roughness in the surface increases and more pore structure appears. Those are the good signs for a higher adsorption capability. It is obvious in Table 1 that for both kinds of sludge, the particle



(sludge from sediment tank) (SAC 1)



(dewatering sludge) (SAC 2)

Figure 1. *The SEM images of sludge powder before and after modification.*

sizes are smaller after modification. In addition, the sludge from the sedimentation tanks shows better performance than the dewatering sludge no matter they are before or after modification.

The heavy metal in the leachate of the modified sludge should be concerned when the modified sludge was used. It can been seen in Table 3 that the contents of the main heavy metals in the leachate are acceptable (GB5086.2.3-1997), that is to say it is safe and applicable to use the modified sludge in water treatment except for drinking water treatment.

3.2. Adsorption Curve of the Sludge Activated Carbon

3.2.1. Adsorption Isotherm of the Sludge Activated Carbon

The relationship between adsorption and concentration under certain temperature is called adsorption isotherm, which is generally used to describe the adsorption equilibrium. In this study, a series of solution with a certain concentration gradient was prepared, after 72 h adsorption, a basic equilibrium was reached and the

Table 1. Particle Size Distribution and Surface Area of Different Materials.

Adsorbents	***d*** **(0.1) μm**	***d*** **(0.5) μm**	***d*** **(0.9) μm**	**Surface Mean Diameter μm**	**Volume Average Particle Size μm**
Sludge from sediment tank	47.41	176	406	87.825	205.251
SAC 1	11.60	43.1	131	24.125	131.031
Dewatering sludge	47.8	165	380	87.126	192.889
SAC 2	24.5	117.0	282	50.373	137.168

Table 2. Zeta Potential of Different Materials.

Adsorbents	Sludge from Sediment Tank	SAC 1	Dewatering Sludge	SAC 2
Zeta potential	–2.3	4.4	–11.3	–1.1

Table 3. Contents of Heavy Metals in the Leachate of the Modified Sludge

Heavy Metal	Concentration of Leachate SAC 1 (mg/L)	Concentration of Leachate SAC 2 (mg/L)	Limitation of the Leachate (mg/L)
Pb	0.004	0.001	3
Cr	not be detected	not be detected	0.3
Cd	not be detected	not be detected	10
Ni	0.0018	0.0012	10
Cu	not be detected	not be detected	50
Zn	0.056	0.030	50
As	0.108	not be detected	1.5
Be	not be detected	not be detected	0.1
Ba	0.563	0.324	100
As	0.002	0.001	1.5
F	0.256	0.214	50
CN	not be detected	not be detected	1.0
Hg	not be detected	not be detected	0.05

absorbance was determined under the balance status. Each sample was done in triplicate and the blank used as control. The adsorption capacity was calculated based on the standard curve equation. The commonly used adsorption isotherms are linear-type isotherm, Freundlich isotherm and langmuir isotherm which are shown in Figure 2.

1. Linear adsorption isotherm

$$C_s = K_d \cdot C_{\mathrm{eq}}$$

2. Freundlich adsorption isotherm

$$C_s = K_f \cdot C_{\mathrm{eq}}^{1/n}$$

3. Langmuir adsorption isotherm

$$C_{\mathrm{eq}}/C_s = 1/(Q_b) + C_{\mathrm{eq}}/Q$$

Where C_s is the adsorption capacity per unit mass adsorbent, mg/g; C_{eq} is the adsorbate concentration in aqueous solution, mg/L; K_d is a adsorption constant; K_f is the Freundlich coefficient; n is the Freundlich empirical constant , normally greater than 1; Q is the adsorption capacity under monolayer adsorption; b is the surface adsorption affinity constant. Q and b can be obtained by calculating or drawing.

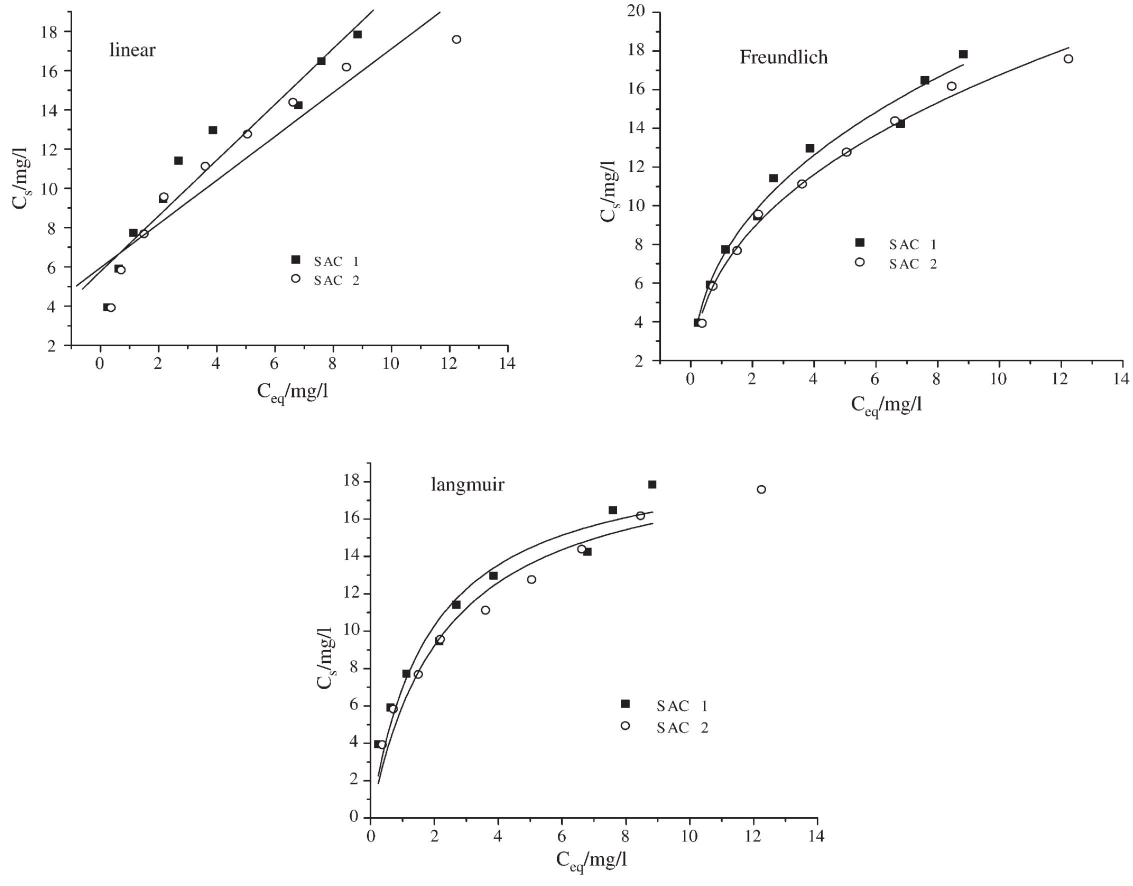


***Figure 2.** Absorption isotherms of activated sludge.*

Table 4. Isotherm Parameters of Activated Sludge Adsorption.

	Equations		Parameters	Correlation
SAC 1	Linear	$C_s = 1.4202\ C_{eq} + 5.7596$	$K_d = 1.4202$, $b = 5.7596$	0.9240
	Freundlich	$C_s = 7.192 \cdot C_{eq}$ 0.4061	$K_f = 7.192$, n = 2.4624	0.9913
	Langmuir	$C_{eq}/C_s = 1/10.7256 + C_{eq}/19.7963$	$Q = 19.7963$, $b = 0.5418$	0.9463
SAC 2	Linear	$C_s = 1.115 C_{eq} + 5.9564$	$K_d = 1.115$, $b = 5.9464$	0.9044
	Freundlich	$C_s = 6.5372 \cdot C_{eq}$ 0.4215	$K_f = 6.4478$, $n = 2.4183$	0.9509
	Langmuir	$C_{eq}/C_s = 1/0.8603 + C_{eq}/19.8989$	$Q = 19.8989$, $b = 0.43235$	0.9617

All isotherm parameters of the activicated sludge adsorption are summarized in Table 4. The higher coefficient in the Freundlich equation indicated that these adsorbents fit the Freundlich equation better than the linear and Langmuir equations. So it can be concluded that the adsorption of Gatifloxacin on two types of sludge activated carbon shows a non-linear relationship which is associated with gatifloxacin's physical and chemical properties and the adsorption maybe caused by both distribution and internal spreading.

In the Freundlich equation, K_f is used to measure the adsorption capacity of the adsorbent. n is the degree of deviation from the linear absorption. It can be seen in table 4 that the parameters of the modified sludge are better than the modified sludge 1, which is consistent with the specific surface area and particle size distribution. The adsorption capacity is higher for the particles with larger surface area and smaller size. While the modified sludge 1 has a higher n value than the modified sludge 2. It is observed from the SEM pictures that two types of modified sludge have looser structure and more pore distribution, and the performance of the sludge activated carbon 1 is better than the sludge activated carbon 2, but the difference between them is not so significant.

According to the study of Hall *et al.*, the matching of the Langmuir equation can be determined by R_L [6] which is a balance parameter and defined as follows,

$$R_L = \frac{1}{1 + bC_0}$$

Where C_0 is the initial concentration of solution (mg/L) b is the Langmuir constant. It can not be matched with Langmuir equation if R_L is greater than 1, while it is a good matching when R_L is ranged between 0 and 1. When R_L is 0, it is a linear relationship. It is obvious in Table 3 that it is a good matching since the value of R_L is ranged between 0 and 1, which indicates the Langmuir equation is appropriate to describe the adsorption and the adsorption process is mainly a single-layer adsorption.

3.2.2. The Adsorption Kinetics of the Sludge Activated Carbon

The kinetics study on the adsorption will change over the time and is used to describe the velocity of adsorption. There are a number of different models, such as the pseudo-first-order kinetic equation, the pseudo-secondary kinetic equation, the Elovinch kinetic equation, as well as the inner spread model equations?which are shown in Figure 3.

It can be seen from Table 5 that the Elovich equation fit the experimental data best in term of the highest coefficient, followed by the quasi-two dynamic equations and the quasi-first-order kinetic equation. So the adsorption process of gatifloxacin is very complicated caused by the combined effects of many reaction mechanisms including the fast surface adsportion process and the slow internal migration process.

The different a value indicates the different adsorp-

Table 5. Kinetics Parameters of Activated Sludge Carbon.

	Kinetics Equation		Parameters	Correlation
SAC 1	Pseudo-first-order kinetic	$\ln 8.7338/(8.7338 - C_s) = 0.7857$	$C_{eq} = 8.7337$; $K_d = 0.7857$	0.6547
	Pseudo-secondary kinetic	$t/C_s = 1/11.1818 + t/9.2178$	$C_{eq} = 9.2178$; $K_s = 0.1316$	0.8770
	Elovinch	$C_s = 5.8904 + 0.8958 \ln t$	$a = 5.8904$; $b = 0.8958$	0.9629
	Inner spread equations	$C_s = 0.4105t^{1/2} + 6.3558$	$K_p = 0.4105$; $X_i = 6.3558$	0.7928
SAC 2	Pseudo-first-order kinetic	$\ln 8.4050/(8.4050 - C_s) = 0.4932$	$C_{eq} = 8.4050$; $K_d = 0.4932$	0.7791
	Pseudo-secondary kinetic	$t/C_s = 1/6.2120 + t/9.0528$	$C_{eq} = 9.05282$; $K_s = 0.0758$	0.9343
	Elovinch	$C_s = 4.6534 + 1.1356 \ln t$	$a = 4.6534$; $b = 1.1356$	0.9732
	Inner spread equations	$C_s = 0.5191t^{1/2} + 5.2491$	$K_p = 0.5191$; $X_i = 5.2491$	0.7973

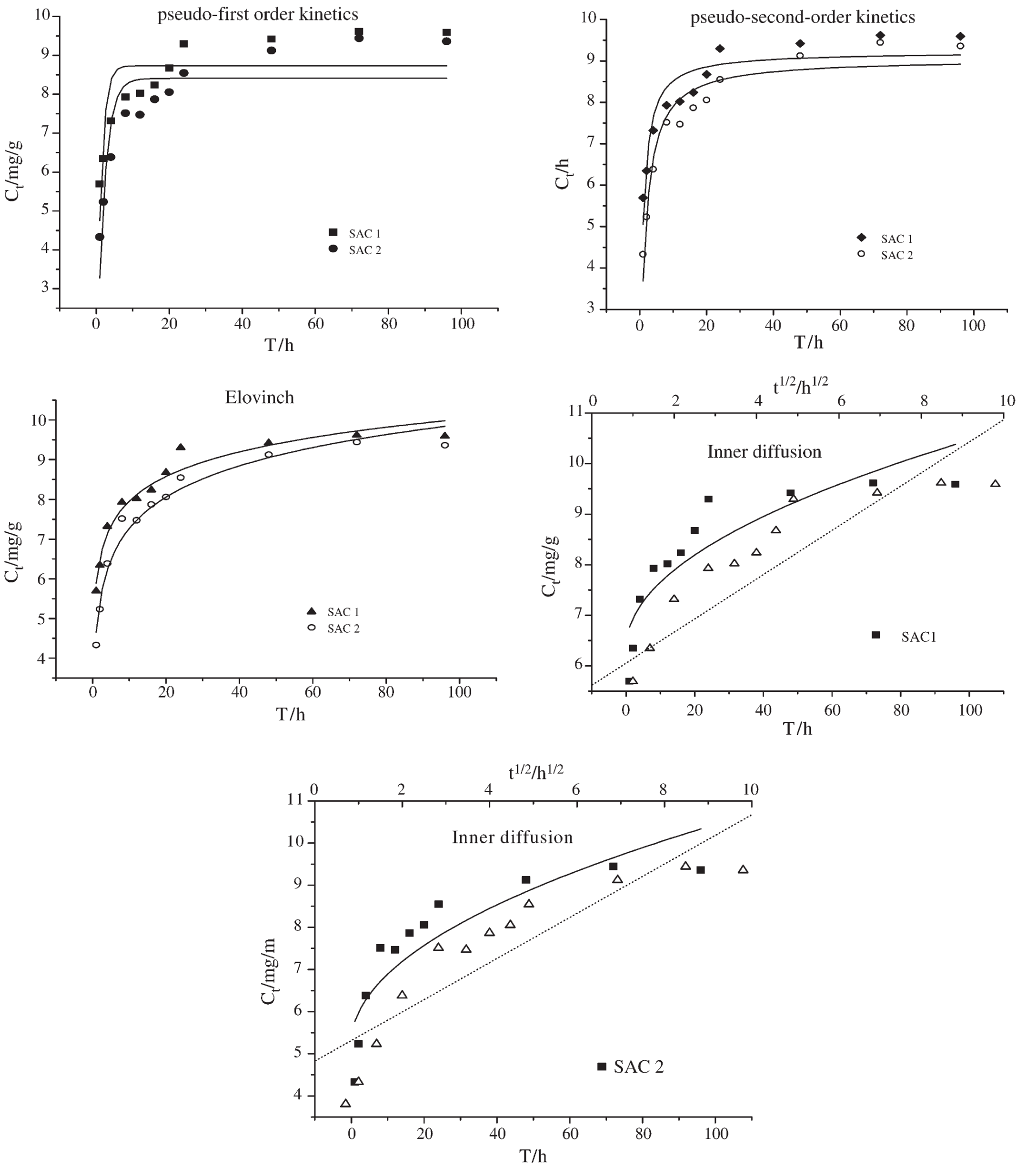


Figure 3. *Kinetics curve of activated sludge carbon.*

tion capacities for different adsorbents, which is match with the results in the single and two dynamic equations shown in Table 5 that the sludge activated carbon 1 is better than the sludge activated carbon 2. In addition, based on the b value which is used to measure the adsorption rate, the sludge activated carbon 2 is better than the sludge activated carbon 1.

Considering the inner diffusion model, there is a good matching in the middle part, while there is a large variation at the beginning and in the late part of the process. This phenomenon reflects the three different reactions which are diffusion of membrane, inner diffusion and adsorption respectively. That also indicates that adsorption of gatifloxacin is a two-stage process. Mckay *et al.* thought that the inner diffusion is the rate-limiting step in the adsorption when C_s and $t_{0.5}$ (dotted line shown in Figure 3) go through the zero point in the inner diffusion model and show a good linear relationship [7]. The inner diffusion curve shown in Figure 3 indicates that the adsorption rate of gatifloxacin is not only controlled by the inner diffusion.

4. CONCLUSIONS AND RECOMMENDATIONS

1. The physical and chemical properties of the sludge were changed to be favorable for adsorption after modification. The sludge activated carbon modified with $ZnCl_2$ can adsorb gatifloxacin effec-

tively. In this study, the performance of the sludge activated carbon modified from the sludge of sedimentation tank is better than the dewatering sludge, but the dewatering sludge is more cost-effective.

2. The adsorption isotherm of gatifloxacin is mostly matched with the Freundlich empirical equation and it is a non-linear process. On the other hand, the Langmuir equation can also be used to describe the adsorption process due to the high R_L value. The most probable process in this adsorption is a monolayer adsorption.
3. In this study, the Elovich dynamics equation fit the data best. So the adsorption is a complex process with both fast and slow stages, and the inner diffusion is not the rate-limiting step. When the time is ranged between 5 and 10 hours, the adsorption capability is 6–7 mg/g. Thus, the 5-hour adsorption is recommended in practical application to control the residence.
4. This study give a good way for using waste sludge as a resourse while it is also benefit for treatment of refractory wastewater.

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Impacts of Pre-sun-drying on Sewage Sludge Compost

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ABSTRACT: The aim of this study was to analyze the impacts of pre-sun-drying on sewage sludge compost. Comparative analysis was focused on the following parameters: moisture content (MC), pH value, total organic carbon (TOC), volatile solids (VS), water soluble total nitrogen (WSTN), ammonia nitrogen (AN), and dehydrogenase activity (DA). The results show that: the sun-drying process can quickly reduce initial moisture content from 82% to 77.7%. But the initial TOC and VS decreased from 356 g/kg and 59% to 326 g/kg and 50%, and the initial WSTN content was also decrease from 3.5 g/kg to 1.9 g/kg. As compost proceeded, the lower moisture content had slowed down the dehydrogenase activity (with an average of 271 μg TF/(g·h) vs. 199 μg TF/(g·h)) . And pH value reached a maximum of 9.35 (non-drying) and 8.79 (air-drying) respectively, which had something to do with the more NH_3-N (12.2 g/kg vs. 4.4 g/kg) formed in the non-drying compost of the thermophilic phase.

1. INTRODUCTION

TODAY, instead of burning or landfilling sewage sludge, new avenues such as composting are actively being developed in order to dispose of these residues in a more natural preservation manner. Composting is defined as the microbial degradation of organic solid material that involves aerobic respiration and passed through a thermophilic stage. By this process, many advantages are reached such as sanitation, mass reduction, decrease of carbon to nitrogen ratio (C:N) in addition to upgrading the organic waste into a useful end-product called compost (M.H. Charest *et al.*, 2004).

Several studies have mentioned the importance of early stage control over different physico-chemical parameters such as temperature, moisture, PH, aeration, particle size and nutrient balance (J.H. Craford,1983). For moisture, most of the moisture content of dewatering sewage sludge from the waste water plant is around 80%, however, the optimum moisture content for the sludge composting ranges from 50% to 60% (J.S. Jeris and R.W. Regan, 1973). Therefore, the sludge pretreatments are always necessary to reduce the initial moisture content to satisfy the needs of the sludge compost. For the sludge composting plants, there are two main sludge pre-drying methods currently, the natural sun-drying method and the heat-drying method. Using solar energy for drying sludge, with the advantage of energy-saving and low operating costs, is proved to be an effective as well as an economic pretreatment method (Zheng Zonghe *et al.*, 2003). And compared to the sun-drying, the later one increases compost cost largely due to the high energy consumption. So most composting plants are inclined to sun-drying as the pre-treatment method for the sludge compost. However, many impacts brought by sun-drying were usually ignored, such as the pre-consumption of the organic matter, duration of thermophilic phase, enzymes activities, and the nitrogen loss problem *et al.* And how to reduce nitrogen loss and increase the nitrogen content of compost has always been one of the hot spots of compost research (A. Meijide *et al.*, 2009).

Hence, this research has focused on impacts of the pre-air-drying on sewage sludge compost and devoted to provide the theoretical basis for coupling sludge pre-drying with following composting and to reduce the loss of nutrients in the pre-treatment, and to improve the composting efficiency as well as the composting quality.

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2. MATERIALS AND METHODS

2.1. Experiment Material

Sewage sludge: The dewatering sewage sludge from Taiping sewage treatment plant in Harbin, and the initial moisture content is around 80%.
Bulking agent: An special inert bulking agent.

2.2. Experiment Device

As shown in Figure 1, the 2400 mm-high cylinder reactor with a diameter of 400 mm and 300 L of the total volume has six main systems: the air flow metering system, combined time-temperature control systems, insulation systems and air pumping systems.

2.3. Experiment Design

Two rounds of the composting experiment were conducted in the same reactor. In the first round, 100 L dewatering sludge were mixed with 200 L inert bulking agents(with a ratio of 1:2) directly. In the second round, 100 L dewatering sludge were exposed to the outdoor for 5 days, with 80 L sludge being left due to the lose of water, and then mixed with 160 L inert bulking agent in order to keep the same ratio(1:2) as the first round. And then over a period of 20-day composting experiment respectively, relevant parameters were mensurated and analyzed.

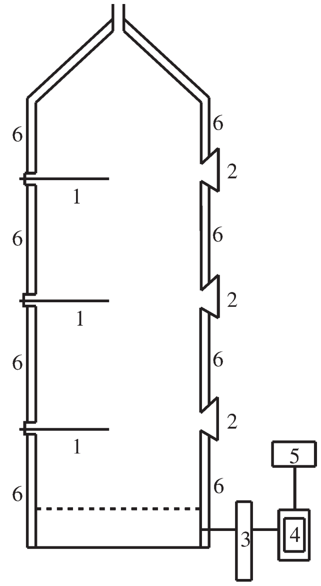

Figure 1. *Composting reactor. 1. Thermometer ; 2. Sampling mouth; 3. Gas flowmeter; 4. Air pump; 5. Combined time-temperature controller; 6. Rubber insulation.*

2.4. Parameters and Analysis Method

Table 1. The Parameters and Analysis Methods of Aerobic Composting Process.

Parameters	Condition	Analysis Method and Apparatus	Sample
MC	105°C, 24h	weight loss–oven	fresh sludge
TOC	900°C	weight loss–TOC-4100	drying sludge
VS	550°C,4h	weight loss–RTM-28-10	drying sludge
pH	1–10 water	glass electrode (PHS-3C)	fresh sludge
AN	1–10 water	Nessler's reagent colorimetry	drying sludge
WSTN	1–10 water	Postassium persulfate oxidation	drying sludge
DA	1–10 water	TTC-DHA	fresh sludge

3. RESULTS AND CONCLUDES

3.1. Temperature Variation and Comparative Analysis

Composting is a natural process by which mocroorganisms decompose organic matters into simpler nutrients(C.Liang *et al.*, 2002).And temperature is one of the most important index during the composting process, which also affects the composting microbial biomass, microbial type and the microbial activity, which in turn affects the efficiency of the biochemical reaction during the decomposition of the organic matters (OM)(L i Yanxia *et al.*, 1999). More importantly, the temperature may indicate that the compost meets the requirements of hygienics (Stentiford E.I., 1996). According to the hygiene requirements of the compost, the temperature is required over 50 ~ 55°C to maintain at least 5 days or more, or above 55°C for more than 3 days, which will kill pathogenic bacteria and parasite eggs effectively (USEPA, 1994). But the over-high temperature (> 70°C) will inhibit the decomposition of the OM, resulting a poor compost quality as well. Research shows that the optimum temperature for the composting ranging from 55°C to 65°C, with the most efficient decompositon (Liang C,Dds KC *et al.*, 2003).

Comparative variation of composting temperature is obvious, even thought the small-scale compost, which thermophilic phase is ralative shorter, and compared to the non-drying compost, the temperature of the sun-drying one is lower even for the relative higher initial ambient temperature (Figure 2); And the sun-drying compost, with less than four-day thermophilic period

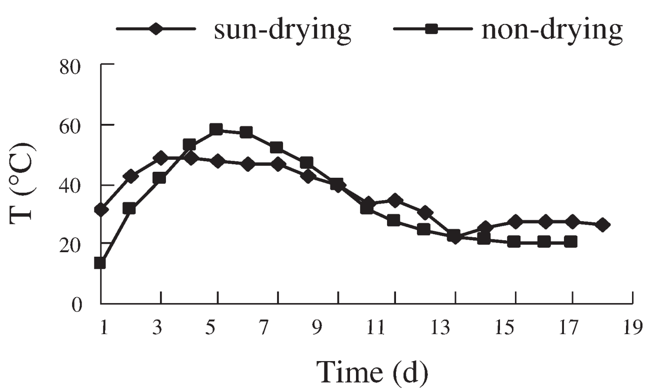

Figure 2. *Comparative variation of composting temperature.*

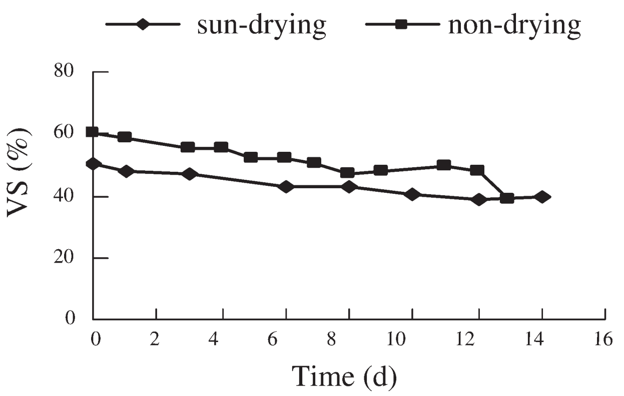

Figure 4. *Comparative variation of composting VS.*

over 50°C, did not meet the composting standard, which mainly because of the microbial metabolism during the sun-drying process. Because, the biodegradable organic matters(the source of nutrition for the microbes), are pre-consumed in a large scale before composting, which can be reflected from the diversity of volatile solids [VS (Figure 4)]. And VS is the combustion-volatile part of the organic matters, including the BVS and NBVS (non-volatile bio-solids, that is, non-bio-decomposition organics). As the change of NBVS in the composting process is very small, therefore, VS content can reflect the degradation extent of the degradable organic matter in the composting process (Naylor L.M., 1996). From the Figure 4, the initial VS decreased by 8.13, from 59% to 51%, indicating that the process of sun-drying had consumed some kind of organic matter in the pile, which can explain why the thermophilic phrase has maintained such a relative shorter time. Compared to the non-drying sludge, the TOC content of the sun-drying one decreased by about 8.02% (Figure 3).This also mainly attributes to the consumption by the biochemical reaction of microbes in the sludge during the sun-drying process. Due to the relative low C/N ratio of the sewage sludge (about 10~15%), the loss of carbon make the composting process more difficult to reach higher temperature.

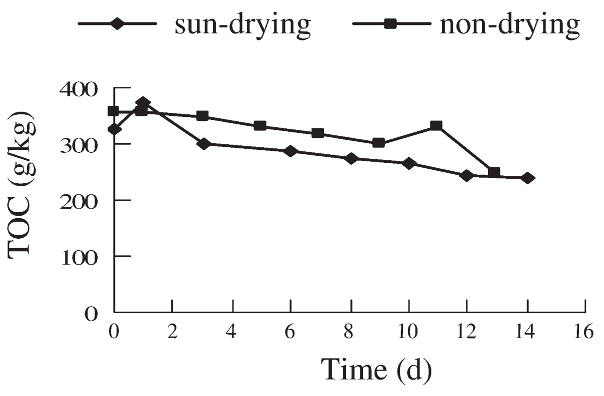

Figure 3. *Comparative variation of composting TOC.*

3.2. Comparative Analysis of Moisture Content and Dehydrogenase Activity

The moisture content of sludge is a key factor to the success of the compost. As the high water content (80%) of the dewatering sludge, if no regulation, it will bring the ventilation problems, resulting in partial anaerobic areas and affecting the composting efficiency. And the only purpose of sun-drying is to remove the excess water from the sludge, so as to meet the moisture content of compost. As shown in the Figure 5, firstly, the sun-drying process can quickly reduce initial moisture content from 82% to 77.7% (the ralative high moisture content after compost due to without turnover systerm in the composting reactor), and the sludge volume decreased by 1/5; Secondly, it indicates that the water removal rate for the two conditions are almost equivalent, both reduced by around 10% during the aerobic composting. So, it can not be concluded that the

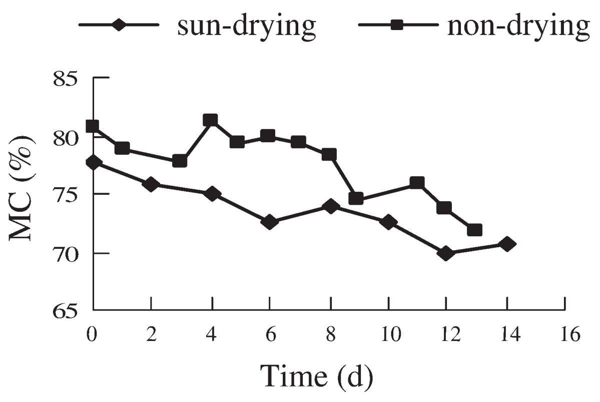

Figure 5. *Comparative variation of composting MC.*

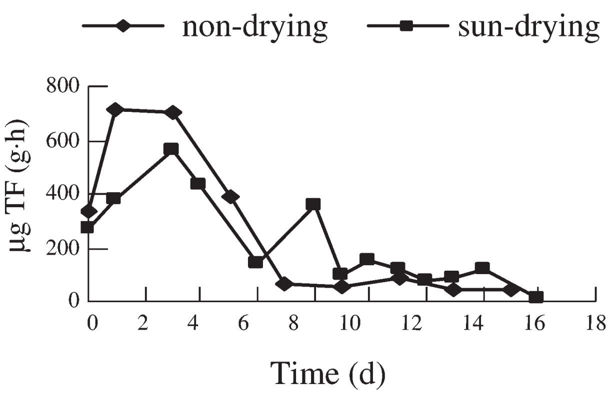

Figure 6. *Comparative variation of composting dehydrogenase activity.*

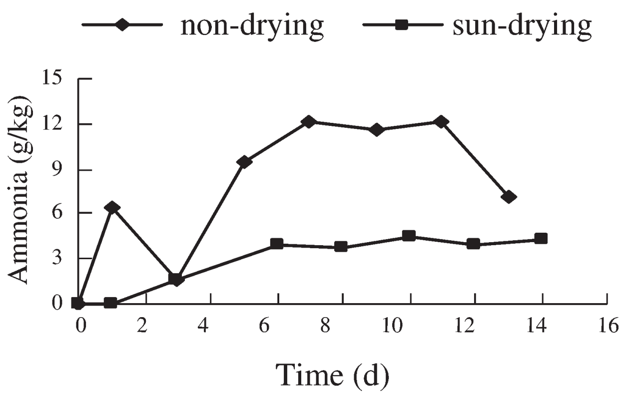

Figure 8. *Comparative variation of composting ammonia.*

more water the sludge lost before the compost, the more efficient the water removal rate will be. This is because the microbes can not use the solid-state components directly, and only when the solid-state components are dissolved in water, the components can be absorbed by the microbes, and high moisture content contributes to the nutrition transfer and absorption for the microbes, leading to enhancement of the microbial activity. Since the dehydrogenase is the trunk enzymes in the respiratory chain, the mass of the dehydrogenase can reflect the microbial activity in a large extent. From the contrastion of the dehydrogenase activity (Figure 6), the non-drying composting dehydrogenase activity is comparatively higher than the air-drying one during the first five-day composting (with an average of 271 μg TF/(g·h) vs. 199 μg TF/(g·h)), and after 9 days, both of the two dehydrogenase activity are significantly reduced, this is mainly because of the quickly reduction of the biodegradable organic matter, resulting to the decrease of the biomass, and more difficult to the dehydrogenation of the hardly biodegradable organic matter for the microbes seems another important reason. So, just in terms of microbial activity, non-drying sludge compost is suggested because of its relative higher microbial activity than compost which sludge experienced pre-sun-drying process.

3.3. Comparative Analysis of the pH and Composting Nitrogen

During the aerobic thermophilic composting, the activities of microbes need a Micro-acid or neutral conditions, and pH of the sewage sludge is neutral under normal circumstances. Since at the beginning of pile-fermentation, organic acids will be formed, and the pH will descend, and as the organic acids are further decomposed, the pH will rise, and continuously, the pH will ascend to its peak, and then down again. And this is quite the same as the Figure 7 showed: pH value experienced HHHa little down in the initial phase and then rebounds quickly. Especially in high-temperature phase, due to the formation of a large number of NH_3-N, Both pH value have increased rapidly, reaching a maximum of 8.79 and 9.35, respectively. And this may have something to do with the low ratio of C and N. And according to the U.S. Environmental Protection Agency

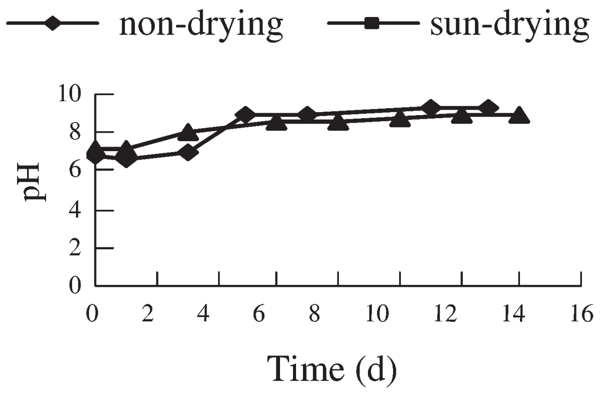

Figure 7. *Comparative variation of composting PH.*

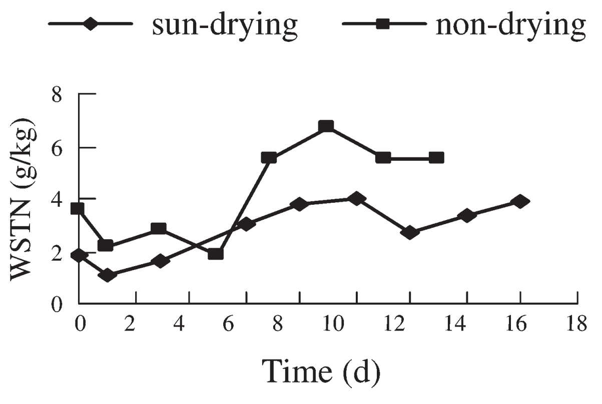

Figure 9. *Comparative variation of composting WSTN.*

(USEPA), the pH value ranging from 6 to 9 is acceptable (C.Liang and K.C.Das, 2003), the high pH value will affect the composting efficiency. Additionally, the over high pH value will lead to more loss of the nitrogen, affecting the quality of the composting product. And the higher pH during the non-drying compost has a great relationship with the more ammonia formed in the non-drying compost of the thermophilic phase (12.2 g/kg vs. 4.4 g/kg (Figure 8).

The nitrogen in the composting mainly consists of organic nitrogen, which usually exists in the form of peptides and proteins (Sanchez-Monedero *et al.*, 2001). And at the initial phase of the composting process, the organic nitrogen transfers into ammonia by ammonification. And in the initial period of the compost, for the volatilization of the excessive ammonia and denitrification of the nitrate, resulting in the loss of nitrogen, and in some cases, the loss could be as high as 70% (Eklind Y., Kirchmann H., 2001).Throughout the composting process, except the volatilization, the part used by the microbes and formed into the other compounds also contribute to the loss of the nitrogen (Tognetti *et al.*, 2007). Compared with the sun-drying compost(the optimum ammonia content just 4.38), the ammonia of the non-drying one(up to 12.17) has a strikingly higher content (Figure 8), which may correspond to the more total nitrogen content of the sludge without the sun-drying process, partly reason is that non-drying sludge has avoided the loss of initial nitrogen during the sun-drying process. This can also be reflected by the reducement of the WSTN from 3.5 g/kg to 1.9g/kg at the beginning of the compost (Figure 9). Hence, from the quality of the composting end-product, non-drying before composting is suggested, because it can avoid the nutrient like nitrogen loss strikingly during the sun-drying process.

4. CONCLUSION

The pre-sun-drying process can reduce the moisture content obviously, but some impacts will be brought in the following compost simultaneously. Firstly, organic materials are partly pre-consumed, resulting in insufficient heat provided by the biodegradation in the following compost. Secondly, dehydrogenase activity is slowed down due to the relative dryer sludge has restrained the transfer and absorption of the nutrients for the microbes. Additionally, the nitrogen is proved to be partly lost before the compost, which may affect the quality of the final compost product. So less drying days and turnover time are suggested in order to reduce the adverse impacts of the pre-sun-drying on the following compost.

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Novel Lightweight Building Bricks Manufactured from Water Treatment Plant Sludge and Agricultural Waste

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ABSTRACT: Novel lightweight bricks have been produced by sintering mixes of dried water treatment plant sludge and agricultural waste. Samples containing up to 40 weight percent rice husk have been sintered using a heating schedule that allowed effective organic burn-out. Rice husk addition increased the porosity of sintered samples and higher sintering temperatures increased compressive strengths. Materials containing 40 weight percent rice husk that were sintered at 1100°C produced low bulk density and relatively high strength materials that were compliant with relevant Taiwan standards for use as lightweight bricks. This research was also evaluated the environmental safety of sintered products by the toxic characteristic leaching procedure (TCLP) concentration. The results indicated that TCLP concentrations of Cu, Zn, Cr, Cd, and Pb in the sintered products were lower than regulation thresholds.

1. INTRODUCTION

IMPROVING drinking water quality has been a priority in Taiwan for many years. Poor soil conservation and the unique geography of Taiwan has caused drinking water shortages, increased the water supply turbidity and reduced drinking water quality. Water consumption in Taiwan increased from 0.18 to 0.242 m^3/day/person between 1986 and 2008. High doses of coagulants and other chemicals are now used in water treatment to improve the drinking water quality (Taiwan Water Corporation, 2009). A typical water treatment plant (WTP) produces about 200,000 m^3 of sludge per day. This amount is expected to increase. Sanitary landfills are normally used for sludge disposal, although the Taiwan Government has a WTP sludge management strategy that aims to reduce landfill disposal by encouraging beneficial reuse. The management of agricultural wastes is also an important environmental issue in Taiwan. Approximately 1.2 million tons of rice paddy waste is produced each year, resulting in approximately 0.24 million tons of waste rice husks (Taiwan Agriculture and Food Agency, 2009). Most of this material is either burnt or stockpiled. Burning causes air pollution and stockpiling is unsightly, uses valuable space and can cause other environmental problems.

Sintering is becoming an attractive option to allow recycling of certain types of inorganic wastes and residues in Taiwan. Over the last decade many researches have investigated the properties of various materials made from sintered wastes. These materials have included pulverized fuel ash (PFA), bottom ash and air pollution control (APC) residues from municipal solid waste (MSW) incinerators, sewage sludge ash, water treatment sludge, dam sediments, slag from steel production, slag from incinerator residues and various other inorganic wastes. Potential applications include lightweight aggregate, bricks, tiles and other construction products (Cheeseman *et al.*, 2003; Chiang *et al.*, 2008; Huang *et al.*, 2001; Mangialardi, 2001; Tay *et al.*, 2002; Xu *et al.*, 2008).

Over the past decade, building brick development has moved toward reducing brick weight and increasing its thermal insulation ability. Considering the modern green building, the amount of inner pores in building bricks is a critical factor. Lightweight bricks were usually manufactured by adding combustible additives as a foaming agent while controlling the appropriate amount of pores, particle size and firing temperature. Plastics have been applied for use as an additive in lightweight brick production. However, the results from previous studies showed that the low apparent density and high water absorption in plasticized lightweight bricks

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resulted in an excessive amount of the pores and decreased compressive strength (Veiseh and Yousefi, 2003). There many unknowns that must be overcome in the key technologies for improving the compressive strength of lightweight bricks.

Rice husk is a major agricultural waste with a unique residue with high ash silica content. The ash contains above 90% silica with a highly porous, lightweight, specific surface area. Rice hull ash has been applied as an amendment in many materials. This is due to its' high porous insulating property. Many industrial applications include refractory brick manufacturing, concrete and lightweight building materials, and the manufacture of insulation and flame retardants etc (Boateng and Skeete, 1990; Chaudhary and Jollands, 2004; Choi *et al.*, 2006). Although rice husk ash applications in cement and steel manufacturing are well-established, silica-enriched ash is usually produced by burning the rice husks. The properties of rice husk ash silica vary according to the firing temperature and time. It is important to control the firing conditions to produce the appropriate ash for the particular application. In this research, rice husks were added to WTP sludge, homogenised and sintered to produce materials with different porosities. The blending ratio and sintering temperature effects on the properties and microstructure of the produced materials is reported.

2. MATERIALS AND METHODS

2.1. Materials

The Fong-Yuan water treatment plant, located in the central part of Taiwan, produces approximately 700,000 m^3/d drinking water from surface water using a conventional coagulation, flocculation and rapid sand filtration process, using poly-aluminum chloride (PAC) as the coagulant. Drinking water is disinfected with a combination of chlorine gas and chlorine dioxide. The drinking water treatment process produces approximately 6,000 tons/year of WTP sludge (based on 50 wt.% moisture content). Representative samples of WTP sludge were collected from the drying beds at Fong-Yuan. The collected sludge cake had agglomerated and was therefore shredded and sieved to give particles between 74 and 300 μm. Rice husks were obtained from the Tai-Nan County Farmers' Association in Southern Taiwan. The rice husks were sieved into particles with sizes between 74 and 300 μm for use in subsequent experiments.

2.2. Characterization of WTP Sludge and Rice Husk

The moisture content of WTP sludge and rice husks was determined by heating samples to 105ºC for 48 hours. The combustible fraction was determined in triplicate using American Public Health Association (APHA) standard methods. X-ray fluorescence (XRF, SPECTRO, X-Lab 2000) was used to determine the chemical composition of WTP sludge. Crystalline minerals were identified by X-ray diffraction (XRD, MAC Science, MXP3). The pH was determined in triplicate using aqueous extracts from dried samples at a 1:10 ratio of solid: distilled water (w/v).

The Pb, Cd, Cu, Cr, and Zn concentrations were determined using nitric acid (HNO_3)/hydrogen peroxide (H_2O_2) digestion, followed by inductive coupled plasma optima optical emission spectroscopy (ICP-OES, Perkin Elmer, Optima 2000DV). The toxicity characteristic leaching procedure (TCLP) test is required by the Environmental Protection Administration of Taiwan (NIEA R201.10T). This involves the addition of an acetic acid solution (0.57% v/v) to dried samples at a constant ratio of liquid-to-solid (20:1). After 18 hours the leachate is filtered and analyzed using ICP-OES for a range of metals including Pb, Cd, Cu, Cr, and Zn.

2.3. Preparation of WTP Sludge Specimen and Sintering Operation Procedure

Dried WTP sludge and rice husk samples with particle sizes between 74 and 300 μm were blended to produce homogenous mixes containing rice husk additions of 0, 5, 10, 20, and 25% (by weight) on a dry basis. Compacted samples were prepared by adding 20 % water to the dry powder and uniaxially pressing at 60 kgf/cm^2 (800 psi) to form 20 mm diameter cylindrical specimens that were approximately 55 mm high.

The temperature was increased at 5ºC/min in an electric furnace (DENGYNG, DF-404) with a first dwell at 105ºC for 120 minutes to evaporate moisture. The dwell at 600ºC for 120 minutes was used to decompose the organic matter in the rice husk. The temperature was then increased to a sintering temperature between 800 and 1100ºC and held for 180 minutes.

2.4. Characterization of Sintered Samples

The bulk density, water absorption, open porosity and dimensional change in the sintered products were determined from their weights and dimensions in term of ASTM C373 and C20-00 standard test methods. The bulk density of the sintered products in grams per cubic centimeter is the quotient of its dry weight (W1) divided by the exterior volume. The exterior volume (V) of the sintered products in cubic centimeters was calculated by subtracting the suspended weight (W2) from the saturated weight (W3). The saturated weight of the sintered products was determined while products were immersed in boiling water for 2 hours. The specimens remained immersed in water for a minimum of 12 hours, surface dried and re-weighed (W3). The suspended weight (W2) was determined after boiling while the specimens were suspended in water. The water absorption was calculated from the ratio between W3–W1 and W1. The open porosity expressed as a percentage the relationship between the open pore volume in the sintered products and the exterior volume, calculated from the ratio between W3–W1 and W3–W2. The change in specimen volume after sintering was also determined.

Unconfined compressive strength was measured using the Taiwan Environmental Protection Administration (EPA) standard method (NIEA R 206.22C). Strengths were obtained in triplicate using a loading rate of 6 kgf/second. The micro-structures of the sintered specimens were examined using scanning electron microscopy (SEM, Hitachi, S3000). Crystalline phases were identified by XRD (MAC Science, MXP3).

3. RESULTS AND DISCUSSION

3.1. Properties of WTP Sludge and Rice Husk

Table 1 shows the pH, moisture content, combustible fraction, percentage ash and metals content (mg/kg) data for the WTP sludge and rice husk. The water content of the WTP sludge and rice husk were 44.4 ± 0.9% and 11.3 ± 0.1 %, respectively. The combustible fraction of the WTP sludge and rice husk were 2.9% and 77.6% respectively. Total metal concentrations in the WTP sludge and rice husk were relatively low. Zn and Cr concentrations were typically 63.8 ± 2.7 mg/kg and 50.4 ± 3.0 mg/kg for rice husk respectively and 71.4 ± 11.0 mg/kg and 128.2 ± 24.8 mg/kg for WTP sludge, respectively. Other metals were present at less than 30 mg/kg or below detection limits.

Table 1. The Principal Properties and the Metal Contents of the Tested Materials.

Items	Sludge	Rice husk
pH (in H_2O)	$6.94^{*1} \pm 0.13^{*2}$	6.39 ± 0.04
Moisture (%)	44.41 ± 0.88	11.34 ± 0.07
Ash (%)	52.67 ± 0.04	11.03 ± 0.07
Combustible (%)	2.92^{*3}	77.63
Total Metal Concentration (mg/kg)		
Cu	28.47 ± 6.1	222.39 ± 1.94
Zn	128.24 ± 24.82	50.39 ± 3.02
Cr	71.09 ± 11.03	63.76 ± 2.69
Cd	N.D.^{*4}	N.D.
Pb	32.52 ± 1.91	18.49 ± 1.15
TCLP Concentration (mg/l)		
Cu	0.01 ± 0.00	0.05 ± 0.00
Zn	0.83 ± 0.07	0.92 ± 0.09
Cr	N.D.	N.D.
Cd	N.D.	N.D.
Pb	0.03 ± 0.00	0.06 ± 0.02
Chemical Composition (%)		
SiO_2 (%)	61.93	16.74
Al_2O_3 (%)	11.37	0.08
Fe_2O_3 (%)	5.28	0.16
K_2O (%)	3.67	0.69
MgO (%)	1.19	0.18
Na_2O (%)	0.62	0.08
CaO (%)	0.49	0.38
TiO_2 (%)	0.50	0.01

TCLP leachate analysis data are given in Table 1. The concentrations of Zn, Pb and Cu leaching from the rice husk and WTP sludge were below the Taiwan EPA regulatory limit. The Cd and Cr leaching concentrations of tested materials were below detection limits. Chemical composition data as percentage of major oxides is also shown in Table 1. This indicates that the main components of WTP sludge are SiO_2 (61.93%), Fe_2O_3 (5.28%), Al_2O_3 (11.37%) and K_2O (3.67%). XRD data is given in Figure 1 for the WTP sludge. Silica (SiO_2) is the major crystalline phase present and relatively low intensity peaks corresponding to those for Al_2O_3 and Fe_2O_3 were also detected.

3.2. Properties of Sintered Specimens

3.2.1. *Bulk Density*

Figure 2 shows that the open porosity of lightweight specimens increased with rice husk addition and decreased with the sintering temperature. With 1100ºC sintering temperature the specimen open porosity increased from 5.2 ± 1.5% to 43.1 ± 1.2% with an increase

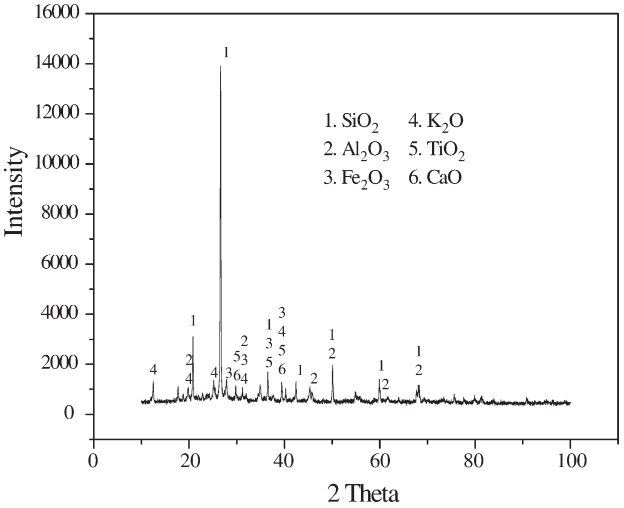

Figure 1. *XRD data for the as-received WTP sludge.*

in added rice husks from 0% to 40%. The larger the rice husk organic matter content, the greater the porosity and shorter the path among particles for gas diffusion. Therefore, a higher rice husk addition ratio increases the open pore volume and decreases the bulk density of sintered specimens.

Samples sintered at the same firing temperature showed increased bulk density in sintered specimens with decreased rice husk addition ratio. Figure 3 shows that a maximum bulk density of 2.38 ± 0.02 g/cm^3 with specimens sintered at 1100ºC. Increasing the rice husk addition from 0% to 40% decreased the sintered specimen bulk density from 2.38 ± 0.02 g/cm^3 to 1.43 ± 0.02 g/cm^3. In the case of 30% rice husk addition and 1050ºC sintering temperature the sintered specimens revealed a bulk density of 1.37 ± 0.07 g/cm^3; lower than that for traditional building brick criteria. These results are in agreement that rice husk addition resulted in low bulk density sintered specimens.

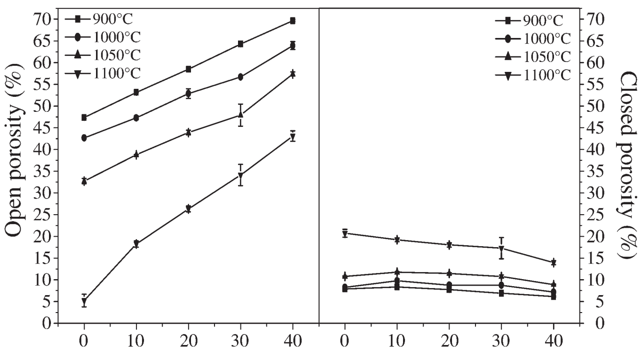

Figure 2. *Rice husks addition effect on the total and open porosity of specimens.*

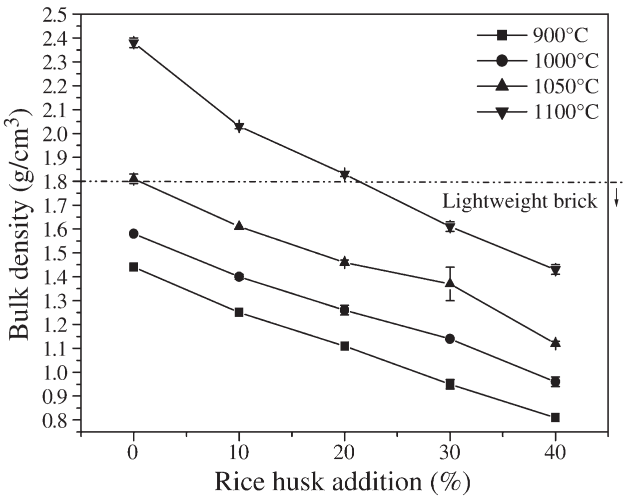

Figure 3. *Rice husks addition effect on the bulk density of specimens.*

3.2.2. *Water Absorption*

The sintering temperature and rice husk addition effects on water absorption are shown in Figure 4. This decreases from 32.9 ± 0.2% to 2.2 ± 0.6% when the sintering temperature is increased from 900 to 1100ºC for samples containing no rice husks. In the case of 40% rice husk addition, the water absorption of sintered specimens decreased from 86.3 ± 0.8% to 30.1 ± 1.4% when the sintering temperature was increased from 900 to 1100°C. Water absorption decreased significantly with increasing sintering temperature. The results also indicated that the water absorption increased with increased rice husk addition ratio.

Figure 4 shows that water absorption increases with the increase in rice husk addition ratio. At 1100ºC sintering temperature, water absorption increases from

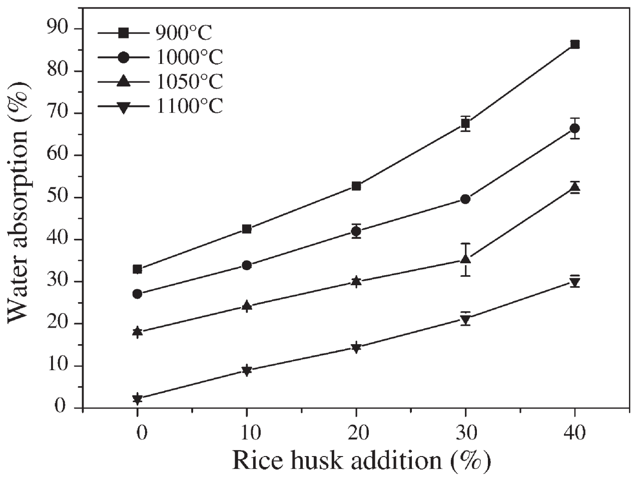

Figure 4. *Rice husks addition effect on the water absorption of specimens.*

2.2 ± 0.6% to 30.1 ± 1.4% as the rice husk addition ratio is increased from 0% to 40%. In samples sintered at 1100ºC with 20% rice husk addition, the water absorption of the sintered specimens was approximately 15% in compliance with the current Taiwan traditional building brick criteria. Lightweight bricks have been applied widely in the inner walls of green buildings, although they have relatively high water absorption. That is, the water absorption of lightweight bricks is an insignificant factor in considering their application. This is because the large number of open pores in sintered specimens provides good thermal insulation properties for green building applications.

3.2.3. Shrinkage After Sintering

Figure 5 shows the shrinkage of samples as a result of sintering. Shrinkage increased with sintering temperature and samples sintered at 1050ºC had shrinkage of approximately 10%. Obviously, the shrinkage of sintered specimen increased significantly with the sintering temperature. A maximum of 15% shrinkage occurs at sintering temperature 1100ºC and 30% rice husk addition and above.

With respect to recycling and reusing sintered specimens, controlling shrinkage or swelling is a critical concern. In general, higher shrinkage rate represented greater densification in sintered specimens. That is, significant densification occurred, resulting in a total shrinkage in volume. The shrinkage rate of the sintered products increased dramatically at 1050°C sintering temperature, as shown in Figure 5. It can be concluded that sintered specimen densification occurred at 1050°C sintering temperature.

3.2.4. Compressive Strength

Figure 6 shows the compressive strength data for sintered specimens as the function sintering temperature for different rice husk percentage addition. The compressive strength increased with increased sintering temperature and decreased with increased added rice husks. Compressive strength increased from 182.6 ± 11.4 kgf/cm^2 to 1590.7 ± 214.5 kgf/cm^2 when the sintering temperature was increased from 900 to 1100ºC for samples containing no rice husks. In the 40% rice husk addition case, the sintered specimen compressive strength increased from 14.1 ± 0.2 kgf/cm^2 to 165.4 ± 11.4 kgf/cm^2 when the sintering temperature was increased from 900 to 1100°C. The higher compressive strength developed at 1050°C sintering temperature with the rice husk ratio at 20% and below, ranging from 240.7 ± 30.0 kgf/cm^2 to 735.5 ± 107.0 kgf/cm^2, thereby fulfilling the code requirement (150 kgf/cm^2) with respect to lightweight bricks for construction work.

The water absorption and compressive strength of the sintered specimens are also key factors in considering their application as construction bricks. Increasing the number of open pores in the sintered specimen implies an increase in water absorption and decrease in bulk density. A contrary trend occurred between water absorption and compressive strength occurs in the sintered specimens. The compressive strength increases with decreasing water absorption. The compressive strength of the proposed sintered products complies with Taiwan's lightweight brick criteria when sintered at 1050ºC with 20% or less added rice husks. The low bulk density and relatively high compressive

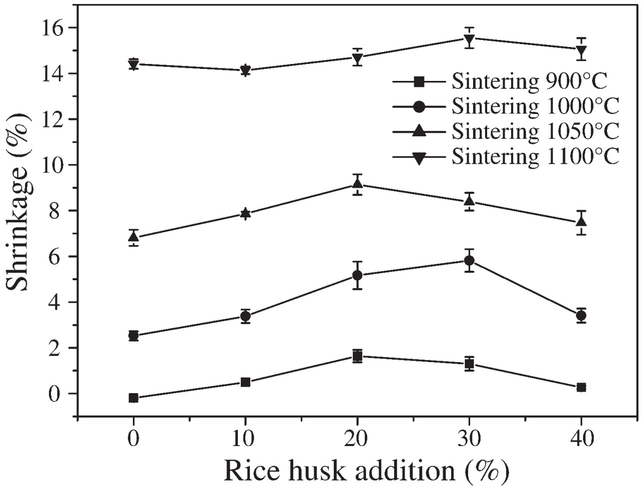

Figure 5. Rice husks addition effect on the shrinkage of specimens.

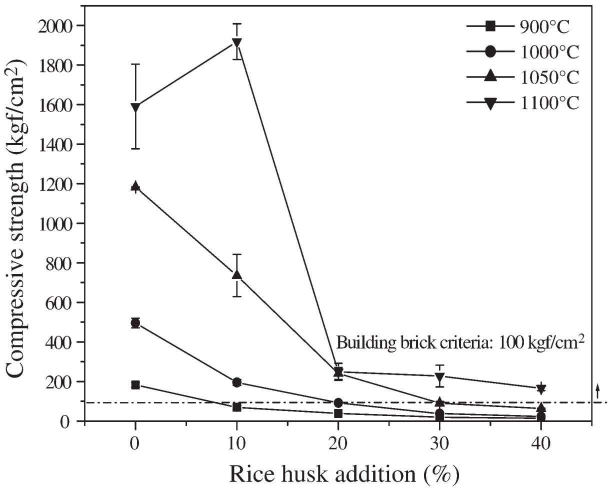

Figure 6. Rice husks addition effect on the compressive strength of specimens.

Table 1. TCLP Metal Leachate Concentrations of Sintered Products.

	1050°C			1100°C			
Metals	**0%**	**10%**	**40%**	**0%**	**10%**	**40%**	**Regulation Thresholds**
Pb	0.01	0.02	0.01	0.04	0.05	0.04	5.0
Cd	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	1.0
Cr	0.007	0.008	0.005	0.016	0.016	0.014	5.0
Cu	0.02	0.01	0.01	0.27	0.63	0.47	25.0
Zn	0.05	0.04	0.04	0.21	0.39	0.29	15.0

strength of lightweight brick were successfully manufactured from WTP sludge and rice husks.

3.2.5. Heavy Metals Characteristics of Sintered Products

Table 2 summarizes the content of Pb, Cd, Cr, Cu and Zn found in specimens sintered in the 1050°C and 1100°C temperature range. The total TCLP leachate concentrations for all tested metals in the sintered specimens revealed a decreasing tendency compared to the WTP sludge properties. Based on these analysis results, the TCLP leachate concentrations for the tested metals in all sintered specimens were in compliance with Taiwan EPA regulatory limits (Pb: 5 mg/l, Cd: 1 mg/l, Cr: 5 mg/l, Zn: 25 mg/l).

3.3. Micro-structural Analysis

Figure 7 shows the XRD data for specimens sintered at 1100°C. Comparison with the XRD data for as-received WTP sludge in Figure 3 shows that no significant changes in the crystalline phases occurred from sintering. The major mineral phases in the sintered specimens were quartz (SiO_2), alumina (Al_2O_3) and hematite (Fe_2O_3). The added rice husk in this work provided the combustible content to produce the appropriate amount of pores and expected lightweight brick under controlled sintering temperature. Although the rice husk ash contains high silica content derived from co-sintering of rice husk and WTP sludge, the rice husk ash content was approximately 16.74% (as shown in Table 1). The crystalline speciation changes in the sintered products were insignificant due to rice husk sintering. The intensities of the major peak (SiO_2) for sintered specimens decreased significantly with increased added rice husk. This means that the SiO_2 compound in the WTP sludge transformed into some non-crystalline phases.

Figure 8 shows the micro-structural analysis of sintered specimens sintered at 1100ºC with different amounts of added rice husk. With 0% rice husk, the sintered specimens produced dense matrix material with good surface characteristics. These results are in agreement with the low water absorption, high compressive strength and bulk density of sintered specimens. The microstructure of sintered specimens at 1100ºC with less than 15% added rice husk showed a similar dense matrix material. However, there was evidence of larger pores in the sintered specimens. The sintered products also had relatively low bulk density and high compressive strength. Theses results are also in compliance with the relevant criteria for lightweight brick applications. The microstructure of sintered specimens at 1100ºC and 20% added rice husk indicated a relatively loose matrix material dominated by the presence of larger open pores in the sintered specimens. The results are in agreement with previous results that the sintered products manufactured from 20% added rice

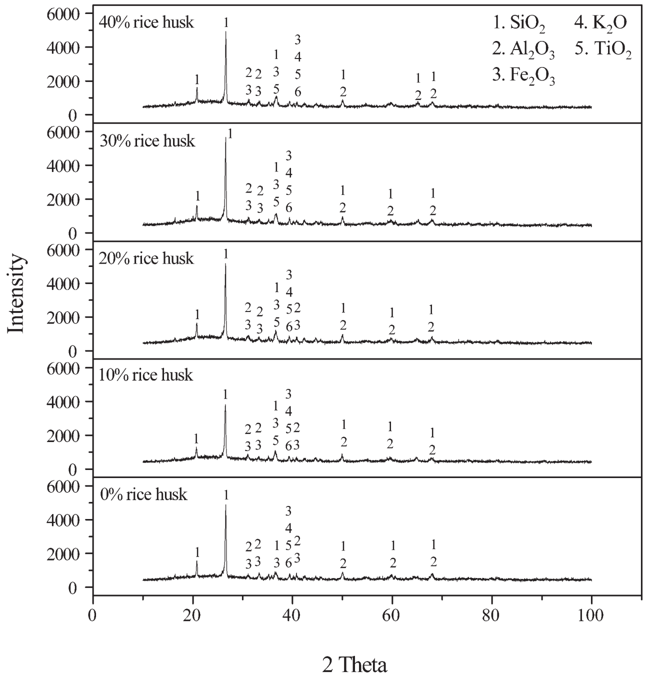

Figure 7. XRD data for WTP sludge and rice husks co-sintered at 1100ºC.

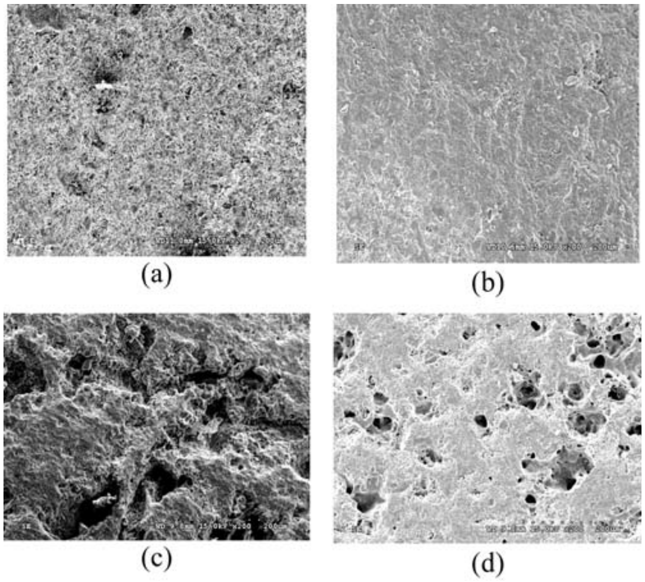

Figure 8. *Scanning electron micrograph images of specimens sintered at 1050^{o}C and 1100^{o}C. (a) 1050℃/WTP sludge (200×), (b) 1100^{o}C/WTP sludge (200×), (C) 1050^{o}C/40% rice husks (200×) (d) 1100^{o}C/40% rice husks (200×).*

husk had a lower compressive strength than that of sintered products produced from 0%~15% added rice husk.

4. CONCLUSIONS

Lightweight bricks have become an important trend for green buildings. This is because lightweight bricks reduce the building weight. The numbers of inner pores in lightweight bricks are much greater than in traditional bricks. Lightweight bricks have a relatively low thermal conductivity property that can be applied to reducing the building's energy use. The lightweight bricks in this research were manufactured from WTP sludge and rice husks by controlling the optimum sintering temperature and amendment ratios. The larger the rice husk organic matter content, the greater the porosity and shorter the path among particles for gas diffusion. Therefore, a higher rice husk addition ratio increases the open pore volume and decreases the bulk density of sintered specimens.

The bulk density of the proposed sintered product decreased significantly with increasing rice husk addition and decreasing sintering temperature. In the 1050°C sintering temperature with 20% rice husk addition, the sintered specimens obtained a bulk density of less than 1.8 g/cm^3. Increasing rice husk addition definitely decreased the bulk density of sintered products due to the increased amount of open pores in the sintered products.

The higher compressive strength of lightweight brick sintered at 1050ºC and below 20% rice husk addition ratio complies with the relevant building brick code requirement (100 kgf/cm^2). In the case of 1100ºC, the compressive strength of the sintered products gradually decreased with increasing rice husk addition. The compressive strengths of sintered products were all in compliance with Taiwan's building bricks criteria.

The amount of open pores in the sintered products manufactured from WTP sludge and rice husk addition increased gradually compared to bricks made from WTP sludge alone. Due to the large amounts of open pores, sintered products have good thermal insulation properties for future green building applications.

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Sludge Treatment by O_3/H_2O_2 and Carbon Source Recovery

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ABSTRACT: Proper disposal of excess sludge has become a tough problem faced by most of wastewater treatment plants. In order to solve this problem, an advanced sludge treatment process combining hydrogen peroxide and ozone was proposed. The impacts of pH value, ratio of hydrogen peroxide to ozone and the original sludge concentration were investigated. As a result, the combination of hydrogen peroxide and ozone process was efficient for sludge disintegration. The optimum molar ratio of hydrogen peroxide to ozone was 1.2 and the pH value was 6. The increase of sludge initial concentration was beneficial for sludge disintegration. The ideal initial concentration of sludge was 9900 mg/L ~ 19600 mg/L. In addition, experimental results also proved that the hydrolysis of sludge could be used as carbon source for nitrogen removal. The average denitrification rate in sludge solution was 2.08 mgNO_3-N/g MLSS·h which was 78% of methanol.

1. INTRODUCTION

With the rapid expansion of sewerage network, sludge disposal has become a tough problem faced by almost all wastewater treatment plants. According to the report of Ministry of Housing and Urban-Rural development of China, about 1250 wastewater treatment plants with total treatment of 7500×10^4 m^3/d have been built and 700 sewerage treatment plants are being built by the end of March 2008. But there are nearly 75% wastewater treatment plants without sludge stabilization facilities (Fang *et al.*, 2009). In order to cope with the awkward situation, the production of sludge should be control firstly (Yasui and Shibata, 1994; Englande and Reimers, 2001; Liu and Tay, 2001). Sludge reduction would not only decrease the operating and disposal costs but also alleviate the environmental impact through sludge disposal by landfill or incineration(Spinosa, 2004).

Many efforts have been made to reduce the production of sludge. Though the underlying principles vary widely, the dissolved of sludge solid phase and the releasing of intracellular is the key step because the organic materials of sludge are mostly in solid phase (Talat and Allan, 2006). In order to disintegrate the sludge, many methods have been adopted, such as biological treatment with thermophilic bacteria (Miah *et al.*, 2005), mechanical disintegration (Kopp e*t al.*, 1997), chemical treatment (such as alkali, acid, hydrogen peroxide, ozone, etc.) (Egemen *et al.*, 1999; Rocher *et al.*, 2001; Saby *et al.*, 2002), thermal hydrolysis, ultrasound and the combination of them (Barjenbruch and Kooplow, 2003; Bougrier *et al.*, 2006; Claire *et al.*, 2007; Zhao *et al.,* 2007).

As one of the most promising technology, sludge ozonation has been paid special attention for its simple operation condition and no second pollutants (Liu, 2003). Ozone is a strong chemical oxidant that can destroy the cell wall of microorganisms and lead to the release of cytoplasm which could be degraded in subsequent biological treatment system (Liao *et al.*, 2007). Many research have proved that the oxidation of ozone would be accelerated by adding hydrogen peroxide to ozone system which constitute the advanced oxidation process (AOP) named ozone / hydrogen peroxide

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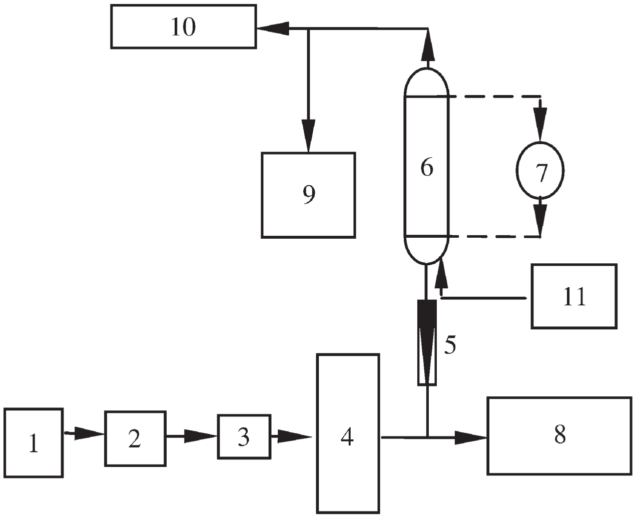
(O_3/H_2O_2) process (Parag and Aniruddha, 2004). In the past decades, O_3/H_2O_2 process have been widely used in water and wastewater treatment, such as the removal of natural organic matters, organochloride compounds, synthetic dyes, etc (Kosaka *et al.*, 2001; Yu *et al.*, 2006). But so far, few studies have focused on the application of waste sludge treatment. Therefore, the purpose of this paper was to develop an advanced sludge treatment process using H_2O_2 and O_3 for the decomposition of sludge. The effects, operating conditions and the reuse of organic materials were investigated.

2. MATERIALS AND METHODS

2.1. Sludge Samples

The waste sludge samples were collected from Xijiao wastewater treatment plant in Changchun city (Jilin province, China) and were stored at 4°C. before use. The sludge had water content of 95% and pH value was 7.03. The initial suspended solids concentrations (SS) were adjusted to 5600~6600 mg/L and volatile solids concentration (VSS) were 80% of SS.

The sludge samples were treated in batch in a 2.0 L bubble column which was made of stainless steel. The reactor system was composed of ozone generator, air generator, exsiccator, cylindrical shape ozone contactor and reflux pump. Figure 1 illustrates the experimental set-up.



1. Air generator 2. Condensator 3. Exsiccator
4. Ozone generator 5. Flow meter 6. Ozone contactor
7. Reflux pump 8. Analytic system of inlet concentration
9. Analytic system of outlet concentration
10. Absorber of exhaust 11. H_2O_2 adding system

Figure 1. Schematic diagram of sludge treatment process.

Ozone was generated with drying air by an XZF-5 ozone generator and was introduced into the column through the distributing plate equipped at the bottom of the column. In order to solve the foaming problem, an internal recycle loop was installed. The gas flow rate was 0.1 m^3/h and the inlet ozone concentration varied between 14 mg/L and 17 mg/L. The ozone transfer efficiency was determined based on the measurement of ozone in the off-gases. Hydrogen peroxide was introduced into the reactor using a peristaltic pump with the introduction of ozone. Ozone dose and hydrogen peroxide dose were defined as the ratio of the mass of ozone or hydrogen peroxide introduced to the reactor to the mass of the sludge before oxidation.

2.2. Denitrification Batch Test

The denitrification tests were carried out with sludge solution in 1000 mL Erlenmeyer flasks with the active volume of 600 mL. The initial concentration of sludge was adjusted to about 4000 mg/L. KNO_3 solution (1000 mg NO_3-N/L) was used as a nitrogen source and the initial nitrate concentration was 45mg NO_3-N/L. The flask was incubated with shaking at 25°C. and 140 rpm. In order to keep the anoxic condition, flasks were purged with N_2 for 1.0 minute after inoculation and sampling, and then the top of flask was sealed airtight using a rubber stopper. Ammonia, nitrite, nitrate and COD were measured periodically.

2.3. Analytical Methods

The chemical characteristics of sludge were analyzed to evaluate the disintegration degree of sludge. The chemical oxygen demand (COD) of sludge was measured by means of the dichromate method (SEPAC, 2002). In this paper, the COD of sludge was composed of two parts: soluble COD(SCOD) and particle COD(PCOD). The PCOD was measured for the particulate matter of sludge samples and the SCOD was measured for the supernatant only. In order to avoid the interference of some other matters, 10 mL sludge samples were washed with distilled water for three times and then were diluted to 100 mL prepared for the analysis of PCOD.

Soluble carbohydrate was measured by phenol-sulfuric acid method and the standard curve was made with glucose (Herbert *et al.*, 1971). Soluble protein was determined according to the standard protein assay by Bradford with bovine serum albumin as standard protein (Bradford, 2005). The total organic carbon (TOC) was determined by a TOC analyzer (TOC-VCPH, Shimadzu). Sludge concentration (SS), ammonia (NH_4-N), nitrite (NO_2-N) and nitrate (NO_3-N) were determined in accordance with standard methods (SEPAC, 2002). All the samples of sludge supernatants used for the measurement of soluble carbohydrate, soluble protein, NH_4-N, NO_3-N, NO_2-N, SCOD and TOC were obtained by centrifuging at 4500 rpm for 20 minute and filtration with 0.45 μm filters. The pH value was determined using a pH meter (PHS-2S, China).

3. RESULT AND DISCUSSION

3.1. Sludge Disintegration

In the past decades, many parameters had been selected to evaluate the degree of sludge solubilisation, such as the SS, VSS, SCOD, TOC and the change of PCOD (Bougrier *et al.*, 2006), among which SCOD was the popular choice for its simple operation condition and convenience. But, the measurement of SCOD can be affected by the residual hydrogen peroxide in supernatant when sludge was treated by O_3/H_2O_2. So, soluble TOC may be a better replacement for SCOD. On the other hand, the PCOD could reflect the changes of solid phase of sludge directly (Bougrier *et al.*, 2005). Therefore, both the reduction of PCOD and the generation of soluble TOC in sludge supernatant were observed during the whole treatment process. The results are shown in Figure 2.

From Figure 2, it can be seen that the changes of PCOD and TOC have different trend with the adding of oxidants. When ozone dose is 199 mg/gSS (hydrogen peroxide dose is 308 mg/gSS), the soluble TOC reaches to a maximum. Above it, soluble TOC decreases while the reduction of PCOD still goes up. Similar results had been reported by Cui (Cui and Jahng, 2004). The different changes between PCOD and TOC may be due to the stronger oxidizing ability of O_3/H_2O_2 process. With the increase of oxidants, the solid particles dissolved and some extracellular and intracellular materials release which lead to the reduction of PCOD. On the other hand, as an advanced oxidation technology, the combination of hydrogen peroxide and ozone would produce more hydroxyl radicals which may oxidize some organic carbon to CO_2 and reduce the quantity of TOC in liquid phase. Therefore, the operation condition should be control carefully.

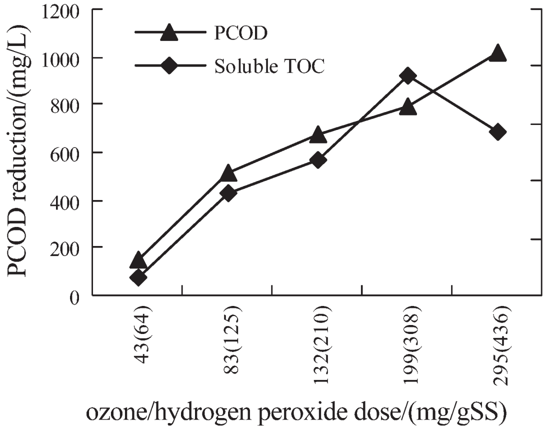


Figure 2. *Changes of PCOD and soluble TOC during whole treatment process. Note: the hydrogen peroxide dose is shown in brackets.*

3.2. Operate Conditions

As well known, the oxidative efficiency of O_3/H_2O_2 process depends on the production of hydroxyl radicals and the oxidative capability of ozone could be enhanced only under proper condition. In normal conditions, the ratio of hydrogen peroxide to ozone, pH value and the original concentration of contaminants are considered firstly.

Ratio of H_2O_2 to O_3

In order to find the optimum ratio of H_2O_2 to O_3, a series of tests were carried out. Specific TOC was chosen as the indicator of sludge disintegration, which could reduce the impacts of weight deviation of sludge samples. The parameter reflects the capacity of soluble TOC generation in sludge supernatant when 1.0 g sludge breaks up. Results are shown in Figure 3.

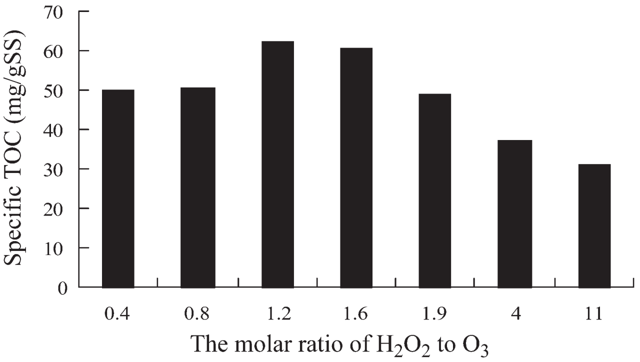


Figure 3. *Sludge solubilisation caused by different molar ratio of H_2O_2 to O_3. Note: ozone dose was 35 mg O_3/gSS with ± 5% deviation.*

As shown in Figure 3, the specific TOC increase when the molar ratio of H_2O_2 to O_3 is less 1.2. But, above this ratio specific TOC begin to decrease. According to the mechanism of hydroxyl radical generation which is shown in Equations (1)–(9) (Staehelin and Hoigne, 1982), the theoretical molar ration of H_2O_2 to O_3 should be 0.5.

$$H_2O_2 \leftrightarrow H^+ \tag{1}$$

$$HO^- + O_3 \rightarrow O_2 + HO_2^- \tag{2}$$

$$HO_2^- + O_3 \rightarrow HO_2^\bullet + O_3^{-\bullet} \tag{3}$$

$$HO_2^\bullet \leftrightarrow H^+ + O_2^{-\bullet} \tag{4}$$

$$O_2^{-\bullet} + O_3 \rightarrow O_2 + O_3^{-\bullet} \tag{5}$$

$$O_3^{-\bullet} + H^+ \rightarrow HO_3^{-\bullet} \tag{6}$$

$$HO_3^{-\bullet} \rightarrow HO^\bullet + O_2 \tag{7}$$

$$HO^\bullet + O_3 \rightarrow HO_2^\bullet + O_2 \tag{8}$$

and thus:

$$2O_3 + H_2O_2 \rightarrow 2HO^\bullet + 3O_2 \cdot \tag{9}$$

But, in tests, the proper ratio of H_2O_2: O_3 is 1.2 which is very different from to the theory. The reason can be explained by the different roles of hydrogen peroxide at low and high concentration. In term of the report of Echigo (Echigo *et al.*, 1996), hydrogen peroxide may react with the hydroxyl radicals and thus inhibit the generation of hydroxyl radicals at higher concentration. Therefore, the ideal ratio of H_2O_2 to O_3 was 1.2 at which the maximum decomposition of sludge was observed.

pH Value

For almost all chemical reactions, the operating pH value is a crucial factor. Especially for H_2O_2/O_3 process, the pH value is very important because it can determine the removal efficiency of pollutants. So, all sludge samples were treated under same conditions except for pH value which was changed from 2 to 12. Figure 4 demonstrates the effects of O_3/H_2O_2 treatment under different pH value.

From Figure 4, it can be seen that the specific TOC released to the supernatant of sludge is maximum for a pH value of 2. But it should be noted that the sludge flocs and the cell wall of microorganism can be also destroyed by acid or alkaline (Neyen *et al.*, 2003). TOC solubilisation caused by pH adjusting without O_3/H_2O_2 addition is also shown in Figure 4. Considering the deducting of TOC caused by pH adjusting, the net releasing of soluble TOC are shown in Figure 5.

As shown in Figure 5, the net releasing of soluble TOC increased with the rising of pH from 2 to 6. When pH value is 6, it gets up to a maximum. Similar results had been obtained by Beltran (Beltran *et al.*, 1999). In his report, the optimum pH value was near neutrality. This can be explained by the delay in generation of free radicals caused by the dissociation reaction of hydrogen peroxide. Another reason may be the decrease of ozone solubility at higher pH value. Therefore, the ideal pH value of this study is 6 and the maximum releasing of TOC is 44.5 mg TOC/g SS which means that there are 44.5 mg of TOC could solubilise from 1.0 g particulate sludge.

Original Sludge Concentration

Many researchers had found that the degradation rate of pollutant could change varying its initial concentration, even though the loads of ozone and hydrogen peroxide were in ideal conditions (Erik *et al.*, 2006). The impact of original concentration of sludge on H_2O_2/O_3 treatment was investigated. The initial concentration of sludge was adjusted to 6600 mg/L, 9900 mg/L and

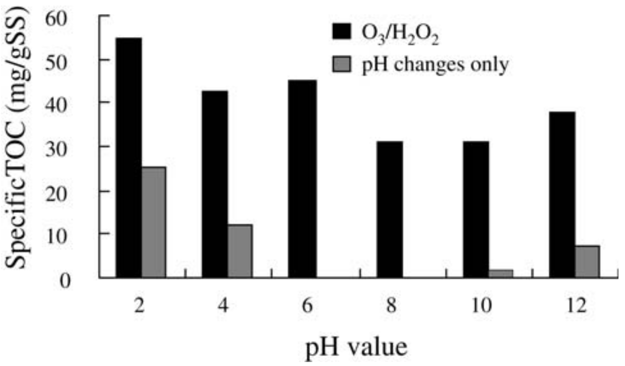


Figure 4. *Sludge solubilization under different pH value. Note: ozone dose was 56 mg O_3/g SS with ±5% deviation and molar ratio of hydrogen peroxide to O_3 was kept 1.2.*

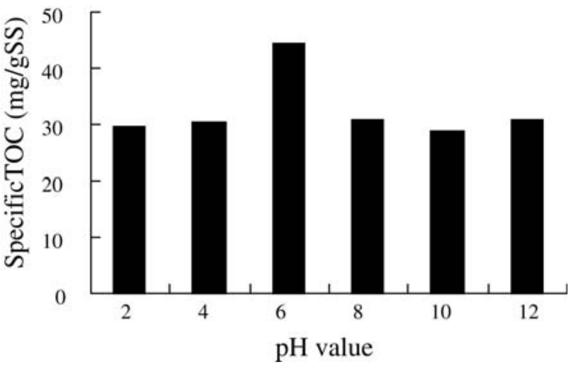


Figure 5. *Net TOC solubilisation under different pH value. Note: ozone dose was 56 mg O_3/g SS with ±5% deviationand molar ratio of hydrogen peroxide to O_3 was kept 1.2.*

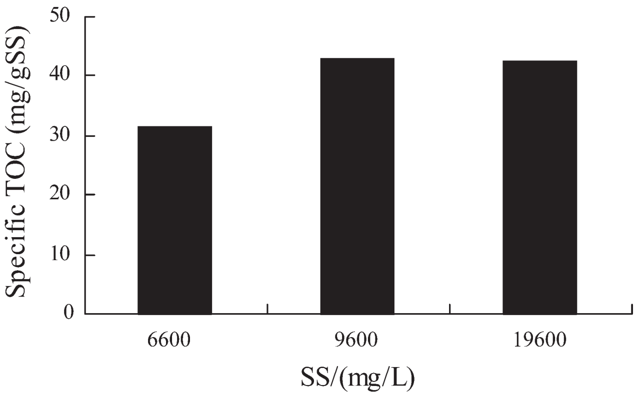


Figure 6. *Impact of sludge original concentration on sludge treatment by H_2O_2/O_3 process. Note: ozone dose was kept 60 mg O_3/g MLSS with ±5% deviation, the molar ratio of hydrogen peroxide to O_3 was kept 1.2 and initial operation pH was 7.05).*

19600 mg/L respectively and the hydrogen peroxide/ozone dose and pH value were in optimum conditions. The results are shown in Figure 6.

From Figure 6, it can be seen that the solubilisation rate of TOC increases from 31.5 mg/g SS to 43.1 mg/g SS when the initial concentration of sludge increase from 6600 mg/L to 9900 mg/L. But it becomes lower when the initial sludge concentration increases from 9900 mg/L to 19600 mg/L. This phenomenon suggests that increasing of sludge concentration would be helpful for the solubilisation of sludge in a certain range and the dilution of sludge concentration should not be recommended. It can be explained by two ways. One is the mass transfer. The high sludge concentration would enhance the contact opportunity between oxidants and decomposable part of sludge and thus accelerate the conversion of solid particulate of sludge to soluble part. The other reason may be due to the reduction of some extraneous substances which can decrease the oxidation efficiency of sludge such as some reducing matters and some inhibitors in supernatant when sludge concentration increase. Therefore, the proper original concentration of sludge is in the range of 9900 mg/L to 19600 mg/L.

3.3. Carbon Source for Denitrification

Generally, protein and carbohydrates, lipids and nucleic acid are the major ingredients of organic matters of sludge which are mostly in the form of solid phase with only a small part in the dissolved form. When these matters were subjected to the advanced oxidation process (O_3/H_2O_2), a significant fraction of the solid matter was dissolved. The characteristics of sludge supernatant were analyzed before and after O_3/H_2O_2 treatment. An example is shown in Table 1.

Table 1. Characteristics of Sludge Supernatant Before and After Treatment by O_3/H_2O_2.

Parameter	Before Treatment	After Treatment
Soluble TOC (mg/L)	20	386
Soluble protein (mg/L)	2.6	23.27
Soluble carbohydrate (mg/L)	4	172.66
Ammonia (mg/L)	0.4	7.9
Nitrite (mg/L)	0.04	0.02
Nitrate(mg/L)	0.5	1.25
pH	7.03	5.9

Note: 2.0g ML were treated, ozone dose was 199 mg/g SS, hydrogen peroxide dose was 308 mgH_2O_2/g SS, initial operation pH was 7.03.

As shown in Table 1, a great increase of soluble TOC and soluble carbohydrate are observed. In literature, the organic matters come from sludge broken, such as soluble TOC and soluble carbohydrate, are considered to be carbon source for denitrification (Magdalena *et al.*, 2007). The microorganism system should be affected if these sludge solution return to the biological system, especially for denitrifying bacteria. In order to find the fact, a series of denitrification tests were carried out with sludge solution and methanol was selected as control. The original concentration of nitrate was adjusted to 45 mg/L. Figure 7 and Figure 8 depict the denitrification behavior of sludge solution system and methanol system respectively.

Comparing Figure 7 to Figure 8, it can be seen that the COD removal rate and denitrification rate of methanol system are bigger than that of sludge solution. For methanol, the average COD removal rate is 14.26 mg COD/g MLSS·h and 71.5% COD are consumed. While,

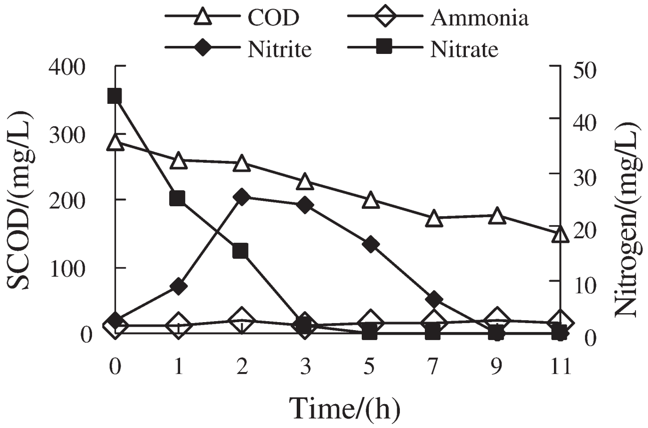


Figure 7. *Batch denitrification using sludge solution as carbon source.*

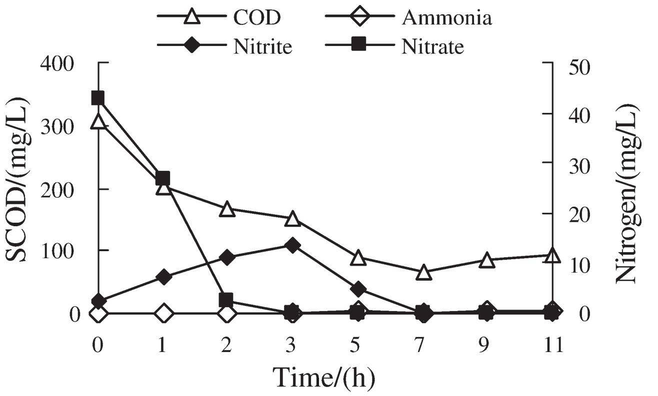


Figure 8. *Batch denitrification using methanol as carbon source.*

for sludge solution, the average removal rate of COD is 9.26 mg COD/g MLSS·h and only 57.1% COD are utilized by microorganism. However, in both systems, the residual nitrate is nearly zero at the end of inoculation. The average denitrification rate of sludge solution system is 2.08 mg NO_3-N/g MLSS·h which is 78% of that of methanol (For methanol, the removal rate of nitrate is 2.68 mg NO_3-N/g MLSS·h). The difference between COD consumption and denitrification rate in two systems may be due to the different biodegradability of organic compounds in sludge solution. Because some organic materials of sludge solution (such as soluble carbohydrate) could be biodegradable as quickly as possible and other matters (such as lipids and chips of cell wall) are difficult to be utilized by the denitrifying bacteria. Therefore, it can be concluded that the solution of sludge treated by O_3/H_2O_2 is suitable for denitrification.

4. CONCLUSIONS

A new advanced sludge treatment process employing hydrogen peroxide and ozone was proposed and the optimal operation conditions were investigated. According to the TOC solubilisation, the optimum molar ratio of H_2O_2 to O_3 was 1.2 and the maximum solution of sludge was observed when operating pH value was 6. In addition, the effect of original sludge concentration was also investigated. Efficiency of sludge disintegration increased when the initial concentration of suspended solids concentrations increased from 6600 mg/L to 19600 mg/L. Finally, denitrification batch experiments using sludge solution were carried out. Comparing with methanol, the average rate of COD consumption of sludge solution was 9.26 mg COD/g MLSS·h which was 65% of methanol. But, at the end of inoculation, the surplus nitrate was nearly zero. Therefore, it can be concluded that the hydrolysis of sludge obtained by H_2O_2/O_3 treatment was biodegradable and the organic matter of sludge solution could be used by microorganisms as carbon source of denitrification.

ACKNOWLEDGEMENTS

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Study on Hydrolysis and Acidification of Primary Sludge

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ABSTRACT: The phenomenon of carbon resource limited is a common problem in the municipal wastewater. In this study, primary sludge which come from primary sediment is been use for generating carbon resource by anaerobic hydrolysis acidification process. In the condition of temperature is 35°C, HRT = 28h and SRT = 3d, ρ(SCOD)and ρ(VFA) of effluents reach the peak value at 975.8 mg/L and 516.4 mg/L during the operate time. When the alkalinity is 725 mg/L and pH is 7.12, hydrolysis acidification process can keep the stable state of hydrolysis acidification efficiency. Appropriate alkalinity and pH value are the key parameters of hydrolysis acidification process for stabile operation. When the hydrolysis acidification process is fluctuated, the changes of ρ(SCOD) and VFA are previous to the alkalinity and pH value.

1. INTRODUCTION

THE phenomenon of carbon resource shortage is a common problem in municipal wastewater. For the kind of wastewater, the wastewater engineers and scientists have been focusing on how to obtain economical carbon source or make the nutrients in urban wastewater meet emission standards by other technologies. In addition, there is not any perfect technology for the primary sludge treatment and disposal at present. The hydrolytic acidification technology may be considered due to the large quantities of organic matter of the primary sludge, and the various volatile fatty acids (VFA) of the acidification product can be reused for biological phosphorus and nitrogen removal process. This way is an effective solution to the carbon source shortage in WWTP, and achieving the sludge production stability and less at certain degree.

Anaerobic digestion of sludge is a complex process of biological degradation, which involves a variety of microbes that can be divided into acidogenic bacteria and methanogens. For the first has many classifications and fast growth rate, and is not very sensitive to the toxicology and environmental conditions such as temperature, pH and ORP; the latter can only be existed under anaerobic condition, it has small species with slow growth rate, and is extremely sensitive to the changes of the environmental conditions. That is just the large differences of the physiological and biochemical characteristics between the two types bacteria in the anaerobic process, leading to production imbalance of acid and methane during the first conventional anaerobic digestion phase, which is not good for developing the bacterial activity; however, separating the two major categories by human and giving the best growing environment for each of them, fully developed their activity, improved the treatment efficiency, and increased operation stability. In 1971, Pohland and Ghosh suggested taking dynamic control to realize two-phase anaerobic digestion. The realizing of two-phase anaerobic digestion will make the acidogenic bacteria and methanogens live in their own best environment respectively. However, it is not saying that there does not existing mthanogens in the acidogenic phase, and acidogenic bacteria do not exist in methanogenic phase; the separation of the two-phase just said that the production of methane is weakened in the acidogenic phase, and vice versa.

If the anaerobic digestion of sludge can be controlled at the acidogenic stage, the product of the acidification, which contains numerous volatile fatty acids (VFA), can be used in biological nitrogen removal process, and is an effective solution to the shortage of carbon source

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in the WWTP. Therefore, how to improve the acidogenic production, and weaken the methanogenic production at the acidification stage should be the key point of the study. Generally speaking, methanogen is divided into hydrogen methanogen and acetic methanogen, and the two different species utilize different substrates in methanogenic stage; the first use hydrogen as substrate in methanogenic metabolism, and the latter make use of acetic acid. Based on the carbon source exploitation at anaerobic digestion of sludge, acetate methanogenic metabolism is not what we want, because it consumed acetic acid which is the effective carbon source in biological nitrogen removal process. Therefore, how to control the growth of acetic methanogen, realize the isolation of acetic methanogen bacteria and acidogenic bacteria shall be the keys for operating the experiment successfully. Because the two species have different growth rate, we can separate them effectively through controlling the sludge retention time. In this experiment, we studied the startup process of the hydrolysis acidification of primary sludge by controlling hydraulic retention time (HRT) and sludge retention time (SRT) and sludge recycle ratio.

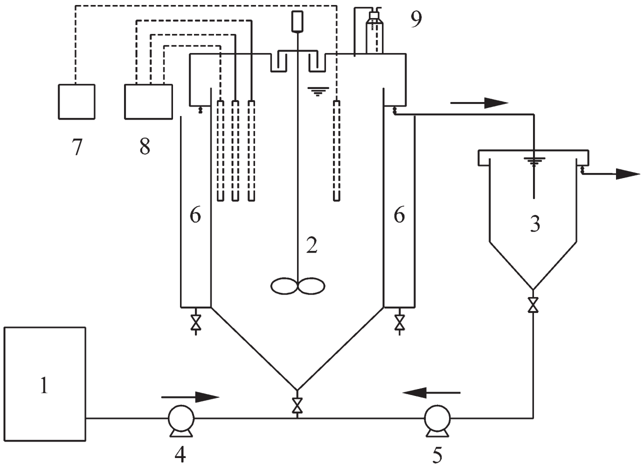
2. MATERIALS AND METHODS

2.1. Source of Primary Sludge

The primary sludge used in this study was obtained from the primary sedimentation tank of a municipal WWTP in Beijing, China. The main characteristics are as follows: pH 6.7–6.9, alkalinity ($CaCO_3$) 475–590 mg/L, total chemical oxygen demand (TCOD) 21.3–25.0 g/L, soluble chemical oxygen demand (SCOD) 175–280 mg/L, total organic carbon (TOC) 57–72 mg/L, violate fatty acids (VFAs) 82–106 mg/L, NH_3-N 65.6–102.4 mg/L, soluble orthophosphate 9.5–11.6 mg/L.

2.2. Reactor and Device

The continuous-flow reactor was made of plexiglass and consisted of hydrolysis and acidification tank and thickening tank. The process was shown in Figure 1, hydrolysis and acidification tank was stirred at a speed of 75 rpm (revolutions per minute) for mixing the contents and the temperature was controlled by waterbath at 35°C. The aim of this study was confirming the feasibility of startup the primary sludge hydrolysis and acidification process by controlling the SRT, HRT and sludge recycle ratio.



1- Sludge reserved tank; 2-Ferment tank; 3-Concentrated tank
4- Inlet pump; 5-Sludge recirculation pump; 6-Waterbath;
7-Automatic temperature controlling device;
8-Online monitors; 9-Gas collection device

Figure 1. *Primary sludge hydrolysis and acidification process.*

2.3. Analytical Methods

All analyses on conventional parameters were performed as defined in Standard Methods for the Examination of Water and Wastewater (fourth edition) .The determination of pH, alkalinity, MLSS, MLVSS, SCOD, VFA, TOC, soluble orthophosphate and ammonia nitrogen and sample pretreatment methods were the same as described in our previous publications (Li *et al.*, 2008; Ren *et al.*, 2009).

3. RESULT AND DISCUSSION

3.1. Variation of Chemical Oxygen Demand (COD) during the Startup and Operation Stages

Researched the feasibility of intensify acidification and weakening the effect of mathanation in the process of primary sludge hydrolysis and acidification by controlling HRT and SRT and sludge recycle ratio. In the experiment, HRT, SRT and sludge recycle ratio were controlled at 28h, 3d and 1, the startup and operation detail in the hydrolytic acidification system has been studied. The determination of TCOD and SCOD in sludge of hydrolytic acidification tank, inlet and outlet has been conducted everyday. Figure 2 reveals the trends of each parameters during 30 days' runtime. As the inoculation bacteria come from the digestion sludge of anaerobic digestion tank in Gao Beidian WWTP, which contains much more acidogenic bacteria and

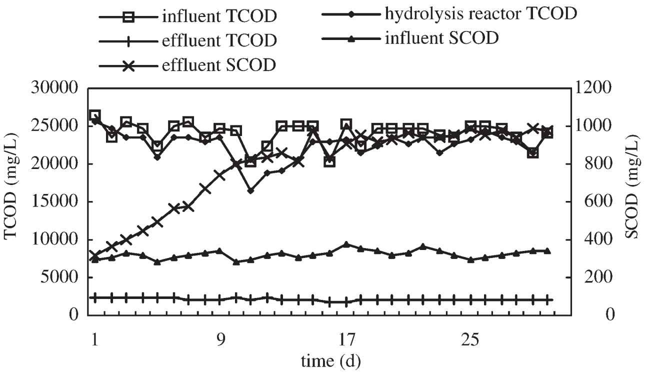


Figure 2. *Variation of COD during the start-up process.*

methanogenic bacteria, it is prone to be startup quickly. From the TCOD curve, by controlling HRT and SRT effectively, it is easy to get the segregation of acid methanogenic bacteria and acidogenic bacteria, and the acid methanogenic bacteria has been washed out. The segregation and the washed out of the acid methanogenic bacteria effectively enhanced acidogenic effect, and weakened methanogenic effect. From the first to 12 days, the outlet SCOD kept increasing, after 13 days, the outlet SCOD fluctuated at a bound, and then gone to stabilization, the hydrolysis acidification system had a more stable acidogenic effect, the SCOD and VFA was 857.9 mg/L and 412.6 mg/L, respectively. From the SCOD curve of influent sludge we can see that the primary sedimentation in the sludge reservoir also can be hydrolysis acidified. In a dredging cycle, (cycle is uncertain, normally around 4d), the sludge SCOD of reservoir had an increased trend. It should be noted that: generally speaking, as the TCOD of the primary sedimentation sludge and hydrolysis acidification sludge are exceeding 20 g/L, it was need to be diluted 50 times before determination, and there were a certain degree fluctuation in the result of the determination, but they were basically stand at 22 g/L or so.

At the function of acidogenic bacteria, the refractory biodegradable organic is transited into easily biodegradable organic (VFA, etc.) in the hydrolysis acidogenic process, and in existence of soluble COD. Therefore, theoretically speaking, the sludge TCOD about inlet and hydrolytic acidification tank will not change. Study investigated that the maximum theoretical COD removal efficiency of common organic (protein, polysaccharide, fat) in the wastewater is 33.3% in anaerobic acidification process [Zhao J.Q., 1994]. However, the removal efficiency of actual anaerobic acidification process is far behind this magnitude, commonly less than 20%. Nevertheless, from Figure 2, most of the 30 days operation time, the outlet TCOD of hydrolysis acidification reactor is less than the inlet, shows the removal of COD happened. On the base of exploring effective carbon resource, the removal of COD do harm to our object, because the methanogenic effect is taking place, the VFA which was produced by acid hydrolysis process may be utilized by the methanogenic bacteria, and also the outcome of the reaction CH_4 and CO_2 escaped. Further, this demonstrated in the data is the outlet TCOD of hydrolytic acidification reactor less than the inlet. As mentioned above, methanogen is divided into hydrogen methanogen and acetic methanogen, the heterogamous of hydrogen methanogen is similar to the acidogenic bacteria. So the loss of methanogen is the process of the loss of acetic methanogen mostly. Hydrogen methanogen and acidogenic bacteria co-exist in the hydrolysis acidogenic systems, hydrogen methanogens make use of H which was produced by the dehydrogenation in the hydrolysis acidogenic process, which can eliminate the inhibition of acidogenic bacteria by H, thus the existence of hydrogen methanogen is useful at the hydrolysis acidification of primary sludge. The existence of dehydrogenation leads to the outlet TCOD of hydrolytic acidification reactor less than the inlet. In essence, in the dehydrogenation of organic, 1 mol organic (CaHbOc) remove Xmol H_2, the cut in organic is 16X (g). At the same time, in the hydrogenation of organic, 1 mol organic (CaHbOc) fortify X mol H_2, the accretion in organic is 16X (g).

The reason of the decrease of COD was bringing by the hydrogen methanogen but acetic methanogen can be explained like this, that in accordance with the TCOD curve, based on the outlet TCOD of hydrolytic acidification reactor less than the inlet, not only the outlet SCOD is not minish, but also it increase steadily. If the reduction of ρTCOD is caused by acetic methanogen, the outlet SCOD will greatly reduced.

3.2. The Changes of pH and Alkalinity during the Startup and Operation Process of Hydrolysis Acidification Reactor

Alkalinity of water refers to the material corresponsive with total acidity, alkalinity sources including: carbonate, bicarbonate, hydroxide, borate, phosphate, silicate, organic alkalinity and metal hydrolysis of salts, etc.. In anaerobic systems, the total alkalinity including bicarbonate alkalinity and VFA alkalinity (about 20% of the former, the latter about 80%) [Anderson,G K, 1992]. Alkalinity changing has a large infection on the treatment efficiency of anaerobic system, because all kinds of bacteria have their own best adaptable pH extent. The feasible pH of acidogenic bacteria at 5.0–8.5, and it can growth at pH less than 5.0 all the same, but the feasible pH of sensitive methanogen is 6.5–7.8, and this is familiar with the pH anaerobic treatment system commonly controlled. Study investigated that the pH and alkalinity are the most important control parameter in an acidogenic reactor [Qin Z, *et al.*, 2003]. If the environment pH is under the tolerance of anaerobic active sludge, it will lead to the activity loss, and the inhibition of the physiology metabolizability, even the death of bacterial. The existence of alkalinity can mitigate the fall of pH in reactor, and enhance the stability of system. [Raghid Lepisto,1999] believe that at the methanogen phase, if there is not enough alkalinity to neutralize the VFA, and the growth of methanogen may be restrained by uncorrupted VFA, resulting the accumulation of VFA and the acidification of anaerobic reactor.

The accumulation of VFA is the mainly objection for generating carbon resource by strengthen hydrolysis acidification process. Because pH and alkalinity is the most important control parameter in anaerobic reactor, the changes of pH and alkalinity in startup and operation process has been studied, shown in Figure 3.

From the picture, it indicated that the SCOD and VFA homologous changed in accompany of the operation time went on, the SCOD as a token of organic is mostly VFA, and the ratio of VFA and SCOD increased gradually. In the hydrolysis acidification process of primary sludge, the alkalinity in system increased continuously. In the hydrolysis acidogenic process of protein, a certain amount of ammonia was produced by deamination, ammonia take a reaction of CO_2, and produced ammonium bicarbonate, so the alkalinity of system increased continuously. The change of VFA in outlet in accordance with the change of alkalinity in hydrolysis acidogenic reactor, and it can be thought that the increase of outlet VFA is in accordance with the addition of alkalinity, on the basis of the hydrolysis acidogenic reactor operation stably. At the 15 day, there was a small fluctuation in the SCOD and VFA of outlet, but the fluctuation of alkalinity didn't happened at the same time, and then it took place at 16day. This phenomenon indicated that the change of system will be best described by the organic index such as SCOD and VFA, then, it can be exhibited by the change of alkalinity and pH subsequently. The alkalinity in a steadily hydrolysis acidogenic effectiveness was fluctuating at 725 mg/L in this system. In the whole operation period, the change of pH is not obviously, in according with the operation went on, the pH increased from 6.83 to 7.12 in the hydrolysis acidogenic reactor, and then it fluctuated at 7.12. The reason of the change of pH is not obvious as follows: in accordance of the operation went on, the alkalinity increased continuously, the alkalinity amortizes the changes of pH in system, make the pH changing relatively smooth in the whole process.

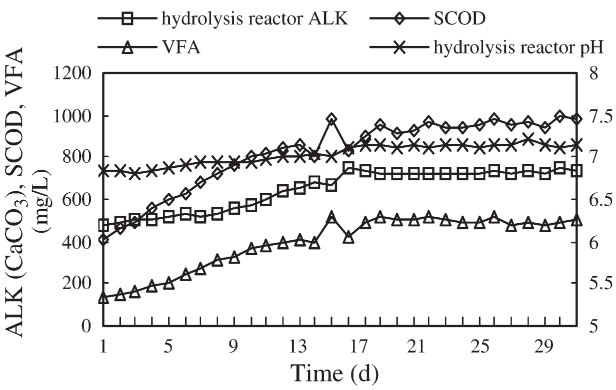


Figure 3. *Change trend map of alkalinity and pH value during the start-up.*

4. CONCLUSIONS

By analyzing the COD changing in startup and operation process, the hydrolysis and acidification system can be startup successfully when HRT, SRT and sludge recycle ratio controlled at 28h, 3d and 1 respectively.

Alkalinity and pH was the key parameters of hydrolysis and acidification system. When the system had a good effect on developing carbon source with primary sludge, the alkalinity was fluctuating at 725 mg/L, and pH was around 7.12, after a stable acidogenic effect took place.

When the state of hydrolysis and acidification reactor was in fluctuation, the first changing may be appeared at the SCOD and VFA, then alkalinity and pH followed subsequently. Therefore, it is needed to attention those parameter's variation of anaerobic active sludge system.

The confirmation of the best kinetic parameters in hydrolysis and acidification system of primary sludge need to be further studied.

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The Adsorption of Dyes in Water by using Modified Sludge

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ABSTRACT: Adsorption of direct scarlet dyes in water was conducted at three different temperatures by using the modified sludge, which is made of the discarded activated sludge from municipal wastewater treatment plant. The dynamic and thermodynamics in the adsorption process were discussed and provided the theoretical understanding for activated sludge recycling. The results showed that the adsorption rates at 25°C, 35°C, 45°C followed the second-order kinetic model, while it also can be expressed by using the first-order kinetic model at 35°C. The adsorptions at three different temperatures were matched with Langmuir model. Meanwhile they were also matched with Freundlich model at 25°C, 35°C, which indicated both physical and chemical adsorptions happened in the adsorption of direct scarlet dyes in water by using the modified sludge. The maximum adsorption capacities increased with temperature increasing and were 142.86 mg/g, 172.41 mg/g and 188.68 mg/g at 25°C, 35°C and 45°C respectively.

1. INTRODUCTION

ACTIVATED sludge has been widely employed in wastewater treatment, although it produced a large amount of excess sludge which are mainly organic matter, nitrogen, phosphorus, heavy metal and pathogenic germ primarily constituting. With the amount of the wastewater increasing, excess sludge will become a huge burden for both environment and economy development. Due to the abundant carbon in the sludge, it can be used to produce adsorbent by adding some activators. The state of the art in the relevant study has been reported recently [1–4]. In this paper, the adsorbent was made of the excess sludge through a series of modification and showed good performance in dyes adsorption. This research showed a promising way to reuse the excess sludge due to low cost and high commercial value.

2. MATERIALS AND METHODS

2.1. Reagent and Apparatus

Reagent: direct scarlet, commercial; sodium chloride, analytical grade.
Equipment: water bath oscillator (SHA-CA) Muffle Furnaces ICP-AES ultraviolet and visible spectrophotometer (HACA) scanning electron microscope FEI QUANTA 200 Fourier-Transform Infrared spectrometer Differential Scanning Calorimeter, (DSC) 6200.

2.2. The Methods for Producing the Modified Sludge

The sludge collected from sewage treatment plant was put into oven at 105°C for 24h. When the moisture content of sludge was below 10%, the dry sludge was grinded and sieved with a 60 sifter. The sludge under sifters was mixed with $ZnCl_2$ in the ratio of 5:3 and dissolved in water followed by water bath at 105°C for 24h. Then the pre-treated sludge was put into the Muffle furnaces at 550°C for 1h followed by cooling in a dryer, grinding and sieving with a 60 sifter. After washing with distilled water for 3 times to wipe off $ZnCl_2$ and articles, the sludge sample under sifter was kept in a dryer for use.

2.3. The Methods

The Experiment for Adsorption Kinetics

The experiments were conducted in triplicates in 50 mL Erlen meyer flasks containing 40 mL direct scarlet solutions and 0.01 g (garded to 0.0001) modified sludge. The flasks were put in a shaker (with a constant temperature water bath oscillator) at 170 r/min; The

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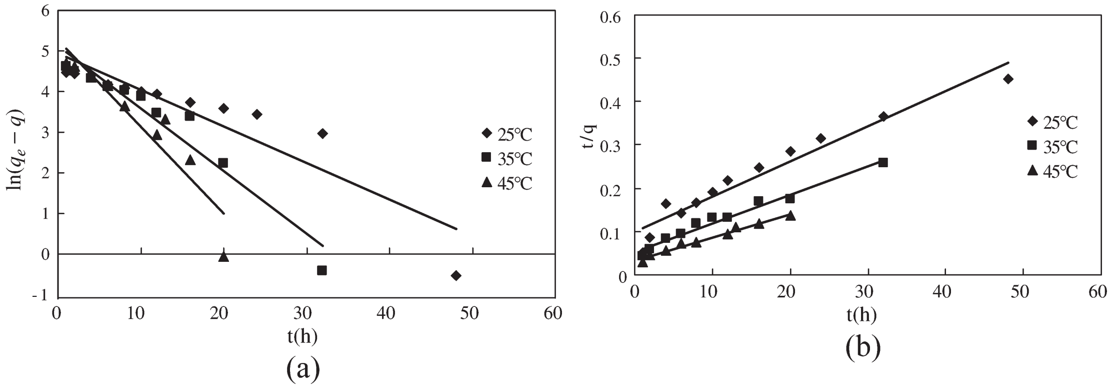


Figure 1. The adsorption dynamics curve of the modified sludge. (a) The first-order kinetic, (b) the second-order kinetic.

sample was taken at certain timing interval and filtered through a 0.45 μm membrane. The absorbency of the solution was tested using a UV/Visible Spectrophotometer ($\lambda = 500$ nm). The residual dye concentration and the quantity of adsorption were calculated by using the calibration curve which was used to counteract the effect of the membrane when done. Based on the above data, the curve of adsorption kinetics was drawn.

The Experiment for Adsorption Isotherms

The experiments were conducted in triplicates in 50 mL Erlen meyer flasks containing 40 mL direct scarlet solutions with concentrations of l0, 20,100 mg/L, and 0.01g (garded to 0.0001) modified sludge. The flasks were put in a shaker (with a constant temperature water bath oscillator) at 170 r/min to reach a equilibrium status. The sample was filtered through a 0.45 μm membrane and the residual dye concentration in the solution was tested in the UV/Visible Spectrophotometer (λ = 500 nm).

3. RESULTS AND DISCUSSIONS

3.1. Kinetic Modeling

Assuming the measured concentrations are equal to the cell surface concentrations, the kinetic models such as the pseudo first-order and the pseudo second-order equations [5,6] can be used in this study. The first-order Lagergren model based on solid capacity is generally expressed as follows:

$$\ln(q_e - q) = \ln q_e - k_1 t \qquad (1)$$

Where q_e and q are the amounts of adsorbed dye on the sorbent at equilibrium status and at time t, respectively (mg/g) and k_1 is the constant rate of first-order adsorption (h^{-1}).

A straight line of $\ln(q_e - q)$ versus t indicates a good match of this kinetic model. In order to figure out the Equation (1) to the experimental data, the equilibrium sorption capacity, q_e must be known. However, in many cases, qe is unknown and as the adsorption tends to become unmeasurable slowly, the amount absorbed is still significantly smaller than the equilibrium amount.

The pseudo second-order model is also based on the sorption capacity in the solid phase. Unlike the other model of adsorption models, it is in agreement with an adsorption mechanism being the rate controlling step. If the sorption rate is followed a second-order mechanism, the pseudo second-order chemisorption kinetic rate equation is expressed as:

$$\frac{t}{q} = \frac{1}{k_2 \cdot q_e^2} + \frac{1}{q_e} t \qquad (2)$$

Table 1. The Dynamics Parameters of the Modified Sludge at Different Temperatures.

	The First-order Kinetic			The Second-order Kinetic			
Temperature (°C)	**q_{ec} (mg/g)**	**K_1 (1/h)**	**R^2**	**q_{ec} (mg/g)**	**K_2 (g/(mg·h))**	**R^2**	**q_e (experimental) (mg/g)**
25°C	122.56	0.0796	0.8991	125	6.3×10^{-4}	0.9743	107
35°C	128.548	0.1239	0.9241	144.928	9.39×10^{-4}	0.9893	124
45°C	196.66	0.214	0.8737	185.2	8.92×10^{-4}	0.9788	146

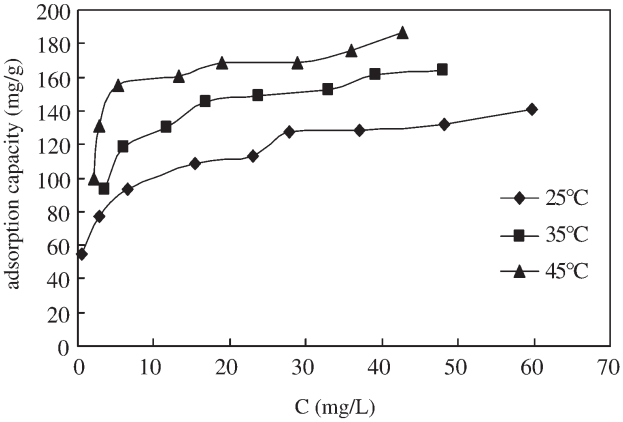


Figure 2. *The adsorption isotherm of the modified sludge.*

Where k_2 is the constant rate of second-order sorption (g/mg·h). The adsorption kinetic curve is shown in Figure 1.

It can be seen in Table 1 that the modified sludge adsorption to the dye at 25°C, 35°C and 45°C can be expressed by the second-order equation. Meanwhile, the adsorption 35°C can also be expressed by the first-order equation. The second-order equation at there different temperatures are $t/q = 1/0.0006 \times 1252 + t/125$, $t/q = 1/0.0009 \times 144.9282 + t/144.928$, and $t/q = 1/0.00089 \times 185.22 + t/185.2$ respectively.

The speed of the adsorption can be judged by k_1 [7,8]. The k_1 at different temperatures shown in Table 1were 0.0796 h^{-1}, 0.1239 h^{-1}, 0.214 h^{-1} respectively. The results indicated that temperature is an important factor for adsorption. When temperature increased, the adsorption speeded up, and then the adsorption capacity augmented, so the modified sludge adsorption process to the dye is a heat absorbing process.

3.2. Equilibrium Modeling

Equilibrium data, commonly known as adsorption isotherms, are basic required parameters to design a adsorption systems. The linear model, Langmuir model and Freundlich model are most used classical adsorption models to describe the equilibrium in solution at a constant temperature [9].

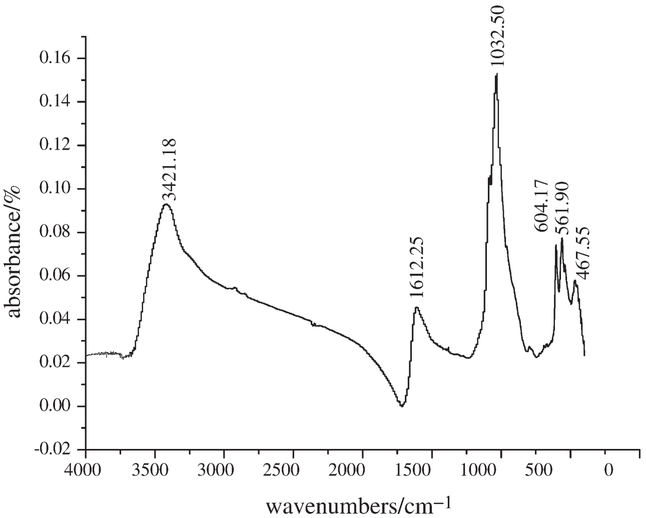


Figure 3. *The FTIR chart of the modified sludge.*

The linear models is given by Equation (3).

$$C_s = K_d C_{eq} + b$$

The empirical Freundich equation based on the sorption on a hererogeneous surface is given by Equation (4).

$$C_s = K_f C_{eq}^{1/n}$$

Where K_f and n are the Freundich constants in the system which indicate adsorption capacity and adsorption intensity, respecticely.

The Langmuir equation for monolayer sorption on a surface in a finite number of identical sites is given by Equation (5).

$$\frac{C_{eq}}{C_s} = \frac{C_{eq}}{Q} + \frac{1}{QK_L} \tag{5}$$

Where Q (mg/g) is the maximum amount of dye per unit weight of the modified sludge adsorption to form a complete monolayer on the surface bound at high C_{eq}. K_L (l/mg) is a constant related to the affinity of the binding sites. Q represents a practical limiting adsorption capacity when the surface is fully covered with dye and assists in the comparison of adsorption performance, particularly in cases where the sorbent did not

Table 2. The Adsorption Isothermal Model of the Modified Sludge at Different Temperatures.

Temperature	Linear Equation	Freundich Equation	Languir Equation
25°C	$C_s = 1.2371C_{eq} + 77.895$	$C_s = 61.744C_{eq}$ 0.2032	$C_{eq}/C_s = 0.007C_{eq} + 0.0238$
35°C	$C_s = 1.3479C_{eq} + 108.66$	$C_s = 78.344C_{eq}$ 0.1991	$C_{eq}/C_s = 0.0058C_{eq} + 0.0189$
45°C	$C_s = 1.4707C_{eq} + 128.11$	$C_s = 103.95C_{eq}$ 0.1572	$C_{eq}/C_s = 0.0053C_{eq} + 0.0095$

Table 3. The Adsorption Isothermal Parameter of the Modified Sludge at Different Temperatures.

	Linear Model			Freundlich Model			Langmuir Model		
Temperature (T)	K_d	b	R_2	K_f	$1/n$	(R_2)	Q (mg/g)	K_L	R_2
25°C	1.2371	77.895	0.8095	61.744	0.2032	0.9921	142.86	0.294	0.9932
35°C	1.3479	108.66	0.8101	78.344	0.1991	0.9451	172.41	0.387	0.9984
45°C	1.4707	128.11	0.6757	103.95	0.1572	0.8087	188.68	0.558	0.9965

reach its full saturation in experiments. Q and K_L can be determined from the linear of C_{eq}/C_s versus C_{eq}. The adsorption isotherms are shown in Figure 2.

It can be seen from Table 2 and Table 3 that the adsorption processes of the modified sludge to dye conform to The Langmuir model, which are $C_{eq}/C_s = 0.007C_{eq} + 0.0238$, $C_{eq}/C_s = 0.0058C_{eq} + 0.0189$ and $C_{eq}/C_s = 0.0053C_{eq} + 0.0095$ at 25°C, 35°C and 45°C respectively. All the correlation coefficient are above 0.99, which indicated there is a good match with experimental data. The maximum adsorption of the adsorbenty at three different temperatures are 142.86 mg/g, 172.41 mg/g and 188.68 mg/g. At 25°C and 35°C, the process also could be described by Freundlich model,. In this case, both physical adsorption and chemical adsorption happened.

3.3. The Infrared Spectrum Analysis of the Modified Sludge

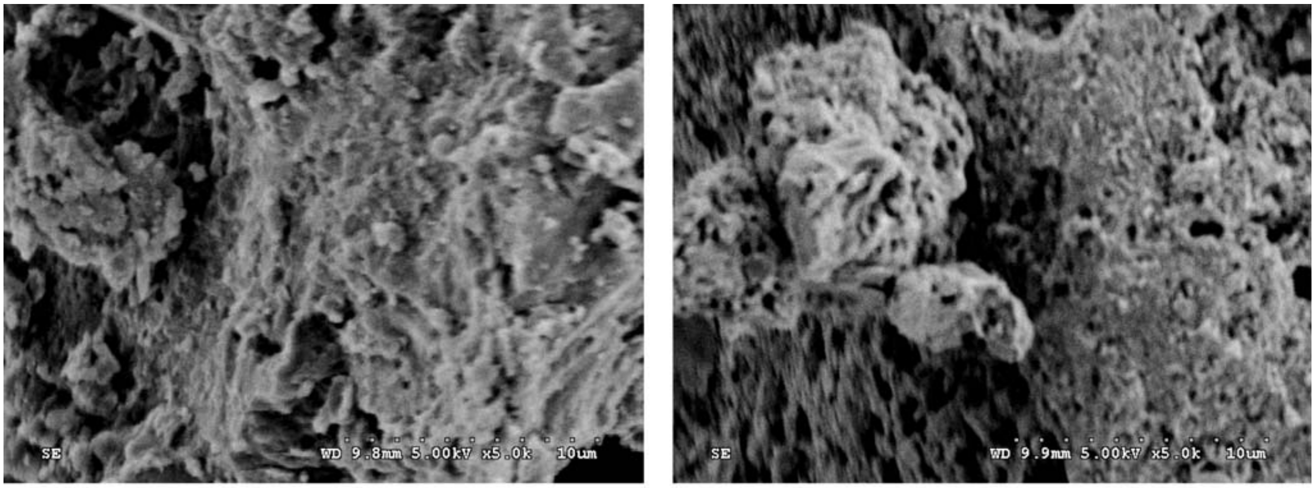
The Figure 3 shows that there were peaks at 3421.18 cm^{-1}, 1612.25 cm^{-1}, 1032.5 cm^{-1}, the functional groups in the surface of the modified sludge can be association –O–H (3700–3200 cm^{-1}), aromatic ring (at about 1600 cm^{-1}), –C–O– (at about 1300–1000 cm^{-1}).

3.4. The Scanning Electron Microscopy (SEM) Observations of the Modified Sludge and the Unmodified Sludge

The structures of the modified and un-modified sludge are compared and shown in Figure 4. Unlike the tight surface of the un-modified sludge, the modified sludge has a rough surface with flake structures. A variety of gaps with different sizes and shapes are distributed irregularly in the surface of the modified sludge, which makes a very complex structure composed of refined concave-convex, wrinkles and defects. That is why the modified sludge has high adsorption properties.

3.5. The Heavy Metal in Leachate of the Modified Sludge

The heavy metal in the leachate of the modified sludge is always a big concern when the modified sludge was used. It can been seen in Table 4 that the contents of the main heavy metals in the leachate are acceptable under the standard limitation (GB5086.2.3-1997), which means that it is safe and applicable to use the modified sludge in water treatment except for drinking water treatment.



(a) (b)

Figure 4. The SEM picture of the modified sludge and un- modified sludge. (a) Un-modified sludge, (b) modified sludge.

Table 3. The Contents of Heavy Metals in the Leachate of the Modified Sludge.

Heavy Metal	Concentration of Leachate (mg/L)	Limitation of the Leachate (mg/L)
Pb	0.003	3
Cr	Not Detected	0.3
Cd	Not Detected	10
Ni	0.0019	10
Cu	Not Detected	50
Zn	0.063	50
As	0.123	1.5
Be	Not Detected	0.1
Ba	0.564	100
As	0.010	1.5
F	0.254	50
CN	Not Detected	1.0
Hg	Not Detected	0.05

4. CONCLUSIONS

1. The results show that the modified sludge produced from sewage treatment plant in Gaobeidian of Beijing is applicabe to water treatment after the chemical modification. This provides a new direction excess sludge utilization and post-treatment of dye wastewater.
2. At 25°C, 35°C, and 45°C, the adsorption of the dye on to the modified sludge followed the second-order kinetic model, while at 35°C, it could also be described by the first-order kinetic model.
3. At 25°C, 35°C and 45°C, the adsorption of the dye on to the modified sludge followed Langmuir isotherm model, while at 25°C and 35°C, it could also be described by the Freundlich isotherm model, which indicate both physical and chemical adsorptions happened in the adsorption process of direct scarlet to the modified sludge. The highest adsorption amount at different temperatures were 142.86 mg/g, 172.41 mg/g and 188.68 mg/g. The saturation adsorption amount increases with temperature increasing.
4. The contents of heavy metals in the leachate of the modified sludge are under the limitation in the GB5086.2.3-1997. It is safe to use the modified sludge in water treatment.

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Bismaleimide (H795)	282	>400	48
VPSP/Bismaleimide copolymer			
C379: H795 = 1.9	245	>400	50
C379: H795 = 1.4	285	>400	53

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