

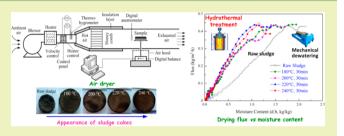
Effect of Hydrothermal Pretreatment on Convective Drying Characteristics of Paper Sludge

Peitao Zhao,*^{,†,‡} Shifu Ge,*^{,†} Dachao Ma,[‡] Chinnathan Areeprasert,[‡] and Kunio Yoshikawa[‡]

[†]Key Laboratory of Energy Thermal Conversion and Control of Ministry of Education, School of Energy and Environment, Southeast University, No. 2 Sipailou, XuanWu District, Nanjing 210096, P.R. China

[‡]Department of Environmental Science and Technology, Tokyo Institute of Technology, G5-8 4259 Nagatsuta-cho, Midori-ku, Yokohama, Kanagawa 226-8503, Japan

ABSTRACT: This work concerns the influence of hydrothermal (HT) pretreatment on sludge drying performance. Sludge was dried in an air duct dryer at a temperature of $30.4 \pm$ 0.4 °C with a constant air velocity of 1.34 ± 0.04 m/s and a relative humidity of about 56%. Drying rate curves, defined as the mass flux (kg/(m² h)) versus the dry basis moisture content (kg/kg), showed that the drying process mainly took place in the falling rate period. HT pretreatment can improve drying speed and shorten drying time. Six classical semi-theoretical



drying models, including Lewis, Page, Logarithmic, Henderson and Pabis, Wang and Singh, and Approximation of Diffusion, were evaluated to represent the experimental results in terms of the coefficient of determination (R^2), reduced chi-square (χ^2), and root means square error ($E_{\rm RMS}$). The Approximation of Diffusion model was the best one to reproduce the experimental data with R^2 close to 1, χ^2 around 0.00001–0.00005, and $E_{\rm RMS}$ of 0.00371–0.00686. The HT pretreatment changed the model constants. The expression was $M_{\rm R} = 0.4868 \exp(-0.0036\tau) + 0.5132 \exp(-0.0014\tau)$ for the untreated sludge and $M_{\rm R} = -0.8945 \exp(-0.0071\tau) + 1.8945 \exp(-0.0045\tau)$ for the HT pretreated sludge. The increase in the effective diffusivity accounted for the improvement in the drying performance.

KEYWORDS: Hydrothermal pretreatment, Drying performance, Convective drying, Mathematical modeling, Effective diffusivity

INTRODUCTION

Paper sludge has been increasing because of the rapid growth in the pulp and paper industries.¹ It is generally composed of organic fibers (cellulose, hemicellulose, and/or lignin), inorganic fillers, and coating materials, such as kaolinite, limestone, and talc.² Its disposal is becoming a matter of public concern because of its potential environmental and human health impacts. On the other hand, the most common disposal method in current practice—landfilling—is becoming more and more difficult to implement due to rapidly shrinking landfill space, public opposition to opening new landfill sites, leachate-related issues, and poor economics.³ The other methods, such as cropland application and ocean dumping, are no longer feasible because of their high cost, as well as strict environmental regulations.⁴

Accordingly, thermal utilization technologies, including pyrolysis, gasification, and combustion, have become attractive and been applied widely to extract carbon-neutral energy from these kinds of biomass wastes.⁵ However, the sludge has to be dried first to allow for less transportation cost, easier storage for the pyrolysis, and gasification.⁶ Sludge combustion provides a large volume reduction, toxicity reduction, and heavy metal control of sludge treatment with energy recovering.^{7,8} On the other hand, direct sludge incineration is not acceptable (especially for developing countries) due to its high cost and some possible gaseous pollutants caused by unstable burning resulting from its high moisture content.⁹ The moisture has

therefore been one main obstacle to sludge utilization and to some extent determined energy and economic efficiencies. Consequently, the reduction of water within sludge is the key issue for efficient sludge treatment, recycling, and disposal.

Mechanical dewatering and thermal drying are two main methods used to remove water. Practically, mechanical dewatering is much more convenient and economic than thermal drying. However, after mechanical dewatering, the wet basis (w.b.) moisture content of sludge was still about 70–80%; thermal drying seems to be inevitable for sludge thermal utilization. Significant economic, industrial, and environmental interests have consequently promoted the development of sludge drying technologies, including waste heat drying,¹⁰ fry drying,⁶ solar drying,¹¹ biodrying,¹² and hydrothermal (HT) drying.¹³ In order to know more about sludge drying characteristics, scientists focused on the skin layer¹⁴ and volume shrinkage by means of X-ray microtomography¹⁵ and crack formation within the drying process;^{16,17} they have made great contributions on developing models to simulate the drying behavior.

HT treatment is another new approach applicable to sludge, which was developed to improve sludge mechanical dewater-

```
Received:September 13, 2013Revised:January 14, 2014Published:January 23, 2014
```

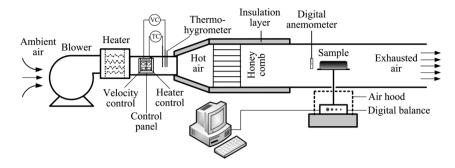


Figure 1. Schematic diagram of the convective drying equipment.

model name	expression	references
Lewis	$M_{\rm R} = \exp(-k\tau)$	18,19
Page	$M_{\rm R} = \exp(-k\tau^n)$	20
Logarithmic	$M_{\rm R} = a \exp(-k\tau) + c$	19
Henderson and Pabis	$M_{\rm R} = a \exp(-k\tau)$	21
Wang and Singh	$M_{\rm R} = 1 + a\tau + b\tau^2$	19,25
Approximation of Diffusion	$M_{\rm R} = a \exp(-k\tau) + (1-a) \exp(-kb\tau)$	26

ability.^{13,14,18} Its energy consumption was only about 30% of that demanded in the conventional thermal drying process when reducing the sludge water content from 80% (w.b.) to around 45% (w.b.).^{9,18} If combining the HT pretreatment with mechanical dewatering, the water content of sludge could be reduced to about 45%. At this level, it is possible to realize sludge self-sustainable combustion. However, to recover energy, the moisture has to be further reduced, and thermal drying is still required. Many works can be found in the literature dealing with kinetics and modeling of sludge thermal drying.¹⁹⁻²¹ Nevertheless, few works focused on the drying behavior of the HT pretreated sludge. In the other words, no data on the drying behavior of this product is available for the engineering design. Even though some of them reported the natural drying behavior of the HT pretreated sludge, the conclusion is still worth discussing because the samples were not prepared under the same conditions as in these studies. Moreover, in order to lower the operating cost, both the dewatering and drying performance are vital for the design and optimization of the commercial plant. Thus, it is necessary to investigate the drying performance of the HT pretreated sludge and to provide some experimental data for the engineering design of the commercial hydrothermal drying plant.

The present study aims to (1) investigate the influence of HT pretreatment on the sludge drying behavior and to find the optimal operating parameters and (2) fit the experimental drying data to several thin-layer models widely applied in the literature and evaluate a suitable drying model for describing the drying process of the HT pretreated sludge.

The HT pretreated and untreated sludge was dried in an air duct dryer at a temperature of 30.4 ± 0.4 °C, constant air velocity of 1.34 ± 0.04 m/s, and relative humidity of about 56%. All the samples were prepared under the same conditions, and an independent variable, drying flux (kg/(m² h)), was used as the only index to evaluate the drying performance.

EXPERIMENT SETUP AND PROCEDURES

Sample Preparation and Experimental equipment. The sludge was taken from Thailand. The HT treatment process was conducted as follows. The sludge was mixed with pure water (Wako Pure Chemical Industries, Ltd., Japan), and the mass ratio was 5:1 (100 g sludge:20 g pure water) to simulate the HT condition. Then the mixture was poured into a glass tube with a volume of 500 mL. After that, the tube was put into the reactor, and the reactor was sealed. Subsequently, the argon was imported into the reactor from a cylinder to create an oxygen-free circumstance. According to our previous experimental experiences, the holding time was fixed as 30 min, and the HT temperature ranged from 180 to 240 °C with an interval of 20 °C. After finishing the reaction, the electronic heater was turned off, and the residual steam was discharged and cooled with a water condenser (details are in ref 22). After the pressure and temperature fell to atmospheric pressure and 100 °C, the products were taken out from the tube and kept in a bottle. The experiment was repeated three times, and the products were mixed. At last, the products were dehydrated for 15 min by a self-made dewatering machine (as introduced in ref 9), and the dewatered product with a diameter of 40.00 mm was used to conduct the drying experiment.

The drying experiments were carried out in a wind tunnel as shown in Figure 1. The dryer is composed of a blower, heater, wind tunnel, tray made of wire meshes, and some measurement instruments. The air was sucked by the blower and heated to the target temperature of 30.4 ± 0.4 °C by an electronic heater. The air velocity was controlled by a revolution speed regulator and kept at 1.34 ± 0.04 m/s all the time. The drying started after the target condition was steady for about 1 h. During the drying process, the sample weight was continuously measured by an electronic balance ASP-4100 (AS-one, Japan) and registered in a computer with .XLS format every 6 min. It stopped after the sample weight was kept constant for 2 h. This weight was recorded as the equilibrium mass, which was expressed as $m_{\rm eq}$ (g) to calculate the equilibrium moisture content $M_{\rm eq}$ (kg/kg).

Data Analysis and Mathematical Modeling. The dry basis (d.b.) moisture content (kg/kg) at time τ (M_{τ}) was calculated using the equation

$$M_{\tau} = \frac{(m_{\tau} - m_{\rm s})}{m_{\rm s}} \tag{1}$$

where M_{τ} was the moisture content (d.d.), kg/kg, and m_{τ} was the sample weight at time τ , g. The m_s (g) was the solid weight (final weight) of the sample, which was obtained by drying the final product in an oven under about 105 °C for 12 h.

The mass flux $\left(kg/(m^2\,h)\right)$ during each drying process was expressed as

$$\dot{m} = 60 \times \frac{\mathrm{d}m}{\mathrm{d}\tau} / 1000 \times A \tag{2}$$

which was calculated by importing these .XLS files into the Origin 8.6 (Originlab, America). $A (m^2)$ was the drying airflow surface area of the sample; $dm/d\tau$ was the weight loss rate of the sample (g/min).

The drying curve was obtained by plotting the mass flux \dot{m} versus with the moisture content M_{τ} (d.b). It was used to evaluate the influence of the HT pretreatment on the drying behavior.

Semi-theoretical models often offer a compromise between theory and ease of use, which is valid within the temperature, relative humidity, air velocity, and moisture content range for which they were developed. Semi-theoretical models are generally derived by simplifying general series solution of Fick's second law or modification of simplified models.²³ Among these models, the Lewis model, Page model, Logarithmic model, Henderson and Pabis model, Wang and Singh model, and Approximation of Diffusion model are used frequently (Table 1). The Henderson and Pabis model is the first term of a general series solution of Fick's second law. The Lewis model is a special case of the Henderson and Pabis model. The Page model is modification of the Lewis model to overcome its shortcomings. The Wang and Singh model is an empirical model, which was directly derived from the relationship between average moisture content and drying time.²³ The Logarithmic equation assumed the resist to water diffusion occurs in the outer layer of the sample.²⁴

The moisture ratio ($M_{R_{J}}$, dimensionless moisture content) of the sample was calculated using the following equation

$$M_{\rm R} = \frac{M_{\tau} - M_{\rm eq}}{M_{\rm ini} - M_{\rm eq}} \tag{3}$$

where $M_{\rm ini}$ and $M_{\rm eq}$ are the initial moisture content and the equilibrium moisture content (d.b., kg/kg), respectively.

The M_{eq} is expressed as

$$M_{\rm eq} = \frac{m_{\rm eq} - m_{\rm s}}{m_{\rm s}} \tag{4}$$

The regression analysis was performed in Origin 8.6 (OriginLab, U.S.A.). The estimation method was based on the Levenberg–Marguardt model, and the fittingness of the models was evaluated by means of the correlation coefficient (R^2), reduced chi-square χ^2 , and root-mean-square error $E_{\rm RMS}$. The higher the R^2 value and lower values of χ^2 and $E_{\rm RMS}$, the better the fitness.¹⁸ The χ^2 and $E_{\rm RMS}$ can be expressed as

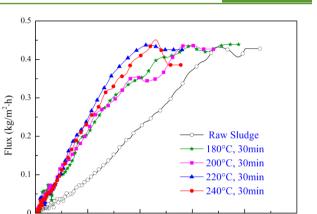
$$\chi^{2} = \frac{1}{N-z} \sum_{i=1}^{N} (M_{\text{R,exp},i} - M_{\text{R,pre},i})^{2}$$
(5)

$$E_{\rm RMS} = \left[\frac{1}{N} \sum_{i=1}^{N} \left(M_{\rm R,exp,i} - M_{\rm R,pre,i}\right)^2\right]^{1/2}$$
(6)

where $M_{\text{R,exp},i}$ is the *i*th experimental M_{R} ; $M_{\text{R,pre},i}$ is the *i*th predicted M_{R} ; N is the number of the experimental data points; and z is the number of model constant.

RESULTS AND DISCUSSION

Influence of HT Pretreatment on Drying Behavior. The variation of the drying rate with the moisture content (d.b.) is shown in Figure 2. It shows the M_{ini} of the sample kept decreasing with increasing HT temperature until the temperature reached to 220 °C. As all these samples come from the same procedure, the difference between the M_{ini} evidently indicated that the HT pretreatment could improve the sludge dewaterability. In the case of drying, it mainly happened in the falling rate period, and its constant drying rate period was very short. The reason is that most of the free water contained in the sludge has been removed by mechanical dewatering. The water evaporation rate consequently depended mainly on the water diffusion speed in the sample. Under the same moisture content, the drying rate of the HT pretreated sludge was much higher than that of the



Moisture Content (d.b, kg/kg)

1.5

Figure 2. Influence of HT pretreatment on drying kinetics.

1.0

0.5

0.0

untreated one. At a moisture content of 0.96 kg/kg (d.b), the drying rate of HT sludge pretreated under the condition of 220 °C and 30 min was twice as much as that of the raw sludge. This implied that HT pretreatment could improve drying performance. In our previous studies, Jiang et al.¹³ and Meng et al.²⁷ also reported that HT pretreatment could improve the natural drying performance of sludge.

The difference between the initial and critical moisture content (moisture of the transition from the constant drying period to the falling rate period) was very similar for all these samples. The most plausible reason was that the water evaporating at this stage was the water on or close to the sample surface. For the HT sample pretreated at 240 $^{\circ}$ C and 30 min, no constant drying period was observed. This could be attributed to the difference existing in the initial temperature between these samples. It is possible because the product from HT was kept in a 4 $^{\circ}$ C refrigerator, and the variation in time spent on sample preparations will cause this difference.

Figure 3 shows the appearance of all the samples after drying. The untreated sludge shrank significantly compared with the HT pretreated one during the drying process. Its thickness dramatically decreased from 6 mm to around 3.5 mm. This was because the HT pretreatment has destroyed the structure of

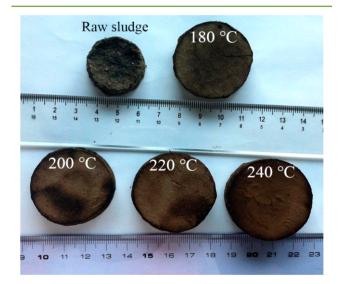


Figure 3. Appearance of the dry sample before and after HT.

2.5

2.0

ACS Sustainable Chemistry & Engineering

the holocellulose, lignins, and cells present in the paper sludge at 180 °C²⁸ and released the bound water, thus reducing the shrinkage stress. The difference in the initial moisture content would also contribute to this shrinkage. However, it could be neglected if compared with that caused by the HT pretreatment. This could be verified by comparing the appearance of the HT sample pretreated at 180 °C with that pretreated under other conditions because if the volume density of the solid plays the main role in the shrinkage, significant difference will be also observed in these samples. The sludge pretreated under 180 °C shrank more than that pretreated under the other temperatures, and the color was also a little light. The reason is that there is still some complex holocellulose was not degraded at 180 °C. The sludge dewaterability was improved due to the transferring of bound water into free water. Moreover, without shrinkage, more pores will be formed along with water evaporation, which would increase the drying rate and promote the drying process. That was the reason that the drying flux of HT pretreated sludge was higher than that of the raw one in the falling rate-drying period. At the drying rate constant stage, the drying flux of all the samples was almost the same, indicating that the transferring of bound water into free water, but not the change of water properties especially chemical properties, improved the sludge dewaterability and drying performance.

Figure 4 shows the moisture content (w.b.) of these samples as a function of drying time. As expected, the moisture decreased

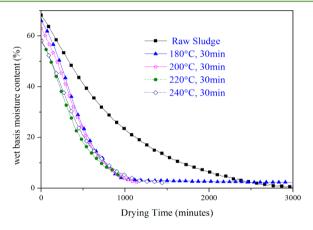


Figure 4. Evolution of wet basis moisture content vs time.

substantially with extending the drying time. The time required to reduce the moisture to a certain level was highly shortened by HT pretreatment. With drying, the time spent on removing the moisture content from 58% w.b. to 5% w.b. was 1956 min for the untreated sludge; whereas, the corresponding values were 780, 846, 923, and 1008 min for the HT sludge pretreated under the holding of 30 min and temperatures of 180, 200, 220, and 240 °C, respectively. The time was reduced by about 60.12%, 56.75%, 52.81%, and 48.47%, respectively. A similar result was also observed by Sacilik et al.,²⁶ indicating the hot water predipping Üryani plum saved about one-third of the time. It is evident in all of the results that the HT pretreatment can highly improve the sludge dewatering performance, both mechanical dewatering and thermal drying.

Models Evaluation. Experimental results of $M_{\rm R}$ variation with drying time were fitted to some outstanding semitheoretical models as shown in Table 1, which were used widely in the literature to depict the kinetics of the drying process. Table 2 presents the statistical results and estimated constants of the nonlinear regression analysis of these models. For all the samples, all the models provided an R^2 value higher than 0.99 except the Wang and Singh model. The highest R^2 value and lowest χ^2 and $E_{\rm RMS}$ values were obtained from the Page and Approximation of Diffusion models, with an R^2 , χ^2 , and $E_{\rm RMS}$ values varying between 0.9984–0.9997, 0.00005–0.00012, and 0.00479– 0.01097, and 0.9994–0.9998, 0.00001–0.00005, and 0.00371– 0.00686, respectively. The most unsuitable was the Wang and Singh model, especially for the raw sludge and the HT 180 °C pretreated sludge, with an R^2 , χ^2 , and $E_{\rm RMS}$ values of 0.5657, 0.01936, and 0.13892, and 0.4102, 0.02666, and 0.16294, respectively. This result implies that the water diffusion properties of the inner the sample, but not the outer layer of the sample, controlled the drying process.

Observing from Table 2, the model constants of the Approximation of Diffusion model were very close for all the HT samples. Therefore, it would be possible to use one universal model constant to represent the drying characteristics of all the HT samples. Figure 5 shows an illustration of modeling the HT pretreated and untreated sludge with the Approximation of Diffusion model. It clearly indicates that this model can predict the drying behavior of both the HT pretreated and untreated sludge. For the model constants of the HT sample, the predicted value was lower than the experimental data when replacing the separated model constant from the average value of all the HT samples. It would be more applicable to adopt the constant from nonlinear regression analysis of the experimental data of "200 °C and 30 min" as a universal model constant to predict the drying behavior of all the HT sludge. Figure 6 compares the experimental data with those predicted with the Approximation of Diffusion model by using the model constant of "200 °C for 30 min". It shows that the predicted value was a little low for the sample pretreated at 220 °C. However, it was still acceptable as this gap was very small. Thus, the most suitable model to predict the drying behavior for the raw sludge was $M_R = 0.4868$ $\exp(-0.0036\tau) + 0.5132 \exp(-0.0014\tau)$ and $M_R = -0.8945$ $\exp(-0.0071\tau) + 1.8945 \exp(-0.0045\tau)$ for the HT sludge.

The HT treatment could destroy the microstructure of sludge and correspondingly improve the hydrophobicity and reduce the viscosity of sludge. The shrinkage stress and resistance to water diffusion were therefore reduced. That was the reason that the HT sludge has a higher water evaporation rate and negligible shrinkage compared with those of raw sludge. Some authors have verified that the HT treatment could decrease sludge viscosity.^{29,30} Park et al.³¹ investigated the effects of hydrothermally pretreated sewage sludge on the stability and dispersibilty of slurry fuel and reported that the HT treatment improved sludge particle size distribution and stability, affecting the sludge atomization, transportation, and viscosity. The hydrophobicity of sludge could be improved because sludge particles would be carbonized during HT processing.^{31,32} This would also result in the improvement of water diffusion properties inside the HT samples.

Evaluation of Effective Diffusivity of the HT Sample. Fick's second diffusion law has been widely applied to interpret the falling rate period within the drying process. According to Figure 2, the drying process mainly happened in the falling rate period. It is possible to analyze it with Fick's diffusion equation, which was developed by Crank.³³ For slab geometry, if the sample's initial moisture is distributed uniformly, its shrinkage is negligible and its diffusivity is constant. The analytical solution of Fick's diffusion equation can be expressed as

Table 2. Constants and Statistical Results from Various Semi-Theoretical Models

model		Lewis				Page			Logarithmic			
items	constant	R^2	χ ²	E _{RMS}	constant	R^2	χ^2	E _{RMS}	constant	R^2	χ ²	E _{RMS}
raw	k = 0.00211	0.9941	0.00026	0.01628	k = 0.0044	0.9986	0.00006	0.00780	k = 0.0021	0.9966	0.00015	0.01228
					n = 0.8852				n = 0.9554			
									c = 0.0100			
180 °C	k = 0.00335	0.9921	0.00059	0.02421	k = 0.0011	0.9994	0.00005	0.00680	<i>k</i> = 0.0035	0.9966	0.00025	0.01582
					n = 1.1838				n = 1.0761			
									c = -0.0110			
200 °C	k = 0.00327	0.9922	0.00062	0.02481	<i>k</i> = 0.0012	0.9997	0.00002	0.00479	<i>k</i> = 0.0032	0.9976	0.00019	0.01384
					n = 1.1744				<i>n</i> = 1.0766			
aa a 0 <i>G</i>	1 0 000 (0	0.001/	0.000.41		1 0 0010				c = -0.0282		0.0001.(
220 °C	<i>k</i> = 0.00348	0.9946	0.00041	0.02015	k = 0.0018	0.9984	0.00012	0.01097	k = 0.0037	0.9979	0.00016	0.01253
					n = 1.1176				n = 1.0587 c=-0.0025			
240 °C	<i>k</i> = 0.00317	0.9969	0.00021	0.01448	<i>k</i> = 0.0018	0.9991	0.00006	0.00775	k = 0.0023	0.9987	0.00009	0.00937
240 C	$\kappa = 0.00317$	0.9909	0.00021	0.01448	$\kappa = 0.0018$ n = 1.0976	0.9991	0.00006	0.00775	$\kappa = 0.0033$ n = 1.0477	0.9987	0.00009	0.00937
					<i>n</i> = 1.0970				c = 0.0011			
model Henderson and Pabis		Wang and Singh			Approximation of Diffusion							
model]	Henderson	and Pabis			Wang and	Singh		Ap	proximation	of Diffusion	
items	constant	Henderson and R ²	and Pabis χ^2	E _{RMS}	constant	Wang and R^2	Singh χ^2	E _{RMS}	Ap constant	proximation R ²	of Diffusion χ^2	E _{RMS}
				E _{RMS} 0.01405	constant $a = -0.0009$	0	0	<i>E</i> _{RMS} 0.13892		1		<i>E</i> _{RMS} 0.00425
items	constant	R ²	χ ²			R ²	χ ²		constant	R ²	χ ²	
items	constant k = 0.0020	R ²	χ ²		a = -0.0009	R ²	χ ²		$\frac{1}{constant}$ $k = 0.0036$	R ²	χ ²	
items	constant k = 0.0020	R ²	χ ²		a = -0.0009	R ²	χ ²		constant $k = 0.0036$ $a = 0.4868$	R ²	χ ²	
items raw	constant k = 0.0020 n = 0.9541	R ² 0.9956	χ ² 0.00020	0.01405	a = -0.0009 $b = 1.82 \times 10^{-7}$	R ² 0.5657	χ^2 0.01936	0.13892	constant $k = 0.0036$ $a = 0.4868$ $b = 0.3909$ $b = 0.3909$	R ² 0.9996	χ ² 0.00002	0.00425
items raw	constant $k = 0.0020$ $n = 0.9541$ $k = 0.0036$	R ² 0.9956	χ ² 0.00020	0.01405	a = -0.0009 $b = 1.82 \times 10^{-7}$ a = -0.0012	R ² 0.5657	χ^2 0.01936	0.13892	constant $k = 0.0036$ $a = 0.4868$ $b = 0.3909$ $k = 0.0101$	R ² 0.9996	χ ² 0.00002	0.00425
items raw	constant $k = 0.0020$ $n = 0.9541$ $k = 0.0036$	R ² 0.9956	χ ² 0.00020	0.01405	a = -0.0009 $b = 1.82 \times 10^{-7}$ a = -0.0012	R ² 0.5657	χ^2 0.01936	0.13892	constant k = 0.0036 a = 0.4868 b = 0.3909 k = 0.0101 a = -0.3961 constant k = 0.0101 constant c	R ² 0.9996	χ ² 0.00002	0.00425
items raw 180 °C	constant $k = 0.0020$ $n = 0.9541$ $k = 0.0036$ $n = 1.0731$	<i>R</i> ² 0.9956 0.9962	χ ² 0.00020 0.00028	0.01405	a = -0.0009 $b = 1.82 \times 10^{-7}$ a = -0.0012 $b = 3.30 \times 10^{-7}$	R ² 0.5657 0.4102	χ^2 0.01936 0.02666	0.13892 0.16294	constant k = 0.0036 a = 0.4868 b = 0.3909 k = 0.0101 a = -0.3961 b = 0.4165	R ² 0.9996 0.9996	χ ² 0.00002 0.00003	0.00425
items raw 180 °C 200 °C	constant $k = 0.0020$ $n = 0.9541$ $k = 0.0036$ $n = 1.0731$ $k = 0.0035$ $n = 1.0656$	R ² 0.9956 0.9962 0.9960	χ ² 0.00020 0.00028 0.00032	0.01405 0.01680 0.01780	a = -0.0009 $b = 1.82 \times 10^{-7}$ a = -0.0012 $b = 3.30 \times 10^{-7}$ a = -0.0023 $b = 1.29 \times 10^{-6}$	R ² 0.5657 0.4102 0.9853	χ ² 0.01936 0.02666 0.00117	0.13892 0.16294 0.03402	constant k = 0.0036 a = 0.4868 b = 0.3909 k = 0.0101 a = -0.3961 b = 0.4165 k = 0.0071	R ² 0.9996 0.9996 0.9998	χ ² 0.00002 0.00003 0.00001	0.00425 0.00540 0.00371
items raw 180 °C	constant $k = 0.0020$ $n = 0.9541$ $k = 0.0036$ $n = 1.0731$ $k = 0.0035$	<i>R</i> ² 0.9956 0.9962	χ ² 0.00020 0.00028	0.01405	a = -0.0009 $b = 1.82 \times 10^{-7}$ a = -0.0012 $b = 3.30 \times 10^{-7}$ a = -0.0023 $b = 1.29 \times 10^{-6}$ a = -0.0026	R ² 0.5657 0.4102	χ^2 0.01936 0.02666	0.13892 0.16294	constant k = 0.0036 a = 0.4868 b = 0.3909 k = 0.0101 a = -0.3961 b = 0.4165 k = 0.0071 a = -0.8945	R ² 0.9996 0.9996	χ ² 0.00002 0.00003	0.00425
items raw 180 °C 200 °C	constant $k = 0.0020$ $n = 0.9541$ $k = 0.0036$ $n = 1.0731$ $k = 0.0035$ $n = 1.0656$	R ² 0.9956 0.9962 0.9960	χ ² 0.00020 0.00028 0.00032	0.01405 0.01680 0.01780	a = -0.0009 $b = 1.82 \times 10^{-7}$ a = -0.0012 $b = 3.30 \times 10^{-7}$ a = -0.0023 $b = 1.29 \times 10^{-6}$	R ² 0.5657 0.4102 0.9853	χ ² 0.01936 0.02666 0.00117	0.13892 0.16294 0.03402	constant k = 0.0036 a = 0.4868 b = 0.3909 k = 0.0101 a = -0.3961 b = 0.4165 k = 0.0071 a = -0.8945 b = 0.6338 k = 0.0243 a = -0.1178	R ² 0.9996 0.9996 0.9998	χ ² 0.00002 0.00003 0.00001	0.00425 0.00540 0.00371
items raw 180 °C 200 °C 220 °C	constant $k = 0.0020$ $n = 0.9541$ $k = 0.0036$ $n = 1.0731$ $k = 0.0035$ $n = 1.0656$ $k = 0.0037$ $n = 1.0577$	R ² 0.9956 0.9962 0.9960 0.9979	χ ² 0.00020 0.00028 0.00032 0.00016	0.01405 0.01680 0.01780 0.01256	a = -0.0009 $b = 1.82 \times 10^{-7}$ a = -0.0012 $b = 3.30 \times 10^{-7}$ a = -0.0023 $b = 1.29 \times 10^{-6}$ a = -0.0026 $b = 1.68 \times 10^{-6}$	R ² 0.5657 0.4102 0.9853 0.9862	χ ² 0.01936 0.02666 0.00117 0.00105	0.13892 0.16294 0.03402 0.03223	constant k = 0.0036 a = 0.4868 b = 0.3909 k = 0.0101 a = -0.3961 b = 0.4165 k = 0.0071 a = -0.8945 b = 0.6338 k = 0.0243 a = -0.1178 b = 0.1591	R ² 0.9996 0.9996 0.9998 0.9998	χ ² 0.00002 0.00003 0.00001 0.00005	0.00425 0.00540 0.00371 0.00686
items raw 180 °C 200 °C	constant $k = 0.0020$ $n = 0.9541$ $k = 0.0036$ $n = 1.0731$ $k = 0.0035$ $n = 1.0656$ $k = 0.0037$ $n = 1.0577$ $k = 0.0033$	R ² 0.9956 0.9962 0.9960	χ ² 0.00020 0.00028 0.00032	0.01405 0.01680 0.01780	a = -0.0009 $b = 1.82 \times 10^{-7}$ a = -0.0012 $b = 3.30 \times 10^{-7}$ a = -0.0023 $b = 1.29 \times 10^{-6}$ a = -0.0026 $b = 1.68 \times 10^{-6}$ a = -0.0020	R ² 0.5657 0.4102 0.9853	χ ² 0.01936 0.02666 0.00117	0.13892 0.16294 0.03402	constant $k = 0.0036$ $a = 0.4868$ $b = 0.3909$ $k = 0.0101$ $a = -0.3961$ $b = 0.4165$ $k = 0.0071$ $a = -0.8945$ $b = 0.6338$ $k = 0.0243$ $a = -0.1178$ $b = 0.1591$ $k = 0.0194$	R ² 0.9996 0.9996 0.9998	χ ² 0.00002 0.00003 0.00001	0.00425 0.00540 0.00371
items raw 180 °C 200 °C 220 °C	constant $k = 0.0020$ $n = 0.9541$ $k = 0.0036$ $n = 1.0731$ $k = 0.0035$ $n = 1.0656$ $k = 0.0037$ $n = 1.0577$	R ² 0.9956 0.9962 0.9960 0.9979	χ ² 0.00020 0.00028 0.00032 0.00016	0.01405 0.01680 0.01780 0.01256	a = -0.0009 $b = 1.82 \times 10^{-7}$ a = -0.0012 $b = 3.30 \times 10^{-7}$ a = -0.0023 $b = 1.29 \times 10^{-6}$ a = -0.0026 $b = 1.68 \times 10^{-6}$	R ² 0.5657 0.4102 0.9853 0.9862	χ ² 0.01936 0.02666 0.00117 0.00105	0.13892 0.16294 0.03402 0.03223	constant k = 0.0036 a = 0.4868 b = 0.3909 k = 0.0101 a = -0.3961 b = 0.4165 k = 0.0071 a = -0.8945 b = 0.6338 k = 0.0243 a = -0.1178 b = 0.1591	R ² 0.9996 0.9996 0.9998 0.9998	χ ² 0.00002 0.00003 0.00001 0.00005	0.00425 0.00540 0.00371 0.00686

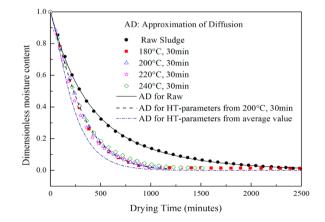


Figure 5. Approximation of Diffusion modeling of HT pretreated or untreated sludge.

$$M_{\rm R} = \frac{M_{\tau} - M_{\rm eq}}{M_{\rm ini} - M_{\rm eq}}$$

= $\frac{8}{\pi^2} \sum_{n=0}^{\infty} \frac{1}{(2n+1)^2} \exp\left(-\frac{(2n+1)^2 \pi^2 D_{\rm e} \tau}{4L^2}\right)$ (7)

where D_e is the effective diffusivity, m^2/s ; *L* is the half—thickness of the slab for dying from two sides, m; and *n* is a positive integer, representing the number of terms being taken into consideration.

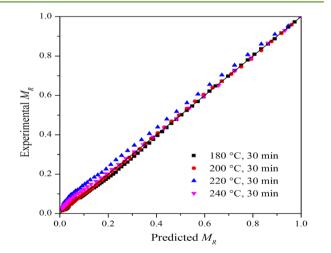


Figure 6. Comparison of the actual $M_{\rm R}$ and predicted $M_{\rm R}$ by the Approximation of Diffusion model.

For a long drying period, $M_{\rm R}$ < 0.6, the expression can be simplified by considering only the first term as

$$M_{\rm R} = \frac{8}{\pi^2} \exp\left(-\frac{\pi^2 D_{\rm e} \tau}{4L^2}\right) \tag{8}$$

Taking a natural logarithm on both sides of this equation and plotting ln $M_{\rm R}$ versus the drying time τ , the effective diffusivity can be obtained

$$D_{\rm e} = -\frac{4kL^2}{\pi^2} \tag{9}$$

where *k* is the slope of the straight line of $\ln M_{\rm R}$ versus τ .

Obviously, as indicated in Figure 3, the shrinkage of the raw sludge is not negligible. Thus, only the effective diffusivity of the HT sludge was analyzed using the Fick's second diffusion in this study. The values were 1.27×10^{-9} , 1.26×10^{-9} , 1.71×10^{-9} , and 1.63×10^{-9} m²/s for the sludge with HT pretreated under the holding time of 30 min and a temperature of 180, 200, 220, and 240 °C, respectively. Compared with that of the raw sludge, which was $(7.42 \pm 0.56) \times 10^{-10} \text{ m}^2/\text{s}$,³⁴ the diffusivity has been improved almost twice. Moreover, the order of the effective diffusivity was the same as that of the drying rate of all these samples. It verified that the drying process was mainly controlled by the inner diffusion properties.

CONCLUSION

This work experimentally investigated the influence of HT pretreatment on sludge drying kinetics. The main conclusions are summarized as the following: (1) HT pretreatment can improve the drying performance of the paper sludge. The optimal operating condition was a HT temperature of 220 and holding time of 30 min for a good dewatering performance within the range studied in this work. (2) The Approximation of Diffusion model was the best model to predict the sludge drying behavior. Its predicted values are in good agreement with the experimental data, with R^2 close to 1 and the lowest χ^2 and $E_{\rm RMS}$ values. Nevertheless, the model constant depended on the sludge origin. To predict the drying behavior, the expression for the raw sludge was $M_{\rm R} = 0.4868 \exp(-0.0036\tau) + 0.5132 \exp(-0.0014\tau)$ and $M_{\rm R} = -0.8945 \exp(-0.0071\tau) + 1.8945 \exp(-0.0071\tau)$ (-0.0045τ) for the HT sludge. (3) The effective diffusivities were 1.27×10^{-9} , 1.26×10^{-9} , 1.71×10^{-9} , and 1.63×10^{-9} m²/s for the HT sludge pretreated under the holding time of 30 min and a temperature of 180, 200, 220, and 240 °C, respectively. This indicated that the drying process was mainly controlled by the inner diffusion properties, which was improved by HT pretreatment.

Although these results are a preliminary investigation on the convective drying behavior of HT pretreated sludge, it is still important to optimize the design and operation of the HT dewatering process (both mechanical dewatering and drying). On the other hand, even if we have experimentally verified that the HT pretreatment can improve the drying performance, future works should be carried out by focusing on the impact of HT pretreatment on the bound energy of water, water distribution, particle size distribution, porosity, and rheological properties of sludge in order to fully explore the mechanism. Also, the effect of other operating parameters, such as the HT temperature, HT holding time, drying temperature, air velocity, humidity, and sample thickness, on the drying behaviors will be studied to reveal how HT pretreatment affects drying behaviors.

AUTHOR INFORMATION

Corresponding Authors

*E-mail: pt.zhaoseu@gmail.com (P.Z.).

*E-mail: ge1962@126.com (S.G.).

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

This work was financially supported by Strategic China-Japan Cooperative Program on "Science and Technology (S&T) for Environmental Conservation and Construction of a Society with Less Environmental Burden" of the National Nature Science Foundation of China and Japan Science and Technology Agency (21161140329). It was also supported by the State Scholarship Fund of China (2011609050), and National Science and Technology Major Project of China (Water Program) (2010ZX07319-002).

REFERENCES

(1) Liao, Y.; Ma, X. Thermogravimetric analysis of the co-combustion of coal and paper mill sludge. Appl. Energy 2010, 87, 3526-3532.

(2) Hojamberdiev, M.; Kameshima, Y.; Nakajima, A.; Okada, K.; Kadirova, Z. Preparation and sorption properties of materials from paper sludge. J. Hazard. Mater. 2008, 151, 710-719.

(3) Mahmood, T.; Elliott, A. A review of secondary sludge reduction technologies for the pulp and paper industry. Water Res. 2006, 40, 2093-2112.

(4) Vamvuka, D.; Salpigidou, N.; Kastanaki, E.; Sfakiotakis, S. Possibility of using paper sludge in co-firing applications. Fuel 2009, 88, 637-643.

(5) Werther, J.; Ogada, T. Sewage sludge combustion. Prog. Energy Combust. Sci. 1999, 25, 55-116.

(6) Hong, S.; Ryu, C.; Ko, H S; Ohm, T I; Chae, J S. Process consideration of fry-drying combined with steam compression for efficient fuel production from sewage sludge. Appl. Energy 2013, 103, 468 - 476

(7) Dewil, R.; Baeyens, J.; Appels, L. Enhancing the use of waste activated sludge as bio-fuel through selectively reducing its heavy metal content. J. Hazard. Mater. 2007, 144, 703-707.

(8) Jiang, J.; Du, X.; Yang, S. Analysis of the combustion of sewage sludge-derived fuel by a thermogravimetric method in China. Waste Manage. 2010, 30, 1407-1413.

(9) Zhao, P.; Ge, S.; Yoshikawa, K. An orthogonal experimental study on solid fuel production from sewage sludge by employing steam explosion. Appl. Energy 2013, 112, 1213-1221.

(10) Ma, X.-w.; Weng, H.-x.; Su, M.-h.; Pan, L. Drying sewage sludge using flue gas from power plants in China. Environ. Earth. Sci. 2012, 65, 1841-1846.

(11) Bennamoun, L. Solar drying of wastewater sludge: A review. Renewable Sustainable Energy Rev. 2012, 16, 1061-1073.

(12) Navaee-Ardeh, S.; Bertrand, F.; Stuart, P R. Key variables analysis of a novel continuous biodrying process for drying mixed sludge. Bioresour. Technol. 2010, 101, 3379-3387.

(13) Jiang, Z. L.; Meng, D. W.; Mu, H. Y.; Yoshikawa, K. Study on the hydrothermal drying technology of sewage sludge. Sci. China, Ser. E: Technol. Sci. 2010, 53, 160-163.

(14) Tao, T.; Peng, X. F.; Lee, D. J. Skin layer on thermally dried sludge cake. Drying Technol. 2006, 24, 1047-1052.

(15) Léonard, A.; Blacher, S.; Marchot, P.; Crine, M. Use of X-ray microtomography to follow the convective heat drying of wastewater sludges. Drying Technol. 2002, 20, 1053-1069.

(16) Tao, T.; Peng, X. F.; Lee, D. J. Structure of crack in thermally dried sludge cake. Drying Technol. 2005, 23, 1555-1568.

(17) Chen, J.; Peng, X.; Tao, T.; Lee, D. Thermal drying of wastewater sludge with crack formation. Water Sci. Technol. 2004, 50, 177-182.

(18) Doymaz, İ. Convective drying kinetics of strawberry. Chem. Eng. Process. 2008, 47, 914-919.

(19) Toğrul, İ. T.; Pehlivan, D. Modelling of drying kinetics of single apricot. J. Food Eng. 2003, 58, 23-32.

(20) Benamoun; L., Belhamri; A., Léonard A., econdary Benamoun; L., Belhamri; A., Léonard A., Eds. Magdeburg, Germany, 2010; pp 828-833.

ACS Sustainable Chemistry & Engineering

(21) Doymaz, İ. The kinetics of forced convective air-drying of pumpkin slices. J. Food Eng. 2007, 79, 243–248.

(22) Lu, L.; Namioka, T.; Yoshikawa, K. Effects of hydrothermal treatment on characteristics and combustion behaviors of municipal solid wastes. *Appl. Energy* **2011**, *88*, 3659–3664.

(23) Özdemir, M.; Onur Devres, Y. The thin layer drying characteristics of hazelnuts during roasting. *J. Food Eng.* **1999**, 42, 225–233.

(24) Xanthopoulos, G.; Oikonomou, N.; Lambrinos, G. Applicability of a single-layer drying model to predict the drying rate of whole figs. *J. Food Eng.* **2007**, *81*, 553–559.

(25) Wang, C.; Singh, R. Use of variable equilibrium moisture content in modeling rice drying. *Trans. ASAE* **1978**, *11*, 668–672.

(26) Sacilik, K.; Elicin, A. K.; Unal, G. Drying kinetics of Üryani plum in a convective hot-air dryer. *J. Food Eng.* **2006**, *76*, 362–368.

(27) Meng, D.; Jiang, Z.; Yoshikawa, K.; Mu, H. The effect of operation parameters on the hydrothermal drying treatment. *Renew. Energ.* **2012**, 42, 90–94.

(28) Binod, P.; Kuttiraja, M.; Archana, M.; Janu, K. U.; Sindhu, R.; Sukumaran, R. K.; Pandey, A. High temperature pretreatment and hydrolysis of cotton stalk for producing sugars for bioethanol production. *Fuel* **2012**, *92*, 340–345.

(29) Orikawa, M.; Kamahara, H.; Atsuta, Y.; Daimon, H. Application of hydrothermal treatment to high concentrated sewage sludge for anaerobic digestion process. *Int. J. Renewable Energy Dev.* **2013**, *2*, 165–168.

(30) Pérez-Elvira, S. I.; Fernández-Polanco, F.; Fernández-Polanco, M.; Rodríguez, P.; Rouge, P. Hydrothermal multivariable approach: Full-scale feasibility study. *Electron. J. Biotechnol.* **2008**, *11*, 7–8.

(31) Park, S.-J.; Bae, J.-S.; Lee, D.-W.; Ra, H. W.; Hong, J.-C.; Choi, Y.-C. Effects of hydrothermally pretreated sewage sludge on the stability and dispersibility of slurry fuel using pulverized coal. *Energy Fuel* **2011**, 25, 3934–3939.

(32) Zhao, P.; Shen, Y.; Ge, S.; Yoshikawa, K. Energy recycling from sewage sludge by producing solid biofuel with hydrothermal carbonization. *Energy Convers. Manage.* **2014**, *78*, 815–821.

(33) Crank, J. The Mathematics of Diffusion; Oxford University Press: Oxford, 1979.

(34) Smith, P.; Coackley, P. Diffusivity, tortuosity and pore structure of activated sludge. *Water Res.* **1984**, *18*, 117–122.