



# Properties improvement of paper mill sludge-based granular activated carbon fillers for fluidized-bed bioreactor by bentonite (Na) added and acid washing

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## ARTICLE INFO

### Article history:

Received 17 June 2011

Received in revised form

13 September 2011

Accepted 13 September 2011

Available online 17 September 2011

### Keywords:

Properties improvement

Granular activated carbon

Filler

Acid washing

## ABSTRACT

Properties improvement of paper mill sludge (PMS) based granular activated carbon fillers for fluidized-bed bioreactor (FBBR) was investigated in this study. Bentonite (Na) powders were blended in the dewatered paper mill sludge powders to strengthen the abrasion resistance strength of the fillers. Different acid washing treatments were studied to produce FBBR fillers with optimum performance. The results indicated that granulation was easy and the abrasion resistance strength of the fillers increased by 15% with 8 wt% of bentonite (Na) added. Acid washing treatment prior to activation had a better effect on the removal of Fe than post-activation acid washing treatment. HCl was the most appropriate acid during the acid washing treatment. The optimum acid washing treatment was carried out prior to activation with 2 M HCl soaking for 6 h. After acid washing treatment, the fillers with grain density of 1170 kg/m<sup>3</sup>, specific surface area of 176 m<sup>2</sup>/g were obtained.

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## 1. Introduction

Fluidized-bed bioreactor (FBBR) is an advanced wastewater treatment system, which has proven superior to traditional of reactors [1–5]. The FBBR has a variety advantages, such as high biomass concentration, very short hydraulic retention time (HRT) with high treatment efficiency and larger surface area for nutrient transfer [6–8]. It has been successfully applied to the treatment of several kinds of wastewater, such as coke oven wastewater, ammonium-rich wastewater and phenolic wastewater [9–13]. The selection of appropriate fillers is a core issue in FBBR system. Appropriate grain density and developed porous structure are the main characteristics required for the fillers. A variety of support particles have been used in the FBBR system such as granular activated carbon (GAC), sand, perlite, zeolite, lava rocks and sponge [14–16]. Among the particles, GAC with developed porosity is a perfect particle for its easy fluidization characteristics and suitability for the proliferation of bacteria. Most of the GAC used as fillers were commercial GAC. The high cost of granular activated carbon products restricts its application as filler in the fluidized-bed bioreactor.

At present, wood and coal are the most common raw material in the production of granular activated carbon, but they are expensive, non-renewable or not readily available [17]. Thus many alternative materials are used as the raw materials to produce granular acti-

vated carbon, such as oil palm, fruit stones, nutshells, waste walnut shell and sludge [18–20]. Of the above alternatives, the manufacturing of paper mill sludge (PMS) into carbon adsorbents has been studied by some researchers, such as Bagreev [21]. According to Khalili [22], ZnCl<sub>2</sub> was used in the chemical activation process and HF was used to produce pure activated carbon without any mineral substrate, but this method involved a high cost and HF was harmful to the environment. In this study, steam was used in the physical activation process and HCl washing treatment was used to improve the characteristics of the PMS-based activation carbon fillers for FBBR, which reduced the cost and the environmental pollution compared to the former.

More and more PMS are produced with the development of pulp and paper industry. The PMS with high contents of organic components can be used as a raw material in the production of activated carbon. At the same time, the production of PMS based activated carbon solves the problem of sludge treatment. In the present study, the paper mill sludge based activated carbon was mostly used as an adsorbent to dispose of the pollutants in the gas and the wastewater. There is hardly any research on the use of paper mill sludge-based granular activated carbon as fillers for FBBR.

In the previous experiment by the author, the preparation of paper mill sludge-based granular activated carbon fillers for fluidized-bed bioreactor was studied. Through steam activation, granular activated carbon fillers with developed pore structure were obtained. But there were some problems related to the production. There was a large amount of tiny plant fibers, which

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contributed to the high content of organic components in the dewatered paper mill sludge (DPMS), but the plant fibers caused the poor viscosity between the DPMS powders. It was difficult to granulate the DPMS powders into pellets. Even with the above-mentioned adhesive, the abrasion resistance strength of GAC fillers did not reach a satisfactory level. Meanwhile, the ash content of the PMS used in this study was 38.82% with chemical composition of 14.92% Al<sub>2</sub>O<sub>3</sub>, 22.08% CaO, 15.35% Fe<sub>2</sub>O<sub>3</sub>, a high content Fe, Al and Ca were harmful to the propagation of microorganisms and led to the increase of the grain density of the fillers to some extent. Thus, some measures were needed to solve these problems. In this study, property improvement of paper mill sludge-based granular activated carbon fillers for fluidized-bed bioreactor (FBBR) was investigated. Bentonite (Na) with strong bonding effect was blended in the dewatered paper mill sludge powders to solve the problem that the dewatered PMS powders were not easily granulated into pellets during the granulation process. Different acid washing treatment methods were studied to improve the characteristic of FBBR fillers.

## 2. Materials and methods

### 2.1. Production of GAC fillers from paper mill sludge

DPMS was obtained from the biologic treatment of the waste waters of the mill in Dezhou Chenming Paperboard Factory, Shandong Province, China. The sludge was dried at 105 °C for 4 h, and then was crushed with an electromagnetic pulverizer to pass through 100 mesh (the diameter of mesh was 0.154 mm). The organic material content of the dried paper mill sludge was 58.00% and the ash content was 38.63%.

Raw pellets with diameter of 0.4–1.0 mm was produced by a pelletizer (DZ-20 equipment) and 0.5 wt% of polyvinyl alcohol and 1.5 wt% of carboxymethylcellulose sodium (NaCMC) mixed solution was used as the adhesive in the granulation process. Then the raw pellets were dried at 105 °C for 2 h. The raw bentonite used in this study was Na<sup>+</sup>-exchanged form of bentonite (Na-bentonite) obtained from Weifang Bentonite Co., Shandong, China, without any further purification. It contained about 95% montmorillonite with chemical composition of 69.32% SiO<sub>2</sub>, 14.27% Al<sub>2</sub>O<sub>3</sub>, 1.99% CaO, 2.69% MgO, 1.84% Fe<sub>2</sub>O<sub>3</sub>, 1.85% Na<sub>2</sub>O, and 1.38% K<sub>2</sub>O.

#### 2.1.1. The carbonization treatment

The carbonization process was carried out in an electric furnace (KSY-D-16, made in China). The dried raw pellets were sent into the heated zone of the electric tube furnace and preheated for 50 min at 450 °C. Then the pellets were transferred to an iron sealed container until they cooled to room temperature. In the carbonization process, the electric tube furnace was sealed to prevent air infiltration. The experiment was conducted in triplicate to obtain three batches of samples.

#### 2.1.2. The activation treatment

The steam activation process was carried out in the same electric tube furnace. The steam was produced by a steam generator (HY-7-5D). The carbonized pellets were kept in the heated zone at the temperature of 800 °C for 60 min, with a steam flow rate of 6 L/min. Then the products were transferred to an iron sealed container until they cooled to room temperature. The experiment was conducted in triplicate to obtain three batches of samples.

### 2.2. The acid washing treatment

The acid washing treatment was carried out in a 500 ml beaker. In the acid washing treatment, 50 g pellets were placed in the

beaker with 100 ml acid solution added. The experiment was conducted in triplicate to obtain three batches of samples.

### 2.3. Characterization

The content of ash was measured according to the process as follows: approximately 1 g of oven-dried sample was weighed and placed in a cylindrical silica crucible. The crucible was heated in a muffle furnace at 815 °C for 2 h. The remaining ash was weighed when the crucible cooled to room temperature in a desiccator. The ash content was calculated on the basis of the original samples mass.

Bulk density and grain density were measured in this research. Before the tests, the samples were settled into an oven (105 °C) for 4 h. After cooling down to the room temperature, 100 g of samples was settled in a measuring cylinder (500 ml) with certain volume of water. Grain density of the samples was calculated according to Eq. (1).

$$\text{Grain density} = \frac{\text{Mass of dried pellets}}{\text{Change of the water volume}} \text{Kg m}^{-3} \quad (1)$$

Fluidization conditions were simulated in a 250 ml measuring cylinder with a micropore aerator in the bottom and 50 g fillers were added in the measuring cylinder. The aeration rate was changed to make the fillers fluidized. After running continuously for two days, the fillers were removed from the measuring cylinder and dried in an oven (105 °C) for 4 h, then weighted. The abrasion resistance strength of the fillers was calculated by using Eq. (2)

$$\text{Abrasion resistance strength} = \frac{\text{Mass of dry residual fillers}}{\text{Mass of the initial fillers}} \times 100\% \quad (2)$$

The iodine adsorption value was evaluated by Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> titration according to GB/T7702.7-2008 [23].

All the above measurements of each sample were determined in three replicates.

The surface area of GAC fillers was determined according to the BET method with nitrogen adsorption/desorption isotherms that were performed at 77 K using a ST-08A4 (Beijing, China) surface area analyzer.

The chemical components of GAC fillers were determined by energy dispersive X-ray fluorescence spectrometer (EDX) and surface physical morphology of GAC was observed by a scanning microscopy (Hitachi S-520).

## 3. Results and discussion

### 3.1. Bentonite (Na) added during the granulation process

To improve the abrasion resistance strength of GAC fillers, bentonite (Na), which had strong bonding effect was mixed with DPMS during the granulation process. In this experiment, the additive amount of bentonite (Na) varied from 2 wt% to 10 wt% of the total mass. It was found that granulation was easy when the additive amount of bentonite (Na) was 8 wt%.

Table 1 presented the comparison of GAC and BGAC. The abrasion resistance strength of the fillers also became better with the

**Table 1**  
Comparison of GAC and BGAC.

	Abrasion resistance strength (%)	Ash content (%)	Grain density (kg/m <sup>3</sup> )	S <sub>BET</sub> (m <sup>2</sup> /g)
GAC	84.07 ± 1.25 <sup>a</sup>	73.82 ± 0.26	1340 ± 14	130 ± 7
BGAC	95.12 ± 2.10	74.61 ± 0.43	1376 ± 20	122 ± 7

<sup>a</sup> All experiments were replicated three times and only mean values were presented. Data were presented as the mean of replicated samples ± standard deviation (n = 3).

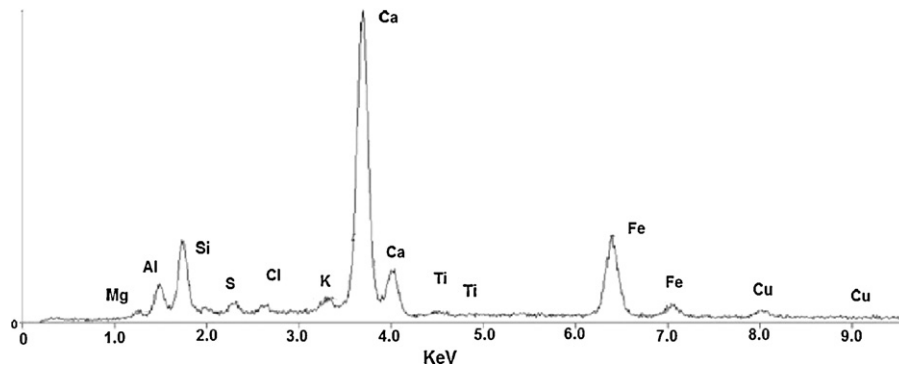


Fig. 1. EDX measurement of the BGAC fillers.

bentonite (Na) added. The abrasion resistance strength of bentonite (Na) with added GAC (BGAC) fillers increased by 15% compared to the GAC fillers. But with the bentonite (Na) added, there was no obvious change to the grain density and specific surface area of BGAC compared to GAC.

### 3.2. The acid washing treatment

EDX was a good approximation for the elemental composition in materials analysis [24]. In this experiment, EDX was used to investigate the elemental changes of fillers after acid washing treatment. Four to five measurements were conducted to determine the average compositions of the BGAC fillers.

Fig. 1 showed the EDX measurement of the BGAC fillers. It could be found that calcium oxide, aluminum sesquioxide, and silicon dioxide were the most abundant oxides in the BGAC fillers. The elemental contents of Fe and Al were at a high level, which were harmful to the propagation of microorganisms. And the leaching solution of the BGAC fillers was alkaline due to the high content of Ca. The inorganic components were removed by the acid washing treatment and the grain density of the fillers was smaller at the same time.

In the previous study, Fitzmorris et al. and Ros et al. have both investigated HCl washing. It could be observed that the BET surface areas of the fillers increased by HCl washing and the ash contents were reduced [25–27]. In this study, in order to obtain fillers with better properties for FBBR, acid treatment was used to reduce the content of Fe, Al and Ca and different acid washing treatment methods were used to investigate the appropriate practices.

#### 3.2.1. Acid washing treatment in different processes

In this section, acid washing treatments were carried out prior to and after the activation stage, respectively. 2 M HCl was used and the soaking time was set to 6 h. The grain density and the specific surface area of the BGAC fillers with acid washing treatment were tested to determine the superior acid washing methods.

Table 2 presented the grain density and the specific surface area of the fillers with different acid washing processes. As shown in Table 2, the grain density of the BGAC fillers with the acid washing treatment prior to activation (BGACA) was smaller than the BGAC fillers with post-activation acid washing treatment (BGACB), and

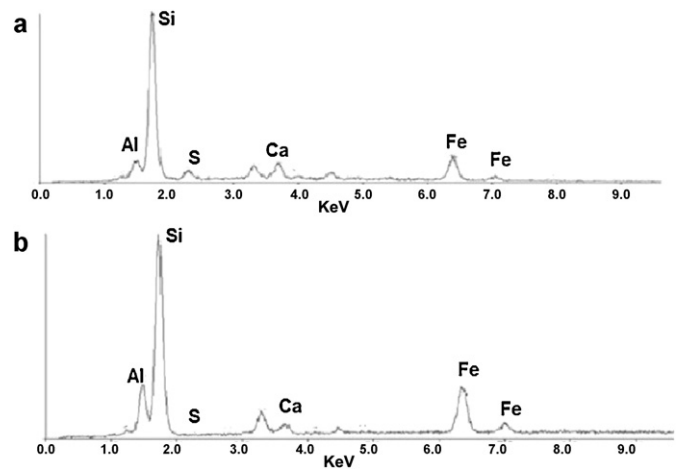


Fig. 2. EDX measurement of the BGACA (a) and BGACB (b) fillers.

the specific surface area of BGACA was slightly bigger than BGACB. This difference could be explained by the analysis of EDX.

The EDX measurements of the BGACA and BGACB fillers were shown in Fig. 2a and b, respectively. During the acid washing treatment, a large amount of Fe, Al and Ca were removed. The acid washing treatment reduced the inorganic content through releasing the partial dissolution of the inorganic fraction [28].

In the acidic conditions,  $\text{SiO}_3^{2-}$  reacted with the  $\text{H}^+$  to generate  $\text{H}_2\text{SiO}_3$  as the reaction product and  $\text{H}_2\text{SiO}_3$  was insoluble in water (Eq. (3)). In this experiment, there was no visible deposit in the acid solution after the acid washing treatment. It indicated that there was no significant removal of silicon during the acid washing treatment. So the silicon content could be used as a background value to evaluate the removal efficiency of Ca, Si and Al.



As shown in Table 3, the ratio of Ca:Si and Al:Si in BGACA was similar to that in BGACB. But the ratio of Si:Fe in BGACA was 10:1.34, compared to 10:3.30 in BGACB. It proved that the removal efficiency of Fe in BGACA was much better than BGACB. The temperature was up to 800 °C during the activation process. It was possible that Fe was encapsulated by carbon phase and mineral-like compound

Table 2

The grain density, specific surface area and ash content of different fillers.

	BGAC	BGACA	BGACB	BGACA <sub>HCl</sub>	BGACA <sub>H<sub>2</sub>SO<sub>4</sub></sub>	BGACA <sub>HNO<sub>3</sub></sub>
Grain density (kg/m <sup>3</sup> )	1376 ± 20 <sup>a</sup>	1170 ± 35	1240 ± 28	1170 ± 35	1430 ± 27	1184 ± 15
S <sub>BET</sub> (m <sup>2</sup> /g)	122 ± 7	176 ± 8	160 ± 9	176 ± 8	167 ± 5	174 ± 10
Ash content (%)	74.61 ± 0.43	69.18 ± 0.064	70.42 ± 0.14	69.18 ± 0.064	73.82 ± 0.17	68.85 ± 1.43

<sup>a</sup> All experiments were replicated three times and only mean values were presented. Data were presented as the mean of replicated samples ± standard deviation (n=3).

**Table 3**  
Ratio of Si:Ca:Al:Fe of the different fillers.

	BGAC	BGACA	BGACB
Si:Ca	10:(15.32 ± 0.63 <sup>a</sup> )	10:(0.52 ± 0.051)	10:(0.93 ± 0.045)
Si:Al	10:(7.9 ± 0.22)	10:(1.33 ± 0.043)	10:(1.77 ± 0.025)
Si:Fe	10:(9.43 ± 0.059)	10:(1.34 ± 0.10)	10:(3.30 ± 0.16)

<sup>a</sup> All experiments were replicated three times and only mean values were presented. Data were presented as the mean of replicated samples ± standard deviation ( $n=3$ ).

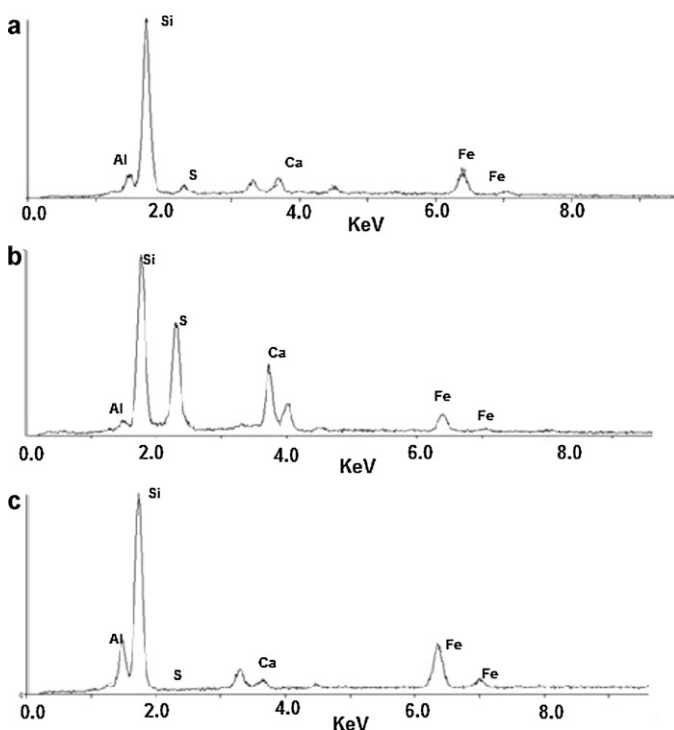
formatted at such a high temperature, which led to the poor removal efficiency of Fe in the post activation acid washing treatment [29]. Previous studies also had the same view, but more extensive studies need to be done obtain more definite conclusions. It could be found that the removal efficiency of Fe had little effect on the specific surface area of BGAC fillers, but the higher Fe removal efficiency led to the decrease of the density.

The acid washing treatment prior to activation had a better effect on the performance of the fillers, so this method was selected.

### 3.2.2. Different acids used in acid washing treatment

Three conventional acids (HCl, H<sub>2</sub>SO<sub>4</sub> and HNO<sub>3</sub>) were used to investigate the effect of different acids on the acid washing treatment. Table 1 showed the grain density and the specific surface area of the BGACA fillers with different acids used in acid washing treatment. The acid washing treatment was carried out prior to activation process and 2 M H<sup>+</sup> existed in all of the acid solutions (HCl 2 M, H<sub>2</sub>SO<sub>4</sub> 1 M, HNO<sub>3</sub> 2 M). As shown in Table 2, the grain density and the specific surface area were almost the same between the BGACA fillers with HCl treatment (BGACA<sub>HCl</sub>) and BGACA fillers with HNO<sub>3</sub> treatment (BGACA<sub>HNO3</sub>). But a slightly smaller specific surface area and an obviously increased grain density existed in the BGACA fillers with H<sub>2</sub>SO<sub>4</sub> (BGACA<sub>H2SO4</sub>) compared to the former two. This difference could be explained by the analysis of EDX.

Fig. 3 shows the EDX measurements of BGACA<sub>HCl</sub>, BGACA<sub>H2SO4</sub> and BGACA<sub>HNO3</sub>, respectively. As shown in Fig. 3 the residual ratio



**Fig. 3.** EDX measurement of the BGACA<sub>HCl</sub> (a) and BGACA<sub>H2SO4</sub> (b) and BGACA<sub>HNO3</sub> (c).

**Table 4**  
Ratio of Si:Ca:Al:Fe of the different fillers.

	BGACA <sub>HCl</sub>	BGACA <sub>H2SO4</sub>	BGACA <sub>HNO3</sub>
Si:Ca	10:0.52	10:14.5	10:0.519
Si:Al	10:1.33	10:1.56	10:1.09
Si:Fe	10:1.34	10:3.46	10:2.06

of Ca:Si in BGACA<sub>H2SO4</sub> was much bigger than BGACA<sub>HCl</sub>, and meanwhile the content of sulfur was much bigger in BGACA<sub>H2SO4</sub> than the others. It indicated that HCl and HNO<sub>3</sub> had a better Ca removal efficiency than H<sub>2</sub>SO<sub>4</sub>. Some white substances appeared in the surface of BGACA<sub>H2SO4</sub>, which was CaSO<sub>4</sub> as a reaction product in the acid washing treatment. CaSO<sub>4</sub> was slightly soluble in water and formatted precipitation, which caused the obvious increase in grain density of BGACA<sub>H2SO4</sub>. The ash content of BGACA<sub>H2SO4</sub> was bigger than BGACA<sub>HCl</sub> and BGACA<sub>HNO3</sub>, which also confirmed this point. On the basis of the above findings, H<sub>2</sub>SO<sub>4</sub> was inappropriate to be used in this experiment.

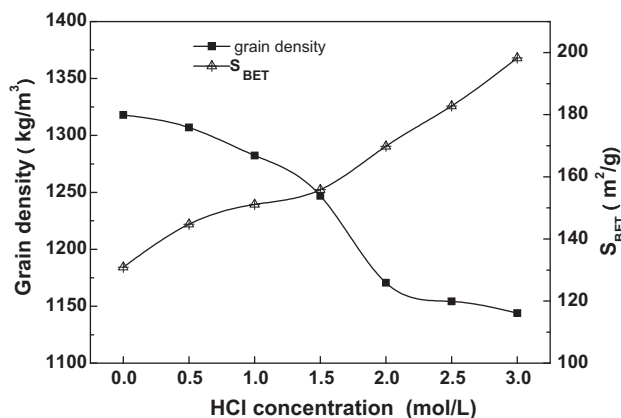
According to Fig. 3 and Table 4, the residual ratio of Si:Ca:Al and the grain density and the specific surface area of BGACA<sub>HCl</sub> were almost the same as those of BGACA<sub>HNO3</sub>. Thus, HCl had almost the same effect on acid washing treatment as HNO<sub>3</sub> with the same concentration. Taking into account the cost and the impact on the environment, HCl was used in the acid washing treatment.

### 3.2.3. Effect of initial concentration

The effect of initial concentration of HCl in acid washing treatment was investigated in this section and the HCl solution ranged from 0 to 3 M (the soaking solution was H<sub>2</sub>O when the initial concentration was 0). The soaking time was selected as 6 h to make the reaction complete and the results were shown in Fig. 4.

It was shown in Fig. 4 that the specific surface area of the BGACA<sub>HCl</sub> fillers became bigger with the increase of the initial concentration of HCl, while the grain density of the BGACA<sub>HCl</sub> fillers showed the opposite trend.

When the initial concentration of HCl was 2 M, the grain density of BGACA<sub>HCl</sub> fillers was 1170 kg/m<sup>3</sup>. There was no obvious change in the grain density of the fillers when the concentration of acid increased. The low cost of BGACA<sub>HCl</sub> fillers with PMS as raw materials was a main advantage compared to the chemical activation carbon. During the acid washing treatment, higher initial concentration of HCl had a better effect on the specific surface area and the grain density of the BGACA<sub>HCl</sub> fillers, but it inevitably increased the costs. Thus, a balanced initial concentration of HCl should be adopted.



**Fig. 4.** Effect of the HCl concentration on the specific surface area and grain density of the BGACA<sub>HCl</sub> fillers.



When the initial concentration of HCl was 2 M, the specific surface area of  $BGACA_{HCl}$  reached  $176 \text{ m}^2/\text{g}$  and most of the Fe and Al were removed. Compared to the perlite with  $S_{BET}$  of  $7.030 \text{ m}^2/\text{g}$  used as fillers in FBBR [14], the  $BGACA_{HCl}$  had a much bigger specific area than the traditional fillers used in FBBR, and  $BGACA_{HCl}$  fillers had a suitable grain density for FBBR.

Thus, considering the costs and the effect of acid washing treatment, 2 M HCl was appropriate in the acid washing treatment prior to activation.

### 3.2.4. Effect of soak time

Experimental series were conducted in order to investigate the effect of HCl soaking time on the characteristic of the  $BGACA_{HCl}$  fillers. During the experiment, the initial concentration of HCl was selected as 2 M based on Section 3.2.3. The soaking time varied from 3 h to 24 h with a 3-h interval.

Experimental data series were shown in Fig. 5. The grain density of the  $BGACA_{HCl}$  was gradually smaller during the first 9 h, but there was no more obvious change afterwards. At the same time, the specific surface area increased in the first 6 h but showed a small decline with time. The changes of the grain density were mainly due to the reduction of the inorganic components, which were removed in the initial phase. It could be deduced that some organic components reacted with the acid solution, which led to the decrease of the specific surface area of the  $BGACA_{HCl}$  fillers [30].

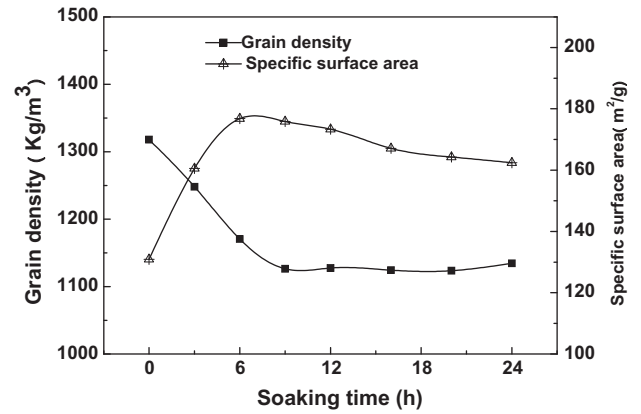


Fig. 5. Effect of soaking time on the specific surface area and grain density of the  $BGACA_{HCl}$  fillers.

Considering these two aspects, it could be found that soaking time of 6 h was optimum to produce  $BGACA_{HCl}$  fillers when the initial concentration of HCl was 2 M.

### 3.2.5. The reaction consideration of the acid washing treatment

According to the above discussion, acid washing treatment was carried out prior to the activation stage with 2 M HCl soaking 6 h.

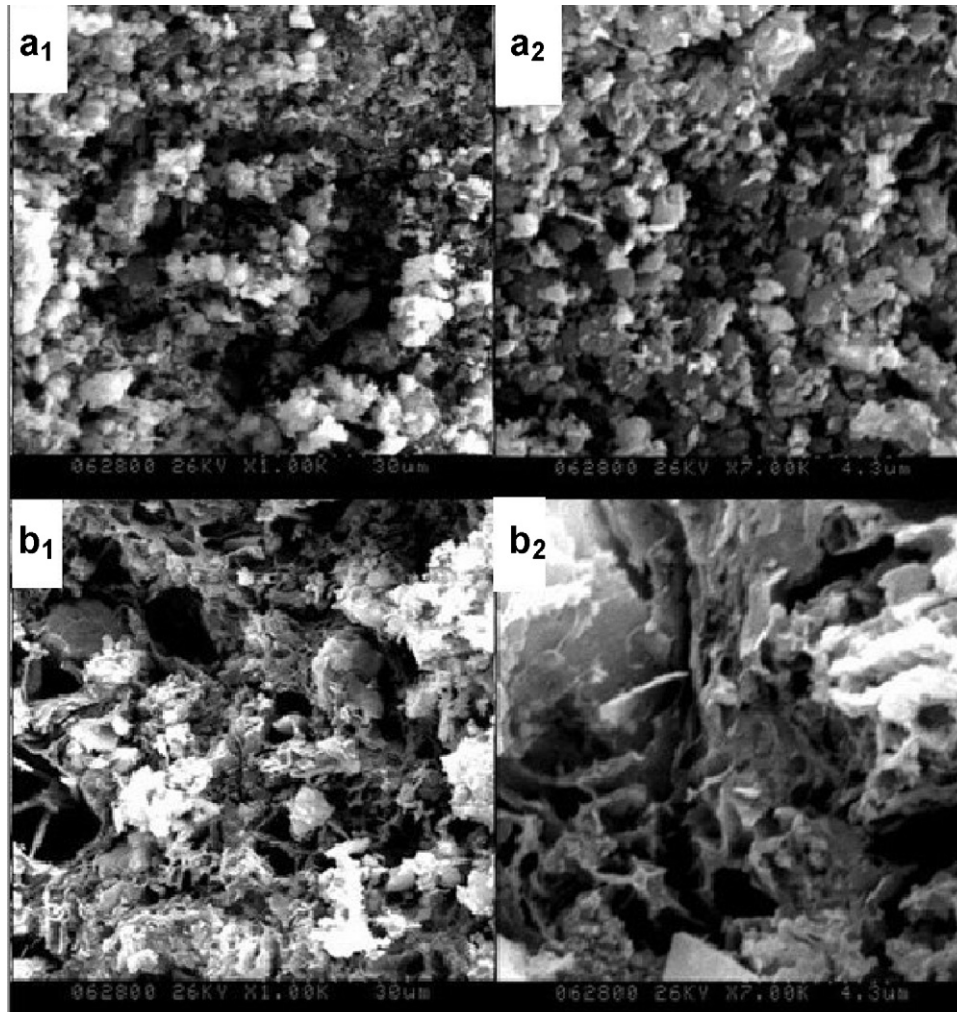


Fig. 6. SEM images of the BGAC ( $a_1 \times 1.00k$ ,  $a_2 \times 7.00k$ ) and  $BGACA_{HCl}$  ( $b_1 \times 1.00k$ ,  $b_2 \times 7.00k$ ) fillers.

**Table 5**  
Comparison of BGACA<sub>HCl</sub> and GAC fillers.

	Grain density (kg/m <sup>3</sup> )	Iodine adsorption value (mg/g)	S <sub>BET</sub> (m <sup>2</sup> /g)
BGACA <sub>HCl</sub>	1170 ± 35 <sup>a</sup>	218 ± 6	176 ± 8
GAC	1340 ± 14	137 ± 7	130 ± 7

<sup>a</sup> All experiments were replicated three times and only mean values were presented. Data were presented as the mean of replicated samples ± standard deviation ( $n = 3$ ).

The organic components played the most important role in the development of the pore structures. The ash level neither has an effect on the activation process nor on the porous development and it only acted as an inert material, which did not contribute to the porosity [31].

Regardless the impact of ash yield, the specific surface area could be recalculated by using Eq. (4)

$$R_{S_{BET}} = \frac{S_{BET}}{1 - \text{ash yield}\%/100} \quad (4)$$

According to Table 2, the specific surface area of BGAC and BGACA<sub>HCl</sub> could be recalculated as 481 m<sup>2</sup>/g and 572 m<sup>2</sup>/g, respectively. An obvious increase of recalculated specific surface area occurred in the BGACA<sub>HCl</sub> compared to the untreated BGAC. It indicated that the increase was not only due to the removal of the inorganic matters in the BGAC, but also might be due to the better accessibility to the remaining carbon in the carbonized particles. The reaction between the remaining carbon and the steam easily occurred due to removal of the inorganic matters [32].

### 3.3. Characterization of the BGAC fillers with acid washing treatment

Fig. 6 shows the SEM images of the BGAC fillers and BGACA<sub>HCl</sub> fillers. As shown in Fig. 6a<sub>1</sub> and a<sub>2</sub>, there was a mass of impurities filled in the pore structures of the BGAC fillers. Fig. 6b<sub>1</sub> and b<sub>2</sub> showed the pore structures of the BGACA<sub>HCl</sub> fillers. The inert materials between the pore were greatly reduced and the pore structures became well developed in BGACA<sub>HCl</sub> fillers. The impurities in BGAC were inorganic components rich in Fe, Al, Si and Ca, which limited the development of the pores. After the acid washing treatment, the impurities reacted with HCl and were removed. In this process, the reaction between the impurities and HCl led to the formation of some pores and provided better activation conditions.

During the steam activation, mesopores (2 nm <  $d$  < 50 nm) were developed on the surface and inside the fillers [33–37], which was suitable for the proliferation of bacteria and the formation of biofilm. Iodine number is considered as a simple and quick test for evaluating the surface area of activated carbon associated with pores with  $d > 1$  nm, so it can be used as a reference standard to evaluate the appropriateness of the fillers for FBBR. As presented in Table 5, the iodine number of BGACA<sub>HCl</sub> was 218 mg/g, which had a more significant growth than that of GAC fillers (137 mg/g). So it indicated that BGACA<sub>HCl</sub> fillers were more appropriate for FBBR than GAC fillers.

Some characterizations of the GAC and GACA<sub>HCl</sub> fillers were presented in Table 5. The GACA<sub>HCl</sub> fillers were resistant to mechanical damage [38] and had excellent biomass retention owing to the extensive surface area [39] after acid washing treatment.

## 4. Conclusions

In this study, properties improvement of paper mill sludge-based granular activated carbon fillers for fluidized-bed bioreactor (FBBR) was investigated.

- (1) The granular activated carbon fillers with 8 wt% of bentonite (Na) added had a good performance in the granulation and the abrasion resistance strength of BGAC fillers increased by 15% compared to the GAC fillers.
- (2) The acid washing treatment prior to activation had a better effect on the removal of Fe. BGAC fillers with smaller grain density and higher specific surface area were produced by this method.
- (3) HCl was the most appropriate acid during the acid washing treatment.
- (4) The optimum HCl concentration was 2 M HCl and the soaking time was selected as 6 h.
- (5) After the acid washing treatment, the grain density, specific surface area and iodine number of BGACA<sub>HCl</sub> were 1170 kg/m<sup>3</sup>, 176 m<sup>2</sup>/g and 218 mg/g, respectively. It had a better performance than GAC fillers.

## Acknowledgement

This work was supported by a grant from the Ph.D. Programs Foundation of Ministry of Education of China (No. 20100131110005)

## References

- [1] J.C. Van Den Heuvel, H.H. Beertink, Kinetic effects of simultaneous inhibition by substrate and product, *Biotechnol. Bioeng.* 31 (1988) 718–723.
- [2] D.W. Holladay, C.W. Hancher, C.D. Scott, D.D. Chilcote, Biodegradation of phenolic waste liquors in stirred-tank, packed bed and fluidized-bed bioreactors, *J. Water Pollut. Control Fed.* 50 (1978) 2573–2578.
- [3] M. Denac, I.J. Dunn, Packed and fluidized bed biofilm reactor performance for anaerobic wastewater treatment, *Biotechnol. Bioeng.* 32 (1986) 159–173.
- [4] W.T. Tang, K. Wisecarver, L.S. Fan, Dynamics of a draft tube gas–liquid–solid FBBR for phenol degradation, *Chem. Eng. Sci.* 42 (1987) 2123–2134.
- [5] W.T. Tang, L.S. Fan, Steady state phenol degradation in a draft-tube fluidized bed bioreactor, *AIChE J.* 33 (1987) 239–249.
- [6] I. Karapinar, F. Kargi, Effect of particle number density on wastewater treatment performance of a fluidized bed bioreactor, *Enzyme Microb. Technol.* 19 (1996) 140–144.
- [7] R. Saravanane, D.V.S. Murthy, Application of anaerobic fluidized bed reactors in wastewater treatment: a review, *Environ. Manage. Health.* 11 (2000) 97–117.
- [8] D. Mowla, M. Ahmadi, Theoretical and experimental investigation of biodegradation of hydrocarbon polluted water in a three-phase fluidized-bed bioreactor with PVC biofilm support, *Biochem. Eng. J.* 36 (2007) 147–156.
- [9] A. Hirata, C. Takahashi, M. Arai, Biological treatment of coke-oven wastewater in three-phase fluidized bed, *Environ. Conservation Eng.* 20 (1991) 183–192.
- [10] A. Hirata, H.S. Lee, S. Tsuneda, T. Takai, Treatment of photographic processing wastewater using anaerobic–aerobic biofilm reactor, *Water Sci. Technol.* 36 (1997) 91–99.
- [11] W. Lin, S. Weber, Aerobic biological activated carbon (BAC) treatment of a phenolic wastewater, *Environ. Prog.* 11 (1991) 145–154.
- [12] R.M. Worden, T.L. Donaldson, Dynamics of a biological fixed film for phenol degradation in a fluidized bed bioreactor, *Biotechnol. Bioeng.* 30 (1987) 398–412.
- [13] K.D. Wisecarver, L.S. Fan, Biological phenol degradation in a gas–liquid fluidized bed reactor, *Biotechnol. Bioeng.* 33 (1989) 1029–1038.
- [14] R. Sowmeyan, G. Swaminathan, Evaluation of inverse anaerobic fluidized bed reactor for treating high strength organic wastewater, *Bioresour. Technol.* 99 (2008) 3877–3880.
- [15] N. Fernandez, S. Montalvo, L. Guerrero, E. Sanchez, I. Cortes, L. Travieso, Anaerobic fluidized bed reactor application to tropical fruit wine effluent, *Water Sci. Technol.* 56 (2007) 33–38.
- [16] P. Yu, Y. Luo, Novel water treatment process–combined cationic ion-exchange bed and degasifier in a three-phase fluidized bed, *Desalination* 151 (2002) 145–152.
- [17] I.M. Lima, W.E. Marshall, Granular activated carbons from broiler manure: physical chemical and adsorptive properties, *Bioresour. Technol.* 96 (2005) 699–706.
- [18] Arash Arami-Niya, Wan Mohd Ashri Wan Daud, Farouq S. Mjalli, Using granular activated carbon prepared from oil palm shell by ZnCl<sub>2</sub> and physical activation for methane adsorption, *J. Anal. Appl. Pyrolysis* 89 (2010) 197–203.
- [19] A. Aygun, S. Yeniso-Karakas, I. Duman, Production of granular activated carbon from fruit stones and nutshells and evaluation of their physical, chemical and adsorption properties, *Microporous Mesoporous Mater.* 66 (2003) 189–195.
- [20] Jin-Wha Kim, Myoung-Hoi Sohn, Dong-Su Kim, Seung-Man Sohn, Young-Shik Kwon, Production of granular activated carbon from waste walnut shell and its adsorption characteristics for Cu<sup>2+</sup> ion, *J. Hazard. Mater.* 30 (2001) 1–315.

- [21] A. Bagreev, T.J. Bandosz, Efficient hydrogen sulfide adsorbents obtained by pyrolysis of sewage sludge derived fertilizer modified with spent mineral oil, *Environ. Sci. Technol.* 38 (2004) 345–351.
- [22] N.R. Khalili, J.D. Vyas, W. Weangkaew, S.J. Westfall, S.J. Parulekar, R. Sherwood, Synthesis and characterization of activated carbon and bioactive adsorbent produced from paper mill sludge, *Sep. Purif. Technol.* 26 (2002) 295–305.
- [23] GB/T7702.7-2008, China, Test method for granular activated carbon from coal—Determination of iodine number.
- [24] S. Brodowski, W. Amelung, L. Haumaier, C. Abetz, W. Zech, Morphological and chemical properties of black carbon in physical soil fractions as revealed by scanning electron microscopy and energy-dispersive X-ray spectroscopy, *Geoderma* 128 (2005) 116–129.
- [25] A. Ros, M.A. Lillo-Rodenas, E. Fuente, M.A. Montes-Moran, M.J. Martin, A. Linares-Solano, High surface area materials prepared from sewage sludge-based precursors, *Chemosphere* 65 (2006) 132–140.
- [26] A. Ros, M.A. Lillo-Rodenas, C. Canals-Battle, E. Fuente, M.A. Montes-Moran, M.J. Martin, A. Linares-Solano, A new generation of sludge-based adsorbents for H<sub>2</sub>S abatement at room temperature, *Environ. Sci. Technol.* 41 (2007) 4375–4381.
- [27] K.B. Fitzmorris, I.M. Lima, W.E. Marshall, R.S. Reimers, Anion and cation removal from solution using activated carbons from municipal sludge and poultry manure, *J. Residuals Sci. Technol.* 3 (2006) 161–167.
- [28] K.M. Smith, G.D. Fowler, S. Pullket, N.J.D. Graham, Sewage sludge-based adsorbents: a review of their production, properties and use in water treatment applications, *Water Res.* 43 (2009) 2569–2594.
- [29] A. Bagreev, S. Bashkova, D.C. Locke, T.J. Bandosz, Sewage sludge-derived materials as efficient adsorbents for removal of hydrogen sulfide, *Environ. Sci. Technol.* 35 (2001) 1537–1543.
- [30] A. Bagreev, T.J. Bandosz, D.C. Locke, Pore structure and surface chemistry of adsorbents obtained by pyrolysis of sewage sludge-derived fertilizer, *Carbon* 39 (2001) 1971–1979.
- [31] A. Linares-Solano, I. Martín-Gullón, C. Salinas-Martínez de Lecea, B. Serrano-Talavera, Activated carbons from bituminous coal: effect of mineral matter content, *Fuel* 79 (2000) 635–643.
- [32] A. Bagreev, T.J. Bandosz, H<sub>2</sub>S adsorption/oxidation on materials obtained using sulfuric acid activation of sewage sludge-derived fertilizer, *J. Colloid Interface Sci.* 252 (2002) 88–194.
- [33] Z.H. Hu, M.P. Srinivasan, Y.M. Ni, Novel activation process for preparing highly microporous and mesoporous activated carbons, *Carbon* 39 (2001) 877–886.
- [34] A. Linares-Solano, I. Martín-Gullón, L.C. Salinas-Martínez, B. Serrano Talavera, Activated carbons from bituminous coal: effect of mineral matter content, *Fuel* 79 (2000) 635–643.
- [35] S.A. Linares, D. Salinas-Martínez de Lecea, I. Cazorla-Amorós, Martín-Gullón, Porosity development during CO<sub>2</sub> and steam activation in a fluidized bed reactor, *Energy Fuels* 14 (2000) 142–149.
- [36] F. Rodríguez-Reinoso, M. Molina-Sabio, M.T. González, The use of steam and CO<sub>2</sub> as activating agents in the preparation of activated, *Carbon* 33 (1995) 15–23.
- [37] M.F. Tennant, D.W. Mazyck, Steam pyrolysis activation of wood char for superior odorant removal, *Carbon* 41 (2003) 2195–2202.
- [38] M.S. Kuyukina, I.B. Ivshina, M.K. Serebrennikova, A.B. Krivorutchko, E.A. Podorozhko, R.V. Ivanov, V.I. Lozinsky, Petroleum-contaminated water treatment in a fluidized-bed bioreactor with immobilized *Rhodococcus* cells, *Int. Biodeterior. Biodegradation* 63 (2009) 427–432.
- [39] W. Xing, H.H. Ngo, W.S. Guo, A. Listowski, P. Cullum, Evaluation of an integrated sponge – granular activated carbon fluidized bed bioreactor for treating primary treated sewage effluent, *Bioresour. Technol.* 102 (2011) 5448–5453.