Research article

The porous structure effects of skeleton builders in sustainable sludge dewatering process

Xiaochun Zhang\textsuperscript{a}, Huashan Kang\textsuperscript{a}, Qingrui Zhang\textsuperscript{a,b,*}, Xiaoming Hao\textsuperscript{a}, Xin Han\textsuperscript{a}, Wen Zhang\textsuperscript{a}, Tifeng Jiao\textsuperscript{a,b}

\textsuperscript{a} School of Environmental and Chemical Engineering, Yanshan University, Qinhuangdao, 066004, PR China
\textsuperscript{b} State Key Laboratory of Metastable Materials Science and Technology, Yanshan University, Qinhuangdao, 066004, PR China

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\textbf{ABSTRACT}

Dewatering from sludge is an important sustainable issue in recent years, in this work, we found the unique behavior: Skeleton builder additions can improve the dewatering performance greatly, which related to the different pore structure of skeleton builder. As compared to the coal ash, sawdust and rice husk char are easier to construct porous channels in the sludge body, which is responsible for the discharge of water. The dewatering efficiency can increased from approximately 30\%–65\% by pipe network effect and interlayer channel effect, a sufficient amount of skeleton builders establish a complete pipe drainage network in the sludge body, allowing the water to be discharged fluently. Moreover, the skeleton builders can cause the sludge body to form a layered structure. Under the combined action of pipe network effect and interlayer channel effect, the deep-dewatering effect increased largely by the addition of skeleton builders.

1. Introduction

Environment and Energy aspects are two main topics in the world (Du et al., 2018; Zhou et al., 2018), but the waste disposal will become an important environmental issue recently. Domestic sewage treatment by bio-methods can produce a large amount of sewage sludge. The key issue of sludge treatment aims at reducing the moisture content efficiently (Ren et al., 2015; Skinner et al., 2015; Zhang et al., 2015). In order to facilitate the subsequent disposal and resource utilization, the general method of mechanical dehydration can reduce the moisture content of sludge to the level of approximately 80\%, which is far below the requirements of sludge treatment (Yang et al., 2015), and thus, a deep dehydration is necessary and required. Thermal drying and sludge conditioning as well as mechanical dehydration methods are commonly used in sludge deep dewatering process. However, high energy consumption and serious secondary pollution problems will significantly inhibit its efficient application (Mahmoud et al., 2016; Tang et al., 2018; Zhang et al., 2014); therefore, efficient approach is urgent and raised a wide-spread research interests.

As well known, sludge dewatering mainly contains two important procedures, that is solid-liquid separation at first, and the sequent extrusion for separation water from sludge (Christensen et al., 2015). Recent study shows that the surface adsorption water and internal hydration water can be converted into free-water by series sludge pretreatment (To et al., 2016), thence favoring for the solid-liquid separation. However, in fact, it is difficult to achieve the efficient deep dehydration, because the organic matter content of sludge floc will lead to a high compressibility, and the drainage channels in sludge body will be shut down by the high mechanical pressure during the squeeze process (Collard et al., 2017; Li et al., 2014a). Thus, a dense layer will form on the surface of the sludge body, and deep water separation cannot be discharged completely. Therefore, the use of chemical conditioning can only improve the sludge dewatering performance to some extent (Vega et al., 2015; Zhang et al., 2017c) However, because of the supporting effect of skeleton builder, the porous structure still exist in the sludge body under the great mechanical pressure, so the water can flow out of the sludge body easier. The commonly used skeleton builders by researchers are simple and easy available solid materials, such as powdered coal ash (Cieslik et al., 2015), lime (Hu et al., 2017), sawdust (Deng et al., 2017), wheat grits (Guo et al., 2015), gypsum (Nittami et al., 2015), red mud (Zhang et al., 2014), lignite (Hosdley et al., 2015), rice husk char (Wu et al., 2016b) and so on.

Liu et al. (2017) reported that the addition of sawdust could increase the sludge dewatering rate, and the degree of dewatering effect was also significantly improved with the doses additions. Luo et al. (2013) found that the sludge cake can convert relatively incompressible
after sawdust conditioning. Sawdust can maintain the permeability of sludge cake by resisting sludge compression during the squeezing process. The permeability of sludge is improved with the increase of sawdust mass ratios gradually. Jeffery et al. (2011) reported biochar has highly enriched carbon skeleton and the surface compared to the biomass material presented a more porous structure. Wu et al. used biochar as a skeleton builder to construct a porous structure in the sludge body, thereby improving the sludge dewatering effect (Wu et al., 2016a). When the amount of treated bio-char was 70% WS, the moisture content of the cake decreased from 76.9% to 70.3%. Powdered coal ash was also a mechanical mixture of various particles. The cool-down PCA mainly consisted of silica-alumina vitreous body and a small amount of carbon granules. The vitreum was constituted by single bead, linked head body and spongy irregular porous body (Qi et al., 2011). Chen et al. indicated that the addition of unmodified powdered coal ash or sulfuric acid modified powdered coal ash can effectively improve the centrifugal dehydration effect of sludge, but the effect of modified powdered coal was much better than unmodified powdered coal ash (Chen et al., 2010).

Numerous research results reflect that skeleton builder played an indispensable role on deep-dewatering of sludge (Li et al., 2014b; Liu et al., 2016; Nittami et al., 2015). Nowadays, most of research aims at the behaviors of skeleton builder conditioning, or the effect of adding skeleton builder on sludge dewatering performance (Vega et al., 2015). However, little is known that the channel structure effects of the skeleton builders on dehydration of sludge, it will be an important guideline to efficient deep dehydration in application.

In this work, three kind of commonly used skeleton builders, sawdust, rice husk carbon (RHC) and powdered coal ash (PCA) were investigated systematically. Series experiments, including the sludge conditioning by chemical agent, skeleton builders combined with chemical agent, as well as the corresponding dehydration effect tests were performed to prove the different sludge dewatering processes, i.e., solid-liquid separation process and water discharge process. Microcosm observation and analysis were carried out on the filter cake obtained in each of the above experiments and three kind of skeleton builders, in order to get the channel structure form in the sludge constructed by the skeleton builders. Then, contrasting with dehydration effect of different skeleton builders, function mechanism of skeleton builder for sludge dewatering was preliminary discussed in this paper.

2. Materials and methods

2.1. Materials

The pre-dewatered sewage sludge was obtained from Qinhuangdao third sewage treatment plant, and the moisture content was approximately 80%–85%. The three kinds of skeleton builders used in this experiment of sawdust, rice husk char (RHC) and powdered coal ash (PCA) was kindly provided by JIJIANG Water filters Co., China. The chemical conditioners used in this experiment were CTAB (analytic grade) and CPAM (analytic grade) respectively.

2.2. Experiment section

2.2.1. Chemical reagent condition and dehydration experiment

Two kinds of chemical conditioning agent were used in the experiments for conditioning. The dose of CTAB was 0 g, 0.9 g, 1.2 g, and 1.5 g, and the dose of CPAM was 0 g, 0.5 g, 0.65 g, and 0.75 g respectively. The above doses were well dissolved in 50 ml of deionized water with 200 g of sludge addition. Stirring for at least 15 min was necessary to ensure the reaction completely. Finally, the mixture was put into mechanical filter-press equipment and pressed for 20 min under 1.3 MPa.

2.2.2. The hybrid condition and dehydration experiment

In the previous section, the optimal amount of CTAB and CPAM can be obtained. The optimal amount of CTAB and CPAM was combined with sawdust, rice husk and powdered coal ash to perform joint conditioning and dehydration experiments. The dosage of the skeleton builders was 0 g, 5 g, 10 g, 15 g, 20 g, and 25 g respectively.

2.3. Analysis method

Specific surface area of RHC and PCA was measured using BET specific surface area analyzer (Model ASAP 2020) by N2-BET method. The particle size distribution of PCA was measured by BT-9300H type particle size distribution analyzer and that of sawdust was measured by Malvern laser particle size analyzer. In addition, the microscopic structure of cake and the micro-shape of skeleton builders were observed by Field Emission Scanning Electron Microscopy (FE-SEM).

Dewatering rate is defined as the ratio of the amount of the water lost before and after press exerting. Considering the moisture content of cake (After skeleton builder conditioning) is seriously affected by the moisture content of the skeleton builder and the amount of use, so it is difficult to examine the sludge dehydration effect, while dewatering rate is a suitable parameter for it with the following equations.

① The calculative equation of sludge dewatering rate of raw sludge and that conditioned by chemical conditioners alone was as follow:

\[ D = \frac{W_1 - W_2}{W_1} \times 100\% \]  

Where \( P_1 \) is assigned to the moisture content of the sludge before de-watering (%), \( W_1 \) is the amount of the sludge (g), \( W_2 \) is the amount of the filter cake (g), and D reflects the sludge dewatering rate (%).

② The calculative formula of sludge dewatering rate conditioned by skeleton builder alone and by chemical conditioners combined with skeleton builders was as follow:

\[ D = \frac{W_1 + W_2 - W_3}{W_1} \times 100\% \]  

Where \( W_3 \) is the quality of skeleton builder (g), others are the same as the above.

3. Results and discussion

3.1. The properties of the three kinds of skeleton builders

The moisture content, specific surface area, and pore distribution of sawdust, RHC and PCA had been determined with the results of Table 1 and Fig. 1. It can be found that the lowest moisture content is attached onto RHC with the value of 1.03%, comparatively, that of sawdust can obtain a highest value of approximately 5.52%. As for the surface areas, an ultrahigh surface areas of 489.6 m^2/g can be attached, which is equal to 30 times greater than PCA samples. Whereas the pore size of

<table>
<thead>
<tr>
<th>Moisture content (%)</th>
<th>BET specific surface area (m^2/g)</th>
<th>Average pore size (nm)</th>
<th>Pore volume (cm^3/g)</th>
<th>Particle size D50 (µm)</th>
<th>Particle size D90 (µm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sawdust</td>
<td>5.52 ± 0.2</td>
<td>-</td>
<td>-</td>
<td>689.8</td>
<td>1250.4</td>
</tr>
<tr>
<td>RHC</td>
<td>1.03 ± 0.2</td>
<td>489.6</td>
<td>4.21</td>
<td>0.663</td>
<td>408.7</td>
</tr>
<tr>
<td>PCA</td>
<td>2.76 ± 0.3</td>
<td>16.7</td>
<td>8.41</td>
<td>0.0263</td>
<td>38.1</td>
</tr>
</tbody>
</table>

* The definitions of D 50 and D 90 have been added in supporting information.
Fig. 1. Pore size distribution of the skeleton builders. (A) PCA (B) RHC (C) Sawdust.

Fig. 2. SEM images of the given skeleton builders. (A) and (B) sawdust, (C) RHC, (D) PCA.
PCA as was twice as that of RHC, the pore volume of RHC was around 25 times of PCA. Such results suggest that the abundant pore might be obtained onto RHC as compared to the PCA, thus, the RHC is possibly responsible for sludge dewatering. It is noted that the specific surface area, pore size and pore volume of sawdust cannot be determined, due to the limit of the measure method. However, it can be observed by SEM analysis of Fig. 2A and B, it is found that the sawdust contained architectural pore structures with size of tens micrometers gap and 2-5 μm pores. The larger holes were conducive to the discharge of water, suggesting from the particle size distribution (Fig. 1), the particle size of sawdust was slightly larger than that of rice husk char, and the size of sawdust and RHC was about as 10 times as PCA. It also could be seen from Fig. 2A and B that the surface of the sawdust exhibited a large number of striped shape rugged ditch (Su et al., 2018). The surface of RHC (Fig. 2C) also had a rough structure as the rice husk itself. The particle size and pore size of PCA (Fig. 2D) were very small, and its surface was smoother than sawdust and rice husk char.

According to the different properties of the three skeleton builders, it can be found that sawdust and rice husk char are easier to construct porous channels in the sludge body, which is responsible for the discharge of water.

### 3.2. Sludge dewatering experiment conditioned by chemical conditioners

Fig. 3 showed the experimental results of sludge dewatering conditioned by CTAB and CPAM respectively. The same letters suggest the slight differences, while the different letters imply significant variation. It reflects that both CPAM and CTAB can achieve efficient performances in sludge water separation.

Comparatively, it can be seen that the dewatering rate conditioned by CTAB (Fig. 3A) exhibits a gradual improving with dose addition and the maximum dewatering rate (27.5%) can be attached at dose of 0.6 g, while the dehydration effect works still poorly. Thus, CTAB is responsible for separating the water from the sludge particles, but it is difficult to discharge the separated water fluently. The dewatering effect of the sludge conditioned by CPAM (Fig. 3B) also exhibits similar tendency. Comparing with the untreated sludge, the dewatering rate can be slightly elevated to approximately 31.24%, but this dewatering rate conditioned by CPAM was still low, and different CPAM dosage were also exert an insignificant variations. SEM observation (Fig. 4) also get further insights into this point, it is shown that CPAM conditioning can lead to a larger floe formation, while CTAB conditioning will bring about some crushed surfaces. However, it was difficult to find significant water exhausted pores and pipes (Wang et al., 2018; Zhang et al., 2017b).

Therefore, both CPAM and CTAB conditioning cannot significantly improve the dewatering effect of sludge. It is mainly ascribed to the high concentrations of organic matters within sludge, thus, the possible deformation occurs during compression and the corresponding drainage pores of sludge was significantly blocked. Liu et al. (2017) also found that the surfaces of raw sludge cakes were dense, and it turned to be smooth when conditioned by CPAM. Simultaneously, the pore channels of surface were also closed completely. On this account, the separating water cannot flow out fluently and the moisture contents of the sludge was still high.

### 3.3. Sludge dewatering experiment conditioned by the combination of chemical conditioners and skeleton builders

According to the results of chemical conditioning treatment, the optimal doses of CTAB (1.2 g, 0.6%) and CPAM (0.75 g, 0.38%) with three skeletal builders were also selected to combine conditioning dehydration experiment. As depicted in Fig. 5, as compared to the chemical conditioning, the sludge dewatering rate was significantly improved using the combined conditioning treatment, it suggests that the skeleton builder additions exert an important roles for dewatering. Taking RHC sample for an example, the dewatering rate of CTAB conditioning can be increased from 25.2% to approximately 58.5%, while the dewatering rate of CPAM conditioning was also improved from 31.8% to around 68.3%. Similar phenomenon is also observed for other skeleton builder additions.

In addition, we also observe some interesting results with skeleton builder additions. Specifically, as for sawdust or RHC addition with low doses (below 2.5% WS), a slight variation onto dewatering rate is attached, sequentially, a fast dewatering is achieved between 2.5% and 7.5% WS amount of skeletal builder, finally, a saturated dewatering rate is obtained at 7.5%-12.5%WS. It is noteworthy that the low dewatering effects at trace level of dosage can be ascribed to the following reasons, that is the amount of the skeleton builder is trivial and, thus, the volume occupied in the sludge body is not enough, which lead to the difficulty in forming a pipe channel connected to each other in the sludge body. In this way, the separated water cannot be discharged rapidly with poor dehydration. As for the 2.5%–7.5% WS ranging, the dewatering rates increased remarkably, suggesting threshold values of the skeleton builder addition. It can form a complete drainage pipe network in the sludge body, further achieving the efficient dewatering. Whereas, when the dosages are greater than 7.5% WS, the sludge dewatering rates approach the maximum and converts to stability. It can be ascribed to the saturated sawdust and RHC additions, besides, the low moisture content of the sawdust and RCH can also cause the possible water adsorption partly in pressure.

In addition, PCA samples also display a similar trend. the maximum dewatering rate can be attached at 12.5% WS, the a prolong dose additions can be ascribed to the different pore structures. Specifically, the
number of pores in PAC particles was lacking, and the pore volume was less than 1/30 of the RHC. Thus, the high dose of PAC is required to discharge the separated water for pore channels needing. Therefore, the added skeleton builder is responsible for discharged water by the sufficient pore channels in sludge body. The dewatering rates are related to the pore structure and volumes. The abundant pore structure will favor for the dewater discharge. Similar results was also found by Ning's work, the TSIS particles as skeleton builder may contain many channels or voids and the particle surfaces are irregular. The fine sludge particles were incorporated into these channels or voids in the TSIS particles during mixing with the sludge. The reduction of the fine particles in the sludge improved dewatering (Ning et al., 2013).

Based on the above analysis, it is believed that Increasing the amount of skeleton builder (from 2.5% WS to 7.5% WS), the corresponding dewatering rate increased gradually, but it is not linearly related. When the amount of skeleton builder exceeds a certain amount (> 7.5% WS), the dewatering rate no longer increases, indicating that the internal drainage channel of the sludge has been constructed when the amount of the skeleton builder reaches 7.5% WS. A small number of skeleton builders are not connected to each other, thus, it is difficult to form drainage channels in the sludge body. Only a sufficient number of skeleton builders are connected to each other to form a drainage channel in the sludge body and form a pipe network.

The different morphologies (Fig. 6A–C) were also obtained by SEM observation; abundant porous structures of cross-section of the sludge cake were obtained through sawdust or RHC addition, which can produce a great number of pipes for dewatering discharge. Sawdust or rice husk stacked together with each other. Also the gap between them could form a large number of channels (Zhang et al., 2017a, 2018). Water could be discharged fluently along these pipes and channels. Similar results were also proved by Liu's work (Liu et al., 2017). In addition, Fig. 6D shows the cross-section of the sludge cake with PAC addition. Obviously, the dense structure reveals little pores and visible gaps. Therefore, the sludge cake with different skeleton building addition can exhibit a uniform layer or porous structure, which favors for the dewatering effect by the formation of channels between the layers and water interface of the sludge.

### 3.4. The mode of the skeleton builder working

Comparing the sludge dewatering rate before and after the skeleton builder addition (Fig. 7A–B), it can be seen that skeleton builder can significantly improve sludge dewatering. In addition, by microstructure observation (Fig. 2A and C), the role of skeleton builder for dewatering can be ascribed to two aspects: pipe network effect and interlayer channel effect. Next, a pipe pattern chart for sawdust and RHC is constructed. As depicted in Fig. 7A, the structure of sawdust or RHC can be regarded as a pipe-like mechanism, which is called skeleton builder pipe (SBP), with porous structure, and strip grooves along the axial on outer surface. In addition, the strip grooves on the surface of two adjacent SBP can also integrate as a water channel (Fig. 7B).

As the previous results of Fig. 5, It also suggest that the negligible dewatering effect was always detected under low dosages of the skeleton builder, while, it can be well improved by increasing doses. That is similar to some individual or dispersed SBP with low dewatering, and water pipes must be connected each other for networks formation to achieve the water delivery. Specifically, a small amount of SBP cannot form an interconnected pipe network within the sludge body and the drainage channel was still obstructed. Comparatively, the large doses addition suggests an outstanding pipe network construction, which can attach fast dewatering in sludge (Fig. 7C).

In addition, we can also obtain a layered structure of sludge cake with skeleton builders hybridization, resulting from the efficient sludge dewatering process. Especially, the sludge was exerted a high static...
pressure during dehydration, and the internal water was well discharged with a reducing volume and density increase (denoted as compaction). In this process, the colloid particles or solid matter will adhere to the skeleton builders, which is called as cementation. Therefore, compaction cooperated with cementation effects favor for the relatively hard filter cake formation and dewatering. During the dehydration, it is usually a gradual process, while in this work, skeleton builder addition can provide a fluent drainage channels, resulting in a fast rate of dehydration. As for the layered sludge cake, at the beginning, a cake layer with low moisture content formed; then, the water
near to this layer flowed out of the sludge for the second layer formation. Finally the interlayered water was removed and the entire cake can exhibit a multi-layer structure (Fig. S1). While, without adding the skeleton builder, the dehydration process of the sludge body was slow, the filter cake would not form a clear layered structure. Under the combined effect of pipe network effect and interlayer channel effect, the addition of skeleton builders significantly improved the dewatering effect of sludge.

4. Conclusion

In this work, we found that the addition of skeleton builders can significantly improve the dewatering effect of sludge. The sludge dewatering effect of sawdust or RHC was much better than that of PCA. These differences were related to their own properties, such as pore volume, average pore size, surface morphology, at low dose (< 2.5%) of skeleton builder addition, negligible dewatering can be achieved, while higher doses can construct the microstructure with sludge and form a fast water discharging. Especially, the fast dewatering process can also form a layered structure of sludge cake, which further favors the interior water discharging. Pipe network and interlayer channel effects can well explain the improved dewatering of sludge.

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Appendix A. Supplementary data

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References