Bioresource Technology 205 (2016) 258–263

Contents lists available at ScienceDirect

Bioresource Technology

journal homepage: www.elsevier.com/locate/biortech

Short Communication

Possibility of sludge conditioning and dewatering with rice husk biochar modified by ferric chloride

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HIGHLIGHTS

- Positive charge from MRB–Fe surface counteracted negative charge of sludge flocs.
- MRB–Fe effectively improved sewage sludge dewaterability as a skeleton builder.
- Incompressible and permeable sludge cakes were formed through adding MRB–Fe.

ARTICLE INFO

Article history:
Received 9 November 2015
Received in revised form 9 January 2016
Accepted 11 January 2016
Available online 19 January 2016

Keywords:
Modified rice husk biochar by $FeCl_3$ (MRB–Fe)
Sludge dewaterability
Charge neutralization
Incompressibility
Permeability

ABSTRACT

Rice husk biochar modified by $FeCl_3$ (MRB–Fe) was used to enhance sludge dewaterability in this study. MRB–Fe preparation conditions and dosage were optimized. Mechanisms of MRB–Fe improving sludge dewaterability were investigated. The optimal modification conditions were: $FeCl_3$ concentration, 3 mol/L; ultrasound time, 1 h. The optimal MRB–Fe dosage was 60% DS. Compared with raw sludge, the sludge specific resistance to filtration (SRF) decreased by 97.9%, the moisture content of sludge cake decreased from 96.7% to 77.9% for 6 min dewatering through vacuum filtration under 0.03 MPa, the SV_{30}% decreased from 96% to 60%, and the net sludge solids yield (Y_N) increased by 28 times. Positive charge from iron species on MRB–Fe surface counteracted negative charge of sludge flocs to promote sludge settleability and dewaterability. Meanwhile, MRB–Fe kept a certain skeleton structure in sludge cake, making the moisture pass through easily. Using MRB–Fe, therefore, for sludge conditioning and dewatering is promising.

1. Introduction

With the increasing of wastewater generation and wastewater treatment efficiency, the growth rate of sewage sludge, which containing over 90% water, is going up. Sewage sludge management is a challenging issue for water industries (Thapa et al., 2009a). Sludge conditioning and dewatering is the paramount important step in the sludge treatment (He et al., 2015; Zhang et al., 2012). Chemical conditioning, such as adding ferric chloride cationic, polyacrylamide and so on to improve sludge dewatering, is commonly used in wastewater treatment plants (Chen et al., 2015). It is noted that chemical addition could enhance sludge dewaterability in certain extent. But due to the high compressibility of sludge with chemical conditioning, the sludge dewatering rate was hindered by the blinding of filtration media and the filter cake (Qi et al., 2011).

In order to decrease the sludge compressibility, physical conditioners used as skeleton builders were investigated. Gypsum, lignite, slag and construction and demolition waste were also used for sludge condition and dewatering (Asakura et al., 2009; Thapa et al., 2009a,b; Zhao, 2002). In these researches, permeable and more rigid lattice structures were formed and the sludge cakes maintained permeable during the compressed filtration, leading to improvement of sludge dewaterability. But adding physical conditioners had little impact on enhancing the sludge dewaterability unless using in together with chemical conditioners (thus it was complicated to find the optimum combination dosing) or using large amounts of physical conditioners (which would greatly increase the sludge solids). Therefore, physical conditioners modification was investigated. Chen et al. (2010) proved that coal fly ash modified by sulfuric acid had much stronger capacity for sludge

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http://dx.doi.org/10.1016/j.biortech.2016.01.020
0960-8524/

dewatering than raw coal fly ash, and the dosage of coal fly ash modified by sulfuric acid was much less than raw coal fly ash.

In our preliminary study, rice husk biochar was used to improve sludge dewaterability with adding ferric chloride ($FeCl_3$). The specific resistance to filtration (SRF) of sludge decreased by 93.14% and the net sludge solids yield (Y_N) increased by 4.46 times compared with the raw sludge. But the influence of adding rice husk biochar alone in sludge dewaterability was not obvious. Several methods, such as acid and alkali modification, and chemical graft, have been used to modify biochars to enhance biochars adsorption performance for wastewater treatment (Fierro et al., 2009; Jing et al., 2014; Liu et al., 2011; Ma et al., 2014). There is little information on the possibility of modified biochars for sludge dewatering. The challenge of this study is to modify the rice husk biochar by $FeCl_3$ to enhance rice husk biochar capacity for sludge dewatering.

In this paper, the optimal preparation method of rice husk biochar modified by $FeCl_3$ (MRB–Fe) and the possibility of improving sewage sludge dewaterability and settleability with MRB–Fe as skeleton builders were explored. The dosage of MRB–Fe for sludge dewatering was optimized. The changes of zeta potential, the characteristics of raw rice husk biochar (raw RB) and modified rice husk biochar (MRB–Fe), and the microstructure of sludge cakes were investigated to analyze the mechanisms.

2. Methods

2.1. Materials

Sewage sludge was obtained from the sludge thickening tank of a local municipal wastewater treatment plant (WWTP) in Changsha, Hunan, China. A modified oxidation ditch process was used in this WWTP. The sewage sludge was transported to laboratory in an airtight polythene cask and was stored at 4 °C before used. When experiments were carried out, the sewage sludge was firstly kept in a water bath at 20 °C for 30 min (Chen et al., 2010). The main sludge characteristics were: moisture content of 98.4%–98.8%, dry solid (DS) content of 12.05–16.25 g/L, SRF of 1.04×10^{13}–5.13×10^{13} m/kg, Y_N of 0.62–0.98 kg/(m^2·h).

2.2. Preparation of MRB–Fe

Raw rice husk biochar (RB) (80–250 μm) was prepared in an airtight crucible with limited supply of air at 500 °C for 2 h in a muffle furnace which was the optimal preparation condition in preliminary study. $FeCl_3$ with a concentration of 1, 2 and 3 mol/L was used for rice husk biochar modifying respectively. The rice husk biochar of 10 g was firstly soaked in 500 ml of hydrochloric acid (1 mol/L) for 24 h, after which the rice husk biochar was filtered, cleaned and dried in the oven. Then the rice husk biochar, which was soaked in $FeCl_3$ solution (solid–liquid ratio is 1:10), was placed into an ultrasonic cleaner (KQ2200V) at 30 °C for 0.5, 1 and 1.5 h, respectively. Lastly, the rice husk biochar was filtered and dried in the oven and milled. The particle size of MRB–Fe was distributed within a range of 80–250 μm.

2.3. Sludge conditioning and dewatering

MRB–Fe was added into 200 ml sewage sludge. After mixing at rapid agitation (350 r/min, 30 s), followed by slow agitation (40 r/min, 3 min), 100 ml of the conditioned sludge was poured into a 100 ml measuring cylinder and settled for 30 min to measure the sludge settleability. The sludge settleability was evaluated with SV_{30}%. And 100 ml of the conditioned sludge was put into a 9 cm Buchner funnel under a pressure of 0.03 MPa for sludge dewaterability analysis. The sludge dewaterability was evaluated with SRF, Y_N and moisture content of sludge cake. After the sludge filtration, a sludge cake was formed. The microstructure and coefficient of compressibility of sludge cakes, and zeta potential of sludge supernatant were tested to verify the conditioning mechanisms. Each experiment was repeated twice or more, and the average value was used to evaluate the performance of sludge conditioning and dewatering.

2.4. Analytical methods

A standard Buchner funnel test apparatus with a 9 cm Buchner funnel and qualitative filter paper was used for SRF determination (Chen et al., 2010). The sludge solids obviously increase with the addition of MRB–Fe in this study, so the sludge dewaterability should not be evaluated only with SRF. Relative effectiveness of sludge conditioners could be better evaluated with Y_N, when the sludge solid increased. The Y_N expresses the amount of sludge solids filtered per unit area and unit time, and was also used to evaluate the sludge filterability in this study (Rebhun et al., 1989). And the Y_N was calculated according to Rebhun et al. (1989).

The sludge cake was harvested after 6 min for dewatering through vacuum filtration, and dried to constant weight at 105 °C to measure solid content of sludge cake. The moisture content of sludge cake was measured by gravimetric method. SV_{30}% was measured by volumetric method. The MRB–Fe and raw RB were characterized by ESEM (Quanta 200, America) and EDS (EDAX genesis xm-2, USA). The Zeta potential was analyzed by Zetasizer Nano analyzer (ZEN3600, England). The microstructure of sludge cakes was characterized with the ESEM. The coefficient of compressibility of sludge cakes was measured according to Qi et al. (2011).

3. Results and discussion

3.1. Optimization of MRB–Fe preparation condition

Fig. A.1 shows the effect of MRB–Fe preparation condition on sludge dewatering. The MRB–Fe dosage was 30% DS (300 g rice husk flour was added to each 1 kg sludge DS). Raw sludge and the same dosage raw RB were used as controls. Lower SRF and higher Y_N indicated higher sludge dewaterability (Chen et al., 2010). Fig. A.1 shows that the dewaterability of sludge conditioned with MRB–Fe was significantly superior to that of raw sludge or sludge conditioned with raw RB. And the lowest SRF and the highest Y_N were reached with a $FeCl_3$ concentration of 3 mol/L and an ultrasound time of 1 h. The sludge SRF decreased from 10.40×10^{12} m/kg to 1.13×10^{12} m/kg and the Y_N increased from 0.98 kg/(m^2·h) to 14.56 kg/(m^2·h), compared with raw sludge. The iron content increased with the increase of $FeCl_3$ concentration. Ultrasound of a suitable time could benefit iron species covering on the MRB–Fe surface (Chen et al., 2014). The sewage sludge could be flocculated by iron species to improve its dewaterability (Chen et al., 2015).

3.2. Effect of MRB–Fe dosage

The sludge was conditioned with MRB–Fe (prepared with a $FeCl_3$ concentration of 3 mol/L and an ultrasound time of 1 h). Fig. 1 indicates the effect of MRB–Fe dosage on sludge dewatering and settling. By contrast, the effect of raw RB dosage on sludge dewatering was also performed. Lower SV_{30}% value indicated higher sludge settleability (Chen et al., 2010). When the MRB–Fe was used, the sludge SRF, moisture content of sludge cake and SV_{30}% decreased with the increase of MRB–Fe dosage. The sludge Y_N increased with the increase of MRB–Fe dosage, and the highest

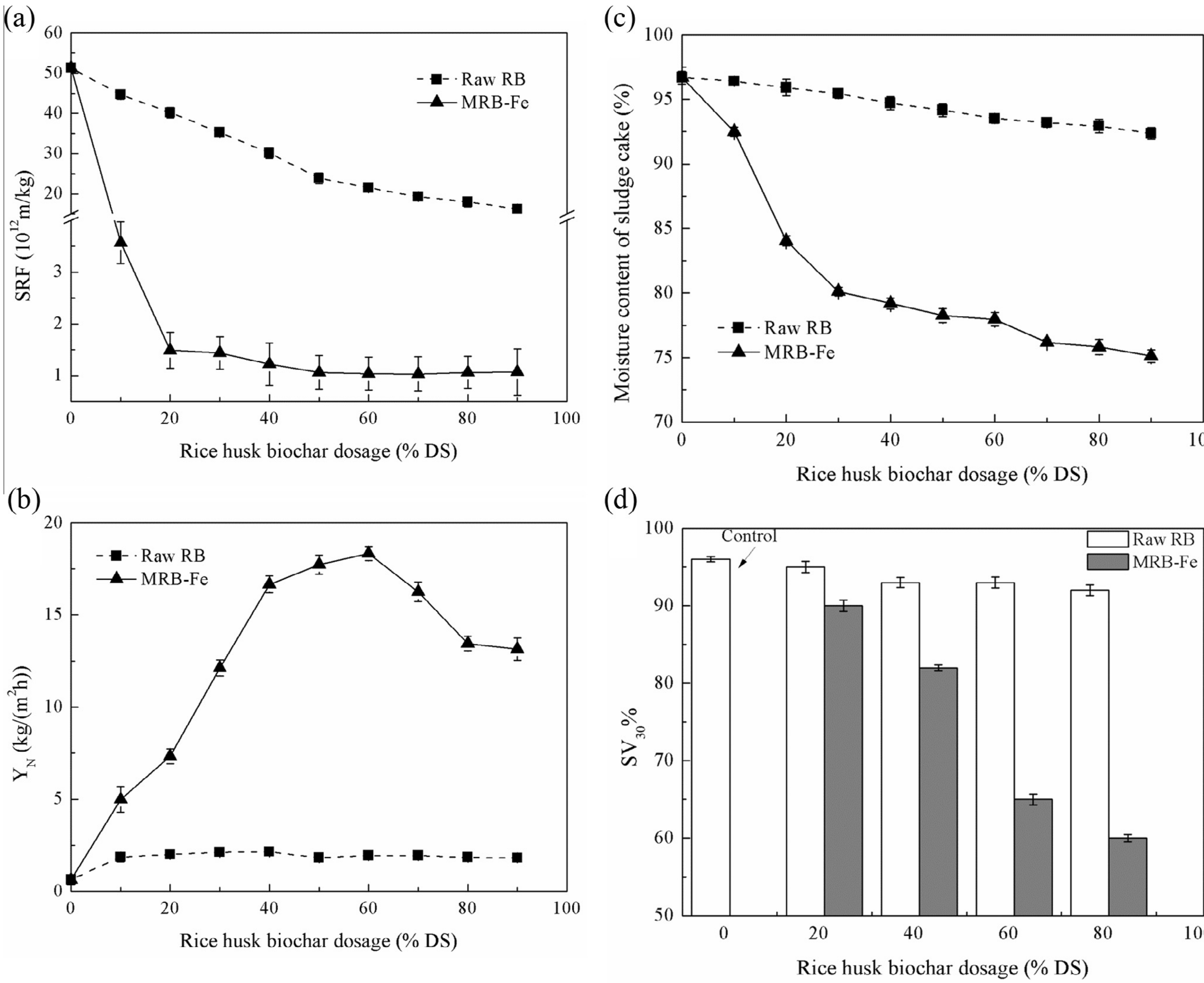


Fig. 1. Effect of rice husk biochar dosage on sludge dewatering. (a) SRF, (b) Y_N, (c) moisture content of sludge cake, (d) sludge settleability.

Y_N of 18.33 kg/(m^2·h) was reached with a MRB–Fe dosage of 60% DS; when the MRB–Fe dosage was more than 60% DS, the sludge Y_N decreased again. Therefore, the optimal MRB–Fe dosage was 60% DS. Compared with raw sludge, when adding the optimal dosage of raw RB (40% DS), the sludge SRF decreased by 41.1%, the moisture content of sludge cake decreased from 96.69% to 94.70%, the SV_{30}% decreased from 96% to 93% and the Y_N increased by 2.4 times. When adding the optimal dosage of MRB–Fe (60% DS), the sludge SRF decreased by 97.9%, the moisture content of sludge cake decreased from 96.69% to 77.97%, the SV_{30}% decreased from 96% to 60% and the Y_N increased by 28 times. These results indicated that the dewaterability and settleability of sludge conditioned with MRB–Fe were obviously superior to that of sludge conditioned with raw RB. Additionally, it is reported that the sludge SRF decreased by 97.7% when adding modified coal fly ash (273% DS), compared with the raw sludge (Chen et al., 2010). Therefore, using MRB–Fe to enhance the sludge dewaterability is significant.

Fig. A.2a shows the microstructures of raw RB and MRB–Fe. The RB soaked in HCl solution was also analyzed as a control because the surface of raw RB was cleaned by HCl solution before modification. There are several tiny particles covering the raw RB surface; after being soaked in HCl solution, the small particles disappeared; after modification with $FeCl_3$ the surface of MRB–Fe was covered by large amount of particles again. Table A.1 indicates that the iron content of MRB–Fe was the most. These iron species on the surface of MRB–Fe could enhance sludge dewaterability and settleability effectively (Chen et al., 2015).

3.3. Possible mechanisms of sludge conditioning with MRB–Fe

The potential stability of sludge colloidal system can be indicated by zeta potential (Lv et al., 2014). Fig. 2a shows the effect of MRB–Fe dosage on zeta potential of sludge supernatant. The zeta potential of raw sludge was −12.1 mV. So the sludge particles excluded each other because of electrostatic interaction and formed a relatively stable system to cause poor settling and dewatering performance of raw sludge (Chen et al., 2010). When MRB–Fe was added, the zeta potential of sludge increased with the increase of MRB–Fe dosages. With the optimal MRB–Fe dosage of 60% DS, the zeta potential of sludge supernatant increased to −1.53 mV. The zeta potential of MRB–Fe suspension (60% DS) was 8.28 mV. While the zeta potential of raw RB (60% DS) was −14.7 mV. The positive charge came from the iron species covering on the MRB–Fe surface. The settleability and dewaterability of sludge were improved because that the stability of sludge colloidal system was destroyed by charge neutralization and the sludge particles congregated with each other. It was also the reason why adding MRB–Fe was superior to adding raw RB for sludge conditioning and dewatering.

The microstructure of sludge cakes was tested by ESEM (as shown in Fig. A.2b). Both the surface and longitudinal section of raw sludge cake showed typically compact and less porous. However, large cracks were found on both the surface and longitudinal section of sludge cake conditioned with MRB–Fe (60% DS). These images indicate that the MRB–Fe played a supportive role in the sludge cake. Fig. 2b showed the change of coefficient of compressibility of sludge cakes. The coefficient of compressibility of raw sludge cake was 1.50, which meant that the high compressibility of sludge hindered the sludge dewatering rate during the filtration stage, and the moisture passed through the sludge cakes became harder and harder. When the MRB–Fe (60% DS) was added, the coefficient of compressibility of sludge cake decreased to 0.86. It meant that the sludge cake could keep a certain skeleton structure and permeability during the filtration stage. So the sludge moisture could be removed out of the sludge cake easily. Therefore, the MRB–Fe improved the sludge dewaterability through changing the sludge microstructures as a skeleton builder.

4. Conclusions

MRB–Fe, prepared from RB modified by $FeCl_3$ solution (3 mol/L) for 1 h, effectively enhanced sludge dewaterability as a skeleton builder. The optimal MRB–Fe dosage was 60% DS. Compared with raw sludge, the sludge SRF decreased by 97.9%, the moisture content of sludge cake decreased by 19.36%, the SV_{30}% decreased by 37.5% and the Y_N increased by 28 times. The positive charge from iron species on MRB–Fe surface could counteract the negative charge of sludge particles to promote sludge settleability and dewaterability. Adding MRB–Fe improved incompressibility and permeability of sludge cakes, so the sludge moisture passed through sludge cakes easily.

Acknowledgements

This research was funded by the National Natural Science Foundation of China (51178047) and Furong Scholar of Hunan Province.

Appendix A

See Figs. A.1, A.2 and Table A.1.

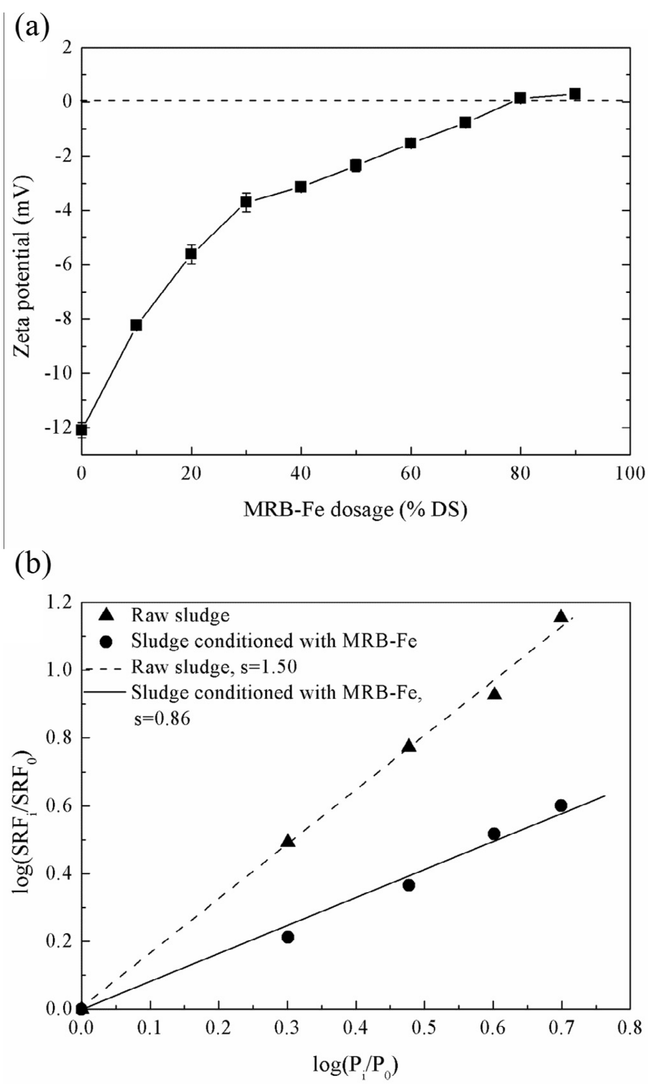


Fig. 2. Change of sludge characteristics. (a) Zeta potential of sludge supernatant, (b) coefficient of compressibility of sludge cakes (MRB–Fe dosage of 60% DS).

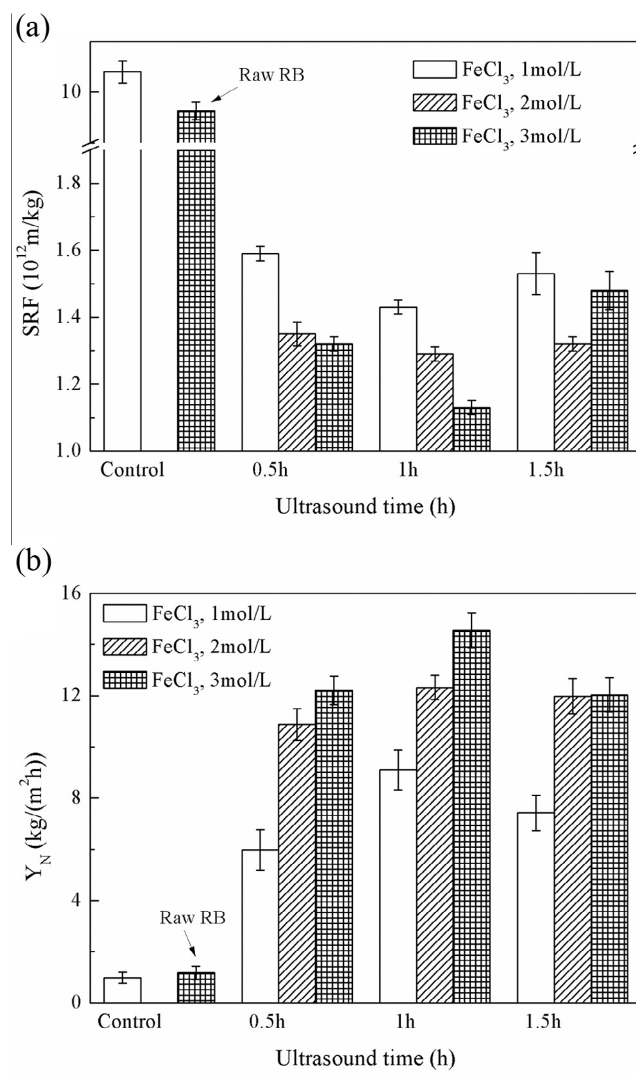
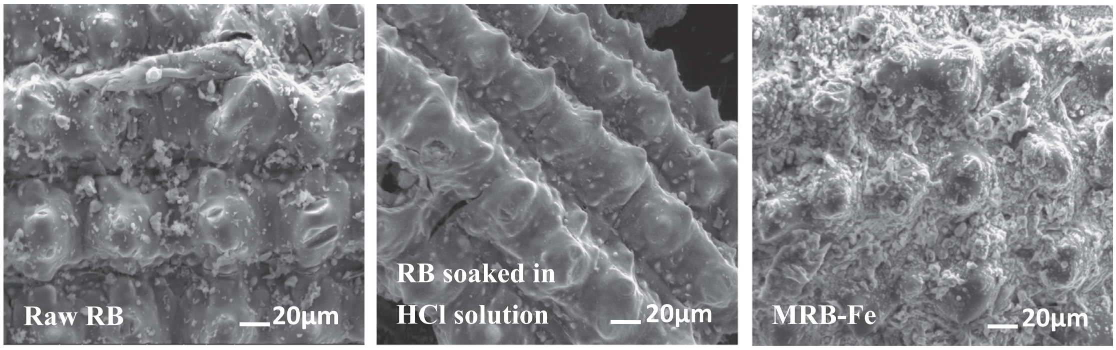
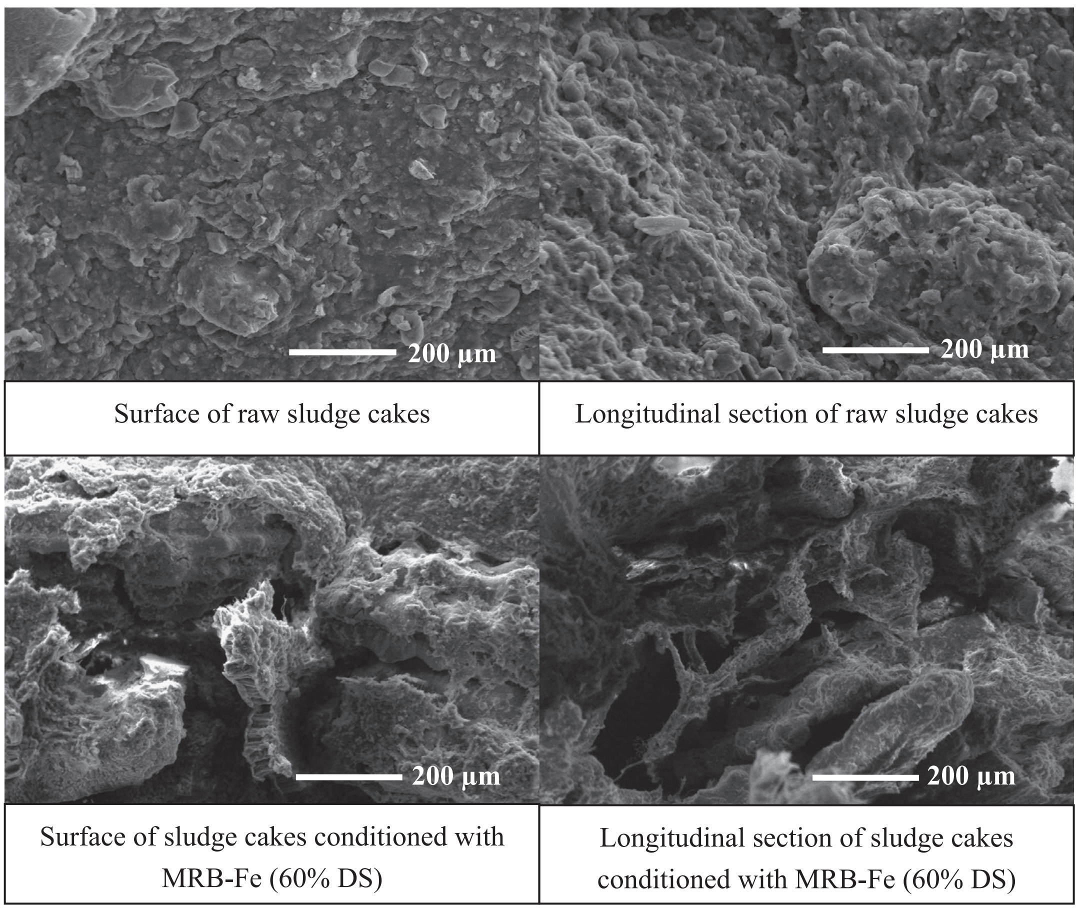


Fig. A.1. Effect of MRB–Fe preparation conditions on sludge filtration dewatering. (MRB–Fe dosage of 30% DS) (a) SRF, (b) Y_N (raw sludge was set as a control).



(a)



(b)

Fig. A.2. Microstructures tested by ESEM. (a) Rice husk biochar, (b) sludge cakes ($FeCl_3$ concentration of 3 mol/L, ultrasound time of 1 h, HCl concentration of 1 mol/L) (MRB–Fe dosage of 60% DS).

Table A.1
Element content of different rice husk biochars tested by EDS (Wt%).

Element	Raw RB	RB soaked in HCl solution	MRB–Fe
C	26.97	26.82	14.84
O	41.69	42.37	27.56
Si	30.84	30.03	17.90
Cl	0.11	0.43	15.46
Fe	0.38	0.35	24.24

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