

# Preparation of a New Granular Acid-Activated Neutralized Red Mud and Evaluation of Its Performance for Phosphate Adsorption

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**(5)** Supporting Information

**ABSTRACT:** A new granular acid-activated neutralized red mud (AaN-RM) was successfully prepared with powdered AaN-RM, powdered straw, and hydroxypropyl methylcellulose (HPMC) for effective phosphate adsorption. The maximum phosphate adsorption capacity of granular AaN-RM reached 86.69 mg/g, which was much higher than that previously reported. Its excellent phosphate adsorption capacity was mainly attributed to high specific surface area caused by complex mineralogy of iron and aluminum and addition of powdered straw. The mass ratio of different ingredients, sintering temperature, and time affected the characteristics of granular AaN-RM greatly. When the mass ratio of powdered straw increased from zero to 33%, the total



pore volume of granular AaN-RM increased from 0.0056 to 0.0375 cm<sup>3</sup>/g; however, the effective chemical compositions reduced when the addition of powdered straw was too high. With increasing the sintering temperature and time, the polymerizability of granular AaN-RM was significantly improved, but a too high sintering temperature and too long sintering time resulted in the conversion of part FeCl<sub>3</sub>·2H<sub>2</sub>O to FeOCl and FeCl<sub>2</sub> and part Al(OH)<sub>3</sub> to Al<sub>2</sub>O<sub>3</sub>, leading to a weaker attraction for phosphate. The optimal mass ratio of powdered AaN-RM, powdered straw, and HPMC was 71:22:7; the sintering temperature and time were 225 °C and 30 min, respectively.

KEYWORDS: Red mud, Granule adsorbent, Mass ratio, Sintering temperature, Sintering time

# INTRODUCTION

Red mud, a solid waste residue formed after the caustic digestion of bauxite ores during alumina production, is highly alkaline (pH 10–13) owing to its large content of sodium hydroxide.<sup>1</sup> The amount of red mud ranges from 0.3 to more than two tons per ton of alumina production, and the global production of red mud is about 120 million tons per year.<sup>2</sup> Consequently, the management of these large quantities of red mud is a major problem. At present, most of the red mud is disposed by landfill, which may pose a huge impact on the environment, including polluting the water and soil and decreasing the useful land area.<sup>3</sup> Therefore, developing novel technologies for red mud disposal and reuse is necessary. Attractive research is to maximize the utilization of red mud for environmental remediation in order to achieve the purpose of treating wastes with wastes.<sup>4</sup>

Various attempts have been tried on the application of red mud as a coagulant, adsorbent, and catalyst.<sup>5,6</sup> Red mud has shown great potential for adsorbing phosphate. The phosphate adsorption capacity depended on the source and activation method of red mud.<sup>7</sup> Akhurst et al. developed a seawater-

activated red mud (Bauxsol), and its phosphate adsorption capacity reached 45.6 mg/g.<sup>8</sup> Li et al. and Huang et al. investigated the effects of acid treatment combined with heat treatment on the adsorptive behavior of red mud and found that all activated red mud samples had higher phosphate adsorption capacities as compared to untreated red mud.<sup>9,10</sup> However, these activated red muds are not suitable for industrial application because the powdered form of them often causes serious problems, like pore clogging, high pressure drop, and mass loss during operation. In addition, the separation of powder adsorbents is difficult.<sup>11</sup> These problems may result in the limitation of reactor configuration and an increase in cost.<sup>12</sup> Thus, it is better to stabilize, fix, and granulate the powdered red mud for practical adsorption processes.

To date, limited researches have been performed on granulation of red mud for phosphate removal and recovery.

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Despland et al. developed porous cement-bound pellets with Bauxsol to remove nutrients from municipal wastewater, and the total phosphorus adsorption capacity was 7.3 mg/g.<sup>13,14</sup> Yue et al. employed dewatered red mud (waste residue from alumina production with sintering process) as raw material to prepare granular red mud adsorbent, and the phosphate adsorption capacity was lower than 10 mg/g.<sup>15</sup> In order to improve the phosphate adsorption performance, novel granular red mud adsorbents should be developed with special structure and surface properties.

Powdered acid-activated neutralized red mud (AaN-RM) was a chemico-physically modified product of red mud and had excellent adsorption performance. Genç-Fuhrman et al. demonstrated that powdered AaN-RM had good potential for arsenate adsorption in the batch and fixed-bed studies.<sup>16,17</sup> Tor et al. investigated the possibility of increasing the phenol adsorption capacity of powdered neutralized red mud by acid treatment, and the phenol adsorption capacity significantly increased after acid activation.<sup>18</sup> In our previous study, the powdered AaN-RM showed good phosphate adsorption performance over a broad pH.<sup>19</sup>

In this research, powdered AaN-RM was chosen for the first time as the main ingredient for granular AaN-RM preparation. Hydroxypropyl methylcellulose (HPMC) was considered to be a promising gelling agent for polymerizability and was applied as a cementing agent to provide binding strength for granular products.<sup>20</sup> Besides, the incorporation of powdered straw was supposed to provide not only the additional binding strength by forming a fibrous mat, but also the additional interconnecting paths for fluid flow by the tissue of xylem and phloem, which could effectively promote the transfer of adsorbates from the external surface to pores of adsorbents.<sup>21</sup>

Therefore, the aims of this paper are to prepare a new granular AaN-RM with powdered AaN-RM, HPMC, and powdered straw and to investigate its potential for phosphate adsorption. Influences of preparation parameters of granular AaN-RM on phosphate adsorption including mass ratio of ingredients, sintering temperature, and sintering time were optimized.

## MATERIALS AND METHODS

**Raw Materials.** The red mud used in this study was provided by Shandong Aluminum Industry Corporation (Zibo, China), which was a residue of alumina production with the Bayer process. The chemical composition of red mud is shown in Table 1 of the Supporting Information. The red mud was primarily a mixture of Fe<sub>2</sub>O<sub>3</sub> (47.39%), Al<sub>2</sub>O<sub>3</sub> (22.38%), Na<sub>2</sub>O (12.76%), SiO<sub>2</sub> (8.88%), and TiO<sub>2</sub> (7.33%). The HPMC was of analytical grade (Alfa Aesar, China). The sun-dried straws were obtained from Hunan, China, which were milled into powders with an average diameter of 0.25 mm.

The phosphate solution was prepared with potassium dihydrogen phosphate, which was of analytical grade (Merck, Germany). In order to investigate the potential of granular AaN-RM for treating wastewater containing high phosphate concentration, the initial phosphate concentration was chosen as 500 mg/L.

**Granular AaN-RM Preparation.** The method for preparing powdered AaN-RM can be found in Ye et al.<sup>19</sup> The powdered AaN-RM, powdered straw, and HPMC were chosen as the main ingredient, pore-forming agent, and cementing agent for granular AaN-RM preparation, respectively. The cementing agent ensures the binding strength of granular products, and its mass ratio was normally 5%-10%.<sup>15</sup> Therefore, the mass ratio of HPMC was fixed as 7% in this research. After evenly mixing the powdered AaN-RM, powdered straw and HPMC at different mass ratios (93:0:7, 82:11:7, 71:22:7, and 60:33:7, respectively), an appropriate amount of pure water was added to form a paste with a thickness of 2 mm. The paste was then cut into pellets with a size of 2 mm × 2 mm in length and width, naturally dried in the open air for 24 h, and sintered at various temperatures (from 150 to 300 °C) for different times (from 5 to 120 min) with a constant-temperature heating air-blowing drybox. Finally, various kinds of granular AaN-RM were obtained after being naturally cooled to room temperature.

Adsorption Study. Adsorption studies were carried out by shaking a phosphate solution with a granular AaN-RM dosage of 3 g/L at 100 r/min for 48 h in Erlenmeyer flasks. The equilibrium time of 48 h was determined according to preliminary experiments. The initial phosphate concentration was 500 mg/L. The solution pH could significantly influence the phosphorus species in solution and then affect the affinity between phosphate ions in solution and functional groups on the adsorbent surface. In this research, the initial solution pH was 7, and  $HPO_4^{2-}$  and  $H_2PO_4^{-}$  were the main existence forms of phosphorus. The adsorption temperature was 20 °C, which was controlled by a gyratory water bath shaker (model G76, New Brunswick Scientific, U.S.A.). The solution turbidity after adsorption equilibrium was quantified by a nephelometer (Hach 2100N Turbidimeter, U.S.A.) and reported in Nephelometric Turbidity Units (NTU). Then, the solution was centrifuged at 3000 r/min for 1 min, and the supernatant was taken to analyze the phosphate concentration. The phosphate adsorbed by per unit of granular AaN-RM was calculated by eq 1:

$$Q = \frac{(C_{\rm i} - C_{\rm f}) \times V}{m} \tag{1}$$

where Q is the phosphate adsorption capacity per unit of granular AaN-RM (mg/g),  $C_i$  (mg/L) and  $C_f$  (mg/L) are the initial and final phosphate concentration, respectively, V is the solution volume (L), and m is the mass of sorbent (g).

The phosphate concentration was determined via the spectrophotometric method DIN-EN-ISO-15681-1 with a QuikChem 8500 flow injection analysis system (Lachat Instruments, U.S.A.). The pH value of phosphate adsorption was measured with a multimeter (model Multiline P4, WTW, Germany). All experiments were conducted in triplicate, and t test was used to evaluate significance analysis for experimental data.

**Characterization of Adsorbents.** The chemical compositions of raw red mud and powdered AaN-RM were determined by an X-ray fluorescence spectrometer (S4 Explorer, Bruker, Germany). With N<sub>2</sub> adsorption/desorption isotherms at 77 K, the Brunauer–Emmett–Teller (BET) surface area and total pore volume of samples were determined (ASAP 2020 V3.04 H, Micromeritics, U.S.A.). The surface structure of granular AaN-RM was analyzed with an electron dispersive X-ray analysis (OXFORD X-Max, Oxford Instruments, U.K.), which was coupled with an electronic detector (LEO 1530, LEO, Germany). The X-ray diffraction (XRD) pattern of granular AaN-RM was detected using an X-ray diffractometer (XRD-6000, Shimadzu, Japan) with Cu K $\alpha$ radiation at 40 kV and 30 mA, which was recorded in a 2 $\theta$ range of 10–70° at a scan speed range of 0.02 deg/s.

Thermogravimetric analysis of granular AaN-RM was conducted using a DTG-60 instrument (DTG-60, Shimadzu, Japan) from 35 to 600 °C at a heating rate of 5 °C/min. A leaching test of the granular AaN-RM was performed according to the standard protocol (US EPA 1313).<sup>2</sup>

#### RESULTS AND DISCUSSION

Characterization of Powdered AaN-RM. The chemical compositions of powdered AaN-RM are also listed in Table 1 of the Supporting Information. Fe and Al elements were the main compositions. The BET surface area of powdered AaN-RM was 80.63  $m^2/g$ , and the total pore volume was 0.0644 cm<sup>3</sup>/g. Figure S1 of the Supporting Information shows the Xray diffraction pattern of powdered AaN-RM, and the specific chemical composition diffraction peaks were observed at different  $2\theta$  (deg), indicating the presence of iron chloride hydrate (FeCl<sub>3</sub>·2H<sub>2</sub>O), gibbsite (Al(OH)<sub>3</sub>), anatase (TiO<sub>2</sub>), and quartz  $(SiO_2)$ . The phosphate adsorption capacity of powdered AaN-RM reached 170.75 mg/g, which was higher than that of neutralized red mud  $(22.40 \text{ mg/g})^{19}$  and other red mud-based adsorbents reported.<sup>9,10,23</sup>

Characterization of Granular AaN-RM. The granular AaN-RM was produced with a mass ratio of powdered AaN-RM, powdered straw, and HPMC of 82:11:7, a sintering temperature of 250 °C, and a sintering time of 30 min. The photograph of granular AaN-RM is shown in Figure 1. The



Figure 1. Photograph image of granular AaN-RM (mass ratio of powdered AaN-RM, powdered straw, and HPMC of 82:11:7; sintering temperature of 250 °C; sintering time of 30 min).

BET surface area of granular AaN-RM reached 90.70 m<sup>2</sup>/g, which increased by 12.49% compared with that of powdered AaN-RM. More channels and pores might be generated when plenty of binder fibers bonded the carbonaceous fragments in granular adsorbents. Ren et al. reported a similar phenomenon that the BET surface area of granular biochar increased from 49.71 to 56.10 m<sup>2</sup>/g after granulation.<sup>24</sup>

Figure 2 shows the thermogravimetric curve of granular AaN-RM, which revealed three stages of mass loss in a range of 35-600 °C. The initial weight loss of 24.40% from 35 to 100 °C could be attributed to the evaporation of moisture adsorbed on the surface of granular AaN-RM.<sup>15</sup> The secondary weight loss of 7.69% from 100 to 200 °C might be due to the release of constitution water from mineral crystals.<sup>25</sup> The final weight loss



Figure 2. Thermogravimetric curve of granular AaN-RM (mass ratio of powdered AaN-RM, powdered straw, and HPMC of 82:11:7; sintering temperature of  $\overline{250}$  °C; sintering time of 30 min).

of 26.68% from 200 to 500 °C could be caused by the decomposition of chemical compositions.<sup>26</sup> The results demonstrated that the granular AaN-RM was thermally unstable. The water of different patterns was first separated out, and the volatile substance could be further decomposed with an increase in temperature.

The phosphate adsorption capacity of this granular AaN-RM was 69.33 mg/g, which was lower than that of powdered AaN-RM (170.75 mg/g); however, the formed granular AaN-RM still showed better phosphate adsorption performance compared with other granular adsorbents because of its higher specific surface area (Table 1). Genç-Fuhrman et al. attributed

### Table 1. Summary of Phosphate Adsorption Capacity of **Different Granular Adsorbents**

adsorbent	specific surface area (cm²/g)	phosphate adsorption capacity (mg/g)	literatures
granular ferric oxides/ biochar hybrid adsorbent	71.45	0.96	24
lanthanum(III) loaded granular ceramic	26.83	2.76	28
granular palygorskite	47.00	13.10	29
red mud granular adsorbent	20.60	5.99	30
granular AaN-RM <sup>a</sup>	90.70	69.33	this work
granular AaN-RM <sup>b</sup>	113.54	86.69	this work

<sup>a</sup>Mass ratio of powdered AaN-RM, powdered straw, and HPMC of 82:11:7; sintering temperature of 250 °C; sintering time of 30 min. <sup>b</sup>Mass ratio of powdered AaN-RM, powdered straw, and HPMC of 71:22:7; sintering temperature of 225 °C; sintering time of 30 min.

the high specific surface area and excellent phosphate adsorption performance to the cleaning of adsorption sites during the acid activation.<sup>16</sup> The generation of amorphous and semi-amorphous precipitates during the preparation of powdered AaN-RM might be also a main reason for higher specific surface area.<sup>27</sup> Furthermore, more channels and pores caused by the addition of powdered straw during the granular AaN-RM preparation might also result in an increase in specific surface area. The complex mineralogy and addition of powdered straw led to excellent phosphate adsorption of granular AaN-RM.

Influence of Preparation Parameters of Granular AaN-RM on Phosphate Adsorption. Influence of Mass Ratio of Different Ingredients. The phosphate adsorption capacity of granular AaN-RM produced with different mass ratios after the adsorption equilibrium is shown in Figure 3. As shown in



Figure 3. Influence of mass ratio of powdered AaN-RM, powdered straw, and HPMC on phosphate adsorption capacity of granular AaN-RM (sintering temperature of 250  $^{\circ}$ C; sintering time of 30 min; initial phosphate concentration of 500 mg/L; AaN-RM dosage of 3 g/L).

Figure 3, the phosphate adsorption capacity of granular AaN-RM produced without powdered straw (mass ratio of 93:0:7) was 36.13 mg/g, which was much lower than that of other

granular AaN-RM. As the mass ratio of the powdered straw increased, the phosphate adsorption capacity of granular AaN-RM first increased and then decreased. The highest phosphate adsorption capacity reached 75.11 mg/g with a mass ratio of 71:22:7. Therefore, the optimal mass ratio of powdered AaN-RM, powdered straw, and HPMC was chosen as 71:22:7.

The SEM images of granular AaN-RM are shown in Figure 4. There were obvious cracks on the surface of granular AaN-RM produced without powdered straw; when the mass ratio of powdered straw increased, a rougher surface was observed. The powdered straw improved the integration of granular AaN-RM. As shown in Table 2 of the Supporting Information, the total pore volume of granular AaN-RM increased from 0.0056 to  $0.0375 \text{ cm}^3/\text{g}$  with an increase in mass ratio of powdered straw from zero to 33%. The increased powdered straw effectively promoted the pore generation of granular AaN-RM. Ren et al. found that the specific surface area and total pore volume of granular ferric oxides also increased after the addition of pulverous biochars.<sup>24</sup> However, the increased powdered straw addition could correspondingly reduce the amount of powdered AaN-RM, which would lead to a decrease in effective chemical compositions reacting with phosphate and further influence the phosphate adsorption performance.

Influence of Sintering Temperature. Sintering temperature affects not only the adsorption performance but also the strength of granular AaN-RM. Too low sintering temperature normally results in the reduction of adsorbent strength, while too high sintering temperature can change the effective chemical compositions of adsorbent due to the transformation



Figure 4. SEM micrographs of granular AaN-RM samples with different mass ratios of powdered AaN-RM, powdered straw, and HPMC: (a) 93:0:7, (b) 82:11:7, (c) 71:22:7, and (d) 60:33:7 (sintering temperature of 250 °C; sintering time of 30 min).

reactions, which further influences the adsorption performance.<sup>15</sup> The strength of granular AaN-RM could be evaluated by the solution turbidity after adsorption equilibrium, which was attributed by the breakage of adsorbents. When the sintering temperature was lower than 225 °C, the powder seriously peeled off from granular AaN-RM during the adsorption process led to a solution turbidity higher than 9.65 NTU (Figure 5). However, when the sintering temper-



**Figure 5.** Influence of sintering temperature on strength and phosphate adsorption capacity of granular AaN-RM (mass ratio of powdered AaN-RM, powdered straw, and HPMC of 71:22:7; sintering time of 30 min; initial phosphate concentration of 500 mg/L; AaN-RM dosage of 3 g/L).

ature was 225 °C or higher, the abrasive resistance of granular AaN-RM was greatly improved, and the solution turbidity after adsorption equilibrium was only 0.16 NTU. It was reported that  $Al(OH)_3$  phase (gibbsite) could evolve similarly to sol–gel  $Al^{3+}$  materials with sufficient heating, which are involved in dehydration of gibbsite together with solid-state topotactic transitions.<sup>24,30</sup> This is speculated to be the reason for strength enhancement of granular AaN-RM when the sintering temperature increased. The sintering temperature should not be lower than 225 °C.

The influence of sintering temperature on the phosphate adsorption capacity of granular AaN-RM is also shown in Figure 5. The phosphate adsorption capacity of granular AaN-RM was 86.89 mg/g when the sintering temperature was 225 °C and decreased with an increase in sintering temperature. With consideration of the strength and phosphate adsorption capacity of granular AaN-RM, the optimal sintering temperature was chosen as 225 °C.

The XRD patterns were used to clarify how the sintering temperature influenced the characteristics of granular AaN-RM. As shown in Figure 6, strong signals of FeOCl were observed in the XRD spectra of granular AaN-RM, and their intensity slightly decreased with an increase in sintering temperatures. When the sintering temperature was 250 °C or higher, new signals of FeCl<sub>2</sub> were observed, and its intensity increased gradually with an increase in sintering temperature. However, only signals of FeCl<sub>3</sub>·2H<sub>2</sub>O were found in the XRD spectra of powdered AaN-RM (Figure S1, Supporting Information). The FeCl<sub>3</sub>·2H<sub>2</sub>O was thermal unstable, and parts of FeCl<sub>3</sub>·2H<sub>2</sub>O was changed to FeOCl and FeCl<sub>2</sub> when the sintering temperature increased, as indicated in eqs 2 and 3):<sup>31</sup>



**Figure 6.** XRD patterns of granular AaN-RM samples sintered at various temperatures (mass ratio of powdered AaN-RM, powdered straw, and HPMC of 71:22:7; sintering time of 30 min).

$$2\text{FeCl}_3 + \text{O}_2 \rightarrow 2\text{FeOCl} + 2\text{Cl}_2\uparrow$$
(2)

$$2\text{FeCl}_3 \rightarrow 2\text{FeCl}_2 + \text{Cl}_2\uparrow \tag{3}$$

The BET surface area and total pore volume of granular AaN-RM increased with an increase in sintering temperature (Table S2, Supporting Information ), which was caused by the gas-producing reaction as in eqs 2 and 3). However, Zhao et al. demonstrated that the transformation of Fe<sup>3+</sup> to Fe<sup>2+</sup> resulted in a weaker attraction for phosphate.<sup>30</sup> Compared with the FeCl<sub>2</sub>, the FeOCl formed at a sintering temperature of 225 °C could easily dissociate into FeO<sup>+</sup> in solution. With the initial solution pH of 7, HPO<sub>4</sub><sup>2-</sup> and H<sub>2</sub>PO<sub>4</sub><sup>-</sup> were the main forms of phosphorus. Therefore, the adsorption process could be described by eqs 4–6.<sup>10</sup>

$$FeOCl \leftrightarrow FeO^+ + Cl^-$$
 (4)

$$\operatorname{FeO}^{+} + \operatorname{HPO}_{4}^{2-} \to \operatorname{FeOPO}_{4}^{2-} + \operatorname{H}^{+}$$
 (5)

$$\text{FeO}^+ + \text{H}_2\text{PO}_4^- \rightarrow \text{FeOHPO}_4^- + \text{H}^+$$
 (6)

With a sintering temperature of 250 °C and higher than 250 °C, part of  $Al(OH)_3$  was decomposed to  $Al_2O_3$  (eq 7).<sup>32</sup> The signals of  $Al_2O_3$  were observed in Figure 6, and their intensity slightly increased with an increase in sintering temperature.

$$2\text{Al}(\text{OH})_3 \rightarrow \text{Al}_2\text{O}_3 + 3\text{H}_2\text{O} \tag{7}$$

As found in our previous study, the FeCl<sub>3</sub>·2H<sub>2</sub>O and Al(OH)<sub>3</sub> played important roles on the phosphate adsorption onto powdered AaN-RM through precipitation, ion exchange, and surface deposition mechanisms, which resulted in the high phosphate adsorption capacity of powdered AaN-RM.<sup>33</sup> The decomposition of Al(OH)<sub>3</sub> and transformation of Fe<sup>3+</sup> to Fe<sup>2+</sup> at a higher sintering temperature resulted in lower phosphate adsorption capacity compared with that at a sintering temperature of 225 °C.

It was reported that the phosphate adsorption capacity of red mud pellet increased with an increase in sintering temperature,<sup>30</sup> which was different from the result of this study. The red mud from the alumina production used in Zhao et al. was produced using sintering processes, and it contained a much higher content of calcite (CaCO<sub>3</sub>) than the red mud produced with the Bayer process.<sup>30</sup> With an increase in sintering temperature, not only the decomposition of CaCO<sub>3</sub> into

CaO resulted in the improvement of porosity, but also the CaO more easily reacted with the phosphate.<sup>34,35</sup>

Influence of Sintering Time. A certain sintering time is required to ensure the strength of granular adsorbent. On the other hand, the chemical compositions of granular adsorbent can be changed or the granular adsorbent can break down when the sintering time is too long.<sup>36,37</sup> When the sintering time was below 30 min, the produced granular AaN-RM crushed out of shape easily and the solution turbidity after adsorption equilibrium was higher than 3.34 NTU (Figure 7). However,



Figure 7. Influence of sintering time on strength and phosphate adsorption capacity of granular AaN-RM (mass ratio of powdered AaN-RM, powdered straw, and HPMC of 71:22:7; sintering temperature of 225 °C; initial phosphate concentration of 500 mg/L; AaN-RM dosage of 3 g/L).

when the sintering time was 30 min or longer, the polymerizability of granular AaN-RM was significantly improved, and the solution turbidity after adsorption equilibrium was only 0.16 NTU. Therefore, the sintering time should not be shorter than 30 min. Figure 7 shows that the phosphate adsorption capacity of granular AaN-RM gradually decreased with an increase in sintering time. Therefore, 30 min was selected as the optimal sintering time.

The XRD patterns shown in Figure 8 could be used to reveal the influence of sintering time on the chemical compositions and phosphate adsorption characteristics of granular AaN-RM.



Figure 8. XRD patterns of granular AaN-RM samples sintered at various times. (mass ratio of powdered AaN-RM, powdered straw, and HPMC of 71:22:7; sintering temperature of 225  $^{\circ}$ C).

As shown in Figure 8, the  $Al(OH)_3$  was stable even if when the sintering time increased from 30 to 120 min. However, the signal peak of FeCl<sub>2</sub> was observed in the XRD spectrum of granular AaN-RM when the sintering time was 60 min or longer. Parts of FeCl<sub>3</sub>·2H<sub>2</sub>O might be decomposed to FeCl<sub>2</sub>, and the intensity of FeCl<sub>2</sub> in granular AaN-RM gradually increased with an increase in sintering time. As a sequence, the phosphate adsorption capacity of granular AaN-RM decreased with an increase in sintering time.

Therefore, the optimal mass ratio of powdered AaN-RM, powdered straw, and HPMC was 71:22:7, and the optimal sintering temperature and sintering time were 225 °C and 30 min, respectively. The components of granular AaN-RM responsible for the phosphate adsorption mainly included FeOCl and Al(OH)<sub>3</sub> under the optimal preparation condition.<sup>36</sup> Meanwhile, the leaching test showed that the leached metals with the initial solution pH of 7 were below detection limit, which demonstrated that the granular AaN-RM was stable under the neutral pH condition.

## CONCLUSIONS

- (1) The granular acid-activated neutralized red mud (AaN-RM) was prepared with powdered AaN-RM, powdered straw, and hydroxypropyl methylcellulose with a maximum phosphate adsorption capacity of 86.69 mg/g, which was much higher than previously reported. The excellent phosphate adsorption capacity was mainly attributed to the high specific surface area caused by complex mineralogy and addition of powdered straw during the preparation of granular AaN-RM.
- (2) The increased mass ratio of powdered straw effectively promoted the pore generation of granular AaN-RM. However, it also resulted in the reduction of effective chemical compositions reacting with phosphate. The optimal mass ratio of powdered AaN-RM, powdered straw, and HPMC was chosen as 71:22:7.
- (3) With an increase of sintering temperature, the strength of granular AaN-RM was significantly improved; however, too high of a sintering temperature led to the conversion of part FeCl<sub>3</sub>·2H<sub>2</sub>O to FeOCl and FeCl<sub>2</sub> and part Al(OH)<sub>3</sub> to Al<sub>2</sub>O<sub>3</sub>, which could result in a weaker attraction for phosphate. The optimal sintering temperature was chosen as 225 °C.
- (4) The sintering time influenced the polymerizability of granular AaN-RM and the transformation of FeCl<sub>3</sub>·2H<sub>2</sub>O to FeOCl and FeCl<sub>2</sub>. Thirty minutes was selected as the optimal sintering time.

## ASSOCIATED CONTENT

#### **S** Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acssuschemeng.5b00932.

Details on the XRD pattern of powdered AaN-RM and main chemical composition of red mud and powdered AaN-RM, as well as the effect of preparation parameters on the physicochemical properties of granular AaN-RM. (PDF)

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#### Notes

The authors declare no competing financial interest.

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