

# Resource Recycling of Mn-Rich Sludge: Effective Separation of Impure Fe/Al and Recovery of High-Purity Hausmannite

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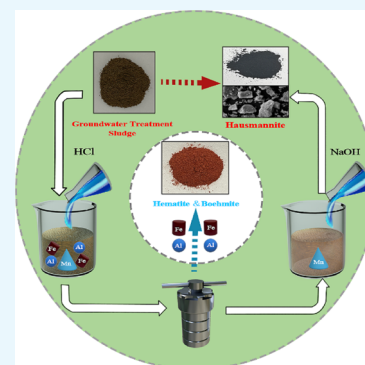
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**ABSTRACT:** Groundwater treatment sludge is a Fe/Mn-rich waste generated in mass production in a groundwater treatment plant for potable water production. The conventional disposal of sludge, such as direct discharge into river/lake, sea, and landfill, is not environmentally sustainable. Herein, a novel method was proposed to effectively separate Fe/Al and recover Mn via a combined hydrochloric acid leaching and hydrothermal route. The sludge contained 14.6% Fe, 6.3% Mn, and 11.5% Al and was first dissolved in 5 M HCl to prepare a leaching solution. Second, the leaching solution was hydrothermally treated, in which 97.1% Fe and 94.8% Al were precipitated as hematite and boehmite and more than 98% Mn was kept. Increasing the reaction temperature to 270 °C was beneficial for Fe/Al removal. With the consumption of abundant H<sup>+</sup>, the reaction of added glucose and nitrate accelerated as the temperature increased. An optimal pH was utilized for Fe/Al hydrolysis and crystallization, leading to extensive removal of Fe/Al. Third, the residual solution was adjusted to pH 8.3 with NaOH, and approximately, 99.2% Mn was removed as hausmannite with a Mn content of 63.6%. This method exhibited efficient separation of impure Fe/Al from Mn-rich groundwater treatment plant iron mud, and the recycled high-purity hausmannite was a marketable active pharmaceutical ingredient.



## 1. INTRODUCTION

Groundwater treatment sludge (GWTS) is a Mn-rich waste and precipitated from backwash wastewater of groundwater treatment plants.<sup>1–3</sup> Approximately, 5 t of sludge is generated in treatment plants with a production of 80,000 m<sup>3</sup>/d. The sludge contains 5.4–8.5 wt % of Mn<sup>4–7</sup> and is usually dumped directly into the river or sea without disposal.<sup>8</sup> With such disposal, the sludge was precipitated on the sediment, where free Fe/Mn was reductively dissolved under the anoxic condition and released to the water.<sup>9</sup> This behavior promoted the transport of Fe/Mn in water body and caused severe Fe/Mn toxicity to aquatic microbes and plants.<sup>10,11</sup> In the normative management of groundwater treatment plants, this sludge is forced to accumulate and sent to landfills after mechanical dewatering, which is costly and occupies landfill areas.<sup>12,13</sup>

The resource utilization of sludge is economic and environmentally friendly, which can not only recover high-purity Mn products but also save disposal cost of sludge. Generally, sludge is recycled in two categories. First, sludge containing abundant Si/Al-bearing oxyhydroxide can be directly recycled as architectural admixtures<sup>14</sup> or soil amendments.<sup>15,16</sup> For instance, Nimwinya et al. mixed sludge with rice husk ash at a weight ratio of 1 and then added a solution containing Na<sub>2</sub>SiO<sub>3</sub> and NaOH at a weight ratio of 9; after curing for 7 days, a geopolymer with an unconfined

compressive strength of 19 MPa was prepared.<sup>14</sup> The Al-bearing oxyhydroxide in sludge has high affinity to adsorb phosphors and other oxyanions<sup>15</sup> and can serve as a soil substitute to control the mobility of soil nutrients.<sup>16</sup> Second, sludge consists of Mn/Fe/Al/Si oxyhydroxide and plenty surface hydroxyl groups. Thus, it can be recycled as an adsorbent for adsorbing contaminants, for example, heavy metals and cationic organics. Ngatenah et al. directly added sludge into wastewater with 10 mg/L Zn and 65 mg/L Cu and found that nearly 100% of Zn and Cu were removed with the addition of 8 g/L sludge.<sup>3</sup> With hydrothermal treatment and/or calcination, the Fe/Mn-bearing oxyhydroxide in sludge can be converted into magnetic species, including jacobsonite,<sup>17</sup> maghemite,<sup>12</sup> and magnetite,<sup>18</sup> so that the treated sludge has good magnetic response and can be magnetically separated from wastewater after use. In the hydrothermal system, Si/Al-bearing compounds can convert into sodalite<sup>19</sup> and/or cancrinite.<sup>20</sup> However, with the abovementioned methods, the corresponding products, including geopolymers, soil

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amendments, and adsorbents, are of low profit and unmarketable; thus, their production at a project scale was restricted.

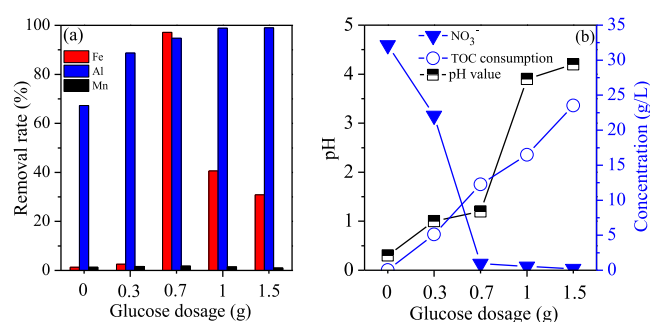
Mn is a valuable metal in sludge, and Mn-bearing reagents, including  $\text{KMnO}_4$ ,  $\text{Mn}_3\text{O}_4$ , and  $\text{MnO}_2$ , are marketable in electronic, biological, and chemical industries.<sup>21,22</sup> Mn recovery from sludge was investigated by Ong et al.<sup>5,23</sup> In this study, sludge with 7.9 wt % Mn was reductively leached by sulphuric acid and hydrogen peroxide to generate an acid solution, and after the impure Fe was precipitated from the solution with KOH, the residual Mn in the supernatant was precipitated as manganese dioxide by adding  $\text{KMnO}_4$ . Mocellin et al. selectively leached Mn from a pyrometallurgical sludge by adding  $\text{H}_2\text{SO}_4$  and  $\text{Na}_2\text{S}_2\text{O}_5$  at pH 4 and found that nearly 77.6% Mn was recovered from the residual solution as rhodochrosite after the leaching solution was readjusted to pH 8.5 with the addition of  $\text{Na}_2\text{CO}_3$ .<sup>22</sup> Among these methods, the sludge was commonly dissolved in strong acid, including  $\text{HNO}_3$ ,  $\text{H}_2\text{SO}_4$ ,<sup>23,24</sup> and  $\text{HCl}$ .<sup>25</sup> Correspondingly, impure Fe/Al is abundant in sludge and also dissolved with Mn in the form of  $\text{Fe}^{3+}$  and  $\text{Al}^{3+}$  in solution. Fe and Al are easily hydrolyzed as Fe/Al-bearing oxyhydroxide in the solution for Mn coordination in the pH adjustment process, which leads to the coprecipitation of Fe/Al/Mn as secondary waste and a low recovery rate of Mn. Mn can be extracted with extraction resin and/or reagents, such as Cyanex 272<sup>26</sup> and di-(2-ethylhexyl)-phosphoric acid.<sup>27</sup> Fe and Al are active metals and also reacted with such extraction reagents along with impure Fe/Al in the recycled Mn product. Therefore, to efficiently recover high-purity Mn products, Fe/Al should be removed from the solution.

Generally, Fe can precipitate at pH 3–3.5 to form Fe-bearing hydrates. These Fe-bearing hydrates have a peculiar structure, in which one Fe is coordinated with six hydroxyls, thereby providing abundant hydroxyl functional groups for cation coordination, including Mn. In particular, the coprecipitation of Fe and heavy metal ions occurs when the concentration of Fe in the solution is high (e.g., >3 mg/L).<sup>28</sup> The hydrolysis of Fe is intensified under high-temperature conditions, which provides a new perspective for Fe removal. Su et al. reported that in Fe/Co/Sr-bearing solution, nearly 55.6% Fe removal was achieved after heating at 160 °C for 10 h, and 99.5% removal was achieved with the introduction of methanol.<sup>29</sup> Compared with Fe, Al has a slower hydrolysis rate, and only 72.9% of Al was removed from Mn-bearing solution using the same method of Su et al.<sup>29</sup> The efficient separation of Al from heavy metal-bearing solution has not been reported.

In the present study, GWTS containing 6.3% Mn, 14.6% Fe, and 11.5% Al was recycled as high-purity hausmannite via a combined hydrochloric acid leaching and hydrothermal route. In the hydrothermal route, Fe and Al were simultaneously separated as hematite and boehmite with the addition of glucose, and the hydrothermal temperature was optimized. Concurrently, the Fe/Al separation and Mn recovery mechanism were also investigated.

## 2. RESULTS AND DISCUSSION

**2.1. Effect of Glucose Dosage.** After acidic leaching, the concentrations of Fe, Al, and Mn in the leachate (supernatant 1) were 6259, 9122, and 2903 mg/L, respectively. When supernatant 1 was hydrothermally treated, Fe/Al removal occurred, where 1.4% Fe and 67.3% Al were removed from the solution (Figure 1a), demonstrating that Al removal took

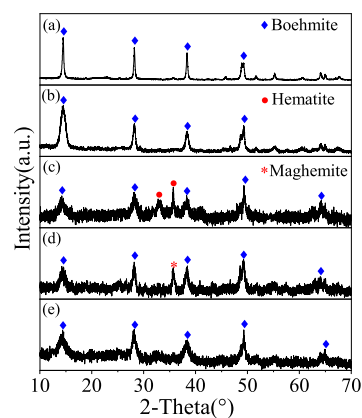


**Figure 1.** Effect of glucose dosage on Fe/Al/Mn removal. (a) Fe/Al/Mn removal rate and (b) pH value change, TOC consumption, and nitrate concentration (the initial pH of supernatant 1 was 0.5, the initial nitrate was 70 g/L, and the hydrothermal temperature was 270 °C).

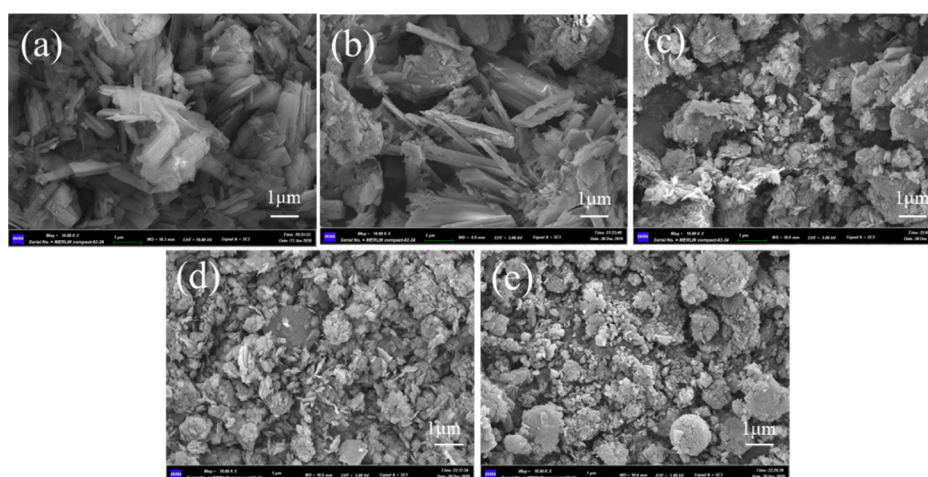
precedence over Fe due to the high concentration of Al. With Fe/Al removal, the pH of the solution also decreased from 0.5 to 0.3 due to the generation of  $\text{H}^+$  in Al hydrolysis, and the nitrate concentration decreased from 70 to 32.2 g/L, which is consistent with the decomposition of nitrate at 220 °C.<sup>30</sup>

When glucose was introduced in the hydrothermal system, the Fe removal efficiency was 2.6% with 0.3 g of glucose and considerably increased to 97.1% with 0.7 g of glucose. However, it gradually dropped to 40.6% with 1 g of glucose and 30.9% with 1.5 g of glucose. This demonstrated that 0.7 g of glucose was the optimal dosage for Fe removal. For Al removal, its efficiency increased from 88.7 to 94.8% with 0.3–0.7 g of glucose and further increased up to 99% with 1.5 g of glucose. During Fe/Al removal, Mn loss was less than 2%, indicating that Mn was rich in the residual solution. When the glucose dosage increased from 0.3 to 1.5 g, the nitrate concentration further decreased from 3.2 to 0.2 g/L, and conversely, consumed TOC increased from 0.5 to 23 g/L. Meanwhile, the pH of the solution constantly increased from 1 to 4.2. This was due to the consumption of  $\text{H}^+$  in the redox reaction of nitrate and organics (e.g., glucose) in the hydrothermal system.

In the absence of glucose, the boehmite peak of the generated precipitates was sharp, and no Fe peak was observed (Figure 2a). The boehmite peak remained almost unchanged when 0.3 g of glucose was added in the hydrothermal system (Figure 2b). By adding 0.7 g of glucose, the boehmite peak became weak, and new peaks of hematite were recorded



**Figure 2.** XRD patterns of the precipitates generated at a glucose dosage of (a) 0, (b) 0.3, (c) 0.7, (d) 1, and (e) 1.5 g.

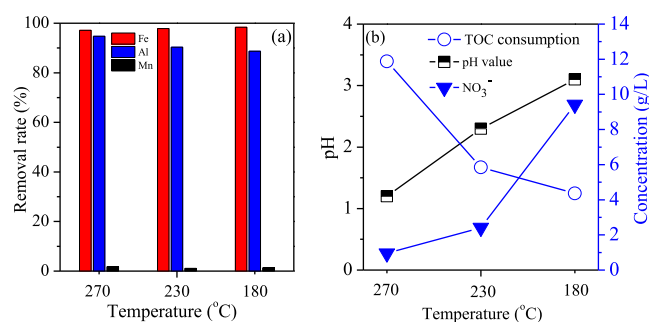


**Figure 3.** SEM images of the precipitates generated at a glucose dosage of (a) 0, (b) 0.3, (c) 0.7, (d) 1, and (e) 1.5 g.

(Figure 2c), which is in agreement with the extensive removal of Fe. When the glucose dosage increased from 0.7 to 1 g, the boehmite peaks remained unchanged; however, the peaks of hematite disappeared, and a new peak of maghemite was observed. At a glucose dosage of 1.5 g, the maghemite peak was not observed (Figure 2d,e).

When the glucose dosage was less than 0.3 g, Al was precipitated as boehmite rods with a diameter and length of 0.5 and 2  $\mu\text{m}$ , respectively (Figure 3). However, only a small portion of Fe was involved in the precipitation. With the addition of glucose at a dosage >0.7 g, irregular particles comprising boehmite and/or hematite and maghemite were generated. The formation mechanism of irregular particles will be discussed in Section 2.4.

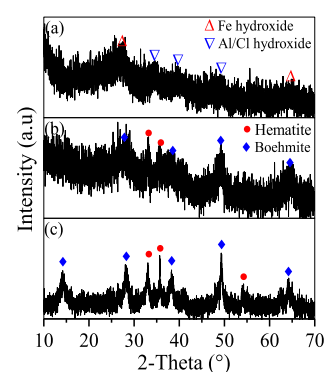
**2.2. Effect of Reaction Temperature.** The hydrothermal temperature is an important parameter for Fe/Al removal, and it was also investigated, as shown in Figure 4. As the



**Figure 4.** Effect of temperature on Fe/Al/Mn removal. (a) Fe/Al/Mn removal rate and (b) pH value change and nitrate and TOC concentration (the initial pH of supernatant 1 was 0.5; the initial nitrate and TOC were 70 and 12.62 g/L, respectively; and the glucose dosage was 0.7 g).

temperature increased from 180 to 230 °C and 270 °C, the removal efficiency of Fe slightly decreased from 98.4 to 97.9% and 97.1%, respectively. However, the removal efficiency of Al steadily increased from 88.7 to 90.4% and 94.8%, respectively, indicating that high temperature evidently promoted Al removal and hardly promoted Fe removal. Accordingly, the residual nitrate concentration decreased from 9.4 g/L to 2.4 and 0.9 g/L along with the decrease in the pH of the solution from 3.2 to 2.3 and 1.2.

Fe/Al was precipitated as an irregular mixture of Fe hydroxide and Al/Cl hydroxide at 180 °C (Figures 5a and



**Figure 5.** XRD patterns of the precipitates generated at (a) 180, (b) 230, and (c) 270 °C.

6a). When the temperature increased from 180 to 230 °C, the precipitates were hematite and boehmite particles (Figures 5b and 6b), suggesting the conversion of Fe/Al hydroxide to well-crystallized hematite and boehmite. At 270 °C, the peaks of hematite and boehmite became sharp (Figure 5c), and accordingly, small boehmite chips with a length of 200 nm were observed (Figure 6c), indicating the crystal growth of hematite and boehmite.

### 2.3. Composition of Recycled Mn-Bearing Particles.

When the concentrations of Fe, Al, and Mn in the residual solution were 181, 477, and 2850 mg/L, respectively, optimal Fe/Al removal was achieved by adding 0.7 g of glucose at 270 °C. After the pH of the solution was adjusted to 8.3, Mn was precipitated as a hausmannite block (Figure 7a,b). The hausmannite block contained 0.5% Fe, 0.7% Al, and 63.6% Mn (Figure 7c), suggesting that Mn was recycled as highly purified hausmannite. The major composition of recycled hausmannite was close to that of a chemical active pharmaceutical ingredient (API) trimanganese tetroxide.

The recycled hausmannite was directly used as a Mn source to prepare  $\gamma$ -MnOOH nanorods. After acid leaching and hydrothermal treatment according to the method of Shin and Varghese et al.,<sup>31,32</sup>  $\gamma$ -MnOOH nanorods were generated (Figure 8a) and showed well-formed peaks of manganese (Figure 8b). The product is of great importance in the area of

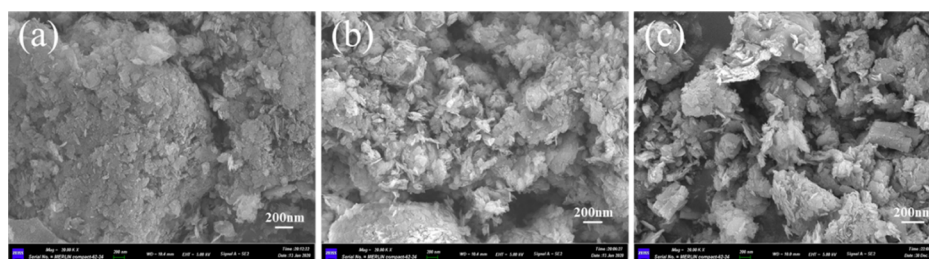


Figure 6. SEM images of the precipitates generated at (a) 180, (b) 230, and (c) 270 °C.

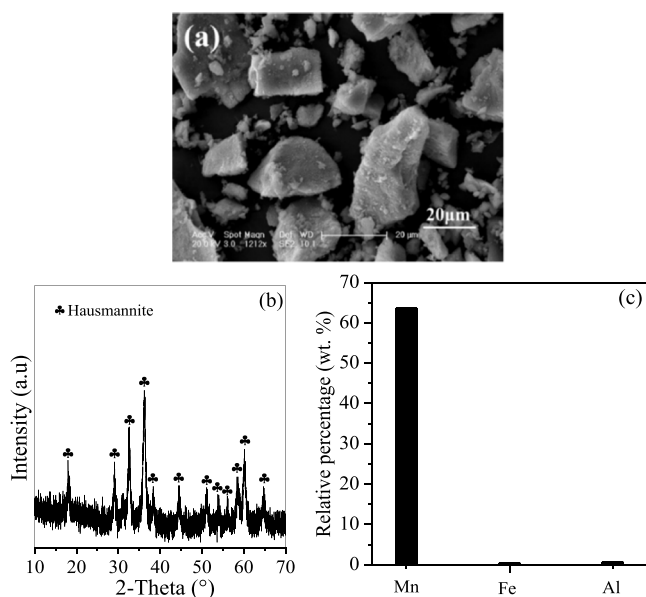


Figure 7. (a) SEM image, (b) XRD pattern, and (c) composition of the Mn-bearing precipitate.

separation membranes,<sup>33</sup> dye adsorbents,<sup>31</sup> and electrocatalysts in the reduction of  $O_2$ ,<sup>34</sup> indicating that the recycled hausmannite was acceptable in these areas.

The mass balance of Mn recovery was calculated (Figure 9). In the dissolution process, nearly 93% Mn, 90.2% Fe, and 100% Al in the sludge were leached and released to acid solution, while the undissolved residue was a Si/Ca-bearing compound. After further hydrothermal treatment, Fe and Al were almost completely removed as a hematite and boehmite mixture, with a Mn loss of <2 wt %. By adjusting the solution pH, more than 99.2% Mn was precipitated as hausmannite. In summary, approximately, 97.1% Fe, 94.8% Al, and 98% Mn in the leachate were recycled as a hematite/boehmite mixture and hausmannite.

The operation cost is an important parameter for Mn recovery from the sludge (Table 1). The sludge was commonly collected and solidified before it is safely landfilled, of which the total cost is approximately US\$ 66.1/t.<sup>13</sup> Herein, Mn was recycled from the sludge. To treat 1-ton sludge, 7.53 ton of hydrochloric acid, 0.49 ton of caustic soda, 0.54 ton of glucose, and 45 kW h power were needed, which amounted to a total cost of US\$ 1128.4 (Table 1), with the generation of only 0.1 ton residual. The sludge production was considerably reduced, and the corresponding cost of sludge reduction can be deducted from the Mn recovery. Moreover, in the recovery process, the heating energy can be recycled via a thermal circulation system, and the hausmannite product was highly marketable, thereby reducing the cost of Mn recovery. In

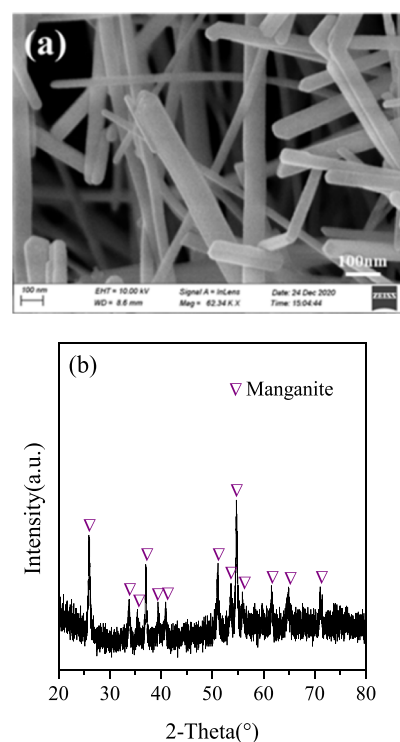


Figure 8. (a) SEM image and (b) XRD pattern of the product prepared from the recycled hausmannite.

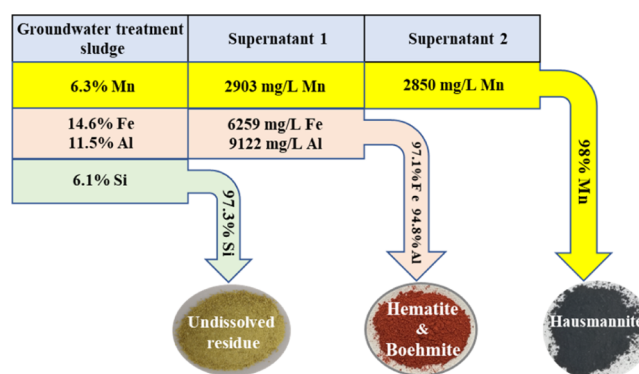


Figure 9. Mass balance graph of Mn recovery from GWTS.

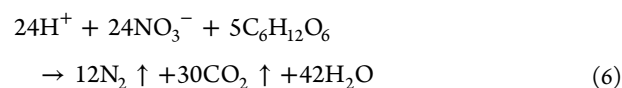
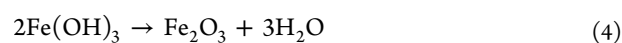
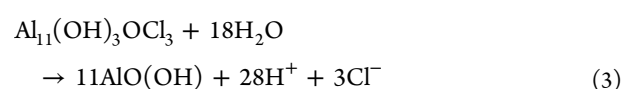
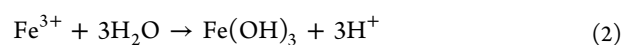
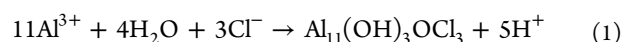
summary, the processing method for Mn recovery from the sludge had potential application.

**2.4. Fe/Al Separation Mechanism.** High temperature (e.g., 270 °C) provided enough energy to expedite Al hydrolysis,<sup>35</sup> where Al was easily polymerized as hydroxy aluminum  $Al_{13}$  and  $Al_{30}$ <sup>36</sup> in the form of Lewis acids and precipitated as an Al-bearing polymer (e.g., boehmite). While

Table 1. Cost of Mn Recovery from the Sludge

	reagent and processing	price	usage/product per ton	subtotal price per ton (US\$)
sludge disposal	drying power	0.32 US\$/kW h	10 kW h (total 10 h)	3.20
recycling processing	undissolved residue	122.5 US\$/ton	0.1 ton	12.25
	hydrochloric acid	103.7 US\$/ton	7.53 ton	780.86
	glucose	336.9 US\$/ton	0.54 ton	181.93
	power	0.32 US\$/kW h	30 kW h (total 20 h)	9.60
	caustic soda	283.6 US\$/ton	0.49 ton	138.96
	drying power	0.32 US\$/kW h	5 kW h (total 5 h)	1.60
major product	hausmannite	2968.1 US\$/ton	0.38 ton	1127.88
	hematite/boehmite mixture	765.7 US\$/ton	0.49 ton	375.19

the polymerization of Fe as Lewis acids did not occur, only a small portion of Fe was hydrolyzed. Thus, Al was hydrolyzed prior to Fe at 270 °C, leading to the removal of 67.3% Al and only 1.4% Fe in the absence of glucose. During Al/Fe hydrolysis, H<sup>+</sup> was produced (eqs 1 and 2), which caused a drop in the pH of the solution from 3.1 to 1.2. With the accumulation of H<sup>+</sup>, Al and Fe were gradually in equilibrium and then became residual at high concentrations in the solution. Al and Fe were first hydrolyzed to Al/Fe-bearing flocs, and then, the conjunction reaction between two adjacent hydroxyls of each floc occurred with the release of one water molecule to produce AlO–Al and/or FeO–Fe bonds. As the conjunction reaction proceeded, well-crystallized Al/Fe minerals (e.g., boehmite and hematite<sup>37</sup>) were produced (eqs 3 and 4). Although the Al/Fe-bearing compounds, including flocs and minerals, had many surface hydroxyls for Mn coordination, H<sup>+</sup> was rich in the solution and competed with Mn to coordinate with surface hydroxyls. Hence, Mn was extensively residual in the solution. In addition, the decomposition of nitrate also occurred at high temperature, with the generation of NO<sub>2</sub> and O<sub>2</sub><sup>30</sup> via eq 5, which led to the decrease in nitrate concentration.



When glucose was introduced in the hydrothermal system, it served as a reducing reagent and reacted with nitrate via eq 6 to generate CO<sub>2</sub>, H<sub>2</sub>O, and N<sub>2</sub>, where H<sup>+</sup> was consumed. With the consumption of H<sup>+</sup>, Al hydrolysis intensified, where Fe hydrolysis was also expedited. However, Fe removal peaked at 97.1% with 0.7 g of glucose and dropped dramatically to 40.6% with 1 g of glucose. By adding 0.7 g of glucose, approximately, 98.6% nitrate was consumed, and the residual TOC was less than 375 mg/L in the solution. With the addition of 1 g of glucose, the complete depletion of nitrate occurred, but TOC was residual at 1232 mg/L in the solution, revealing that the added glucose was too high. Such an overdose of glucose and its intermediates first reduced Mn<sup>3+</sup> as Mn<sup>2+</sup> and then reacted

with Fe<sup>3+</sup> to produce Fe<sup>2+</sup>. The newly produced Fe<sup>2+</sup> had a small hydrolysis constant compared with Fe<sup>3+</sup> and did not hydrolyze significantly in the hydrothermal system, leading to the high level of residual Fe<sup>2+</sup>. The added glucose and its intermediates were also adsorbed by Al/Fe-bearing flocs and/or minerals to generate an organic cover. This cover prevented contact between particles and restrained the crystal growth. Thus, fine boehmite rods disappeared, and the replacement of hematite by maghemite occurred at a glucose dosage of >1 g. Consequently, overdosed glucose had two effects: one was curbing reduction from Fe<sup>3+</sup> to Fe<sup>2+</sup>; the other was restraining the generation of well-crystallized boehmite and hematite. Besides glucose, other organics, for example, methanol,<sup>38</sup> ethanol,<sup>39</sup> levulinic acid,<sup>30</sup> and ascorbic acid,<sup>40,41</sup> also reacted with nitrate. Such a reaction also accelerated in the presence of enough H<sup>+</sup> and became slow with the increase in solution pH,<sup>42,43</sup> where the solution pH was controlled and the hydrolysis of Fe was effective. In general, the higher the molecular weight of organics, the more the nitrate consumption. For instance, by adding ethanol, double amount of nitrate and H<sup>+</sup> was consumed, in comparison with methanol.<sup>39</sup> Thus, organics with high molecular weight was acceptable in the pH adjustment. Among the abovementioned organics, glucose was a macromolecular organic matter, which was cheap and marketable after calculating its dosage in the hydrothermal reaction. Therefore, glucose can be served as a cheap reagent in the recovery of Mn from GWTS.

The phase transition of Al/Fe hydrolysates to boehmite and hematite was retarded when the hydrothermal temperature decreased from 270 to 180 °C. Only weakly crystallized Fe hydroxide and Al/Cl hydroxide were generated. More importantly, the polymerization of Al became significantly slower, but Fe hydrolysis was enhanced. Al hydrolysis consumed higher energy than Fe. Thus, Al showed a slow hydrolysis rate at 180 °C, which caused a low removal rate of Al. The decrease in the Al removal rate generated a low amount of H<sup>+</sup>. Correspondingly, Fe hydrolysis became intensified, resulting in an increase in Fe removal efficiency.

In the sludge, the Mn ion valence state was Mn<sup>3+</sup>, which was dissolved in the acid solution. In the hydrothermal process, Mn<sup>3+</sup> had high redox potential and preferentially reacted with glucose compared with Fe<sup>3+</sup>. This was effective for restraining Fe<sup>3+</sup> reduction and facilitating Fe<sup>3+</sup> hydrolysis and removal. Thus, at an optimal glucose dosage of 0.7 g, a part of Mn<sup>3+</sup> reacted with glucose to produce Mn<sup>2+</sup>. Mn<sup>3+</sup> and the newly reduced Mn<sup>2+</sup> were coprecipitated when the pH of the solution was adjusted to 8.3 in order to generate hausmannite as the final product.

**2.5. Potential Application in Waste Recycling.** With the novel method, impure Al and Fe were effectively

Table 2. Recycling Method of Mn from Mn-Bearing Waste

Mn-bearing waste	major composition	Mn recycling method	product and residue	refs
dry cells	29.0% Mn	acid leaching—ozonation—electroreduction	Mn	47
	23.0% Zn		MnO	
	9.0% C		ZnO C	
electrolytic manganese anode mud	8.0% Si 2.6% Al 2.4% Mn 1.4% Fe	water leaching—carbonate precipitation process	MnCO <sub>3</sub>	48
electric-arc furnace slag	38.1% Ca	improved hydrometallurgical process	Mn <sub>3</sub> O <sub>4</sub>	39
	19.2% Fe		CaSO <sub>4</sub>	
	7.7% Si		Fe <sub>2</sub> O <sub>3</sub>	
	7.3% Mn		Si-undissolved	
	0.5% Al			
GWTS	9.0% Fe	acid leaching—hydroxide precipitation process	MnO <sub>2</sub>	5
	7.9% Mn		Fe(OH) <sub>3</sub>	
GWTS	14.6% Fe	improved hydrothermal route	Mn <sub>3</sub> O <sub>4</sub>	this study
	11.5% Al		Fe <sub>2</sub> O <sub>3</sub>	
	6.3% Mn		AlO(OH)	
	6.1% Si		Si-undissolved	

precipitated from Mn-bearing acidic solution and became residual at 477 and 181 mg/L in the treated solution, respectively. More than 98% of Mn was retained and recycled as hausmannite by adding NaOH, along with the minimum of impure Al/Fe. The recycled hausmannite was highly purified with a Mn content of 63.6%, which is close to the composition of trimanganese tetraoxide. The recycled hausmannite was directly used as a Mn source to prepare  $\gamma$ -MnOOH nanorods after further treatment. Thus, it can be directly used as a chemical API and used to produce separation membranes, dye adsorbents, and electrocatalysts in the reduction of O<sub>2</sub>. The byproduct was a mixture of boehmite and hematite with an Al and Fe content of 39.3% and 41.7%, respectively, in which the Mn content was less than 0.3%. This byproduct is an essential component of inorganic pigments and can be used to produce colorful cement and glass.<sup>24,44</sup>

In the Al/Fe separation, Mn was cationic and did not attach onto the surface of Al/Fe-bearing hydroxide and/or minerals (e.g., boehmite and hematite), resulting in high levels of residual Mn in the solution. Other heavy metals, such as Zn, Cu, and Ni, were also adsorbed by an Al/Fe-bearing adsorbent and then released into the solution when the pH of the solution was adjusted to <3.<sup>13,45,46</sup> This finding revealed that such heavy metals showed similar characteristics to Mn and can be kept in the acidic solution during Al/Fe separation. Moreover, the heavy metal-rich solution is an important resource and can be treated with conventional methods (e.g., resin column and extraction reagent) to prepare highly valuable products. Many hazardous wastes, including electroplating sludge, waste battery, and slag, are rich in heavy metals and can be purified with the abovementioned method, which not only reduces the total production of hazardous wastes but also produces valuable heavy metal-bearing products.

Other Mn-bearing wastes, for example, dry cells, electrolytic manganese anode mud, and electric-arc furnace slag, are categorized in Table 2. When the sludge was dissolved in hydrochloric acid, an acidic leachate was generated, where more than 98% Mn was recycled as hausmannite with a Mn content of 63.6% after the separation of Fe/Al via a hydrothermal route. Even though Fe/Al reacted with an

extractant to cause pollution,<sup>49</sup> Cyanex 923 was used to be an extractant with acid leaching and chemical precipitation method, in which 97% Mn was recycled.<sup>47</sup> Ong et al. employed H<sub>2</sub>SO<sub>4</sub> and H<sub>2</sub>O<sub>2</sub> leaching Mn and then precipitated Mn as MnO<sub>2</sub> with the addition of exogenous KMnO<sub>4</sub>,<sup>5</sup> where KMnO<sub>4</sub> was residual in the rest solution and should be further removed.

With our method, separation of Fe/Al prior to the Mn recovery is important because it avoids expensive extractants/resins and additional manganese sources. Moreover, the separated Fe/Al was a mixture of hematite and boehmite with a Mn content of <0.3% and can be inorganic pigments to produce colorful cement and glass.<sup>24,44</sup> Besides that, the supernatant with Fe, Al, Mn concentration <3 mg/L after Mn precipitation can be directly discharged according to the discharge standard for electroplating industries of China. Such results showed that secondary waste was not generated. Therefore, this method exhibited obvious advantages of efficient Mn recovery with secondary pollutants.

This method also employed an alternative strategy to purify Fe/Al from industrial wastes, for example, saline slag,<sup>50,51</sup> lamination waste,<sup>52–54</sup> and rare-earth extraction residue.<sup>55</sup> For instance, pretreatment Al-bearing waste with an Al content of >50% was discharged from fusion processing of aluminum industry<sup>50,51</sup> and can be purified as hydrotalcites and boehmite, with the enrichment of SiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub> in the residual solution. Accordingly, the iron-concentrated powder precipitated from the separation of rare earths from Nd-Fe-B waste<sup>55</sup> can also be purified so that the Fe content in the powder dramatically increased up to 65 wt %. Even though abundant of acid and heating energy were consumed in the purification of Fe/Al waste, the obtained product with high purity was marketable.

### 3. CONCLUSIONS

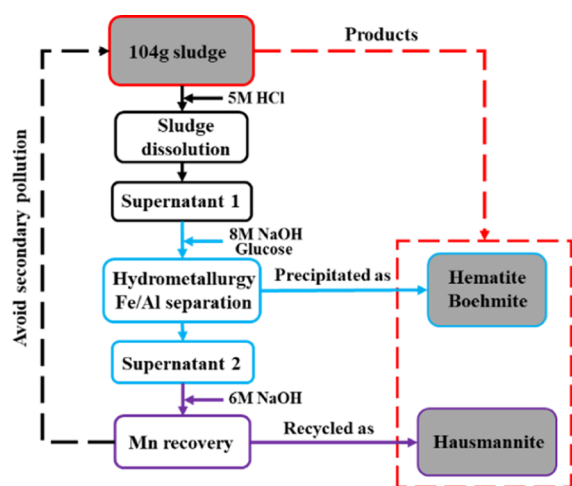
GWTS is a solid waste rich in Mn. It was purified as hausmannite via an acid dissolution and hydrothermal method. With the novel method, Mn was recycled in three steps as follows: First, the sludge was dissolved in hydrochloric acid to generate an acidic solution with Mn/Al/Fe concentrations of 2903, 9122, and 6259 g/L, respectively. Second, the acid

solution was hydrothermally treated to precipitate Al/Fe as boehmite and hematite particles. The hydrothermal temperature and glucose dosage were optimized to 270 °C and 0.7 g, where 94.8% Al and 97.1% Fe were precipitated in the form of irregular particles, along with a Mn loss of <2%. Third, the concentration of Mn in the solution was kept at 2850 mg/L, and Al and Fe were residual at 477 and 181 mg/L, which were further precipitated by adjusting the pH of the solution to 8.3 with NaOH. The recycled product contained 63.6% Mn, 0.7% Al, and 0.5% Fe and showed a similar composition to the chemical API trimanganese tetraoxide. In summary, the method effectively purified Mn-rich waste as hausmannite and had potential application in recycling of Mn-bearing waste.

## 4. MATERIALS AND METHODS

**4.1. Sludge Generation and Pretreatment.** Groundwater treatment plant iron mud was obtained from the sedimentation tank of Shuangyang water treatment plant (Changchun, China). It was generated in the following steps: In the plant, groundwater containing 1.3 mg/L  $\text{Mn}^{2+}$  and 6.2 mg/L  $\text{Fe}^{2+}$  was first pumped and rapidly oxidized by bubbling with gas aeration. Afterward, the groundwater was further treated by chlorine oxidation to oxidize  $\text{Mn}^{2+}$ . Subsequently, polyaluminum chloride (PAC) was added to coagulate the groundwater and precipitate oxidized  $\text{Fe}^{2+}$  and  $\text{Mn}^{2+}$ , generating GWTS. The sludge was vacuum-dried at 50 °C for 48 h and then characterized by chemical composition analysis. Its major composition was 14.6% Fe, 6.3% Mn, 11.5% Al, 3.2 Si, and 0.2% Ca.

**4.2. Fe/Al Precipitation and Mn Recovery Experiment.** Fe/Al separation and Mn recovery were performed in the following steps (Figure 10): First, 10.4 g of sludge was



**Figure 10.** Flow sheet of the Fe/Al separation and Mn recovery experiment.

dissolved in 5 M HCl at 70 °C under stirring at 90 rpm for 30 min. After cooling the acid to room temperature, 500 mL of the supernatant (named as supernatant 1) was gathered and then adjusted to pH 0.5 with 8 M NaOH. No precipitate was generated in supernatant 1, and the concentrations of Fe, Mn, and Al were 6259, 2903, and 9122 mg/L, respectively. The major composition of the undissolved residual was 32.4% Si, 4.4% Fe, 2.1% Mn, and 0.8% Ca. Second, 20 mL of supernatant 1 was transferred into a 50 mL Teflon vessel and added with 1.9 g of  $\text{NaNO}_3$  and 0.7 g of glucose. The

vessel was heated at 270 °C for 20 h and then cooled down to room temperature. The deposit was collected at the vessel bottom, and the generated supernatant (named as supernatant 2) was also collected. Control experiments were performed in accordance with the abovementioned procedures, in which the glucose dosage varied from 0 to 1.5 g. Subsequently, the hydrothermal temperature was also optimized in the range of 180–270 °C.

Optimal Fe/Al removal was achieved by heating at 270 °C for 20 h with the addition of 0.7 g of glucose. The corresponding supernatant 2 was further neutralized to pH 8.3 with 6 M NaOH to precipitate Mn. The collected Mn-bearing precipitates were vacuum-dried at 60 °C for 12 h and then characterized by X-ray diffraction (XRD), scanning electron microscope (SEM), and X-ray fluorescence (XRF) along with the Fe/Al precipitates.

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## Notes

The authors declare no competing financial interest.

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