Extraction of Valuable Metals and Preparation of Mesoporous Materials from Circulating Fluidized Bed-Derived Fly Ash via an Acid–Alkali-Based Alternate Method

Zhibin Ma,* Xueli Zhang, Yanxia Guo, and Fangqin Cheng*

ABSTRACT: Stringent leaching conditions including high pressure, temperature, and chemical consumption limit the extraction of valuable metals from circulating fluidized bed-derived high-alumina fly ash (CFB-HAFA) via the acid leaching method. In the present study, a complex utilization of CFB-HAFA, including the extraction of valuable metals (Al, Li, and Ga) and preparation of mesoporous material, is realized via a moderate acid–alkali-based alternate method. The results show that 82, 78, and 69% of Al, Li, and Ga, respectively, in CFB-HAFA are extracted by two treatments of acid leaching under moderate conditions of 15 wt % HCl concentration and 90 °C leaching temperature. The leaching behaviors of metals follow a shrinking core model, and the leaching process is first controlled by the surface chemical reaction at the initial stage and H+ diffusion thereafter. Numerous slit-shaped mesopores form in the residue during acid leaching. The final residue with a specific surface area of 273 m²/g can be used as an efficient adsorbent for removing methylene blue from dye wastewater. The maximum adsorption capacity is approximately 140.0 mg/g at room temperature. The Langmuir adsorption isotherm and pseudo second-order model can well describe the adsorption process and kinetics, implying that the adsorption is a monolayer and chemical adsorption.

1. INTRODUCTION

Coal is the major energy resource in China. In recent years, coal enriched in valuable metals, including aluminum (Al), lithium (Li), gallium (Ga), germanium (Ge), and rare earth elements (REEs), has been found in specific areas of China.¹ For example, coals from Jungar Coalfield, Inner Mongolia, China, have been found to be enriched in Al, Li, Ga, and REE.² Coals from Ningwu Coalfield, Shanxi Province, China contain abundant amounts of Al, Li, and Ga.³ Most of these valuable metals in coal transform into coal fly ash during coal combustion.⁴ Coal fly ash with high contents of alumina (Al₂O₃) is generally called “high-alumina fly ash” (HFAA), which can be used to produce Al-based products as a substitute for bauxite.⁵,⁶

According to boiler types and combustion conditions, HFAA can be divided into two categories: pulverized coal furnace-derived HFAA (PC-HFAA) and circulating fluidized bed boiler-derived HFAA (CFB-HFAA).⁷ Although the emission of PC-HFAA is currently greater than that of CFB-HFAA, the emission of CFB-HFAA is increasing each year in China. Large amounts of low-quality coal and solid wastes, such as coal gangue and coal slime, are generated annually during coal mine production and coal washing process in main coal-producing areas, and this situation may result in various environmental problems.⁸ As a response to the urgent demand to burn these inferior fuels at a massive scale, CFB boilers have been widely applied to generate electricity and supply heat.⁹ Therefore, CFB-HFAA emissions are rapidly increasing, and the amounts of CFB-HFAA are accumulating, especially in the major coal-producing areas.¹⁰ Recycling the valuable metals including Al, Li, and Ga from CFB-HFAA can achieve ash utilization with high economic benefits and also reduce...
environmental impacts caused by bauxite mining and ash storage.

At present, numerous studies have investigated various methods for extracting valuable metals from PC-HAFA. However, few works have focused on extracting metals from CFB-HAFA. Given that the combustion temperature (800–950 °C) of a CFB boiler is considerably lower than that of a traditional PC furnace (1300–1700 °C), the mineral composition and micromorphology of CFB-HAFA substantially differ from those of PC-HAFA. In PC-HAFA, Al is present in the glass phase and mullite with a stable structure. Al in the glass phase is easily dissolved by acid leaching, whereas Al in the mullite is not. This condition limits the extraction efficiency of Al in PC-HAFA. By contrast, Al is present in the amorphous aluminosilicate of CFB-HAFA. The extraction efficiency of Al in the amorphous aluminosilicate of CFB-HAFA during acid leaching directly is higher than those in mullite of PC-HAFA, indicating that Al in CFB-HAFA is extracted more easily than that in PC-HAFA under the same leaching conditions. Li et al. found that the extraction efficiency of Al from CFB-HAFA can reach 85.84% using a one-step pressurized hydrochloric acid (HCl) leaching treatment under a liquid volume to solid mass ratio (denoted L/S) of 3.85, HCl concentration of 9.81 mol/L, leaching temperature of 160 °C, and leaching time of 3 h. However, HCl exhibits strong corrosiveness to equipment under pressurized conditions, and the acid leaching residue cannot be effectively utilized. These drawbacks substantially increase operation costs and limit its further development. Yang et al. reported that the extraction efficiency of Al₂O₃ from CFB-HAFA by using the hydrochemical process can achieve 92.31% under optimum conditions at 280 °C, 45 wt % NaOH solution with CaO, a L/S of 9 mL/g, and a residence time of 1 h. It is very difficult to extract Al from CFB-HAFA economically. The extraction process generally requires high chemical consumption or application of stringent reaction conditions, such as high temperature or pressure. A comprehensive technology for extracting multiple metals from CFB-HAFA under moderate conditions that also considers the utilization of the leaching residue would have broad application prospects.

In a previous study, we applied a moderate acid–alkali-based alternate method for extracting multiple metals from CFB-HAFA. The method extracted 78, 80, 72, and 55% of Al, Li, Ga, and REE, respectively, from CFB-HAFA in the HCl solution via three treatments of acid leaching at a temperature of 90 °C, a 20% HCl solution, a L/S of 5 mL/g, and a residence time of 2 h. In addition, the final leaching residue had abundant mesopores and a high specific surface area of 205 m²/g. However, the process flow is tedious because CFB-HAFA is treated by three treatments of acid leaching and two treatments of alkali leaching, which greatly limits the application and further development of this technology. In addition, excessive amounts of solvents (HCl and NaOH) were used to dissolve metals and reveal the separation mechanism of Al and Si in ash during the leaching process. Thus, the leaching kinetics of metals from CFB-HAFA should be explored. However, little information regarding this aspect is available in the literature.

The present study investigated the effect of mechanical grinding of CFB-HAFA on the extraction efficiencies of Al, Li, and Ga, under acid–alkali-based alternate leaching conditions. Effects of key process parameters, including solvent concentration, L/S, and leaching temperature, on the extraction efficiencies were also examined. Furthermore, we also investigated the adsorption performance of the leaching residue for methylene blue (MB) in aqueous solution. This study aims to not only extract valuable metals from CFB-HAFA under moderate conditions but also explores the use of the leaching residue.

2. RESULTS AND DISCUSSION

2.1. Properties of Raw Fly Ash. The major composition and rare element concentration of CFB-HAFA are given in Table 1. Figure 1 shows that the major mineral matters in the CFB-HAFA are quartz (SiO₂), anhydrite (CaSO₄), calcite (CaCO₃), and hematite (Fe₂O₃). The total contents of crystal minerals only accounts for 26.3% of the CFB-HAFA; the rest is amorphous. All Al₂O₃ in the CFB-HAFA is in the form of amorphous aluminosilicate.

2.2. Effect of Particle Size Distribution of CFB-HAFA on Extraction Efficiency. The effects of mechanical grinding on the particle size distribution of CFB-HAFA are shown in Figure 2 and Table 2. The particle size distribution of ash particles is changed by mechanical grinding. The sharp peak between 10 and 100 μm in the particle size distribution curve of HAFAs shifts to the left, which belongs to the fine particle range, and its intensity dramatically decreases at the first stage (0–3 h) of grinding. Meanwhile, the intensities of peaks...
between 0.1 and 10 μm increase and the values of Dv (50) and Dv (90) evidently decrease. These results indicate that the increase in fineness of ground ash particles is sharp at the first stage (0–3 h), and then gradually decreases at the second stage (3–5 h). The fine particles tend to absorb moisture in the air and agglomerate. Hence, the particle size starts to increase slightly when grinding time exceeds 7 h.

The variation in extraction efficiencies of Al, Li, and Ga from CFB-HAFA under different grinding times is shown in Figure 3. The extraction efficiency of Al from raw ash samples is approximately 52% and that from ground ash samples with a grinding time of 3 h reaches approximately 62%. The extraction efficiency of Al from ground ash samples at a grinding time of 0–3 h increases as grinding time increases, implying that the reduction of the average particle size of CFB-HAFA is beneficial to Al dissolution. The increase in fineness of ash samples enhances the specific surface area of particles and results in the formation of a new surface that promotes the contact between Al and H+, thus increasing extraction efficiency of Al. Furthermore, several new structural defects (imperfections in ordered structures) appear in the ash particles during the milling process that improves the dissolution reactivity of components in ash samples. For the ground ash samples with a grinding time of 3–5 h, the extraction efficiency of Al slightly increases as grinding time increases, and then remains constant when grinding time exceeds 7 h. When the grinding time exceeds 3 h, the particle size of ground ash does not readily decrease to a great extent. Thus, the extraction efficiency of Al does not easily improve continually. Like the variations in Al extraction efficiency, the extraction efficiencies of Li and Ga from ground ash samples initially increase as grinding time increases and then remain constant when grinding time exceeds 3 h. However, the increase in the extraction efficiencies of Li and Ga is lower than that of Al because the concentrations of Li and Ga in the ash samples are relatively low and thus small amounts of Li and Ga are exposed to the new surfaces after grinding. The extraction efficiencies of Li and Ga from the ground ash samples with a grinding time of 3 h are approximately 47 and 58%, respectively. Therefore, a grinding time of 3 h is suitable for extracting Al, Li, and Ga from ground CFB-HAFA. The ground CFB-HAFA samples with a grinding time of 3 h were used as raw materials in subsequent experiments.

### 2.3. Effects of Leaching Parameters on Extraction Efficiency

#### 2.3.1. Dissolution of Al, Li, and Ga during the First Acid Leaching

Leaching of metal ions from ash samples is an important step in the recovery of valuable metals. The dissolution of Al, Li, and Ga from the ground CFB-HAFA is a complex process that depends on several factors such as HCl concentration and L/S ratio. The effect of HCl concentration and L/S ratio on the extraction efficiency is shown in Figure 4. The extraction efficiency of Al is approximately 62% under 20% HCl concentration and L/S of 5 mL/g. It slightly decreases when the HCl concentration increases to 25% because AlCl3 solubility decreases at high HCl concentrations. Therefore, increasing the HCl concentration does not improve the extraction efficiency of Al in the 20% HCl solution does not substantially decrease when the L/S decreases from 5 to 4 mL/g. However, it decreases from 61 to 57% when the L/S decreases from 4 to 3 mL/g. The extraction efficiency of Al under the 15% HCl and L/S of 5 mL/g is similar to that under the 20% HCl and L/S of 4 mL/g but higher than that under the 20% HCl and L/S of 3 mL/g. As the L/S decreases, the extraction efficiency of Al gradually decreases in the 15% HCl solution because the probability of H+ colliding with Al is gradually reduced. Unlike the extraction efficiency of Al, the extraction efficiencies of Li and Ga in these solutions remain stable, except when the HCl concentration and L/S are 15% and 3 mL/g, respectively, in which the extraction efficiencies evidently decrease. Although the amounts of H+ in the solution are excessive for Li and Ga in ash samples, some H+ does not readily contact with Li and Ga distributed in the ash samples, thus decreasing the extraction efficiency. Based on the high extraction efficiency and low acid consumption, the appropriate conditions for the first acid leaching treatment are 15% HCl and L/S of 5 mL/g. The extraction efficiencies of Al, Li,
and Ga under this condition are approximately 61, 48, and 57%, respectively. The first acid leaching residue (denoted as HR-1) obtained under optimum conditions was used in subsequent alkali leaching experiments.

Figure 5 shows that the extraction efficiencies of Al, Li, and Ga increase as temperature increases. The dissolution of metals in HCl solution could be divided into two stages according to the dissolution rate. In stage I, the metals in ash rapidly dissolve in the first 20 min. In stage II, the dissolution rate decreases after 20 min. As temperature increases, the trend becomes obvious. The dissolution of metals in the HCl solution becomes stable after 100 min.

In acidic leaching, the heterogeneous reaction kinetics of most solid particles can be interpreted by shrinking core models. The mechanisms of these models are generally represented as diffusion, chemical, and mixed control models.22 The extraction process is usually controlled by one of these steps. Shrinking core model equations can be expressed as eqs 1 or 2 according to the surface chemical reaction or diffusion-controlled processes.

Figure 4. Variations in extraction efficiencies of Al, Li, and Ga from ground CFB-HAFA samples at 90 °C under different HCl concentrations and L/S.

Figure 5. Variations in extraction efficiencies of (a) Al, (b) Li, and (c) Ga during the first acid leaching treatment over time between 60 °C and 90 °C (15% HCl; L/S = 5 mL/g).
\[ 1 - (1 - r)^{1/3} = K_c t \text{ (chemical reaction controlled process)} \quad (1) \]

\[ 1 - 3(1 - r)^{2/3} + 2(1 - r) = K_d t \text{ (diffusion-controlled process)} \quad (2) \]

where \( r \) is the extraction efficiency of metal, \( t \) is the reaction time (min), and \( K_c \) and \( K_d \) are rate constants.

Experimental data were fitted against the eqs 1 and 2 to analyze leaching kinetics, and the results were attached in the Supporting Information (Figure S1). Figure S1 shows that the kinetics data of Al, Li, and Ga in stage I fit well to the chemical control model because of high \( R^2 \) values, whereas the data in stage II fit well to the diffusion control model. In stage I, the metals on the ash surface react with \( H^+ \) and then dissolve in the solution. The leaching process is controlled by a surface chemical reaction because the metals on the particle surface and \( H^+ \) are abundant in this stage. As the reaction progresses, the amounts of Al, Li, and Ga on the particle surface dramatically decrease, and the undissolved Si atoms remain on the particle surface. \(^{18}\) \( H^+ \) has to pass through the silicon layer to react with metals in the interior of ash particles. Therefore, the leaching process is controlled by \( H^+ \) diffusion in stage II.

2.3.2. Removal of Si Accumulated on the Particle Surface by Alkali Leaching. Si atoms in the ash samples are insoluble in the HCl solution. Thus, large amounts of Si atoms accumulate on the particle surface during acid leaching, thereby hindering the dissolution of Al further. By contrast, Si atoms can be dissolved in the NaOH solution, thereby separating Si and Al. The effects of NaOH concentration and \( L/S \) on the dissolution ratio of Si from HR-1 were investigated (Figure 6a). The dissolution ratio of Si initially increases as the NaOH concentration increases from 10 to 15\% and then decreases when the NaOH concentration reaches 20\%. The mineral phases of alkali leaching residues obtained under different NaOH concentrations were analyzed to explain the reason for the decline, and the results are shown in the Supporting Information (Figure S2). Figure S2 shows that sodalite \((Na_4Al_3Si_3O_12Cl)\) forms and deposits on the residue in 20\% NaOH solution, thereby decreasing the dissolution ratio of Si. The dissolution ratio of Si does not dramatically decrease under 15\% NaOH when the \( L/S \) decreases from 5 to 4 mL/g but it evidently decreases when the \( L/S \) decreases to 3 mL/g. Therefore, the optimum parameters for alkali leaching are 15\% NaOH and \( L/S \) of 4 mL/g. Under these conditions, the dissolution ratio of Si is approximately 56\% and approximately 3.5\% of Al dissolves in the NaOH solution. The concentrations of Li and Ga in the alkali filtrate are measy, indicating that Li and Ga in CFH-HAFA mainly dissolve in the HCl solution.

Figure 6b shows that as the temperature increases, the dissolution ratio of Si gradually increases. Certain amounts of Si atoms accumulated on the surface of HR-1 rapidly dissolve
and its dissolution rate in the slowly dissolved during the second acid leaching treatment, increases as the temperature increases. The Al atoms in SR are mentioned previously, the extraction e
bonds of several Si
exposes numerous Al atoms to SR. In addition, the chemical Leaching.

Dissolution of Si atoms during alkali leaching obtained under optimum conditions was used in the fi
treatment. They decrease to 15, 28, and 7%, respectively, when the L/S decreases from 4 to 3 mL/
g. Therefore, the optimum conditions were 15% HCl and L/S of 5 mL/g during the second acid leaching treatments. The SR obtained under 15% NaOH and L/S of 4 mL/g was used in the experiments.

Figure 7a shows the effects of L/S on the extraction efficiencies of Al, Li, and Ga. Approximately 21, 30, and 12% of Al, Li, and Ga, respectively, in SR are extracted by 15% HCl solution and L/S of 5 mL/g. When the L/S were 5 and 4 mL/
g, the extraction efficiencies of Al, Li, and Ga are similar during the first acid leaching treatment. Considering that Al content in SR was lower than that in raw ash samples, the solution with 15% HCl was used in the second acid leaching treatments. The SR obtained under 15% NaOH and L/S of 4 mL/g was used in the experiments.

Figure 7b shows the dissolution behavior of Al in SR during the second acid leaching treatment between 60 and 90 °C. As mentioned previously, the extraction efficiency of Al gradually increases as the temperature increases. The Al atoms in SR are slowly dissolved during the second acid leaching treatment, and its dissolution rate in the first 20 min is lower than that during the first acid leaching treatment. The extraction efficiencies of Al between 60 and 90 °C during the second acid leaching treatment were fitted against eq 2 to analyze leaching kinetics, and the results were attached in the Supporting Information (Figure S3). Figure S3 shows that the kinetics data are fitted well to the diffusion-controlled model, indicating that Al dissolution during the second acid leaching treatment is mainly controlled by H⁺ diffusion. Although some Al atoms are liberated and exposed on the particle surface during alkali leaching, the content of Al on the particle surface is lower than that on raw ash particles because approximately 61% of Al in ash is extracted during the first acid leaching treatment.

2.3.3. Dissolution of Al, Li, and Ga during the Second Acid Leaching. Dissolution of Si atoms during alkali leaching exposes numerous Al atoms to SR. In addition, the chemical bonds of several Si–O–Al units in the residue are broken by the NaOH solution, thus liberating some free Al atoms, which can be easily dissolved in HCl solution. The optimum concentration of the HCl solution was 15% during the first acid leaching treatment. Considering that Al content in SR was lower than that in raw ash samples, the solution with 15% HCl was used in the second acid leaching treatments. The SR obtained under 15% NaOH and L/S of 4 mL/g was used in the experiments.

2.3.4. Dissolution of Other Ions during Leaching Treatment. In addition to Al, other metals including Ca, Fe, and Mg in CFB-HAFA are also dissolved in the HCl solution. Approximately 97.4, 88.6, 99.3, 58.2, and 19.7% of Ca, Fe, Mg, K, and Ti, respectively, in CFB-HAFA are dissolved in the HCl solution under the optimum conditions during the first acid leaching treatment. Approximately 0.9, 6.6, 8.5, and 5.9% of Ca, Fe, K, and Ti, respectively, in the ash are dissolved during the second acid leaching treatment. Therefore, almost all of Ca, Fe, and Mg in CFB-HAFA are dissolved in the HCl solution and entered the acid leachate. Approximately 66.7 and 25.6% of K and Ti enter the acid leachate.

In addition to Si, approximately 20.3 and 3.5% of K and Al, respectively, are dissolved in the NaOH solution under the optimum conditions. Other elements cannot enter the alkali leachate under the current conditions.

In summary, approximately 82, 78, and 69% of Al, Li, Ga, respectively, in CFB-HAFA are extracted during two treatments of acid leaching, and 56% of Si is dissolved by the NaOH solution under mild conditions with low concentrations of leaching agents and low L/S values. Although the extraction efficiencies of valuable metals are not the highest, the conditions are mild and the consumption of chemical reagents is relatively low. Li and Ga in the acid leachates can be separated first, and the remaining leachates containing Al can be used to prepare the aluminum chloride flocculant.23 The alkali leachates containing NaOH and Na₂SiO₃ can be used to activate the coal fly ash to prepare geopolymers, which are considered as excellent functional materials.24

2.4. Variations in the Pore Structure of Leaching Residues. Figure 8 depicts the pore size distribution and N₂-adsorption/desorption isotherms of CFB-HAFA and leaching residues. Pore structure parameters are given in Table 3. Almost no mesopore is observed in CFB-HAFA, which has a low specific surface area of 12 m²/g. Large amounts of slit-shaped mesopores (Figure 9a) with a pore diameter of 2–5 nm form in HR-1, as metals in the ash samples are dissolved in the HCl solution after the first acid leaching treatment. During the acid leaching, the pore volumes of the particles dramatically increase and the average pore diameter decreases. Thus, the specific surface area sharply increases from 12 to 150 m²/g. Figure 9b indicates that most mesopores disappear after alkali
leaching because Si dissolution in NaOH solution results in their collapse or enlargement. Consequently, the specific surface area of SR decreases to 38 m²/g. Figure 9c shows that numerous slit-shaped mesopores with a pore diameter of 2−16 nm form again in HR-2 after the second acid leaching treatment, and its specific surface area reaches 273 m²/g.

Although the extraction efficiency of Al during the second acid leaching treatment is considerably lower than that during the first acid leaching treatment, the content of mesopores and specific surface area of HR-2 are higher than those of HR-1. These results indicate that some mesopores formed during the first acid leaching treatment on the particle surface may be blocked by several products generated during alkali leaching, such as sodium silicate hydrate gel.25 These gels are dissolved in HCl solution so that the mesopores are reopened, and thus the specific surface area of the residue sharply increases. The variations in the pore structure of particles during acid and alkali leaching experiments are consistent with those of our previous study.18 However, the specific surface area of the acid leaching residue is larger in the present study because the particle size of the ground ash decreases and the extraction efficiencies of metals increase. Numerous mesopores are created by the dissolution of metals from ash in the HCl solution.

2.5. Adsorption Performance of MB on HR-2. The final residue HR-2 has potential for being used as an adsorbent because of its abundant mesopores and high specific surface area. The adsorption of MB onto it in aqueous solution was investigated. Figure 10 shows the effects of the adsorbent dosage, initial concentration of MB, and contact time on the adsorption capacity.

Langmuir and Freundlich models were used to describe the equilibrium adsorption for MB on HR-2. The linear forms of Langmuir and Freundlich isotherm equations are as follows26

$$C_e = \frac{1}{q_m K_I} \left( 1 + \frac{1}{q_m} C_e \right)$$

(3)

$$\log q_e = \log K_F + \frac{1}{n} \log C_e$$

(4)

where $C_e$ is the equilibrium concentration of MB (g/L), $q_e$ is the amount of MB adsorbed at equilibrium (mg/g), $q_m$ is the maximum adsorption capacity (mg/g), and $K_I$ (L/mg) is the Langmuir isotherm constant. $K_F$ (mg/g) and $1/n$ (dimensionless) are the constants of a Freundlich isotherm. The experimental data are fitted well to the Langmuir model because of the high $R^2$ value (0.9983), and the results are shown in Figure 11. The fitting results of the Freundlich model are not given because of the very low $R^2$ value (0.1608). These
indicate that the adsorption process occurs on a homogeneous surface of HR-2 by monolayer adsorption. The maximum adsorption capacity calculated using the Langmuir model is close to the experimental one, implying that the adsorption process is mainly monolayer.

Adsorption kinetics is very important for the potential applications of the adsorbent. The pseudo first-order and pseudo second-order kinetics models are used to elucidate the adsorption kinetic process. The equations of these models are expressed by eqs 5 and 6:  

\[
\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303}t
\]  

(5)

\[
t = \frac{1}{k_2q_e^2} + \frac{1}{q_e} t
\]  

(6)

where, \(q_e\) and \(q_t\) are the amounts of MB adsorbed per unit of the adsorbent (mg/g) at equilibrium time and at a given time \(t\), respectively, \(k_1\) and \(k_2\) are the rate constants of pseudo first-order and pseudo second-order kinetic models, respectively, for adsorption.

Figure 12a,b depicts the curve-fitting plots of the pseudo first-order and pseudo second-order plots, respectively, and the parameters obtained for the two models are presented in Table 4. The results indicate that the pseudo second-order model is more suitable for the description of the adsorption kinetics of MB on HR-2 because of the high correlation coefficient \((R^2 = 0.9996)\). In addition, the calculated \(q_e\) value according to the pseudo second-order model is 144.1 mg/g and close to the experimental one (140.0 mg/g). Therefore, the mechanism for the adsorption of MB on HR-2 is chemical adsorption, which involves electrostatic interaction between the surface charge of HR-2 and MB+.

3. CONCLUSIONS

(1) Reducing the particle size of CFB-HAFA by mechanical grinding can increase the extraction efficiencies of Al, Li, and Ga from ash in HCl solution. Approximately 82, 78, and 69% of Al, Li, and Ga in CFB-HAFA are extracted after two treatments of acid leaching under 15% HCl solution and a temperature of 90°C. The optimum L/S for the first and second acid leaching treatments are 5 and 4 mL/g, respectively. The leaching kinetics of Al, Li, and Ga during the first acid leaching treatment follow the shrinking core model governed by the surface chemical reaction in the first 20 min and H+ diffusion thereafter. The increase in the extraction efficiencies of valuable metals from CFB-HAFA is mainly limited by H+ diffusion.

(2) Large amounts of slit-shaped mesopores in the residue form during acid leaching treatment. The final residue with a high specific surface area of 273 m²/g can be used as an efficient and low-cost adsorbent for removing MB from dye wastewater. The maximum adsorption capacity reaches approximately 140.0 mg/g at room temperature. The Langmuir adsorption isotherm and pseudo second-order model can well describe the adsorption process and kinetics, implying that the adsorption of MB on the leaching residue yields a monolayer and is by chemical adsorption.

4. MATERIALS AND METHODS

4.1. Materials. CFB-HAFA used in this study was obtained from the Pingshuo Coal Gangue Power Plant in Shanxi Province, China. The chemical reagents include hydrochloric acid (HCl, 15%).
acid (HCl, Beijing Chemical Works, 36–38 wt %), sodium hydroxide (NaOH, Sinopharm Chemical Reagent Co., Ltd., >96 wt %), and MB (C_{16}H_{18}CIN_{3}S, molecular weight: 373.90 g/mol, Sinopharm Chemical Reagent Co., Ltd.).

4.2. Mechanical Grinding. Mechanical grinding of CFB-HAFA was carried out using a planetary ball mill (QM-3SP4, Nanjing NanDa Instrument Plant, China). The weight of CFB-HAFA for each grinding was 30 g and the grinding time was 1, 3, 5, and 7 h, respectively.

4.3. Leaching Experiment. Raw and ground ash samples were used as raw materials for leaching experiments to investigate the effects of mechanical grinding on the extraction efficiencies of valuable metals. About 20 g of the ash sample was mixed with 20 wt % HCl solution of at a L/S of 5 mL/g. Slurries were stirred at a constant rate of 300 rpm for 2 h in a water bath at 90 °C and then filtered to obtain acid leachate and solid residue. The extraction efficiencies of Al, Li, and Ga were calculated on the basis of ion concentrations in the leachate and chemical composition of raw ash.

Ash was ground for 3 h. Ground ash was used as a raw material for optimization experiments of leaching parameters. The concentrations of HCl solution were 15, 20, and 25 wt %. L/S values were 3, 4, and 5 mL/g. Leaching temperature was set to 90 °C. The acid leaching experiments were conducted following the aforementioned methods. The first acid leaching residue (denoted as HR-1) was obtained under the optimum leaching conditions. HR-1 was then treated with the NaOH solution to dissolve Si accumulated on the surface of the residue. The adjustable concentrations of the NaOH solution were 10, 15, and 20 wt %, and the L/S values were 3, 4, and 5 mL/g, respectively. The alkali leaching residue (denoted SR) was obtained under the optimum leaching conditions. SR was then used as a raw material for optimization experiments of the second acid leaching parameters. HCl solution (15 wt %) was used during the second acid leaching treatment. The adjustable L/S values were 3, 4, and 5 mL/g. The second acid leaching residue was denoted HR-2. For the evaluation of kinetic parameters, the leaching experiments were operated under optimum conditions at different holding temperatures of 60, 70, 80, and 90 °C. All leaching experiments were conducted in triplicate with ±4% standard deviation. The results were the average of the three obtained values.

4.4. MB Adsorption Experiment. Cationic dye MB was employed as the adsorbed media to evaluate the adsorption performance of HR-2. The detailed conditions for the adsorption experiments are shown in Table 5. A certain quality of HR-2 and 50 mL of aqueous solution with different concentrations of MB were added to the flasks, and they were shaken with a speed of 170 shakes/min in a shaker at 25 °C for a certain time. Then, the mixture was centrifuged for 10 min at 5000 rpm. The MB concentration in the supernatant solution was analyzed by a UV spectrophotometer (TU-1800, PGENERAL, China) at 665 nm as \( \lambda_{\text{max}} \) of MB.

The adsorption capability \( (q_e, \text{mg/g}) \) of MB on HR-2 was calculated according to eq 7

\[
q_e = (C_0 - C_e) \frac{V}{m}
\]

(7)

where \( q_e \) is the amount of MB adsorbed at equilibrium (mg/g), \( C_0 \) and \( C_e \) are the initial and equilibrium concentrations of MB (g/L), \( m \) is the mass of the adsorbent (g), and \( V \) is the volume of solution (L).

4.5. Analytical Methods. The particle size distribution of CFB-HAFA was determined by a laser particle size analyzer (Mastersizer 3000, Malvern). Powder X-ray diffraction (XRD, D2, Bruker) with Cu Kα radiation was carried out to determine the minerals in the specimens, which were scanned with a 2θ step size of 0.02° in the range of 10–80°. The minerals in the raw CFB-HAFA were quantified according to the XRD patterns using TOPAS software (version 4.2, Bruker) based on the Rietveld method. Zinc oxide (AR, Sinopharm Chemical Reagent Co., Ltd., ≥99.0 wt %) was added to the samples to determine the content of amorphous components. The concentrations of ions in the leachate were determined with an inductively coupled plasma emission spectrometer (iCAP6300, Thermo). N\(_2\) adsorption was measured using an Accelerated Surface Area and Porosimetry System (Micromeritics, ASAP 2460) at 77 K. The specific surface area and pore size distributions of the residues were determined using the Brunauer–Emmett–Teller (BET) method of multilayered adsorption. Transmission electron microscopy (TEM, JEM-2100F, Japan) was applied to observe the pore structure of the leaching residues.

Table 5. Conditions for the Adsorption Experiments

| series | adsorbent dosage (g/L) | initial concentration of MB (g/L) | contact time (min) |
|--------|------------------------|----------------------------------|-------------------|
| A      | 0.5; 1; 2; 4; 7; 10    | 0.7                              | 1440              |
| B      | 2                      | 0.05; 0.1; 0.2; 0.3; 0.4; 0.5; 0.7; 0.9; 1.0; 1.1 | 1440              |
| C      | 2                      | 0.7                              | 5; 10; 20; 40; 60; 180; 300; 420; 600; 840; 1440 | 1440              |

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.0c04737.

Plots of chemical reaction and diffusion-controlled kinetic models of Al, Li, and Ga leaching with time between 60 and 90 °C (15% HCl; L/S = 5 mL/g), XRD patterns of alkali leaching residues obtained under different NaOH concentrations, and plot of diffusion-controlled kinetic models for Al dissolution during second acid leaching treatment between 60 and 90 °C (15% HCl; L/S = 4 mL/g) (PDF)

AUTHOR INFORMATION

Corresponding Authors

Zhibin Ma – State Environmental Protection Key Laboratory of Efficient Utilization Technology of Coal Waste Resources, Collaborative Innovation Center of High Value-Added Utilization of Coal-Related Wastes, Institute of Resources and Environmental Engineering, Shanxi University, Taiyuan 030006, PR China; orcid.org/0000-0003-2648-5002; Phone: +86 351 7018553; Email: mazhibin@sxu.edu.cn

Fangqin Cheng – State Environmental Protection Key Laboratory of Efficient Utilization Technology of Coal Waste Resources, Collaborative Innovation Center of High Value-Added Utilization of Coal-Related Wastes, Institute of Resources and Environmental Engineering, Shanxi University, Taiyuan 030006, PR China; orcid.org/0000-0002-2961-31303

https://dx.doi.org/10.1021/acsomega.0c04737

ACS Omega 2020, 5, 31995–31995
Authors

Xue Li Zhang — State Environmental Protection Key Laboratory of Efficient Utilization Technology of Coal Waste Resources, Collaborative Innovation Center of High Value-Added Utilization of Coal-Related Wastes, Institute of Resources and Environmental Engineering, Shanxi University, Taiyuan 030006, PR China

Yanxia Guo — State Environmental Protection Key Laboratory of Efficient Utilization Technology of Coal Waste Resources, Collaborative Innovation Center of High Value-Added Utilization of Coal-Related Wastes, Institute of Resources and Environmental Engineering, Shanxi University, Taiyuan 030006, PR China

Complete contact information is available at:
https://pubs.acs.org/10.1021/acsomega.0c04737

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

This work was supported by the National Natural Science Foundation of China (U1810205; 21506121) and Graduate Education Innovation Project of Shanxi Province (2020SY009).

ABBREVIATIONS

CFB-HAFA, circulating fluidized bed-derived high-alumina fly ash
PC-HAFA, pulverized coal furnace-derived high-alumina fly ash
L/S, liquid volume to solid mass ratio
HR-1, the acid leaching residue obtained during the first acid treatment
HR-2, the acid leaching residue obtained during the second acid treatment
SR, the alkali leaching residue
MB, methylene blue

REFERENCES

(1) Dai, S.; Finkelman, R. B. Coal as a promising source of critical elements: Progress and future prospects. Int. J. Coal Geol. 2018, 186, 155−164.
(2) Dai, S.; Li, D.; Chou, C.-L.; Zhao, L.; Zhang, Y.; Ren, D.; Ma, Y.; Sun, Y. Mineralogy and geochemistry of boehmite-rich coals: New insights from the Haerwusu Surface Mine, Jungar Coalfield, Inner Mongolia, China. Int. J. Coal Geol. 2008, 74, 185−202.
(3) Wang, J.; Wang, Q.; Shi, J.; Li, Z. Distribution and enrichment mode of Li in the No. 11 Coal Seam from Pingshuo Mining District, Shanxi Province. Energy Explor. Exploit. 2015, 33, 203−215.
(4) Ma, Z.; Shan, X.; Cheng, F. Distribution characteristics of valuable elements, Al, Li, and Ga, and rare earth elements in feed coal, fly ash, and bottom ash from a 300 MW circulating fluidized bed boiler. ACS Omega 2019, 4, 6854−6863.
(5) Shemi, A.; Ndlouvo, S.; Sibanda, V.; Van Dyk, L. D. Extraction of alumina from coal fly ash using an acid leach-sinter-acid leach technique. Hydrometallurgy 2015, 157, 348−355.
(6) Zhang, J.-B.; Li, S.-P.; Li, H.-Q.; He, M.-M. Acid activation for pre-delicitated high-alumina fly ash. Fuel. Technol. 2016, 151, 64−71.
(7) Ding, J.; Ma, S.; Shen, S.; Xie, Z.; Zheng, S.; Zhang, Y. Research and industrialization progress of recovering alumina from fly ash: A concise review. Waste Manage. 2017, 60, 375−387.
(8) Zhang, Y.; Zhao, J.; Ma, Z.; Yang, F.; Cheng, F. Effect of oxygen concentration on oxy-fuel combustion characteristic and interactions of coal gangue and pine sawdust. Waste Manage. 2019, 87, 288−294.
(9) Yue, G.; Cai, R.; Lu, J.; Zhang, H. From a CFB reactor to a CFB boiler—The review of R&D progress of CFB coal combustion technology in China. Powder Technol. 2017, 316, 18−28.
(10) Zhao, J.; Wang, D.; Liao, S. Effect of mechanical grinding on physical and chemical characteristics of circulating fluidized bed fly ash from coal gangue power plant. Constr. Build. Mater. 2015, 101, 851−860.
(11) Li, X.; Wang, H.; Zhou, Q.; Qi, T.; Liu, G.; Peng, Z. Efficient separation of silica and alumina in simulated CFB slag by reduction roast-ignite leaching process. Waste Manage. 2019, 87, 798−804.
(12) Yang, C.; Zhang, J.; Li, S.; Li, H.; Hou, X.; Zhu, G. Mechanisms of mechanochemical activation during comprehensive utilization of high-alumina coal fly ash. Waste Manage. 2020, 116, 190−195.
(13) Valeev, D.; Kunilova, I.; Alpatov, A.; Mikhailova, A.; Goldberg, M.; Kondratiev, A. Complex utilisation of ekibastuz brown coal fly ash: Iron & carbon separation and aluminium extraction. J. Cleaner Prod. 2019, 218, 192−1192.
(14) Guo, C.; Zou, J.; Wei, C.; Jiang, Y. Comparative study on extracting alumina from circulating fluidized-bed and pulverized-coal fly ashes through salt activation. Energy Fuels 2013, 27, 7868−7875.
(15) Li, W. Q.; Zou, P.; Chi, J. Z.; Liu, D. R.; Wu, Y. F. Leaching of alumina from circulating fluidized bed fly ash using hydrochloric acid. Hydrometall. China 2020, 39, 110−113.
(16) Yang, Q.; Ma, S.-h.; Zheng, S.-l.; Zhang, R. Recovery of alumina from circulating fluidized bed combustion Al-rich fly ash using mild hydrochemical process. Trans. Nonferrous Met. Soc. China 2014, 24, 1187−1195.
(17) Tripathy, A. K.; Sarangi, C. K.; Tripathy, B. C.; Sanjay, K.; Bhattacharya, I. N.; Mahapatra, B. K.; Behera, P. K.; Satpathy, B. K. Alumina recovery from NALCO fly ash by acid digestion in the presence of fluoride ion. Int. J. Miner. Process. 2015, 138, 44−48.
(18) Ma, Z.; Zhang, S.; Zhang, H.; Cheng, F. Novel extraction of valuable metals from circulating fluidized bed-derived high-alumina fly ash by acid-alkali-based alternate method. J. Cleaner Prod. 2019, 230, 302−313.
(19) Guo, Y.; Yan, K.; Cui, L.; Cheng, F. Improved extraction of alumina from coal gangue by surface mechanically grinding modification. Power Technol. 2016, 302, 33−41.
(20) Hajimohammadi, A.; van Deventer, J. S. J. Dissolution behaviour of source materials for synthesis of geopolymers binders: A kinetic approach. Int. J. Miner. Process. 2016, 153, 80−86.
(21) Cui, L.; Guo, Y.; Wang, X.; Du, Z.; Cheng, F. Dissolution kinetics of aluminum and iron from coal mining waste by hydrochloric acid. Chin. J. Chem. Eng. 2015, 23, 590−596.
(22) Wang, J.; Huang, X.; Wang, L.; Wang, Q.; Yan, Y.; Zhao, N.; Cui, D.; Feng, Z. Kinetics study on the leaching of rare earth and aluminum from FCC catalyst waste slag using hydrochloric acid. Hydrometallurgy 2017, 171, 312−319.
(23) Zhang, Y.; Li, M.; Liu, D.; Hou, X.; Zou, J.; Ma, X.; Shang, F.; Wang, Z. Aluminum and iron leaching from power plant coal fly ash for preparation of polymeric aluminum ferric chloride. Environ. Technol. 2018, 40, 1568−1575.
(24) Wu, Y.; Lu, B.; Bai, T.; Wang, H.; Du, F.; Zhang, Y.; Cai, L.; Jiang, C.; Wang, W. Geopolymer, green alkali activated cementitious material: Synthesis, applications and challenges. Constr. Build. Mater. 2019, 224, 930−949.
(25) Nath, S. K.; Kumar, S. Role of alkali concentration on reaction kinetics of fly ash geopolymization. J. Non-Cryst. Solids 2019, 505, 241−251.
(26) Zhou, C.; Gao, Q.; Luo, W.; Zhou, Q.; Wang, H.; Yan, C.; Duan, P. Preparation, characterization and adsorption evaluation of spherical mesoporous Al-MCM-41 from coal fly ash. J. Taiwan Inst. Chem. Eng. 2015, 52, 147−157.
(27) Wang, S.; Soudi, M.; Li, L.; Zhu, Z. Coal ash conversion into effective adsorbents for removal of heavy metals and dyes from wastewater. J. Hazard. Mater. 2006, 133, 243−251.
(28) Liu, S.; Chen, X.; Ai, W.; Wei, C. A new method to prepare mesoporous silica from coal gasification fine slag and its application in methylene blue adsorption. *J. Cleaner Prod.* **2019**, *212*, 1062–1071.

(29) Zhu, D.; Zuo, J.; Jiang, Y.; Zhang, J.; Zhang, J.; Wei, C. Carbon-silica mesoporous composite in situ prepared from coal gasification fine slag by acid leaching method and its application in nitrate removing. *Sci. Total Environ.* **2020**, *707*, 136102–136111.