Leaching characteristics and kinetics of the metal impurities present in rice husk during pretreatment for the production of nanosilica particles

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Abstract–Fundamental studies on the removal of metal impurities are essential for the production of nanosilica by combustion. This study reports the leaching characteristics, leaching kinetics and occurrence form of the metal impurities present in rice husk based on acid pretreatment. Acid pretreatment removes most of the metal impurities present in rice husk. In particular, 98 wt% removal of potassium can be reached. The acid concentration, leaching time and reagent type have significant effects on the leaching of metal impurities, and optimal conditions exist for the acid pretreatment process. Furthermore, the leaching of metal impurities occurs through two stages, and parts of the metal impurities exist in organic-bound form, which can be leached through ion exchange. The results show that the pseudo-second-order model is suitable for describing the leaching kinetics of the metal impurities present in rice husk, and empirical formulas for predicting the metal contents leached from rice husk during acid pretreatment at ambient temperature are also obtained. Additionally, the different occurrence form and quantities of metal impurities in rice husk lead to different leaching effects, which strongly influences the chemical properties and quality of the obtained silica particles.

Keywords: Rice Husk, Leaching Characteristics, Metal Impurities, Pretreatment, Kinetics

INTRODUCTION

Rice husk is an abundant agricultural by-product in Asia. In China, approximately 40 million tons of rice husk are produced each year [1]. Silica is a valuable industrial raw material in various industrial applications, such as the synthesis of industrial materials, cement additives, absorbents and rubber reinforcements [2-6]. Rice husk is a promising raw material for the preparation of silica because it contains a large quantity of amorphous bio-silicon, and rice husk ash (RHA) is the main type of silica particles obtained from burned rice husk. Amorphous RHA with the highest chemical activity can be obtained by the combustion or pyrolysis of rice husk at a low temperature of 600-700 °C [7,8]. However, if the combustion temperature is increased, the eutectic reaction between alkali metals, especially potassium, and silica in rice husk occurs during the combustion process and forms a low melting glass-like layer that covers the surface of the rice husk and hinders the further oxidation of carbon. The conversion of amorphous silica to the crystalline state is accelerated by the previous combustion conditions, which results in crystalline RHA with a high carbon content as the final product. In addition, the occurrence of metal and nonmetal impurities also influences the purity of the silica in RHA [9].

Zevenhoven et al. [10] found that elements such as alkali metals and chlorine in biomass fuels not only affected the quality of the ash, but also caused bed agglomeration and corrosion of the heated surface during fluidized bed combustion. The occurrence of metal and nonmetal elements in biomass reduced the thermal conversion efficiency and increased the maintenance costs of the combustion reactors [11]. Thus, the content of metals, chloride and other components in biomass must be reduced before utilizing biomass fuels [12]. A chemical leaching pretreatment process was introduced as an effective method for modifying biomass according to the literature [13-15]. Similarly, chemical pretreatment helped to improve the physicochemical properties of RHA by removing the metal impurities present in rice husk [16-18].

Different grades of nanosilica ash can be obtained from the combustion or pyrolysis of rice husk after various acid pretreatment processes, which indicates that the acid pretreatment process effectively removes the alkali metals and other metal impurities from rice husk. The leaching ratio (leaching efficiency), an intuitive parameter of metal removal, can directly reflect the quality of the resulting RHA to a certain degree, but this parameter is affected by the pretreatment parameters, such as the acid type, acid concentration, leaching temperature and leaching time. So far, no research has been conducted on the leaching patterns of metal impurities in rice husk during acid pretreatment. Furthermore, the occurrence form and leaching mechanism of metal impurities in rice husk are fundamental factors that determine the leaching of metal impurities during acid pretreatment. However, few studies reports a suitable explanation for the leaching mechanism and kinetics of metal impurities in rice husk. All the above shortcomings prompt an in-depth study on the leaching characteristics and mechanism of metal impurities in rice husk during acid pretreatment so that the optimum pretreatment conditions for industrial production can be

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determined.

Fundamental studies on the leaching characteristics of metal impurities in rice husk during acid pretreatment are crucial as a basis for the preparation of pure amorphous silica particles. Given this fact, in this work, the acid pretreatment of rice husk was investigated. In detail, the leaching components of acid solution were quantified by inductively coupled plasma (ICP) emission spectroscopy and ion chromatography (IC); the leaching characteristics of the chemical components in rice husk were analyzed; the effects of pretreatment parameters on the leaching characteristics of the major metal impurities (K, Ca and Na) in rice husk were studied; the leaching kinetics and mechanism of metal impurities were studied by linear regression; and the occurrence form and proportion of metal impurities in rice husk were obtained. All of these experiments provided a theoretical basis for obtaining high quality nanosilica.

MATERIALS AND METHODS

1. Materials

Rice husk samples were collected from a rice processing plant in Harbin, Heilongjiang Province, China. The raw materials were first sieved to remove small particles and subsequently dried at 105 °C in a drum wind drying oven for 2 h according to the national standard (GB/T 28731-2012). The content of metal impurities in the original rice husk is shown in Table 1, where K had the highest content (3.805 mg/g) followed by Ca. Therefore, K, Na and Ca were the primary hindering species in the application of rice husk combustion to produce nanosilica particles.

2. Acid Leaching Pretreatment

In the acid pretreatment experiments, 30 g of dried rice husk was added to 500 mL of an acid solution for a certain duration at ambient temperature with occasional stirring to remove the impurities. The leaching times were 5, 10, 15, 30, 60, 120 and 180 min; the stirring interval was 10 min; citric acid and sulfuric acid were chosen as the reagents; and the concentrations of the reagents were 0.05, 0.1, 0.5, 1 and 1.5 mol/L. The leached rice husk was then filtered and repeatedly washed with deionized water to eliminate the soluble fractions. The as-prepared rice husks were finally dried at 105 °C for 6 h in a drying oven and then collected. The acid leachate and washing solution were filtered through a membrane (0.45 μm) filter, the pH of the acid leachate was also measured, and the leachate and washing solution were mixed and diluted to 1.5 L to determine the contents of metals and nonmetals and the total organic carbon (TOC).

3. Analysis

The content of metal impurities in the original rice husk sample was quantified by a digestion method and ICP emission spectroscopy (Optima 5300DV, USA). The digestion process was conducted as follows: Approximately 0.5 g of dried rice husk (<200 mesh) was

loaded in a flask fitted with a reflux condenser, 10 mL of concentrated nitric acid and 3 mL of hydrofluoric acid were added, and the rice husk was digested under microwave heating. After the reaction was complete, a certain amount of nitric acid was used to rinse the flask walls, and the mixture was heated and concentrated. Finally, the solution was left to stand, after which it was filtered through quantitative filter paper. ICP emission spectroscopy was used to quantify the metal species in the digestion solution and the acid leachates, while the concentrations of the nonmetals were measured by IC (ICS-3000, USA); the average value was taken after three parallel measurements. Additionally, the TOC in the acid leachates was analyzed using an Elementar Analyzer (LiquiTOC II, Germany).

4. Kinetic Model

The leaching curves of the metal impurities in rice husk over time obtained in this study showed a general trend of initially rapid changes followed by slower changes and then an approach towards equilibrium (see within). When studying the leaching kinetics of metal impurities in rice husk, the leaching of metal impurities throughout the pretreatment process must be considered. The leaching of metal impurities during pretreatment can be simply assumed to proceed as follows:

$$\text{Metal}_{(s)} + \text{Acid solution}_{(aq)} \rightarrow \text{Soluble compound}_{(aq)} \tag{1}$$
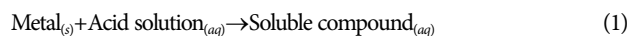
The saturation concentration of the soluble metal impurities leached into solution was considered constant for the same leaching conditions. The solid/liquid ratio of rice husk to acid solution was 0.06 (g/L), which ensured that all the soluble substances in the rice husk could dissolve completely. Studies have shown that the pseudo-second-order model reasonably describes the leaching kinetics of metals in rice husk [19,20]. The second-order kinetic rate equation is shown as follows:

$$\frac{dC_t}{dt} = k(C_s - C_t)^2 \tag{2}$$

where k is the second-order leaching rate constant (L/(mg·min)), C_s is the equilibrium concentration (mg/L), and C_t is the concentration (mg/L) of metal impurities in the acid solution at time t (min). The integrated rate law for second-order leaching with the boundary conditions of t=0 to t and C_t=0 to C_t is given in Eq. (3) and the linear form is shown in Eq. (4).

$$C_t = \frac{C_s^2 kt}{1 + C_s kt} \tag{3}$$

$$\frac{t}{C_t} = \frac{t}{C_s} + \frac{1}{kC_s^2} \tag{4}$$

The initial leaching rate h can be defined by Eq. (5) when t approaches 0.

$$h = kC_s^2 \tag{5}$$

Eq. (3) can be rearranged to obtain the following equation:

$$C_t = \frac{t}{\frac{1}{h} + \frac{t}{C_s}} \tag{6}$$

By fitting the experimental data of t versus t/C_t using the linear

Table 1. Metal contents of the rice husk sample

Metal species (mg/g)						
K	Na	Ca	Mg	Al	Fe	Mn
3.805	0.359	2.188	0.407	0.044	0.197	0.361

Table 2. Content of elements in the acid solution and the water leached from rice husk (mg/g rice husk)

Component	Sulfuric acid	Citric acid	Water
K	3.736	3.643	2.521
Na	0.066	0.056	0.056
Ca	1.164	0.691	0.291
Mg	0.352	0.309	0.109
Al	0.014	0.014	0.002
Fe	0.041	0.050	0.007
Mn	0.342	0.268	0.067
Cl	2.310	2.345	2.253
S	n.d.	0.448	0.293
P	0.351	0.328	0.253
Organic carbon	3.920	n.d.	1.644

n.d.-The content cannot be accurately determined due to interference by the reagent

regression method, the initial leaching rate h, the equilibrium concentration C_s, and the second-order leaching rate constant k can be obtained from the slope and intercept of the fitting plot.

RESULTS AND DISCUSSION

1. Leaching Characteristics of Rice Husk
1-1. Analysis of the Acid Leachate Elemental Composition

To study the relationship between the leaching of impurities in rice husk and the effect of this relationship on the performance of RHA following acid pretreatment, the content of the chemical elements leached into the solution per gram of rice husk during the pretreatment was determined, as shown in Table 2. The leaching parameters were as follows: sulfuric acid and citric acid were used as the pretreatment reagents at a concentration of 0.5 mol/L, the leaching time was 120 min, the process was conducted at ambient temperature, and deionized water was applied as a control leachate. Table 2 shows that various amounts of the metals K, Na, Ca, Mg, Al, Fe and Mn and nonmetals Cl, S and P leached from the rice husk into the leachate. K had the highest leaching content, which was far higher than that of the other metals, and Ca had the next highest leaching content. The first result was due to the fact that K had the highest content in the original rice husk (Table 1), and it also suggested that a large amount of the K present in rice husk was highly mobile. The leaching level of the metal impurities during the acid pretreatment was higher than during water washing, indicating that the metal impurity removal capacity of acid was better than that of water [21]. For the nonmetal impurities, the leaching content of Cl was approximately the same under the three leaching conditions, indicating that most of the Cl present in rice husk existed in a water-soluble form [22]. But the leaching content of S and P was limited, and only trace amounts of N was leached. The leaching process of biomass is usually accompanied by the removal of a certain amount of organic matter [23]. In this study, different contents of organic carbon were indeed detected in the water and sulfuric acid leachates (Table 2); however, the content of leached organic carbon was far less than the total carbon
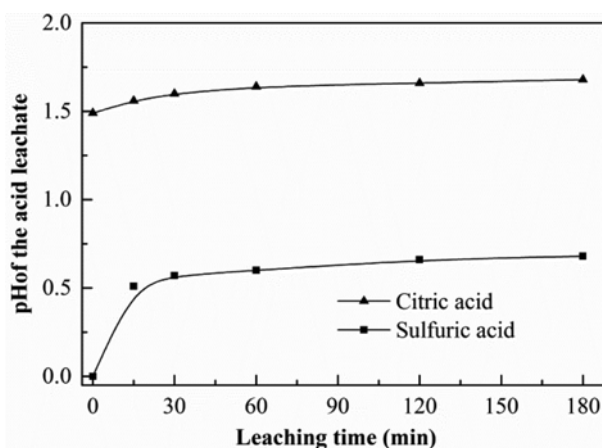
Fig. 1. pH of the acid leachate.

content of rice husk (C_{db}=40.3 wt%). Thus, for the rice husk used as fuel, the energy loss caused by the pretreatment process was negligible.

1-2. pH Analysis of the Acid Leachates

The leaching of various metal impurities strongly depends on their form/mode of occurrence in rice husk. The detection of the nonmetal species Cl, S and P in the acid leachates indicated that at least part of the metal impurities, especially alkali and alkaline earth metals, were likely to be present in the form of water-soluble salts, such as chlorides and part of sulfates and phosphates. In addition to these salts, the metal impurities were also present in larger quantities in other forms. Fig. 1 shows the pH of the two acid leachates at different leaching times. The pH increased rapidly with leaching time (especially sulfuric acid) within the initial 0-30 min, then increased slightly and finally reached equilibrium. This trend indicated that numerous hydrogen ions participated in an ion-exchange reaction with the metal impurities present in rice husk, and this ion-exchange reaction occurred mainly within the initial 30 min of the leaching process. Furthermore, as shown in Table 2, the cation/anion ratios in the acid leachates exceeded 1, suggesting that at least some of the metal impurities present in rice husk exist in forms other than water-soluble salts and were leached by ion exchange. The leaching of organic carbon (TOC) during the pretreatment process further showed that a portion of the leached metal impurities most likely existed in the organic-bound form [24]. Therefore, part of the leachable metal impurities in rice husk existed in the form of water-soluble salts, and the other part that existed in the organic-bound form was leached by ion exchange. In summary, the leaching of metal impurities during acid pretreatment occurs through a highly complicated reaction.

2. Effects of the Pretreatment Parameters on the Leaching of Metal Impurities
2-1. Acid Concentration

The leaching characteristics of metal impurities vary with changes in the pretreatment conditions, so the effect of the pretreatment parameters on the leaching of the main metal impurities in rice husk must be studied. Fig. 2 shows the leaching curves of K, Ca, and Na as a function of the acid concentration (120 min reaction) at a temperature of 25 °C. The acid concentration of 0 represents
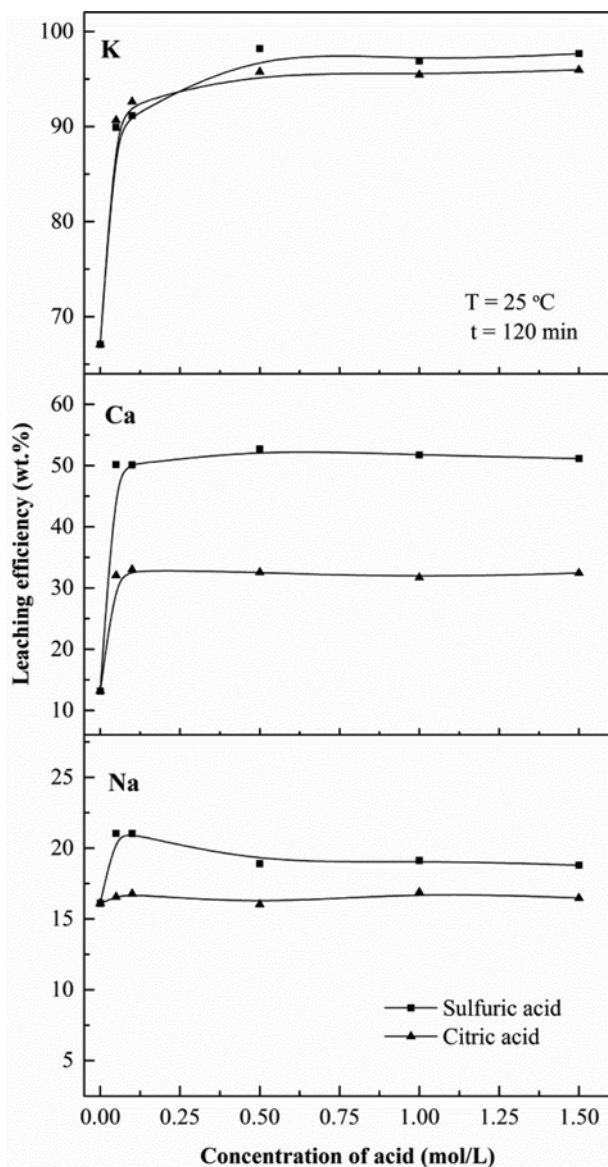
Fig. 2. Leaching ratios of metal impurities from rice husk at different acid concentrations.

Fig. 3. Leaching ratios of metal impurities from rice husk at different leaching times.

leaching by deionized water. The leaching of K and Ca followed similar trends under the two acid pretreatment conditions. The leaching ratios of K and Ca were 67 wt% and 13 wt%, respectively, at an acid concentration of 0. The ratios then increased sharply with increasing acid concentration and finally increased slowly to reach equilibrium. The maximum leaching ratio of K during the sulfuric acid and citric acid pretreatment process reached 98 wt% and 95 wt%, respectively, which was much higher than the K leaching ratio reported by Deng et al. from washing rice husk with water [25]. The high K leaching value obtained in this study further indicated that K was present in rice husk in water-soluble and acid-leachable forms [26]. Moreover, the removal of most of the K during the pretreatment process prevents the melting problem that can occur during the combustion of rice husk. Unfortunately, the final leaching ratios of Ca obtained from the sulfuric acid and cit-

ric acid pretreatment processes were approximately only 52 wt% and 33 wt%, respectively. The low leaching values suggested that the leaching of Ca was limited by other factors [27]. Moreover, it could be concluded that most of the Ca present in rice husk was acid-leachable and insoluble, exhibiting more complex chemical forms, which was consistent with the form of Ca in other biomasses [28,29]. However, the change in the efficiency of Na leaching with increasing acid concentration differed slightly from that of K and Ca. Citric acid had the lowest efficiency in the leaching of Na, where the Na leaching ratio was as low as approximately 16 wt%, consistent with the Na ratio obtained from water leaching. For the sulfuric acid pretreatment process, the Na leaching ratio increased slightly with increasing concentration and then remained unchanged.
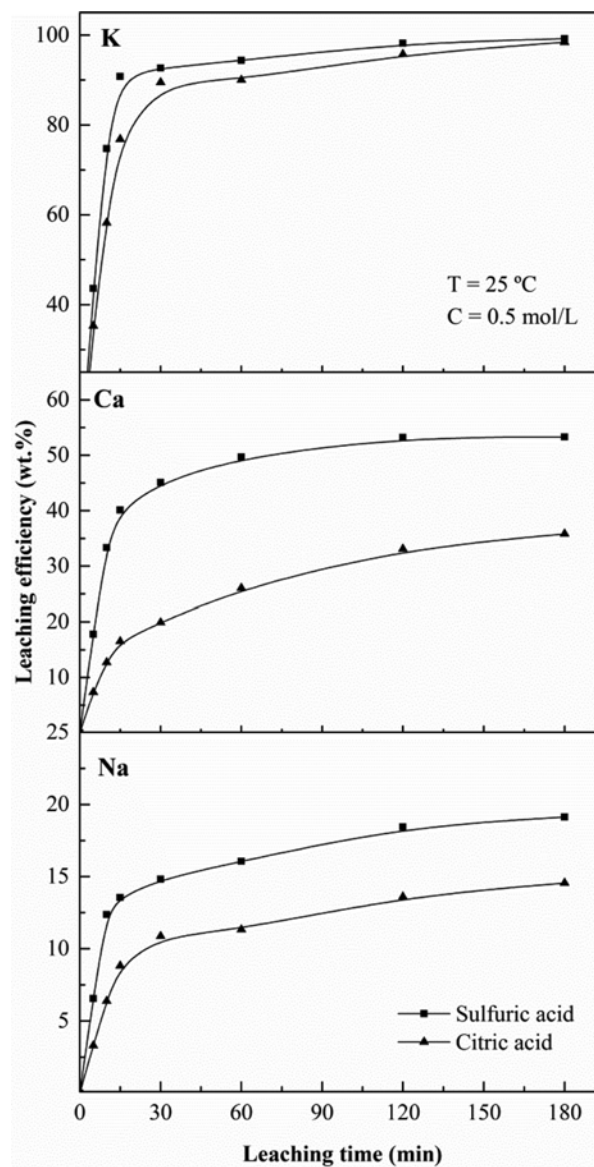
Additionally, according to Fig. 2, the leaching of K, Ca and Na

exhibited an optimal acid concentration at which the highest leaching ratio was achieved and maintained. For K and Ca leaching, the optimal acid concentration was 0.5 mol/L, while for Na, the optimal concentration was 0.1 mol/L. Due to the importance of K in the combustion of rice husk, the optimal acid concentration for K leaching (0.5 mol/L) was utilizaed in further studies.

2-2. Leaching Time

Fig. 3 shows the leaching curves of K, Ca and Na at different leaching times with an acid concentration of 0.5 mol/L and a temperature of 25 °C. The three metal impurities clearly exhibited similar leaching tendencies under the two acid pretreatment conditions. In detail, the leaching ratios increased sharply during the leaching period of 0-15 min, after which leaching became slow with further increases in the leaching time. The leaching curves were all characterized by a sharp bend at t=15-30 min, which demonstrated that the leaching of the metal impurities could be divided into two stages: a rapid leaching stage and a slow leaching stage [23]. During the rapid leaching stage, approximately 76-90 wt% K, 16-47 wt% Ca and 9-13 wt% Na were leached by the two acids. On the one hand, the initial rapid leaching stage was attributed to the driving force of the fresh acid, and on the other hand, this stage also revealed the presence of a large number of metal impurities at the surface of the organic matter framework of rice husk. During the slow leaching stage, only 6-20 wt% of the metal impurities were leached, and these leached impurities came from the metals bound to organic molecules. The final leaching ratios of the three metal impurities varied after the leaching reaction reached equilibrium. K had the highest removal of 99 wt%, whereas the removal ratios of Ca and Na were approximately only 53 wt% and 19 wt%, respectively, under the sulfuric acid pretreatment condition [30]. Additionally, when the leaching time was longer than 120 min, the leaching process of the three metal impurities became very slow, and the lengthening of the leaching time had little effect on the leaching ratio.

2-3. Acid Type

Fig. 2 and Fig. 3 show that the metal impurities exhibited similar leaching tends during the two acid pretreatment processes, but the leaching ratios of the metal impurities during the sulfuric acid pretreatment process were typically higher than those during the citric acid pretreatment process. The higher leaching ratios obtained from sulfuric acid pretreatment resulted from the stronger acidity and ionization ability of the acid, which accelerated the leaching of metal impurities [31], while the leaching by citric acid was relatively slower. The experimental results show that mineral acids remove metal impurities such as K, Ca, and Na more efficiently than organic acids.

3. Leaching Kinetics of Metal Impurities

The leaching of metal impurities during acid pretreatment occurred through the chemical reaction of the metal impurities present in rice husk with the acid solution. The primary purpose of this work was to study the ability of the acid solutions to leach the metal impurities present in the original rice husk (unground) at ambient temperature (25 °C), so an optimum solid/liquid ratio of 0.06 (g/L) and an acid concentration of 0.5 mol/L were chosen to minimize the diffusion resistance caused by the lack of reactive ions in the acid solution. With these parameters, the solid rice husk sufficiently contacted the acid solution, and the leaching ratio of the

metal impurities mainly depended on their solubility. In this study, the leaching curves of the metal impurities present in rice husk as a function of the leaching time showed a general trend of initially rapid changes followed by slower changes and finally an approach towards equilibrium. Therefore, it was assumed that the leaching process could be simplified to a pseudo-second-order chemical reaction, the kinetic equation for which was given in Section 2.4. The experimental data for the leaching of the metal impurities were fitted according to the integrated linear Eq. (3) of the model, and the correlation of the kinetic model was verified. The fitted linear and kinetic parameters are shown in Fig. 4 and Table 3. The fitted correlation coefficients (r^2) of three metal impurities were above 0.99, indicating that the hypothetical pseudo-second-order leaching model was in good agreement with the experimental data of the actual leaching process and could reasonably describe the leach-
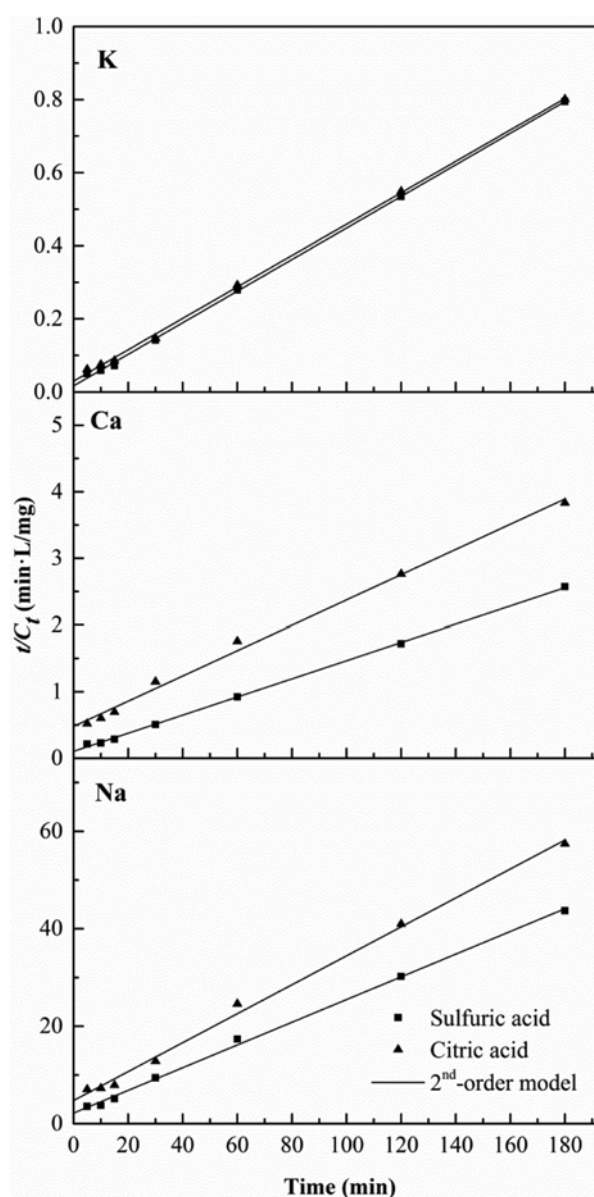

Fig. 4. Pseudo-second-order leaching kinetics of the metal impurities from rice husk with various acids.

Table 3. Fitted kinetic parameters for the acid leaching of rice husk

Acid type	Kinetic parameters for each element											
	K				Ca				Na			
	$k \times 10^3$	C_s	h	r^2	$k \times 10^3$	C_s	h	r^2	$k \times 10^3$	C_s	h	r^2
Sulfuric acid	1.12	231.48	59.81	0.999	6.76	73.36	9.707	0.999	24.90	4.29	0.459	0.998
Citric acid	0.62	232.56	33.68	0.999	0.75	52.74	2.09	0.994	18.55	3.37	0.210	0.996

Units: k is L/(mg·min), h is mg/(min·L) and C_s is mg/L

ing kinetics of the metal impurities. The initial leaching rate constant h of the metal impurities followed the order K>Ca>Na, indicating that a significant amount of K was available to be immediately leached when the rice husk was added to the fresh acid solution, because most of K, a mobile element, was not bound to the organic molecules present in rice husk and therefore rapidly leached in a short amount of time [32]. However, the leaching of Ca and Na required further diffusion of the acid into the matrix pores or osmosis through cells [33]. The acid type had a significant effect on the total leaching rate constant k and the initial leaching rate constant h of the three kinds of metal impurities present in rice husk, and sulfuric acid exhibited a higher equilibrium concentration C_s of metal impurities.

Under ambient temperature and in the presence of excess acid, the leaching kinetic parameters of each metal impurity remained constant. Thus, C_s and h were substituted into Eq. (6) to obtain the leaching rate equation of the metal impurities in terms of C_t and t. Then, the metal concentration C_t was converted to the metal content M (mg/g) leached from rice husk to obtain the empirical formula in terms of M (Table 4). The empirical formula shown in Table 4 represents the general predicted leaching model of the metal impurities in rice husk under acid pretreatment at ambient

temperature, which can be used to predict the leaching content of metal impurities in rice husk at any time under ambient temperature. To verify the accuracy of the empirical expression, sulfuric acid was used to examine the leaching of metal impurities under different pretreatment conditions. The actual and predicted leaching contents are shown in Table 5. When the acid concentration was low (≤ 0.1 mol/L), the actual leaching amounts of K, Ca and Na were inconsistent with the predicted leaching amounts (Table 5), suggesting that the diffusion resistance caused by the low acid concentration had a negative effect on K, Ca and Na leaching. When the acid concentration was above 0.5 mol/L, the error in the predicted values decreased, and the accuracy was higher. Fig. 5 shows the precision of the model for predicting the leaching contents of the metal impurities. Overall, the empirical expression accurately predicted the leaching contents of the metal impurities at various times, but the actual measured values were slightly lower than the predicted values.

4. Further Analysis of Metal Impurities

Although the acid leaching process of metal impurities in rice husk followed pseudo-second-order leaching kinetics (Fig. 4), the final leaching rate constants of all the metals were distinct. The occurrence form and distribution of inorganic elements in bio-

Table 4. Empirical expressions for the leaching content of the metal impurities present in rice husk

Acid type	Empirical expressions		
	K (mg/g)	Ca (mg/g)	Na (mg/g)
Sulfuric acid	$M_K = \dfrac{t}{1.003 + 0.259t}$	$M_{Ca} = \dfrac{t}{6.181 + 0.817t}$	$M_{Na} = \dfrac{t}{130.72 + 13.986t}$
Citric acid	$M_K = \dfrac{t}{1.781 + 0.258t}$	$M_{Ca} = \dfrac{t}{28.708 + 1.138t}$	$M_{Na} = \dfrac{t}{285.71 + 17.804t}$

Note: M_K, M_{Ca} and M_{Na} are the contents of metal impurities leached from rice husk (mg/g)

Table 5. Predicted and actual content of the metal impurities leached from rice husk under various pretreatment conditions

Operation parameters		Actual values (mg/g)			Predicted values (mg/g)		
Acid concentration (mol/L)	Leaching time (min)	K	Ca	Na	K	Ca	Na
0.05	30	3.175	0.852	0.073	3.420	0.977	0.055
0.1	60	3.487	0.954	0.064	3.627	1.087	0.062
0.5	120	3.686	1.164	0.066	3.740	1.151	0.066
1	120	3.670	1.132	0.068	3.740	1.151	0.066
1	180	3.669	1.156	0.065	3.780	1.174	0.068
1.5	15	2.940	0.795	0.044	3.069	0.813	0.044

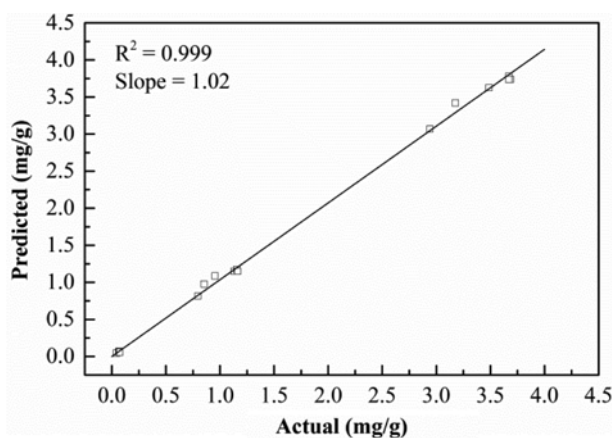Sulfuric acid, leaching temperature: 25 °C

Fig. 5. Plot showing the precisions of the model for predicting the leaching content of the metal impurities present in rice husk.

mass have been reported to have a strong impact on their removal efficiencies [22,34], and rice husk is not exempt from this impact. Based on the leaching characteristics and trends for the metal impurities in rice husk described in the previous section, these impurities were classified into three categories according to their solubility: (1) water-soluble form, (2) acid-leachable form, and (3) insoluble form. Quantification of the water-soluble portion was performed by the leaching of rice husk with deionized water at ambient temperature for 2 h, while the content of the acid-leachable portion was determined via the leaching of rice husk using 0.5 mol/L sulfuric acid for 2 h at ambient temperature. The residual portion was then calculated by difference. The occurrence form and distribution of the alkali and alkaline earth metals in rice husk are plotted in Fig. 6. As shown, more than 60 wt% of the K present in rice husk exists in the form of water-soluble salts, including chlorides, sulfates and phosphates, which are mainly free in the molecular pores. Most of the remaining K is in the acid-leachable form, which is mainly found in the macromolecules or bound to the polysaccharide matrix [35,36]. Approximately only 13 wt% of the Ca is in the water-soluble form, and more than 40 wt% of the Ca exists in
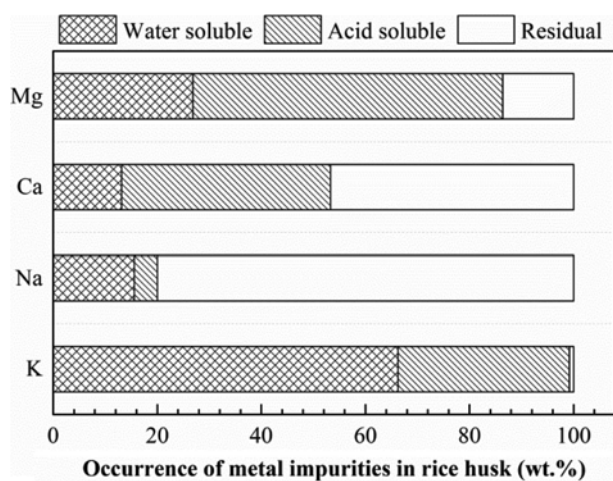
the acid-leachable form. The limited leaching of Ca suggests that Ca mostly exists as organic salts and carbonates that are sparingly soluble in dilute acid and require hydrolysis conditions, such as heating and boiling, to be leached completely [27]. Mg leaches more easily than Ca, and more than 80 wt% is soluble, in which approximately 60 wt% is in the acid-leachable form bound to the organic structure of rice husk only leached through ion-exchange with hydrogen ion from dilute acid or present as water insoluble salts. Approximately 15 wt% of the Na exists as water-soluble salts, and only a small amount of Na could be leached under the present acid pretreatment conditions. Compared with another alkali metal K, Na has a very low solubility by dilute acid. It was reported that Na in biomass has a strong and positive association with Si [37]. Therefore, these Na are likely to be present in silicates.

Most of the acid-leachable metal impurities were extensively leached during the ion-exchange reactions with the dilute acid solutions in the initial rapid stage (Fig. 3), and the leaching of the water-soluble metal impurities in the matrix also occurred during this stage. Beyond the leaching content in the rapid leaching stage, approximately only 8-9 wt% K, 6-16 wt% Ca and 3-5 wt% Na were leached during the slow leaching stage. This limited leaching is due to the fact that the residual metal impurities were bound to the interior molecules of the organic matter, thereby requiring further diffusion of the acid into the matrix pores or osmosis through cells to be leached. The organic carbon matter present in the leachates was shown to be mainly organic acids, including acetic acid, formic acid and oxalic acid, which may also participate in the subsequent slow leaching reactions [23]. Therefore, the slow leaching process is a complex reaction that involves the ion-exchange reaction of the acid solution, and trace amounts of the native organic acid that leached from the rice husk itself [38].

The results reported in this study have important practical implications in several aspects and give direction to the possible follow-up works. First, the results provide guidelines for developing optimum pretreatment condition for the industrial preparation of nanosilica by the combustion of rice husk in a circulating fluidized bed. Under the optimal pretreatment condition, nanosilica powder with a purity of above 98.8 wt% and a high specific surface activity of more than 200 m^2/g was obtained through the rice husk combustion in a lab-scale fluidized bed. Second, the variation of content of the main metal impurities in rice husk and the differences in the occurrence form of these inherent species results in a dissimilarity of leaching of metal impurities in rice husk. Thus, the experiment data provide essential information for estimating the recyclability of the main AAEM species (especially K) in rice husk during the pretreatment process. Third, the results reported in this study also provide insights regarding those elements leaching behavior and its relationship with rice husk. At present, however, systematic studies about the content, occurrence models, behavior of all major and minor elements in biomass fuels (not only in rice husk) are only at an initial stage of investigation, and therefore much more detailed work is required in this topic.

CONCLUSIONS

A series of acid pretreatment experiments of rice husk were

Fig. 6. Forms and distribution of metal impurities in rice husk.

conducted at ambient temperature under laboratory conditions. The leaching characteristics, leaching mechanism and forms of metal impurities in rice husk during acid pretreatment were investigated. The following conclusions can be drawn:

(1) Large amounts of metal impurities as well as some nonmetals are removed from the rice husk during acid pretreatment. Some of metal impurities in rice husk are leached by the ion-exchange reaction with acid and likely exist in the organic-bound form.

(2) The leaching of metal impurities during acid pretreatment at ambient temperature is a two-stage process that includes an initial rapid and short leaching stage followed by a slow and long leaching stage. The pretreatment parameters, such as the acid concentration and leaching time, have positive effects on the leaching of the major metal impurities, K, Ca and Na, and sulfuric acid more effectively removes the metal impurities present in rice husk than citric acid. An optimal condition (0.5 mol/L, 120 min) is obtained for leaching of metal impurities in rice husk.

(3) The leaching experimental data are in good agreement with the pseudo-second-order leaching model, which is suitable for describing the leaching kinetics of the metal impurities in rice husk. An empirical expression for predicting the leaching content of metal impurities in rice husk during acid pretreatment at ambient temperature was obtained using model analysis, which can predict the leaching amount of metals under different pretreatment conditions with good accuracy.

(4) The metal impurities present in rice husk are divided into three forms, where almost all of the K is in the water-soluble and acid-leachable forms, while most of the Na, Ca and Mg are in the acid-leachable or insoluble form. Most importantly, the differences in the forms and distribution of metal impurities in rice husk result in different trends of acid leaching for each metal impurity and ultimately determine the performance and quality of the resulting nanosilica.

REFERENCES

1. P. Fu, S. Hu, J. Xiang, W. Yi, X. Bai, L. Sun and S. Su, *Bioresour. Technol.*, **114**, 691 (2012).
2. D. A. Awizar, N. K. Othman, A. Jalar, A. R. Daud, I. A. Rahman and N. H. Al-Hardan, *Int. J. Electrochem. Sc.*, **8**, 1759 (2013).
3. B. S. Thomas, *Renew. Sust. Energ. Rev.*, **82**, 3913 (2018).
4. Y. Zhou, Z. Tian, R. Fan, S. Zhao, R. Zhou, H. Guo and Z. Wang, *Powder Technol.*, **284**, 365 (2015).
5. Y. Fan, R. Yang, Z. Lei, N. Liu, J. Lv, S. Zhai, B. Zhai and L. Wang, *Korean J. Chem. Eng.*, **33**, 1416 (2016).
6. S. Artkla, *Korean J. Chem. Eng.*, **29**, 555 (2012).
7. M. Sarangi, P. Nayak and T. N. Tiwari, *Compos. Part B-Eng.*, **42**, 1994 (2011).
8. S. Huang, S. Jing, J. Wang, Z. Wang and Y. Jin, *Powder Technol.*, **117**, 232 (2001).
9. R. V. Krishnarao, J. Subrahmanyam and T. Jagadish Kumar, *J. Eur. Ceram. Soc.*, **1**, 99 (2001).
10. M. Zevenhoven, P. Yrjas, B. J. Skrifvars and M. Hupa, *Energy Fuels*, **26**, 6366 (2012).
11. D. J. Nowakowski, J. M. Jones, R. M. D. Brydson and A. B. Ross, *Fuel*, **86**, 2389 (2007).
12. X. Liu and X. T. Bi, *Fuel Process. Technol.*, **92**, 1273 (2011).
13. C. Yu, Y. Zheng, Y. S. Cheng, B. M. Jenkins, R. Zhang and J. S. Vander-Gheynst, *Bioresour. Technol.*, **101**, 4331 (2010).
14. H. Liu, M. Li, X. Cao and R. Sun, *Energy Technol.*, **1**, 70 (2013).
15. S. Al-Zuhair, M. Abualreesh, K. Ahmed and A. Abdul Razak, *Energy Technol.*, **3**, 121 (2015).
16. A. Salas, S. Delvasto, R. Mejia de Gutierrez and D. Lange, *Cement Concrete Res.*, **9**, 773 (2009).
17. H. A. Alyosef, A. Eilert, J. Welscher, S. S. Ibrahim and R. Denecke, *Paticul. Sci. Technol.*, **5**, 524 (2013).
18. S. Chandrasekhar, P. N. Pramada and J. Majeed, *J. Mater. Sci.*, **41**, 7926 (2006).
19. Y. S. Ho, H. A. Harouna-Oumarou, H. Fauduet and C. Porte, *Sep. Purif. Technol.*, **45**, 169 (2005).
20. Y. S. Ho, *Water Res.*, **40**, 119 (2006).
21. S. R. G. Oudenhoven, R. J. M. Westerhof, N. Aldenkamp, D. W. F. Brilman and S. R. A. Kersten, *J. Anal. Appl. Pyrolysis*, **103**, 112 (2013).
22. H. Wu, K. Yip, Z. Kong, C. Z. Li, D. Liu, Y. Yu and X. Gao, *Ind. Eng. Chem. Res.*, **50**, 12143 (2011).
23. S. B. Liaw and H. Wu, *Ind. Eng. Chem. Res.*, **52**, 4280 (2013).
24. P. Chen, W. Gu, W. Fang, X. Ji and R. Bie, *Environ. Prog. Sustain.*, **36**, 830 (2017).
25. L. Deng, T. Zhang and D. Che, *Fuel Process. Technol.*, **106**, 712 (2013).
26. D. S. Scott, L. Paterson, J. Piskorz and D. Radlein, *J. Anal. Appl. Pyrolysis*, **57**, 169 (2001).
27. J. Umeda and K. Kondoh, *Ind. Crop. Prod.*, **32**, 539 (2010).
28. C. Yu, P. Thy, L. Wang, S. N. Anderson, J. S. Vander-Gheynst, S. K. Upadhyaya and B. M. Jenkins, *Fuel Process. Technol.*, **128**, 43 (2014).
29. D. Mourant, Z. Wang, M. He, X. S. Wang, M. Garcia-Perez, K. Ling and C.-Z. Li, *Fuel*, **90**, 2915 (2011).
30. S. Gu, J. Zhou, Z. Luo, Q. Wang and M. Ni, *Ind. Crop. Prod.*, **50**, 540 (2013).
31. J. Umeda, K. Kondoh, *J. Mater. Sci.*, **43**, 7084 (2008).
32. S. V. Vassilev, C. G. Vassileva and D. Baxter, *Fuel*, **129**, 292 (2014).
33. Z. Kong, S. B. Liaw, X. Gao, Y. Yu and H. Wu, *Fuel*, **128**, 433 (2014).
34. D. Lv, M. Xu, X. Liu, Z. Zhan, Z. Li and H. Yao, *Fuel Process. Technol.*, **91**, 903 (2010).
35. S. Zhang, Q. Dong, L. Zhang and Y. Xiong, *Bioresour. Technol.*, **199**, 352 (2016).
36. S. V. Vassilev, D. Baxter and C. G. Vassileva, *Fuel*, **117**, 152 (2014).
37. S. V. Vassilev, D. Baxter, L. K. Anderden and C. G. Vassileva, *Fuel*, **89**, 913 (2010).
38. Z. He, J. Mao, C. W. Honeycutt, T. Ohno, J. F. Hunt and B. J. Cade-Menun, *Biol. Fert. Soils*, **45**, 609 (2009).