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RESEARCH ARTICLE

The effect of NaOH concentration on silica leaching process from rice husk ash in South Sulawesi Province, Indonesia

Herlina Rahim[1], Gyan Prameswara[1,*], Muh. Irfan Wijaya Gusmadi[1], Jamaluddin[2]

[1]Program Studi Teknik Kimia Mineral, Politeknik ATI Makassar, Jl Sunu No. 220, Kota Makassar, 90211, Indonesia
[2]PT Tala Salapang Agro, Gowa Regency, 92173, Indonesia

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OBJECTIVES The issue of waste and raw material sources has become common in the processing industry. The ideal solution is to use waste as a substitute for primary material. The processing of rice husk waste for silica extraction can aid in resolving the issue of solid waste accumulation in the agricultural industry. **METHODS** The extraction process begins with burning and ashing the husk waste to increase the silica content. At 750 °C, the silica content increased to 88.06%. The leaching process was carried out to dissolve Si, and observe the behavior of other major elements, such as K, Ca, and P, from rice husk ash. Leaching was carried out in a 3-neck flask with external heating. The effect of the concentration of NaOH solution on elements recovery was studied in this experiment. **RESULTS** The highest recovery of Si, K, Ca, and P reached 89.94%, 89.04%, 61.37%, and 78.61%, respectively, at 3 N NaOH concentration, 120 minutes, 300 rpm, and 10% S/L ratio. There was also a precipitate of Na_3PO_4 formed in the product solution after being left for 24 hours. **CONCLUSIONS** This provides insight into the decantation process before precipitation using $Al(OH)_3$ in zeolite production.

KEYWORDS effect of concentration; leaching; rice husk ash

1. INTRODUCTION

The world is experiencing two main problems: resource depletion and excess waste production. A solution to this issue is to use waste as the main production feed stream (Steven et al. 2022). All industrial sectors compete to increase revenue by substituting waste as the main raw material (Setyawan et al. 2019). Biomass waste can be used as an alternative to overcome this problem. The accumulation of rice husk waste in Indonesia, which is increasing yearly, is still a challenge for solid waste processing. Indonesia's rice production in 2021 reached 54.42 million tons, of which 20% is husk waste (Badan Pusat Statistik 2021).

Recently, rice husk has been used in various applications such as fertilizers, preparing activated carbon, and as an industrial fuel for gasification or combustion boilers. Another use of rice husk waste processing is for the main ingredient in the manufacture of zeolite. Husk waste usually contains high cellulose, lignin, and ash (Santana Costa and Paranhos, 2018). Typical husk waste composition contains 38% cellulose, 22% lignin, 20% ash, 18% pentosane, and 2% organic matter content. Rice husk ash (RHA) contains amorphous silica as much as 30-35% (Chandrasekhar et al. 2003). The high silica content in RHA has not been utilized optimally for material substitution in amorphous silica-based products. This silica content can be used as raw material for zeolite.

The silica leaching process plays an essential role in the zeolite production from RHA. The purity of the extracted amorphous silica will affect the zeolite product. This extraction process is affected by several factors, such as temperature, solvent type, solvent concentration, RHA size, solid-liquid ratio, and other leaching operating conditions.

Research on the extraction of silica from RHA has been carried out. Ma et al. (2012) developed a leaching technique using acid and NH_4F followed by precipitation in an acidic state. Liou and Yang (2011) investigated silica production by extracting Na_2SiO_3 from rice husk ash using NaOH, followed by precipitation with HCl. 0.15 M Na_2SiO_3 was obtained from the extraction process using NaOH, and the highest surface area was obtained when SiO_2 was formed during the precipitation process. The recovery of SiO_2 formed as a result of precipitation was 99.48%. This is due to the smaller size of the NaCl salt formed in comparison to the salt formed in other types of acids. Fernandes et al. (2017) evaluated the RHA leaching process using 1 M NaOH, followed by precipitation using H_2SO_4. Kalapathy et al. (2001) conducted an acid-leaching experiment followed by NaOH leaching to extract Si from RHA. From previous research, only a few discussed the

*Correspondence: gyan@atim.ac.id

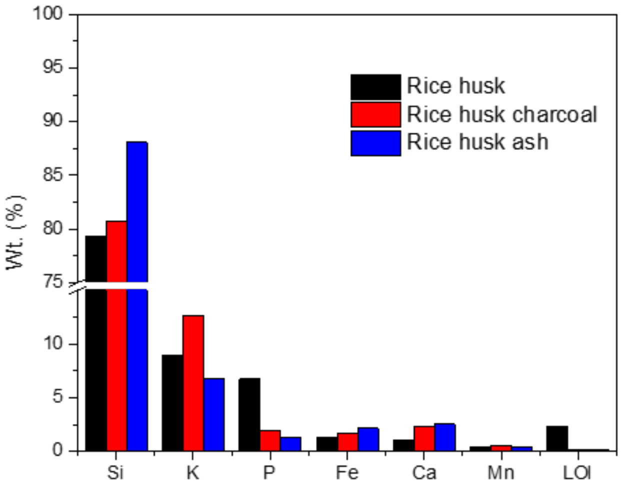

FIGURE 1. Content of major elements on rice husks, husk charcoal, and rice husk ash.

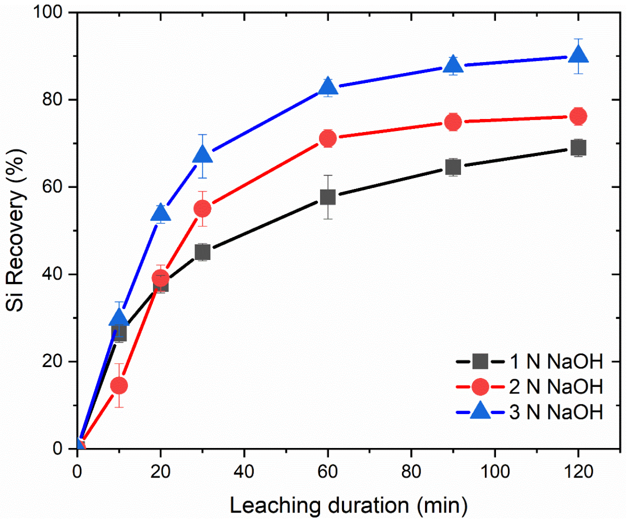

FIGURE 2. Effect of NaOH concentration on Si recovery (S/L ratio = 10%, stirring speed = 300 rpm, leaching temperature = 80 °C).

effect of NaOH concentration on direct RHA leaching without acid pretreatment. Excessive use of acid in the pretreatment process can cause new liquid waste problems without a recycling process. Liquid waste and the use of acid issue will also increase production costs on industrial-scale operations.

The silica leaching process using NaOH solution is crucial for making zeolite. This study aims to characterize the ashing process and the effect of NaOH concentration on Si leaching recovery.

2. MATERIALS AND METHOD

2.1 Materials

Rice husk ash was obtained from PT Tala Salapang Agro (TSA) Gowa Regency, South Sulawesi Province, Indonesia. The material is separated from the soil and other solid waste and washed using tap water. Drying is used to remove water from the rice husks. RHA was crushed and sieved to obtain a particle size of < 180 microns. The solution used for the leaching process is NaOH (prepared from NaOH flakes > 97%, local).

2.2 Method

2.2.1 Rice husk pretreatment

Rice husk, rice husk charcoal, and rice husk ash were analyzed using x-ray fluorescence (XRF) Epsilon 1, Panalytical. X-ray diffraction (XRD) Rigaku Miniplex 600 XRD Rigaku Miniplex 600 was used to determine the dominant phase present in the sample and determine crystallinity.

2.2.2 Heating pretreatment

The ashing process is carried out by burning 1000 g of rice husk into husk charcoal at 400 °C. The husk charcoal was then incinerated using a muffle furnace at 750 °C for 3 hours. The RHA obtained is then fed for the leaching process.

2.2.3 Leaching process

The leaching process was carried out using a 500 mL three-neck flask equipped with a thermometer and a reflux condenser. The heating process uses a hot plate, and stirring uses a magnetic stirrer. 50 mL of NaOH with a concentration of 1, 2, and 3 N was heated to 80 °C, and 5 grams of RHA was added (S/L ratio = 10%). Si, K, Ca, and P recovery is calculated using Equation 1 (Prameswara et al. 2022a,b; Trisnawati et al. 2020).

$$R_i(\%) = \frac{m_f C_{fi} - m_{ri} C_{ri}}{m_f C_{fi}} \times 100 \qquad (1)$$

Where,

1. R_i is element recovery (%),
2. m_f is the mass of the feed (grams),
3. C_{fi} is the concentration of elements in the feed(%), m_{ri} is the mass of the residue (grams), and C_{ri} is the concentration of elements in the residue.

3. RESULT AND DISCUSSION

3.1 Ashing process

The ashing process aims to reduce organic and volatile materials from rice husks. It is known that organic materials such as cellulose and lignin make up 36% of rice husks (Liashenko et al. 2020). It can be seen in Figure 1 that the silica content increases during the ashing process. This is due to reduced organic matter constituents (C, H, and O). The material loses its water content at temperatures of 80-150 °C. In comparison, cellulose and lignin decomposition processes occur at 350 °C and 600 °C, respectively (Bakar et al. 2016). Figure 1 also shows a significant increase in Si concentration from rice husk charcoal to RHA.

K content increased during the combustion process (400 °C) and decreased during the ashing process (750 °C). K in the K_2O phase will be reduced at 740 °C while the content of phosphate (P) in the P_2O_5 phase decreases due to being reduced at 340 °C. Si, K, P, and Ca contents in RHA were 88.06%, 6.77%, 1.29%, and 2.51%, respectively.

3.2 Effect of NaOH concentration

The reaction of SiO_2 with NaOH is presented in Equation 2. It can be seen in Figure 2 that at 1 N NaOH concentration, Si recovery increased significantly from 0 – 120 minutes. At 2 and 3 N NaOH concentrations, the Si recovery reached equilibrium at 60 minutes. The highest recovery in leaching using

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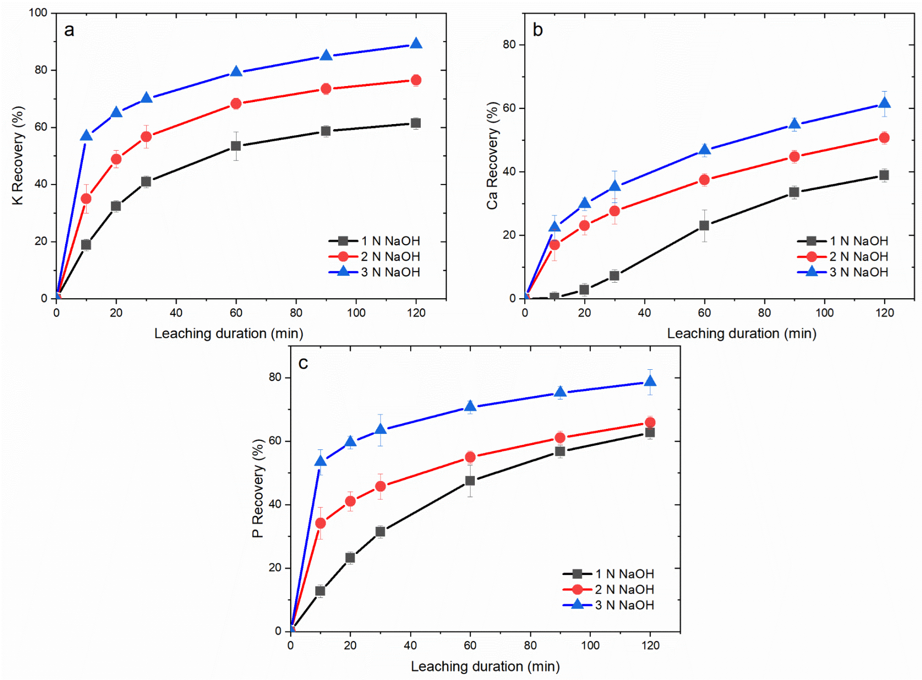

FIGURE 3. Effect of NaOH concentration on (a) K, (b) Ca, and (c) P recovery (S/L ratio = 10%, stirring speed = 300 rpm, leaching temperature = 80 °C).

1 N, 2 N, and 3 N NaOH concentrations were 68.96%, 76.19%, and 89.94%, respectively. This result differs from Mujiyanti et al. (2021), who stated that the highest Si recovery was 61.37% by leaching using NaOH 3 N at an RHA size of 240 mesh. The RHA pretreatment process is also influential. The husk milling process will open the material matrix, facilitating the reduction of organic matter in the ashing process.

$$SiO_{2(s)} + 2NaOH_{(aq)} \rightarrow Na_2SiO_{3(l)} + H_2O_{(l)} \tag{2}$$

Increasing the concentration of NaOH will increase the concentration of Na^+ ions, resulting in more Si reacting. Santana Costa and Paranhos (2018) reported that an increase in NaOH concentration greater than 4 N would not increase Si recovery. An increase in solution viscosity will occur at higher NaOH concentrations, resulting in reduced mobility of Na^+ ions.

Potassium (K) is as much as 6.77%, which is one of the major elements in RHA. The reaction with NaOH is presented in Equation 3.

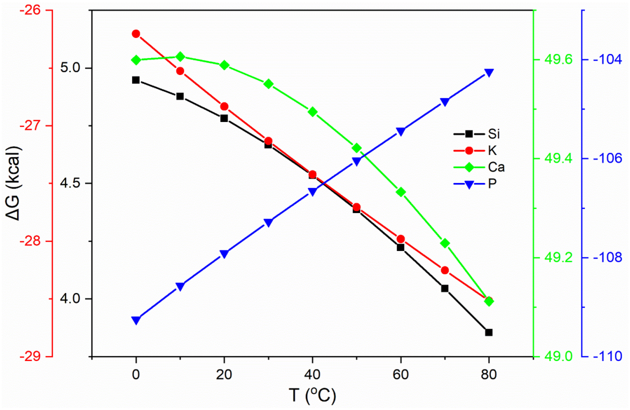

FIGURE 4. ΔG of equation (2)-(5).

$$K_2O_{(s)} + 2NaOH_{(aq)} \rightarrow 2KOH_{(aq)} + Na_2O_{(l)} \tag{3}$$

In Figure 3(a), a significant increase in recovery only occurs at 0-30 minutes. The highest K recovery in leaching using NaOH with concentrations of 1 N, 2 N, and 3 N were 61.39%, 76.51%, and 89.04%, respectively. The K dissolution process occurs spontaneously at high NaOH concentrations due to the negative value of the Gibbs free energy change (ΔG) (Figure 4). The same behavior is shown in phosphate (P) dissolution. The reaction is presented in Equation 4.

$$P_2O_{5(s)} + 6NaOH_{(aq)} \rightarrow 2Na_3PO_{4(aq)} + 3H_2O_{(l)} \tag{4}$$

Figure 3(c) shows P recovery at various concentrations of NaOH solution. P recovery in the leaching process using 2 N and 3 N NaOH reached equilibrium in 30 minutes. However, there was a significant increase in leaching using 1 N NaOH at 10-120 minutes. The highest recovery was achieved at 120 minutes using 1 N, 2 N, and 3 N NaOH were 62.63%, 65.86%, and 78.61%, respectively. In contrast to the K and P recovery behavior, Ca recovery did not reach equilibrium until 120 min (Fig. 3(b)). The reaction is shown in Equation 5.

$$CaO_{(s)} + 2NaOH_{(aq)} \rightarrow Ca(OH)_{2(aq)} + Na_2O_{(l)} \tag{5}$$

The highest Ca recovery (61.37%) was achieved at 3 N NaOH, 80 °C, for 120 minutes.

Another finding from this experiment is the formation of Na_3PO_4 precipitate. It is known that Na_3PO_4 will precipitate at room temperature after being left for 24 hours. This provides a new understanding of the determination of the silica refining process flow. The decantation process can be carried out to separate the Na_3PO_4 precipitate after being left for 24 hours.

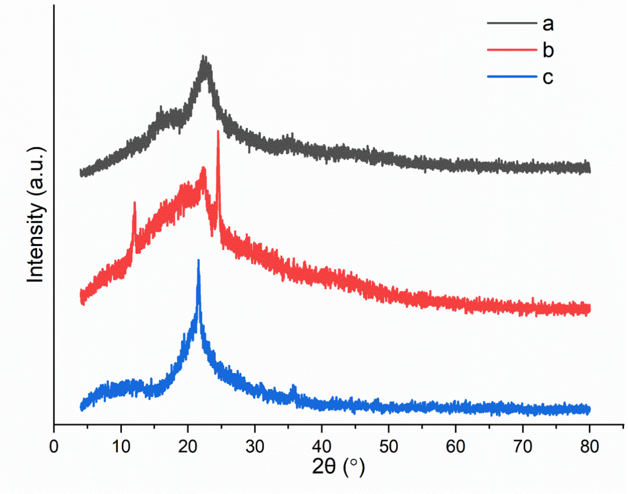

FIGURE 5. XRD pattern of (a) rice husks, (b) rice husk charcoal, and (c) rice husk ash.

Figure 4 shows the Gibbs free energy change values extrapolated from the reference data (298 K, 1 bar). The P and K leaching process have a negative ΔG value at 80 °C, indicating that the reaction can occur spontaneously. It is evident in Figures 3 (a) and (c) that the recovery of K and P reaches equilibrium quickly. So that the dissolution of each element using NaOH solution can be sorted as P > K > Si > Ca. In addition to the increase in NaOH solution concentration, the small particle size of rice husk ash (<180 microns) plays an important role in the rapid dissolution of K, Ca, and P in the NaOH solution, resulting in high recoveries. Recoveries of oxygen (O) are not calculated. When SiO_2 is leached using NaOH, oxygen is released as a gas (in the form of water vapor) (Wang et al. 2014). Instead, the focus is on measuring the extraction efficiency and recovery of silica, which is the desired product.

3.3 Material characterization

Phase analysis of the material was carried out using XRD (Figure 5). The amorphous silica phase is the primary material for making rice husks. With the ashing process, the amorphous silica content increases. The spectrum spreads in the range 2θ of 15 °– 40 °, with the central peak at 22 °. This confirms the behavior of amorphous silica. The presence of cellulose is indicated by a peak at 2θ of 12 and 25 °(Figure 5b). Because cellulose decomposes at a temperature of 250-350 °C during the ashing process, rice husk ash does not show any peaks besides SiO_2 ($2\theta = 22$ °) in Figure 5c (Alshatwi et al. 2022; Rivas et al. 2016). CaO and K_2O were identified at 2θ of 37 and 33 °, respectively, although slightly visible (Istadi et al. 2015). This also shows the presence of CaO and K_2O in rice husk, K and Ca are naturally present in rice plants due to absorption from the environment (Ferreira et al. 2020).

4. CONCLUSION

Increasing the silica content of rice husks was carried out by using the carbonization process at 400 °C and the ashing process at 750 °C resulting in an increase in the silica content from 79.25% to 88.06% in RHA. The RHA leaching process using NaOH was carried out to determine the effect of solvent concentration on Si, K, Ca, and P recovery. The highest silica recovery reached 89.94% at 3 N NaOH concentration, 120 minutes, 300 rpm 10% S/L ratio. The highest K, Ca, and P recoveries were 89.04%, 61.37%, and 78.61% under the same operating conditions. Na_3PO_4 precipitate was found after 24 hours. This precipitate indicates that further silica purification can be done using the decantation process before reacting with $Al(OH)_3$ to form zeolite material.

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