A method for production of pure silica as fertilizer from industrial waste material

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Abstract. Globally, industrial waste such as fly ash, bottom ash, and slag in the thermal power energy, steel, and coal industry has been known as potential soil ameliorant and silica fertilizer. However, the use of those materials as ameliorant or Si fertilizer should consider negative environmental impact. Therefore, to use that material in Indonesia need to deal with the regulation and to prove its positive effect on the soil and plant. One innovative idea for recycling industrial waste is to use those raw materials to produce high purity Si as fertilizer. The objective of this research was to improve the solubility of Si from industrial waste material using a sol-gel technique. High purity of Si from materials was prepared using an acid and base solution. Two kinds of materials were selected to produce high purity Si, namely: bottom ash and fly ash. Silicon concentration of material before and after treatments were extracted by using two extraction method, namely: Na₂CO₃/NH₄NO₃ and 0.5 M HCl. The results show that the Si concentration of materials was higher with the sol-gel technique compared to Si concentration before treatment. In summary, this study provides an effective method to produce available Si from waste material.

1. Introduction

In Indonesia, industrial waste such as fly ash, bottom ash, and slag in the thermal power energy, steel, and coal industry has been potential for environmental impact. Under Environmental Law No P.12/MENLHK/SETJEN/PLB.3/5/2020, those materials are classified as toxic and hazardous waste. Therefore, to use those materials in Indonesia need to deal with the regulation and to prove its positive effect on the soil and plant. This environmental impact has encouraged more research to transform those raw materials into new products that are beneficial for agriculture.

Recently, various industrial by-products, for example, slag from iron and alloy manufacturing that consist of calcium silicate which could meet the demand of Si fertilizer. Several studies have reported the beneficial effects of Si on rice growth and production.

The commercial use of fly ash as a fertilizer in crop production is uncommon in most countries, including Indonesia. As coal ashes may contain non-essential elements that adversely affect soil, crop, and groundwater quality [1-3]. Despite the potential and negative effect on environmental quality, the production of coal in Indonesia is around 437 million t [4] with bottom and fly ash as waste that is likely to remain a serious issue.

Fly ash is a fine particulate residue and a very complex material that is removed from the dust-collection system. The diameter of fly ash particles from <1 µm up to 150 µm. Fly ash is a glassy
material with a very high available Si content which is produced from coal combustion [2, 5, 6]. The chemical composition of fly ash depends on the type of feed coal used in the combustion process [5, 6]. In general, fly ash from the combustion of sub-bituminous coal contains more calcium (Ca), less iron (Fe) and contains very little unburned carbon (C) than fly ash from bituminous coal [5].

Silica is polymers of silicic acid consisting of interlinked SiO$_4$ units in a tetrahedral fashion with the general formula SiO$_2$ or SiO$_2$ x H$_2$O. In nature, it exists as sand, glass, quartz, etc. [7, 8]. Solid forms of Si are divided into two categories: silicates bound to Al or other elements and quartz (SiO$_2$) [9].

Silica fertilizer is not much available in Indonesia and import silicate fertilizer from other countries is relatively expensive. For this reason, it is desirable to explore cheap and abundant local materials as Si fertilizer. There are various methods to prepare pure silica from different materials. Synthesized nanoparticles from rice husk via the sol-gel method and synthesized silica xerogels from bagasse ash [7, 10]. The sol-gel technique is the most common method for silica synthesis that involves simultaneous hydrolysis and condensation reaction. A sol of sodium silicate or silicon alkoxide gets converted into a polymeric network of the gel by that process [7]. This research has mainly focused on improving the solubility of Si from industrial waste material using sol-gel techniques as treatment.

2. Materials and methods

Four materials were selected to produce high purity Si, namely: (1) Bottom ash, (2) Fly ash 1, (3) fly 2, and (4) fly ash 3. Silicon was extracted from materials with 2 extraction method, namely: (1) Na$_2$CO$_3$/NH$_4$NO$_3$ (10 g L$^{-1}$/16 g L$^{-1}$) (1:100 ratio continuous shaking 1h, filter) [11], (2) 0.5 M HCl (1:150 ratio for 1h, filter) [12]. Silicon concentrations in the supernatant were determined by colorimetric analysis with Spectrophotometer UV 1,800 Shimadzu. The wavelength used for Si detection was 810 nm.

The flow diagram of silica synthesis is shown in figure 1. Silica gels were prepared using alkaline and acid solution with three different steps [10, 13]. These steps were (1) pre-treatment, ten grams of fly ash and bottom ash were washed in 40 ml hot distilled water to remove impurities. Then, fly ash and bottom ash were filtered through filter paper and the residues were washed with hot water. The residues were dried in the oven for silica extraction. (2) Silica was extracted from fly ash and bottom ash using a 2N NaOH to dissolve the silica and produce a sodium silicate. During silica extraction, the mixture of materials and NaOH solution was boiled for 1h with constant stirring. After cooling, the material solution was filtered through filter paper Advantec No. 6. (3) The filtrate was sodium silicate which was added with 2N HCl to precipitate soft silica gels when pH decreased to <10. (4) Precipitated gelation was filtered off, into a beaker glass and washed with hot distilled water. (5) The silica gels in filter paper were dried at 105°C for 1h.

The silica content of gel was extracted with 2 extraction method, namely: (1) Na$_2$CO$_3$/NH$_4$NO$_3$ (10 g L$^{-1}$/16 g L$^{-1}$) (1:100 ratio continuous shaking 1h, filter) [11] and 0.5 M HCl (1:150 ratio for 1h, filter) [12].

3. Results and discussion

3.1. Silica concentration

The silica concentration of materials was characterized by two different extraction methods. From table 1, it is shown that after treatment, in which is the materials changed into silica slurry formation, the concentration of Si was increased as shown in table 1. The concentration of silica by the sol-gel technique was higher compared to original materials (before treatment).

In the sol-gel technique, prior to silica extraction, materials were washed hot water to remove sulphur (S). Water extraction most effectively released S from fly ash and bottom ash [14]. Furthermore, Si is soluble in alkaline solution to form sodium silicate as expressed in Eq. (1).

After adding HCl, the pH of silica gel was around 1 to 4. This condition was almost the same with the titration method, which is a sodium silicate solution, was titrated with HCl, and was stopped at certain pH conditions. The soft silica gel was gently broken after filtering and washing by distilled water.
to make a slurry. Sodium silicate that was formed and water purification showed great promise for high purity of silica gel production [10]. NaOH dissolves silica to form a sodium silicate solution [13]. pH is a critical parameter to form silica gel (figure 2). The experiment demonstrated that precipitation of amorphous silica from solutions due to salinity (Eq. 2). Increased salinity will increase both silica polymerization and deposition rates [15]. The presence of ions reduces the repulsive forces allowing the polymer to aggregate and form a gel in saline solution. The chemical reactions of silica powder synthesis in Eq (2) [16]:

The hydrochloric acid solution was added gradually into the suspension to initiate the hydrolysis-condensation reaction [7] at pH < 4. Silica starts to precipitate when the pH decreases less than 10 in acidification reaction [10].

According to the American Society for Testing Materials standard ASTM C618 [17], the ash containing SiO₂+Al₂O₃+Fe₂O₃ content between 50 and 70 wt % are defined as Class C, while those with more than 70 wt % SiO₂+Al₂O₃+Fe₂O₃ are defined as Class F. In this research, the colour of fly ash 1 and 2 was light brown or cream, which indicated a high percentage of calcium oxide (CaO). Meanwhile, fly ash 3 has dark brown or grey colour that is higher organic content class F fly ash possesses pozzolanic properties, meaning it contains silica compounds [18].

\[
\text{SiO}_2 + 2\text{NaOH} \rightarrow \text{Na}_2\text{SiO}_3 + \text{H}_2\text{O} \quad (1)
\]

![Figure 1. The flow diagram of the sol-gel technique](image)

Material (10 g) in hot water

Filter

Dry the residue in the oven

5 g dry residue and add 2 N NaOH

Allow for 1 h

Boil with stirring (1 h)

Filter

Collect filtrate

Gelation by adding 2N HCl

Gel form

Filter

Dry the gel in the oven

Pure silica
Table 1. The silica content of materials by two different extractable Si.

| Materials  | Before treatment | After treatment |
|------------|-----------------|----------------|
|            | HCl 0.5 N        | Na₂CO₃/NH₄NO₃ | HCl 0.5 N        | Na₂CO₃/NH₄NO₃ |
|            | mg SiO₂ kg⁻¹     |                | mg SiO₂ kg⁻¹     |                |
| Bottom ash | 28664            | 381            | 75957            | 9873           |
| Fly ash 1  | 16451            | 165            | 51075            | 3221           |
| Fly ash 2  | 16229            | 349            | 46331            | 2266           |
| Fly ash 3  | 18039            | 1699           | 86448            | 2618           |

Figure 2. Form of silica gel and silica powder

\[ \text{Na}_2\text{SiO}_3 + \text{H}_2\text{O} + 2\text{HCl} \rightarrow \text{Si(OH)}_4 + 2\text{NaCl} \] ………………… (2)

Sodium silicates are slightly basic, and when neutralized by adding hydrochloric acid dropwise by a pipet, hydrolysis will occur and silanol (Si-OH) groups will form. The mixing of silicate salt with an acid will form silica gel. Particles of colloidal size are formed by condensation. The small three-dimensional siloxane networks are gradually formed as condensation proceeds. The pH and the addition of an electrolyte can affect the condensation reaction [8]. In the absence of salts, electrostatic interaction between charged particles limits the aggregation process to form a three-dimensional, porous silica network [10]. Furthermore, the size of primary particles increases and decreases in number (figure 3).

Figure 3. Sol-gel process

3.2. The amount of silica material

The amount of silica material was reduced after treatment (table 2). The quantity of material by the sol-gel technique was 3.0 to 4.8 % from raw material. It was possible as a material through several stages of purification such as hydrolysis, gelation, and drying. During those stages, it might be more Si lost from the material. Another possibility that during the synthesis of Si gel, the raw material was not through an aging process. In this experiment, the remaining Na⁺ in sodium silicate was removed using distilled water on filter paper.

The aging process is when the gel in contact with the pore-filling liquid, its structure and properties keep changing as a function of time [8]. The gel mixture was aged at 60°C for 8 h [7]. The soft gel was aged for 8 to 40 h [10].
Table 2. The amount of Si materials before and after treatment

| Material      | Amount (g) before | Amount (g) after |
|---------------|-------------------|------------------|
| Bottom ash    | 5                 | 0.18             |
| Fly ash 1     | 5                 | 0.23             |
| Fly ash 2     | 5                 | 0.15             |
| Fly ash 3     | 4                 | 0.19             |

4. Conclusions
The Si availability of fly ash and bottom ash can be improved by the sol-gel technique to produce silica gel. The sol-gel technique of fly ash and bottom ash increased Si concentration and Si release than those in initial ones. Although the improvement method was found to be effective, it is needed to be tested on a pilot-scale to evaluate the economic feasibility.

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