Journal of Research in Nanoscience and Nanotechnology

Journal homepage:
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ISSN: 2773-6180

Novel Approach to the Synthesis of Silica Gel: Sequential Mechanical Activation and Sol-Gel Methods from Fly Ash Derived from Coal

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https://doi.org/10.37934/jrnn.13.1.2332

ABSTRACT

Exploration of unconventional resources and the reuse of industrial by-products are critical for advancing environmental sustainability. In this study, we propose a sequential mechano-activation and sol-gel method to synthesize silica gel (SG) from coal fly ash (CFA). The raw CFA used in this study contains 49.54% SiO_2, with 99% of the particles measuring approximately 210 nm in size, as determined by XRF and Particle size analysis. Our findings indicate that the SG surface is rich in SiO- species, evidenced by the presence of silanol (Si-OH) and siloxane (Si-O) groups in FTIR and Raman analyses. XRD analysis confirmed the amorphous nature of the SG produced from CFA. Additionally, the SG obtained had a particle size of around 97 nm for 90% of the population. This work addresses the issue of coal waste management and provides promising material for wide application.

Keywords:
Coal Fly Ash; Silica Gel; Sol-Gel Method; Mechanoactivation; Sustainable technology

Received: 28 May 2024	Revised: 25 Jun. 2024	Accepted: 27 Jul. 2024	Published: 30 Aug. 2024

1. Introduction

Exploration of unconventional resources and reusing industrial leftovers has become critical in the continuously shifting encounter of environmental sustainability. Coal fly ash (CFA), which is a byproduct of coal combustion in power plants [1-4] has long been viewed as an environmental problem due to its large volume and tendency to leak hazardous substances [4,5]. CFA consists primarily of tiny, powdery particles that are mostly spherical, with solid or hollow structures, and an amorphous composition. It exhibits low bulk density and possesses a substantial amount of distinct surface area [6,7]. It was reported that 750 million tons of CFA are generated annually, with at least 75% not being managed in an environmentally friendly way [8].

The present attention has switched to the latent potential hidden in CFA due to its high aluminum (Al) and silicon (Si) content, which might be a beneficial supplemental resource of refined alumina and silica if economically viable technologies can be devised. According to ASTM C618, CFA is categorized into two classes based on its Si, Al, and Fe oxide content: C and F grades. CFA grade C has a high calcium concentration, whereas grade F has a high silica content [6]. Rosita *et al.* reported that in a coal power plant in Indonesia specifically, CFA type F might contain chemical components such as SiO_2 (50.6%), Al_2O_3 (23.6%), Fe_2O_3 (10.9%), CaO (5.1%), and MgO (3.8%), making it an appealing source for silica derivative production [9]. This growing interest in extracting silica from CFA is an exceptional opportunity to solve environmental problems connected with CFA disposal while contributing to the circular economy by converting industrial waste into a valuable and versatile commodity.

The composition of silicates in CFA is a pivotal factor influencing its reactivity and suitability for diverse applications. While silicates exist in both amorphous and crystalline forms within CFA, with approximately 70% constituting quartz, mullite, and sillimanite in crystalline structure [10,11]. It is noteworthy that only the amorphous counterparts demonstrate reactivity with alkali and play a crucial role in extraction efficiency. In contrast, crystalline silicates remain inert, exhibiting rare reactivity with the acids or bases under normal conditions [11]. Eventhough silica sand own high percentage of silica [12], around 95%, agricultural bio-resources are potential to consider. Several studies have successfully acquired silica from various agricultural bio-resources, including sugarcane [13,14], rice husk [15,16], maize cob [17,18], bagasse [19,20], clay [21], and coffee husk ash [22,23] using certain methods such as chemical vapor condensation (CVC) [24], reverse microemulsion (RME) [25], precipitation [26], and the sol–gel method [6,14].

The sol-gel method, involving low-temperature chemical reactions in a solution, stands out for its ability to create an inorganic polymer network [27]. Through the condensation of silicate tetrahedrons with oxygen, siloxane linkages (Si-O-Si) and nanometer-sized particles are formed, resulting in a gel with exceptional purity and homogeneity [28]. Despite its widely acknowledged cost-effectiveness and efficiency, the sol-gel approach necessitates expensive raw materials and employs high-temperature furnaces [29,30].

In our study, we propose a novel approach wherein CFA, a source of silica, undergoes mechanical treatment, specifically ball milling, to enhance surface area and reactivity [31]. Subsequently, the sol-gel process is employed, wherein inorganic and amorphous polymers form through the condensation of silicate tetrahedrons. This technique entails the extraction of silica from CFA in the form of sodium silicate, followed by acid treatment to convert the silica into a gel [11,32,33]. The amorphous silica in CFA, recognized for its solubility in solutions with pH values exceeding 10 [34], is solubilized by treating it with a sodium hydroxide solution. The resulting solubilized silica, a soluble silicate, holds promise for varied applications.

Our research endeavours to harness the efficacy of the sol-gel process to extract amorphous silica from CFA, presenting a viable and cost-effective avenue for the utilization of CFA while contributing to sustainable practices and resource repurposing. This study aspires to contribute significantly to the ongoing discourse on innovative resource utilization and environmentally conscious methodologies.

2. Methodology

2.1. Materials

The coal fly ash (CFA) used in this study was sourced from an Indonesian coal power plant. The CFA underwent a series of treatments, beginning with drying in an oven at 100°C overnight to eliminate water content. The second treatment involved mechanical activation through ball milling for 24 hours, using a mass ratio of 1:20 w/w (CFA to ball). The additional chemical components used in this research included NaOH (Merck), HCl (Merck, 37%), and H_2SO_4 (Merck, 97%).

2.2. Methods

Initially, CFA underwent magnetic separation to remove magnetic substances. Subsequently, other metal contents, particularly aluminium (Al) and iron (Fe), were removed by adding sulfuric acid (H_2SO_4). The extraction of amorphous silica from Indonesian CFA employed a sol-gel, hydrothermal template-free method. In a three-neck reflux flask, 30 g of Indonesian CFA samples were introduced to 150 mL of 5 M NaOH and heated at 100°C for 3 hours using a reflux condenser system. This solution then underwent filtration using Whatman-41 filter paper, and the residue was washed with deionized water. The filtrate was allowed to cool and was then titrated with 1 M HCl to a pH range of 7-8. The mixtures were left to age for 24 hours [2,6,11]. The powder obtained was dried in an oven at 100^0C for 4 hours and lastly calcined at 600^0C under air condition.

2.3. Characterisations

This comprehensive set of characterizations provides detailed insights into the elemental composition, crystallographic structure, surface morphology, chemical bonds, and physical properties of the synthesized amorphous silica from CFA. The elemental composition of CFA was initially determined using X-ray fluorescence (XRF). X-ray diffraction (XRD) was performed using a Rigaku MiniFlex 600 with a Cu-Kα source at 40 kV, with the 2θ angle ranging from 5° to 70°. The chemical bonds in the CFA and amorphous silica were analyzed by Fourier transform infrared spectroscopy (FTIR, Thermo Scientific Nicolet iS10). Raman spectroscopy was conducted using a DXR3xi Raman imaging microscope from Thermo Fisher Scientific, with the laser power set to 1 mW, an exposure time of 0.0222 s, and 35 scans.

To analyze the size distribution and zeta potential, a particle size analyzer (Zetasizer Pro Blue, Malvern) was employed based on the dynamic light scattering method. This instrument is capable of determining particles in the range of 0.3 nm to 10 μm.

3. Results

3.1. Chemical Composition of CFA

The chemical compositions of the CFA were determined using XRF analysis, and the results are presented in Table 1. SiO_2, Al_2O_3, CaO, SO_3, TiO_2, K_2O, and P_2O_5 were identified as major compounds in the chemical composition of CFA. Notably, the silica content was found to be 49.54%.

Table 1
XRF analysis of CFA

Element	Concentration	Unit	Compound	Concentration	Unit (%)
Si	42.689	%	SiO_2	49.540	%
Al	25.916	%	Al_2O_3	30.977	%
Fe	16.938	%	Fe_2O_3	9.469	%
Ca	9.131	%	CaO	5.683	%
S	1.908	%	SO_3	2.234	%
Ti	1.477	%	TiO_2	1.029	%
K	0.781	%	K_2O	0.429	%
Mn	0.287	%	MnO	0.148	%
P	0.154	%	P_2O_5	0.167	%

Prior to extraction, the CFA underwent a preliminary mechanical treatment involving ball milling, acquiring a finely sized CFA, as depicted in Figure 1(a). The particle size distribution indicates that 99% of the CFA particles are approximately 210 nm in size, with a polydispersity index (PI) of 0.48. The zeta potential of the CFA is measured at -7.98 mV, as depicted in Figure 2(a). The mechano-activation treatment provides the necessary energy to reduce the particle size and improve homogeneity [31]. It is essential to recognize that the quantity and size of CFA particles can significantly influence mass transfer efficiency during the extraction process. The reduction in particle size increases the surface area, thereby enhancing the contact between the CFA and the extraction reagents. This increased surface area facilitates better interaction and dissolution of the silica components.

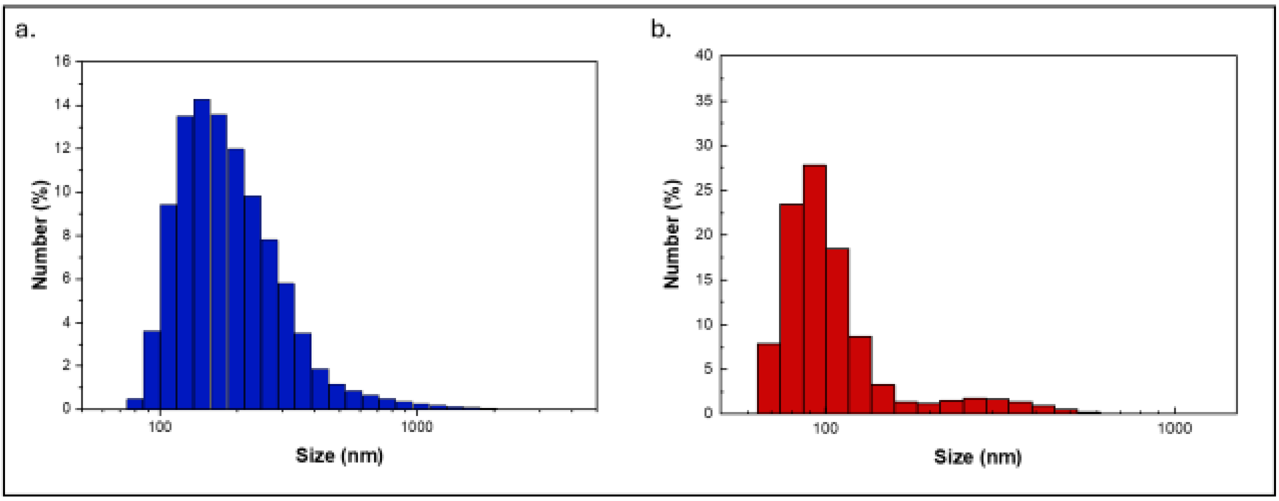

Fig. 1. Particle size analysis of **(a)** CFA and **(b)** SG

3.2. Characterisation of Silica Gel (SG)

The obtained SG exhibits a particle size of approximately 97 nm for 90% of the population, as depicted in Figure 1(b). This uniform particle size distribution is indicative of a controlled synthesis process. Additionally, the SG has a high negative zeta potential of about -24.5 mV as shown in Figure 2(b), which signifies enhanced colloidal stability in solution. The high negative surface charge is primarily attributed to the presence of deprotonated silanol groups (SiO^-) on the surface, which helps prevent particle aggregation and ensures stable dispersion [35].

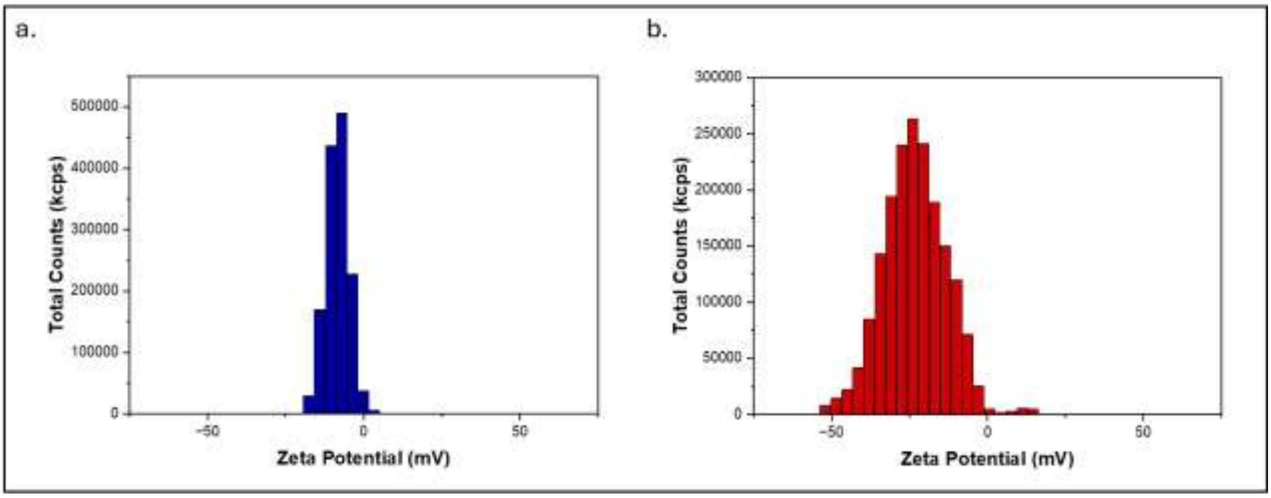

Fig. 2. Zeta potential of **(a)** CFA and **(b)** SG

Figure 3(a) displays the Raman spectra of SG synthesized from coal fly ash (CFA). The Raman analysis reveals five significant peaks located at 480 cm^{-1}, 600 cm^{-1}, 800 cm^{-1}, 980 cm^{-1}, and 1600 cm^{-1}. The peaks at 480 cm^{-1} and 800 cm^{-1} are attributed to the D1 defect mode of silica, which is associated with tetracyclosiloxane rings and oxygen vibrations perpendicular to the Si-Si bond line, respectively. The peak at 600 cm^{-1} corresponds to the D2 defect mode, which is indicative of three-membered cyclosiloxane rings. Additionally, the peak at 980 cm^{-1} is linked to surface silanol groups (Si-OH), while the peak at 1600 cm^{-1} is related to the bending vibrations of O-H bonds, typically due to adsorbed water or hydroxyl groups [36-38].

Additionally, Figure 3(b) presents the FTIR spectra of the SG. The FTIR analysis identified prominent peaks at 1050 cm^{-1} and 800 cm^{-1}, corresponding to the asymmetric and symmetric vibrations of inter-tetrahedral oxygen atoms in Si-O-Si (siloxane), which forms the primary structure of SiO_2 [34,39,40]. The presence of siloxane is crucial as it is a key functional group in the final product, contributing to the structural integrity and properties of the SG [34,41].

In addition to the siloxane peaks, FTIR analysis revealed peaks at approximately 3400 cm^{-1} and 1630 cm^{-1}, corresponding to the stretching and bending vibrations of hydroxyl groups (-OH) attached to the SiO_2 framework, forming silanol groups (Si-OH) [34,39,42]. However, in our sample, these peaks were notably weak, likely due to the calcination process, which effectively removes moisture content and silanol groups from the SG. The high-temperature treatment during calcination dehydrates the silica surface, eliminating adsorbed water and reducing the number of surface hydroxyl groups, resulting in the diminished intensity of these O-H related peaks [43]. The removal of silanol groups during calcination enhances the stability of the SG. Additionally, the high siloxane content contributes to the structural integrity and robustness of the SG.

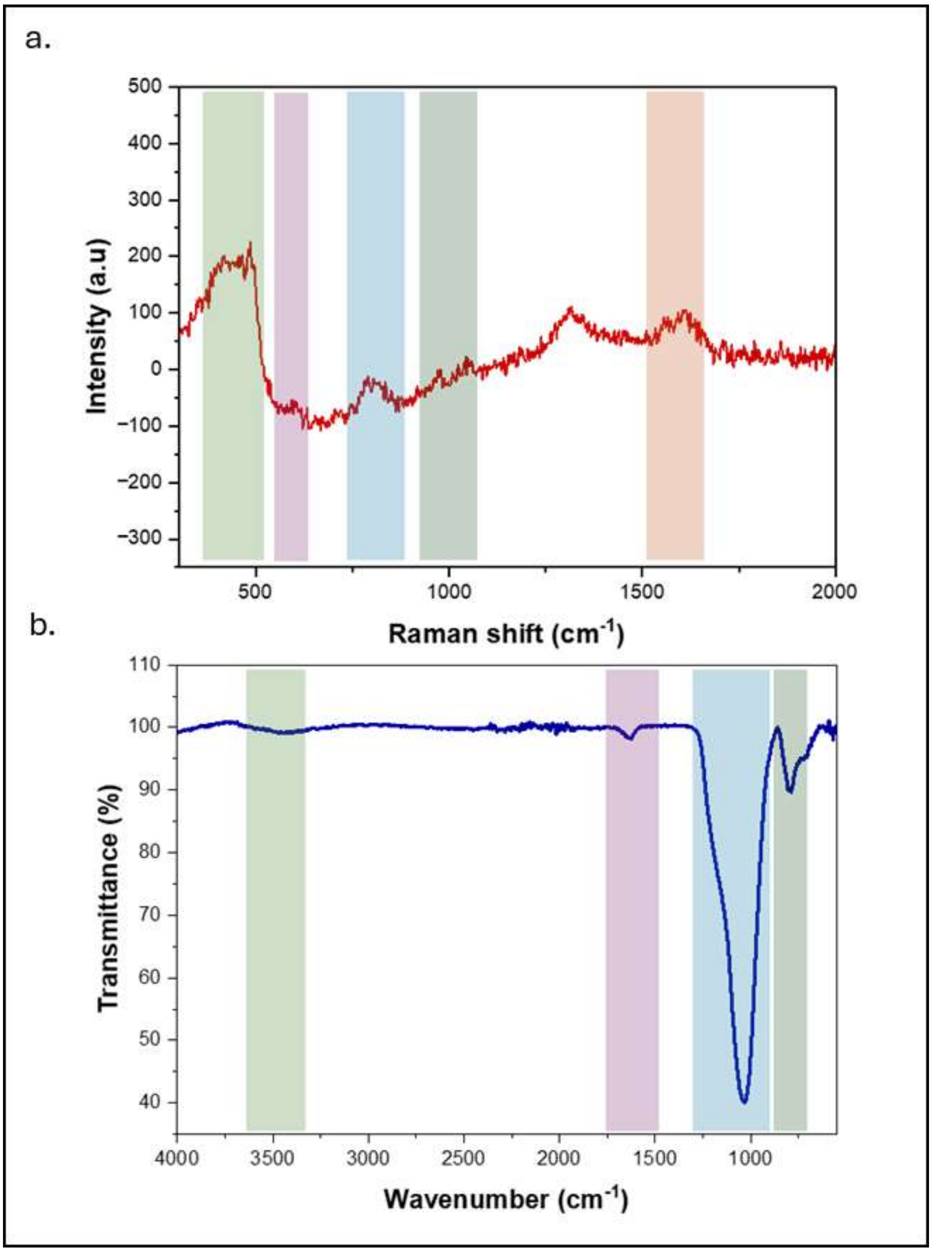

Fig. 3. Spectra of SG **(a)** Raman spectra showing the overall spectral profile; and **(b)** FTIR spectra displaying the characteristic peaks

The XRD pattern of the synthesized SG is presented in Figure 4, revealing a distinctive broad peak at 2θ = 22°. This broad and diffuse scattering suggests that the SG predominantly has an amorphous structure, indicating a lack of long-range crystalline order. The absence of additional sharp peaks in the XRD pattern confirms that there are no other crystalline phases present in the sample.

Several previous studies have demonstrated that silica synthesized from rice husk ash and fly ash typically exhibits a primarily amorphous structure [6,34]**.** This is largely due to the specific chemical processing involved. NaOH is known to selectively dissolve amorphous silica, which is then precipitated during the synthesis process [6,44]. This selective dissolution and precipitation process ensure that the final product is rich in amorphous silica, free from crystalline contaminants. The amorphous nature of the synthesized SG is advantageous for various applications, including adsorption and catalysis, as it provides a high surface area and abundant active sites. The consistency of the amorphous structure, as confirmed by XRD analysis, underscores the effectiveness of the sol-gel synthesis method employed in this study.

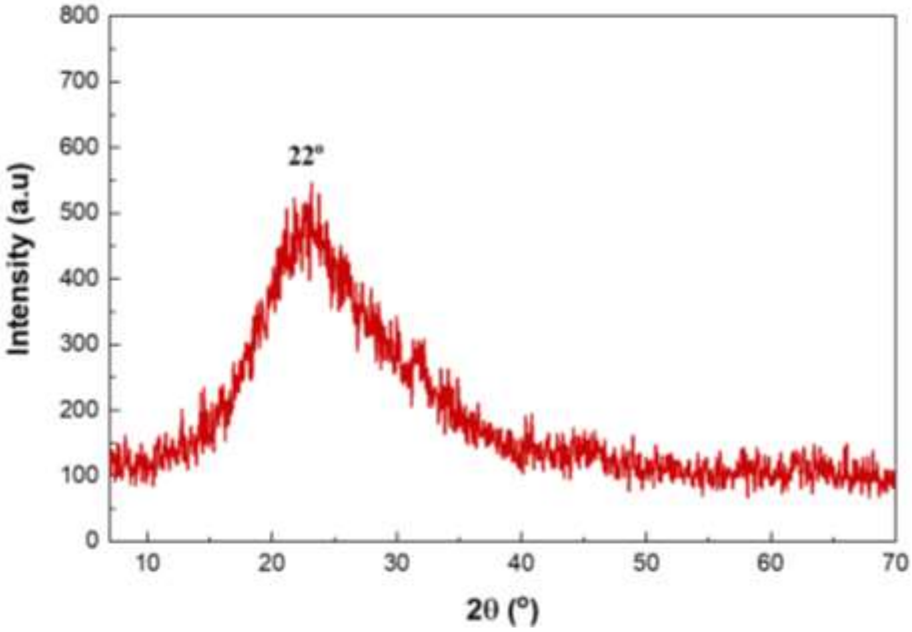

Fig. 4. XRD pattern of SG

4. Conclusions

This study demonstrated that a sequential mechanoactivation and sol-gel approach can effectively produce SG with desirable properties from coal fly ash (CFA). The resulting SG exhibits an amorphous structure, with a particle size of approximately 97 nm for 90% of the population and a zeta potential of around -24.5 mV. The characterization analyses confirmed the presence of functional groups such as silanol (Si-OH) and siloxane (Si-O), which are crucial for adsorption applications. The successful synthesis of SG from CFA highlights the potential of utilizing coal fly ash, a byproduct of coal combustion, as a valuable resource for producing high-performance materials. This approach not only addresses the environmental challenge of coal ash disposal but also provides an effective solution for water treatment through adsorption. The study underscores the feasibility of transforming industrial waste into useful products, contributing to environmental sustainability and resource recovery. Future work should focus on optimizing the synthesis process, scaling up production, and exploring the adsorption capabilities of the synthesized SG for various pollutants in different environmental conditions.

Acknowledgement

The authors would like to express their sincere gratitude to Nano Center Indonesia for their valuable support throughout this research. Additionally, the authors extend their appreciation to PT Nanotech Indonesia Global, Tbk. for providing the start-up research grant that contributed to the success of this study. Author Ande Fudja Rafryanto wishes to acknowledge support from the Indonesian Endowment Fund for Education (LPDP) 202308120119005.

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