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Effect of Ultrasound on Silicon Extraction from Coal Fly Ash

Tam Le Van[a,*], Kien Anh Le[a], Ky Phung Nguyen[b]

[a]Vietnam Institute for Tropical Technology & Environmental Protection, 57A Truong Quoc Dzung, Phu Nhuan Dist., HCMC
[b]Department of Science and Technology of HCMC, 244 Dien Bien Phu, Dist. 3, HCMC
tamvndmt@gmail.com

Coal fly ash from coal-fired power stations in Vietnam, which can cause serious environmental problems if managed improperly, is a promising silicon source for zeolite synthesis. This paper investigated the effects of ultrasound (UTS) energy on the extraction of silicon from the coal fly ash produced by the Duyen Hai thermal power plant using a 20-kHz probe immersed in the reaction mixture. Silicon was extracted from the fly ash in an alkaline solution at different temperatures, times, and ultrasonic powers. The second-order design, or the central composite design, was employed to investigate the effect of each parameter on silicon extraction. Data analysis was performed by Response Surface Methodology (RSM) using Design Expert software. With ultrasound assistance, the efficiency of silicon extraction reached 65.92 %, which is a very high extraction efficiency considering the short extraction time and lack of fusion step. With the use of ultrasound, the extraction efficiency is significantly increased compared to the fusion method. The optimal region predicted from the empirical modeling is around the center point (90 °C, 50 min, 50 % amplitude).

1. Introduction

In Vietnam, coal-fired power plants contribute greatly to global warming by emitting huge amounts of carbon dioxide. The national power development master plan for 2021–2030 with long-term goals to 2045 set out a roadmap to drastically decrease coal power, with only 9.6 % of needs supplied by coal power by 2045. Still the demand for coal remains very large, the coal output for thermal power plants is expected to be about 35 Mt, and more than 10.4 Mt of coal fly ash (CFA) has been estimated to be produced in Vietnam in 2022. CFA from coal-fired power stations, which can cause serious environmental problems if managed improperly, is a useful raw material and promising silicon source for zeolite synthesis. CFA can be used as backfill material for landfills and road subbases, and as raw material for production of concrete, cement, ceramic glass (Ju et al., 2020), and super-light materials, such as aerogels or aerogel composites (Pham and Le, 2021). The zeolites synthesized from CFA are good adsorbents for removing Cr (VI) from industrial wastewater (Thi, 2021).
Fusion with solid NaOH is considered the most efficient method to convert the silicon and aluminum in fly ash into sodium silicate (Na_2SiO_3) and sodium aluminosilicate ($NaAlSiO_4$), which are readily soluble in alkaline solutions. This method does not convert 100 % of the crystalline components in fly ash such as mullite, hematite, and magnetite into a soluble form. In addition, this method consumes a large amount of energy, so it is difficult to develop on a larger scale.
Recently, an extraction method in an alkaline solution with ultrasound has been widely employed. Ojumu et al. (2016) have used an ultrasonic device (600 W, 20 kHz) in the form of a transducer with output power decreasing from 170 W to 80 W in 10 min to replace the fusion step. As a result, the amorphous silicon and aluminum were dissolved, and the crystalline silicon and aluminum were not. The extraction efficiency of the sonication treatment and fusion step were quite similar: 24 % Si and 6 % Al from the original fly ash compared with 32 % Si and 8 % Al. Boycheva et al. (2020) have concluded that 48 min of sonication did not dissolve the crystals in fly ash. Aldahri et al. (2016) have shown that hematite and calcite were partially soluble in 1 M NaOH solution for 4 h at 100 °C, while quartz was insoluble. Mullite is not soluble in mild alkaline conditions, whether 4 h of hydrothermal conditions, 4 h of ultrasonication, or a combination. Ju et al. (2020), with the condition of ultrasonic assistance (pulse-type) with a capacity of 720 W, have increased the extraction efficiency at 110 °C from 34.96 % to 54.42 % in 70 min. This is the maximum extraction efficiency so far considering the short extraction time

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and absence of a fusion step. Many previous studies have shown that the silicon extraction efficiency is lower than 37.5 %. The optimal extraction conditions are a 0.5 g NaOH/1 g fly ash ratio and a temperature of 100–110 °C for 60–70 min. Panek et al. (2017) have achieved an efficiency of 66.77 % at 80 °C with a prolonged extraction time of 36 h.

Ojumu et al. (2016) used the same 20-kHz ultrasonic transducer. Their short reaction time at 105 °C probably caused the extraction efficiency to be lower than that of Ju et al. (2020). Ojumu et al. (2016) used 5 M NaOH alkaline solution with the ratio of 1 g ash: 5 mL 5 M NaOH, ≈ 20 % NaOH solution (mass ratio of NaOH/fly ash=1:1), compared with the work of Ju et al. (2020), which used 1 g ash: 2 mL 25 % NaOH ≈ 6.25 M (mass ratio of NaOH/fly ash=0.5:1). Commonly used ratios of NaOH/fly ash when dissolving fly ash with NaOH solution are between 0.5 and 1.2 NaOH/fly ash. Previous studies have shown that temperature was the limiting factor and strongly affected the silicon extraction efficiency. The optimal temperatures ranged from 80 to 100 °C. Reaction temperatures under 80 °C had low extraction efficiency and reaction temperatures above 100 °C had limited effect.

In this study, an ultrasound-assisted alkaline dissolution strategy was applied. The survey domain was defined over three factors: temperature (°C), time (min) and amplitude (%). An ultrasonic device with a capacity of up to 1.500 W was employed in continuous operation mode. This study aims to investigate the optimal condition to increase the efficiency of the ultrasound-assisted silicon extraction method and determine the contribution of the crystalline components, such as quartz (SiO_2) and mullite ($Al_6Si_2O_{13}$).

2. Materials and methods

2.1 Reagents and characterization techniques

Class F fly ash from Duyen Hai thermal power plant (Vietnam) was used for silicon extraction. The fly ash was collected at the fly ash silo of the power plant before transport to the ash yard. Sodium hydroxide (Analytical Reagent) and deionized (DI) water were used throughout this work.

The components of the original CFA, along with those of other desilicated CFA samples, were confirmed by X-ray fluorescence (XRF) spectroscopy (Model S2 Puma, Bruker, Germany). The mineral phases in the raw materials and zeolite products were identified using qualitative X-ray diffraction (XRD) techniques (Model D2 Phaser, Bruker, Germany). The XRD instrument operated at a voltage of 30 kV and a current of 10 mA. The samples were ground to a fine powder and later mounted onto sample holders. All samples were dried at 105 °C for 12 h to remove moisture prior to analysis. The silicon content was determined using a UV-vis 1800 instrument (Shimadzu Corporation, Kyoto, Japan) according to US EPA method 366.

2.2 Extraction of silicon from CFA

The fly ash was sieved through a 50-μm screen to separate the unburnt coal and residues from the alumino-silicate minerals. The silicon was extracted based on a typical alkaline dissolution method: 75 g of CFA was added to 300 mL of 6 M sodium hydroxide solution using ultrasonic transducer equipment at a frequency of 20 kHz and 1500 W power (VCX 1500 HV2-220, Sonics & Materials, USA). The ultrasonic device was operated in continuous mode. A double-layer reaction vessel with a thermostatic tank and temperature probe was used to control the temperature during the reaction. After the reaction phase, the mixture was processed immediately to minimize error. Vacuum filtration was used to separate the mixture, after which the liquid component was analyzed. Each sample was analyzed three times in parallel experiments, and the mean values obtained are presented in this work.

2.3 Experimental design and data analysis

Many factors influence the extraction of silicon from fly ash. The three factors of temperature, time, and ultrasonic energy strongly affect the silicon extraction process. The experiment was statistically analyzed using a central composite experimental design. In this study, the influence of the independent variables temperature (X1: 81.6, 85, 90, 95, 98.4 °C), time (X2: 33.2, 40, 50, 60, 66.8 min), and amplitude (X3: 25, 35, 50, 65, 75 %) were investigated on the silicon extraction efficiency. A design for three-variable optimization with 17 experimental points, including three replicates at the center points, was selected. The center points defined the experimental error and reproducibility of the data. The actual values of the independent variables must be coded as dimensionless values into coordinates inside a scale, which must be proportional to their localization in the experimental space (Bezerra et al., 2008). The code levels of the correspondence of the independent variables with the real values are described in Table 1. The values of the independent variables are expressed as −α, −1, 0, +1, and +α intervals; the α-value depends on the number of variables. It can be calculated as $\alpha=2^{(k-p)/4}$. For three variables, α is 1.68. Design Expert 12 software (Stat-Ease, Minneapolis, USA) was used to analyze the experimental data.

Table 1: The coded values of the independent variables corresponding to their real values

Coded	Temperature (X1), °C	Time (X2), min	Amplitude (X3), %
−α	81.6	33.2	25
−1	85	40	35
0	90	50	50
+1	95	60	65
+α	98.4	66.8	75

3. Results and discussion

3.1 Raw material characterization

Table 2 illustrates the major oxides and trace elements present in the Duyen Hai CFA as determined by XRF analysis. The SiO_2/Al_2O_3 ratio in the ash was 2.16. This ratio plays an important role in the type of zeolite that can be produced from coal ash (Bukhari, 2016, Ojumu et al., 2016). The $SiO_2 + Al_2O_3 + Fe_2O_3$ mass exceeded 70% of the total ash mass, indicating that the Duyen Hai coal fly ash is in class F and resulted from burning a mixture of bituminous coal and sub-bituminous coal.

Table 2: Composition of Class F Duyen Hai coal fly ash

Chemical Composition	Content (wt%)
SiO_2	55.8
Al_2O_3	25.8
Fe_2O_3	7.4
MgO	1.3
CaO	1.1
K_2O	4.3
C	< 3

Notes: Compounds of less than 1 wt% are not shown in the table.

The crystalline structure of CFA was determined by XRD, and the resulting spectrum is shown in Figure 1. The main crystalline components were quartz, mullite, hematite (Fe_2O_3), and magnetite (Fe_3O_4). In addition, a broad diffraction peak appeared between 15° and 35°, indicating that amorphous silica and aluminum were also present in both the raw and desilicated CFA.

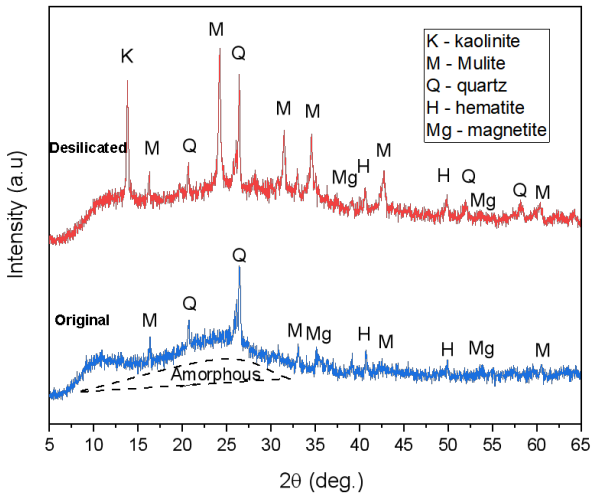

Figure 1: XRD spectra of the raw CFA and desilicated CFA

3.2 The efficiency of silicon extraction from CFA

The optimization of the silicon extraction was conducted with one response of silicon extraction efficiency. Table 3 shows that the silicon extraction efficiency ranged from 21.69 % to 65.92 %. The highest silicon extraction efficiency (65.92 %) was obtained at the temperature of 90 °C, the reaction time of 50 min, and the amplitude of 50 %.

Table 3: Central composite design with three factors and response of Si extraction efficiency

Run	Temperature (X1), °C	Time (X2), min	Amplitude (X3), %	Si extraction efficiency, %
1	−1	−1	−1	34.33
2	1	−1	−1	34.30
3	−1	1	−1	28.73
4	1	1	−1	45.76
5	−1	−1	1	22.39
6	1	−1	1	30.52
7	−1	1	1	21.69
8	1	1	1	30.25
9	−1.68	0	0	33.78
10	1.68	0	0	31.31
11	0	−1.68	0	29.34
12	0	1.68	0	39.21
13	0	0	−1.68	27.20
14	0	0	1.68	21.80
15	0	0	0	64.35
16	0	0	0	65.92
17	0	0	0	64.23

The regression analysis indicated that X3, $X1^2$, $X2^2$, and $X3^2$ were significant model terms (P-values less than 0.05). The F-value of Lack of Fit of the Y response was 42.56, implying that the lack of fit was insignificant. The coefficient of determination (R2) was 0.9447, meaning that more than 94.47 % of the response variability was explained, and the ability of the established model. The model F-value was very high (13.28), and the model p-value was very low (0.0013) on the response, so there is only a 0.13 % chance that a Model F-value this large could occur due to noise. Thus, the accuracy of the polynomial model was adequate. In this case, the regression equation of the silicon extraction efficiency is a quadratic function, as described in Eq(1).

$$Y_1 = 64.663 - 3.47X_3 - 10.83X_1^2 - 10.22X_2^2 - 13.67X_3^2 \quad (1)$$

The visualization of the predicted model equation can be obtained from the surface response plot in Figure 2.

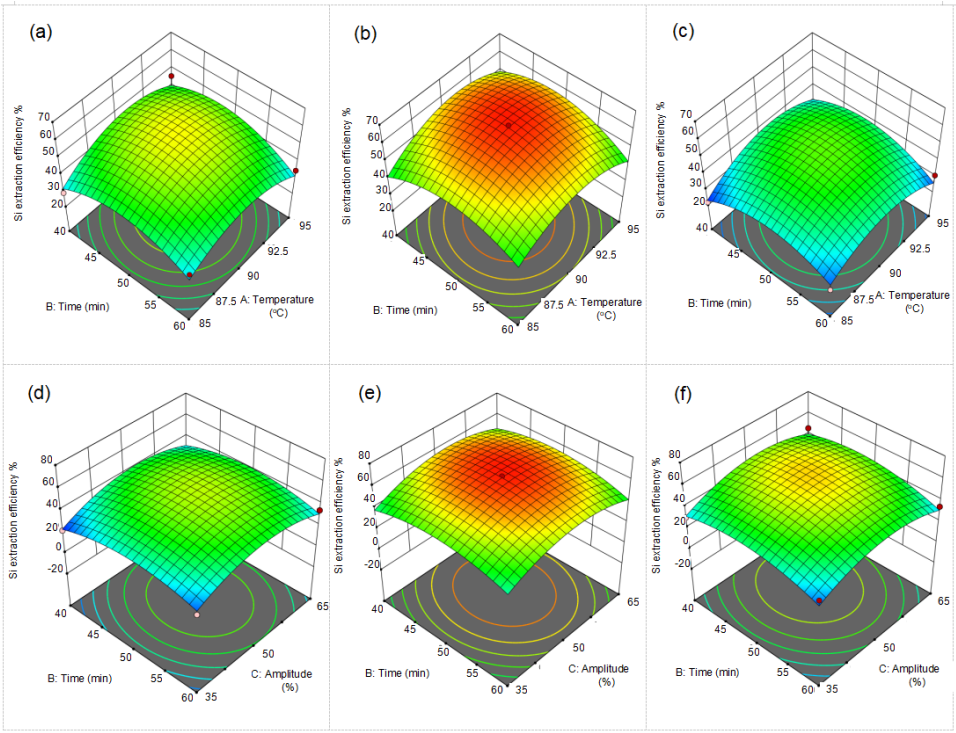

Figure 1: The surface response plot of the extraction efficiency response: (a) amplitude 35%, (b) amplitude 50%, (c) amplitude 65%, (d) temperature 85 °C, (e) temperature 90 °C, and (f) temperature 95 °C

This graphical representation is a two-dimensional surface in the three-dimensional space because one variable is held constant to visualize the plot, as in Figure 2. The optimum region can be found by visually inspecting the surfaces (Bezerra et al., 2008). The optimal condition of the reaction can also be determined by solving the regression equations exported from Design Expert. Figure 2 represents the surfaces where the maximum point is located inside the experimental region, and the optimum region is around the center point (90 °C, 50 min, 50 % amplitude). This position gives the silicon extraction process high flexibility during operation within the optimum region to obtain sufficient extraction efficiency.

3.3 Evaluation on extraction efficiency

Increasing the efficiency of silicon extraction from CFA has always been an area of research interest. With ultrasound assistance, the efficiency of silicon extraction can reach 65.92 %, which is a very high extraction efficiency, especially considering the short extraction time and lack of fusion step. A comparison of silicon extraction efficiency between different studies is shown in Table 4.S

Table 4: Comparison of silicon extraction efficiency between different studies

No.	Method	Extractants /CFA	Fusion		Dissolution		Mass fraction (% Si/CFA)	Extraction efficiency (%)	Ref.
			T (°C)	t (h)	T (°C)	t (h)			
1	Alkali dissolution	0.96	-	-	90	0.83	26.04	65.92	This work
2	Alkali dissolution	0.5	-	-	100	1.17	20.35	37.49	Ju et al. (2020)
3	Alkali dissolution	0.5	-	-	110	0.3	20.35	28.05	Ju et al. (2020)
4	Alkali dissolution	0.5	-	-	110	1.2	20.35	54.42	Ju et al. (2020)
5	Alkali dissolution	0.8	-	-	100	4.5	17.83	19.12	Hui and Chao (2006)
6	Alkali dissolution	0.6	-	-	80	36	24.72	66.77	Panek et al. (2017)
7	Alkali dissolution	0.8	-	-	125	1	24.10	29.76	Zhou et al. (2015)
8	Acid dissolution	1	-	-	25	0.5	21.79	10.22	Li and Qiao (2016)
9	Alkali fusion	1.2	550	1	25	24	23.69	8.6	Yuan et al. (2019)
10	Alkali dissolution	1	-	-	105	0.17	25.87	28	Ojumu et al. (2016)

This research showed that the ultrasound-assisted alkali dissolution method could increase silicon extraction efficiency up to 65.92 %, equivalent to the results of Panek et al. (2017) (66.77 %) without an excessive reaction time. The higher ultrasonic power (1,500 W) probably explains the improvement to the silicon extraction efficiency compared to that (720 W) of the study by Ju et al. (2020). The optimal ultrasonic time (approximately 50 min) is also an important factor affecting the efficiency of silicon extraction. Ojumu et al. (2016) used the same type of 20-kHz ultrasonic transducer at a shorter reaction time, 6 min at 105 °C, which probably caused the extraction efficiency to be lower than that of Ju et al. (2020) and this work.

The percentage of amorphous components in the desilicated fly ash decreased compared to the raw fly ash (74.1 % and 76.1 %), while the percentage of crystalline components in the desilicated fly ash increased (23.9 % and 25.9 %). This indicated that the main source of reactive silicon was amorphous. The percentage of quartz (SiO_2) in desilicated fly ash decreased sharply, from 12.31 % to 6.74 %. However, the percentage of mullite ($Al_6Si_2O_{13}$) in the fly ash after ultrasonic treatment increased from 4.28 % to 7.74 %, showing that under the reaction conditions of this study, quartz (SiO_2) was significantly soluble. In contrast, mullite remained insoluble. Compared with other reaction conditions, for example, after 10 min of sonication (600 W, 20 kHz) in 5 M NaOH with none of quartz or mullite dissolved (Ojumu et al., 2016), after 48 min of sonication with none of quartz or mullite dissolved (Boycheva et al., 2020), after 3 h of sonication (360 W, 20 kHz) in 1 M NaOH with none of quartz or mullite dissolved (Aldahri et al., 2016), and after 70 min of sonication (720 W, 20 kHz) in 6.25 M NaOH with none of quartz or mullite dissolved (Ju et al., 2020). Therefore, mullite remains the most difficult crystal to dissolve. At the same time, quartz can be significantly soluble if the reaction occurs at a high NaOH concentration (≥ 6 M), long enough sonication time (approximately 50 min), and with high sonication power (1,500 W). The dissolution of quartz may contribute to the increased silicon extraction efficiency.

The optimal reaction temperature at 90 °C but not higher is reasonable and similar to previous studies. When the temperature is higher than 90 °C, side reactions and the formation of unexpected zeolites, such as sodalite, may occur in addition to silicon extraction, lowering the silicon extraction efficiency at higher temperatures.

4. Conclusions

In conclusion, silicon was extracted from CFA using an ultrasound-assisted alkaline dissolution strategy. The efficiency of silicon extraction reached 65.92 % for a 50-min reaction under 1500 W ultrasound at 90 °C, which is a high extraction efficiency considering the short extraction time and lack of fusion step. Using the ultrasound-

assisted method, the silicon extraction efficiency was improved with a shorter reaction time and lowered energy consumption.

The results showed that second-order quadratic modeling is compatible with the experimental data (R-squared value of 94.47 %), and all three factors impact the reaction efficiency ($p < 0.05$). The optimal region predicted from the empirical modeling is around the center point (90 °C, 50 min, 50 % amplitude). The regression equation of the silicon extraction efficiency is a quadratic function, given in Eq(1). These results showed that CFA is a promising silicon source for zeolite synthesis.

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