

Alkaline Pre-Treatment of Coal Fly Ash as Bio-Silica Fertilizer

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Abstract

This study deals with the pre-treatment of coal fly ash (CFA) by using alkaline substance to improve water solubility of Si which in turn readily available to the plants. Selected weight ratios of CFA/NaOH (s:s) were tested and the highest H₄SiO₄ yield ratio was selected for further study. X-ray diffraction and scanning electron microscopy analyses were performed to confirm the evidence of structural changes of the CFA upon alkaline treatment. To improve SiO₂ dissolution, seven Si-solubilizing fungi, *i.e.*, *Aspergillus niger* BCC194, *A. niger* K0909, *A. niger* A1601, *Trichoderma polysporum*, *T. viride*, *T. pseudokoningii*, and *Trichoderma* spp, were each inoculated onto pre-treated ash. The results indicated that the relationships between ratio of CFA/NaOH and total and soluble Si were linear ($R^2 = 0.97^{**}$ and 0.96^{**} , respectively). Total SiO₂ values range from 10.43% to 13.02%, whereas soluble Si contents were 2.30% - 2.64% improved about 300 times compared to un-treated CFA. Both XRD and SEM analyses indicated that alkaline treatment to CFA caused particle damages resulting in increasing soluble Si. Inoculation of pre-treated CFA by *T. polysporum* up to twelve days of incubation yielded the highest soluble Si. Each fungal species grown on Bunt & Rovira solid media enriched with CFA as Si-source expressed significantly different ability in solubilizing Si from CFA. Citric acid was shown to be stronger compared to acetic and oxalic acids in solubilizing Si from CFA.

Keywords

Soluble Si, Si-Solubilizing Fungi, Si Fertilizer, Silicic Acid

1. Introduction

As an attempt to implement a circular economy, a coal fly ash (CFA) originated

from fertilizer power plant was intended to be an effective silicon (Si) fertilizer. With considerably high silica (SiO_2) content, this material has very low water-soluble Si (H_4SiO_4). Silicon (Si) has got considerably intensive attention worldwide as new functional fertilizer. As the second largest abundant element on earth [1], this nutrient is required by almost all crops with various functions. However, the crops are capable of absorbing Si when it presents as a unique molecule, *i.e.*, silicic acid (H_4SiO_4) [2] [3]. On the other hand, SiO_2 presents as insoluble material and its dissolution is governed by high pH (alkaline) condition. Although not considered as an essential element as NPK fertilizer, Si has a positive impact on plant development. Silicon fertilization has the potential to mitigate environmental stresses and soil nutrient depletion. Positive effects of Si in supporting better growth and improved yield of many important crops have been widely reported [4] [5] [6] [7]. Many efforts are then spent by many researchers in many countries to formulate the most effective product as Si fertilizer. Previously, we developed an acid-base extraction method of Bangka-Belitung quartz sand to improve water-soluble Si [8]. The formulated Si-fertilizer was shown to be very effective in improving growth and yield as well as water and nutrient use efficiencies of selected crops such as black soybean [9], rice paddy [10], sugarcane [11], corn [12], and oil palm [13].

In order to provide various diversification of Si-fertilizer raw material sources, coal fly ash (CFA) could be considered as a prospective material to be processed further as beneficial fertilizer. Many studies have been reported in relation to the characteristics of coal fly ash originated from a power plant facility. Among others, [14] [15] [16] [17] [18] indicated that CFA was dominated by silica (SiO_2), iron oxides (Fe_2O_3), aluminum oxides (Al_2O_3), and calcium oxides (CaO). The content of soluble Si was however very low ($\ll 1\%$) and therefore it is necessary to process further the CFA as a new Si fertilizer to improve its soluble Si content. We are of the opinion that this effort could be achieved by employing both chemical and biological approaches. The chemical treatment could involve the reaction of CFA with alkaline substance such as sodium hydroxide (NaOH) [8], whereas the biological activation could be employed by using silica-solubilizing microbes, particularly fungi [19].

As consequence of using coal in power plant of some fertilizer companies, CFA is generated in a considerably huge amount depending on the power generated by the plant. This phenomenon will to some extent create environmental problem since CFA in Indonesia is classified as toxic waste [20] and needs additional costs for handling it according to the safe waste management measures. By considering the chemical characteristics of the materials, as part of a circular economy program, CFA could be processed further to be a new Si-fertilizer. However, an effective process required needs to be established. We report here the process of alkaline pre-treatment on CFA and enrichment with selected Si-solubilizing fungus to formulate and evaluate the product specification according to existing regulation of commercial Si-fertilizer.

2. Material and Method

2.1. Coal Fly Ash Characterization

The CFA material was obtained from PT Pupuk Kalimantan Timur in Bontang, East Kalimantan, Indonesia, for chemical characterization. The samples obtained had dark gray color and powder form (about 100 - 200 mesh size). Chemical analyses were conducted at Indonesian Research Institute for Biotechnology and Bioindustry in Bogor, West Java, Indonesia. The analyses included pH (H₂O), total organic C (Spectrophotometry), total N (Kjeldahl), P₂O₅ (25% HCl-AAS), K₂O (25% HCl-AAS), MgO (25% HCl-AAS), CaO (25% HCl-AAS), Sulphur (AAS), total silica (SiO₂) (Gravimetry), soluble Si (H₄SiO₄) (Spectrophotometry), Fe₂O₃ (AAS), Al₂O₃ (AAS), cation exchange capacity (CEC) (Percolation-Titration), selected heavy metals (Pb, Cd, As, Hg, Cr, and Ni) (AAS), and water content (Gravimetry) employing standard analytical procedures [21].

2.2. Si-Solubilizing Fungal (SSF) Isolate Preparation

The silicate-solubilizing fungi (SSF) studied were cultured each in Bunt and Rovira solid standard media including selected strains of *Aspergillus i.e.*, *Aspergillus niger* BCC F194, *A. niger* K0909 and *A. niger* A1601, and of *Trichoderma i.e.*, *Trichoderma sp.*, *T. polysporum*, *T. viride*, and *T. pseudokoningii* as collection of the Microbiology and Environmental Laboratory, IRIBB, Bogor [19]. A piece of inoculant SSF ($\varnothing = 3$ mm) as a source of inoculum was grown on Bunt and Rovira solid medium containing (L⁻¹): 20 g glucose; 1.0 g peptone; 1.0 g yeast extract; 0.5 g (NH₄)₂SO₄; 0.4 g K₂HPO₄; 0.1 g MgCl₂; 0.01 g FeCl₃; 250 mL soil extract; 20 g oxoid agar; 750 mL tap water; and pH 6.6 - 7.0 as described by [22]. These media were supplemented with either 0.25% magnesium trisilicate (Mg₂O₈Si₃) or modified medium using CFA as sources of silicate.

2.3. Silicate-Solubilizing Capacity of the SSF

For assessment of Si-solubilizing capacity potential, petri dishes containing Bunt and Rovira solid medium at each initial pH condition were inoculated with each culture strain of SSF. The culture dishes were kept for seven days incubation at 28°C. The solubilization halo's (translucent area surrounding colonies) diameter was measured after seven days incubation and the Solubilization Index (SI) expressed as halo diameter (mm)/colony diameter (mm) was calculated [23]. The potential capacity of the strains studied was classified based on their SI as demonstrating low (SI < 2.0), intermediate (2.0 ≤ SI < 4.0) and high (SI ≥ 4.0) potential solubilization capacities.

2.4. Effect of Ash/Alkaline Ratio on Soluble Si

In this study, we modified the extraction method from the previously reported for quartz sand [8] by omitting the acid extraction (HCl) and using alkaline substance (NaOH) only to improve solubility of SiO₂ in water (H₄SiO₄). The main reason for this was to reduce the costs and still have sufficient soluble Si content

as Si fertilizer. A 30 gram of CFA was activated by 30, 40, 50, and 60 grams NaOH(s), respectively, to obtain different ratio of CFA/NaOH. Four ratios of CFA/NaOH(s) were evaluated and the most efficient ratio was selected based on soluble Si content. Each mixture was then heated on stove at 330°C while stirred manually until melted and the melted mixture was kept stirred until it dried out and cooled at room temperature [8]. **Figure 1** shows typical physical appearances of original CFA and that after pre-treated with NaOH(s). Soluble Si was then determined from each ratio in two replicates by using spectrophotometer. Regression analysis was performed to determine relationship between soluble Si and the amounts of NaOH(s) added to CFA.

2.5. Mineralogical Analyses

2.5.1. X-Ray Diffraction

X-ray diffraction (XRD) analysis was performed by using a random-oriented sample for both untreated and treated CFA employing XRD-6000 Shimadzu with Cu K α radiation at 40 kV and 30.0 mA equipped with low divergence and receiving slits and a graphite monochromator. The presence of minerals in the CFA sample was identified from random powder diffraction patterns following the procedures given by [24]. As adopted by [8] a continuous scan was applied in a horizontal scale ranging from 3° to 90° 2 θ at a scan speed of 3° 2 θ min⁻¹ and a sampling pitch of 0.02 - 2 θ . Calibration was done by using a 325-mesh Si powder standard of Shimadzu containing 990.0 g·kg⁻¹ SiO₂.

2.5.2. Electron Microscopy

Scanning Electron Microscope (SEM) observation was carried out to treated and un-treated CFA samples. As reported by [8], the electron beam was accelerated through a high voltage 20 kV and pass through a system of apertures and electromagnetic lenses to produce a thin beam of electrons. Prior to analysis, the samples were leveled with a special tool. After sputter coating the cast with 35 nm of gold-palladium (Au-Pd), electron micrographs were recorded using a Jeol JSM-5310LV SEM.



Figure 1. Physical appearance of CFA before (left) and after pre-treated with NaOH(s) (right).

2.6. Effectiveness of Si-Solubilizing Fungal Isolates on Soluble Si

Silica solubilizing capacity was then assayed in 50 mL liquid and solid Bunt and Rovira medium with 0.25% (w/v) CFA as Si source. Inoculation was performed by transferring two pieces of fungal inoculant ($\varnothing = 3$ mm; 10^6 spores) on 250 mL Erlenmeyer flask containing 50 mL of liquid culture Bunt and Rovira medium. The cultures were incubated on a mechanical shaker at 100 rpm (28°C) for four, eight, and twelve days. Silica solubilizing capacities were determined by using American Standard Testing and Material (ASTM D859-16) method. The dissolved silicate in the form of silicic acid (H_2SiO_4) was measured using a spectronic 21 spectrophotometer at 660 nm wavelength [25].

2.7. Effect of Organic Acids on Silica Dissolution

This experiment was carried out to clarify the relative strength of different types of organic acids in solubilizing silica from CFA by using STM D859-16 method with colorimetric measurement. Citrate, acetate and oxalate were added separately in different concentrations (0, 100, 200, 300, 400 and 500 ppm) to 50 mL of Bunt and Rovira medium containing 0.25% (w/v) CFA, then incubated for eight days on a mechanical shaker at 100 rpm in 28°C . The dissolved silicate in the form of silicic acid (H_2SiO_4) was measured using a spectronic 21 spectrophotometer at 660 nm wavelength [25].

2.8. Effect of Citric Acid Produced by SSF Isolates on Silica Dissolution

The SSF producing citric acid [19] [26] [27] was determined in liquid Bunt and Rovira with 0.25% (w/v) CFA as sources of silica. Selected seven strains of SSF were grown in liquid Bunt and Rovira medium for four, eight, and twelve days, then incubated at a mechanical shaker at 100 rpm in 28°C . Citric acid assay was done according to improved pyridine-acetic anhydride acid method suggested by Marier and Boulet [28]. About 1 mL of pyridine and 5 mL of acetic anhydride added and incubated for 30 min in ice bath. The standard was prepared by different volumes of citric acid (100 mg of citric acid was dissolved in 100 mL of deionized water (DW), *i.e.*, 0.2 - 1 mL in 5 different test tubes. The volume was made up to 1 mL with DW. One milliliter of pyridine and 5 mL of acetic anhydride were added. The blank was prepared by taking 1 mL of DW in the place of citric acid. It was then kept for incubation in ice bath for 30 minutes. Concentration of citric acid was found by plotting graph of absorbance versus concentration and measured at 420 nm wavelength with the development of color density.

3. Results and Discussion

3.1. Chemical Characteristic of CFA

Selected chemical analyses were carried out to determine the element composition of CFA before and after treated by NaOH(s) as presented in **Table 1**. The ash has an alkaline reaction with pH 9.5 and contains 0.49% organic C, 0.02% N,

Table 1. Selected chemical properties of CFA originated from Bontang, East Kalimantan, Indonesia (un-treated and treated with alkaline).

Chemical properties	Un-treated CFA	Treated CFA
pH H ₂ O	9.5	12.2
Organic Carbon (%)	0.49	0.24
Nitrogen (%)	0.02	0.01
P ₂ O ₅ HCl 25% (%)	0.53	0.11
K ₂ O HCl 25% (%)	0.1	0.12
MgO HCl 25% (%)	1.96	0.64
CaO 25% (%)	4.82	1.35
Sulphur (%)	0.1	0.28
SiO ₂ (%)	31.4	10.9
H ₄ SiO ₄ (%)	0.008	2.50
Al ₂ O ₃ (%)	28.16	8.6
Fe ₂ O ₃ (%)	20.91	4.4
Pb (ppm)	17.1	20.4
Cd (ppm)	10.5	0.9
As (ppm)	n.d.*	n.d.
Hg (ppm)	n.d.	n.d.
Cr (ppm)	326.8	n.d.
Ni (ppm)	40.0	15.3

*not detected.

0.53% P₂O₅, 0.10% K₂O, 4.82% CaO, 0.10% S, 31.4% SiO₂, 0.008 ppm H₄SiO₄, 28.2% Al₂O₃, and 20.9% Fe₂O₃. All of these values are in the range of those reported by others previously [29]. A special notice should be paid on the very low value of soluble Si (H₄SiO₄) which far below 1 ppm although the total silica (SiO₂) was considerably high (31.4%). This is also the reason for the need to improve Si solubility of CFA by chemical and/or biological approaches. However, the alkaline treatment has improved the soluble Si content up to 2.5%.

3.2. Effect of CFA/NaOH on Soluble Si

Figure 2 shows the relationship between the amount NaOH(s) added to CFA and the total silica content, whereas **Figure 3** indicates the effect of the alkaline to soluble Si of CFA. It is indicative that up to 60 grams of NaOH(s) added to 30 grams of CFA both total and soluble Si were linearly correlated. The more NaOH(s) added, the higher the values of total and soluble Si of the CFA. However, as the value of soluble Si from 30 grams addition of NaOH(s) has passed the minimum requirement for a commercial Si fertilizer set by the government (minimum SiO₂ 10% w/w), then the 1:1 ratio of CFA to NaOH(s) could be recommended as the best activation process for CFA to be Si fertilizer. As shown

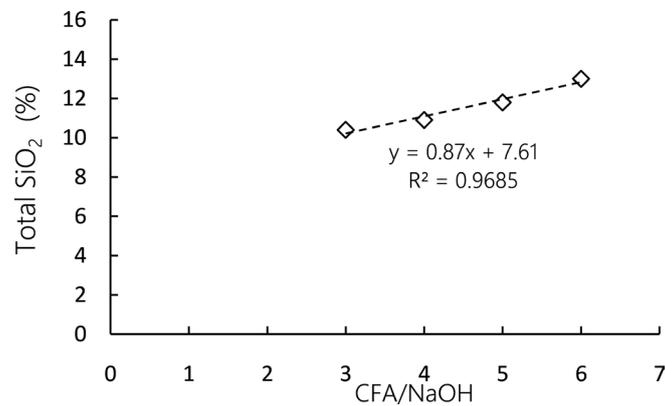


Figure 2. Effects of alkaline amount used for CFA pre-treatment on total SiO₂ content yielded.

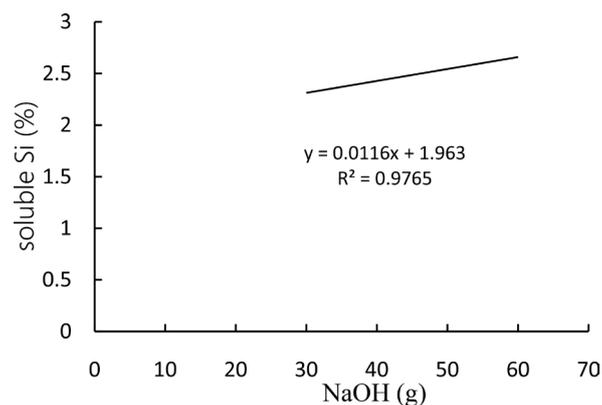


Figure 3. Effects of alkaline amounts used for CFA pre-treatment on soluble Si content yielded.

in **Table 1**, this treatment resulted in much better chemical compositions in term of soluble Si improved more than 300 times, decreased sesquioxide's and heavy metals contents in general. The increase of soluble Si is assumed to take place according to the following reaction [30].

3.3. Changes on Mineralogical Properties

Figure 4 shows the significant difference regarding the X-ray diffractograms between original and NaOH-treated CFA. The emergences of several strong intensity peaks were assumed due to the removal of contaminants, such as Al-Fe oxides, by alkaline solution treatment. These evidences were shown at the 2 degrees below 20 and above 30. Silica minerals, particularly quartz, were indicated by 21.1 (0.421 nm) and 26.5° 2 (0.335 nm) peaks [24] [31]. On the other hand, the peaks present in between 30 and 60° 2 could be considered as other characteristic peaks for quartz as reported by [32]. Alkaline pretreatment has yielded also consequently a disruption of CFA particles as shown by SEM observation. **Figure 5** shows the physical appearances of particle of both original and NaOH-treated CFA. Destruction of mineral surfaces could be assumed as the supporting evidence of increasing Si dissolution from CFA.

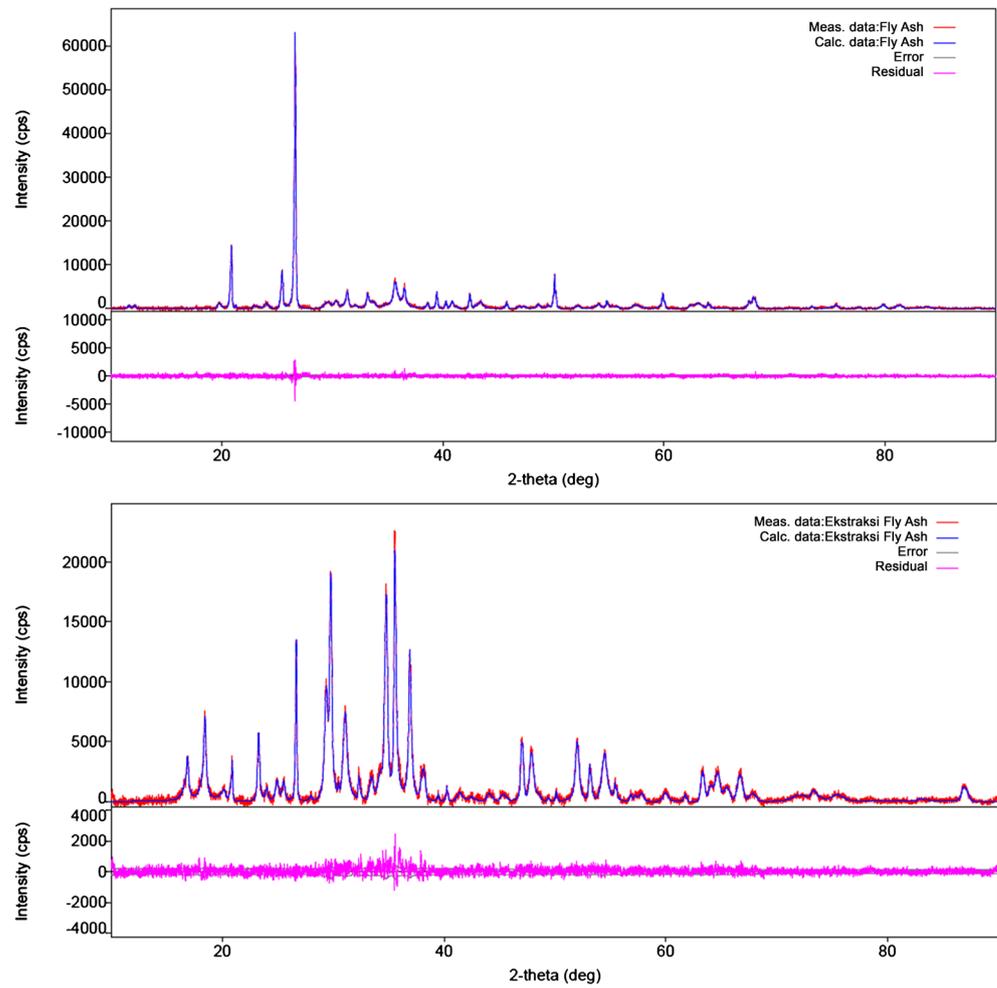


Figure 4. X-ray diffractograms of original (top) and NaOH-treated (bottom) CFA indicating increased intensity of the mineral peaks of Si and others.

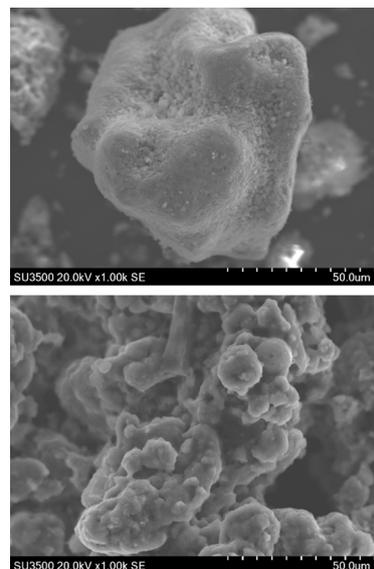


Figure 5. Scanning electron microscopy photographs of original (top) and NaOH-treated (bottom) CFA.

3.4. Effectiveness of Si-Solubilizing Fungal (SSF) Isolates on Soluble Si

In order to improve further the solubility of Si from CFA we applied biological treatment by using selected Si-solubilizing fungus. Data shown in **Table 2** indicate that among seven SSF isolates used in this experiment *A. niger* BCC 194 was the strongest isolate dissolving CFA resulting in the highest amount of soluble Si after twelve days of incubation. This evidence confirmed previous results reported by others in relation to the fact that SSF produces organic acid capable of solubilizing Si [19].

3.5. Effect of Organic Acids on Silica Dissolution

This experiment was carried out in laboratory to confirm the ability of organic acids as produced by SSF isolates in solubilizing Si from CFA. Data presented in **Figure 6** show that there were linear relationships between three organic acids (*i.e.*, oxalate, acetate, and citrate) concentrations and soluble-Si. It is indicative that oxalate was the strongest relationships as an agent for Si dissolution from CFA indicated by the highest coefficient of determination ($R^2 = 0.984^{**}$) compared to the other two organic acids (R^2 -acetate = 0.886^{**} and R^2 -citrate = 0.892^{**}) although the highest amount of soluble Si was obtained by citrate. Based on this evidence, the citrate was selected to be used in the next experiment.

3.6. Effect of Citric Acid Producing SSF Isolates on Silica Dissolution

In order to provide more supporting evidences regarding the capacity of citric acid produced by SSF isolates another experiment was carried out by growing each isolate on liquid culture media consisting CFA as the only Si source. Data shown in **Table 3** indicate that during twelve days of incubation all isolates used produced citric acid with various concentrations. Isolate *A. niger* BCC F194 showed superiority compared to the other isolates by producing 801.5 ppm at

Table 2. Soluble-Si from CFA by selecting SSF isolates during twelve days of incubation.

Species	Day 4	Day 8	Day 12
<i>Trichoderma sp</i>	22.58 ^{bc*}	33.83 ^d	42.97 ^d
<i>T. viride</i>	17.13 ^e	54.40 ^b	63.02 ^b
<i>T. polysporum</i>	19.24 ^{de}	40.86 ^c	64.07 ^b
<i>T. pseudokoningii</i>	20.12 ^{cd}	53.17 ^b	64.07 ^b
<i>A. niger strain</i> BCCF194	26.62 ^a	56.16 ^b	73.92 ^a
<i>A. niger strain</i> Korbe 0909	23.28 ^b	60.91 ^a	76.73 ^a
<i>A. niger strain</i> A1601	20.82 ^{bcd}	34.89 ^d	51.41 ^c
Control (no isolate)	14.31 ^f	17.30 ^e	19.76 ^e

*Figures followed by the same letter(s) are not significantly different according to Duncan Multiple Range Test ($P < 0.05$).

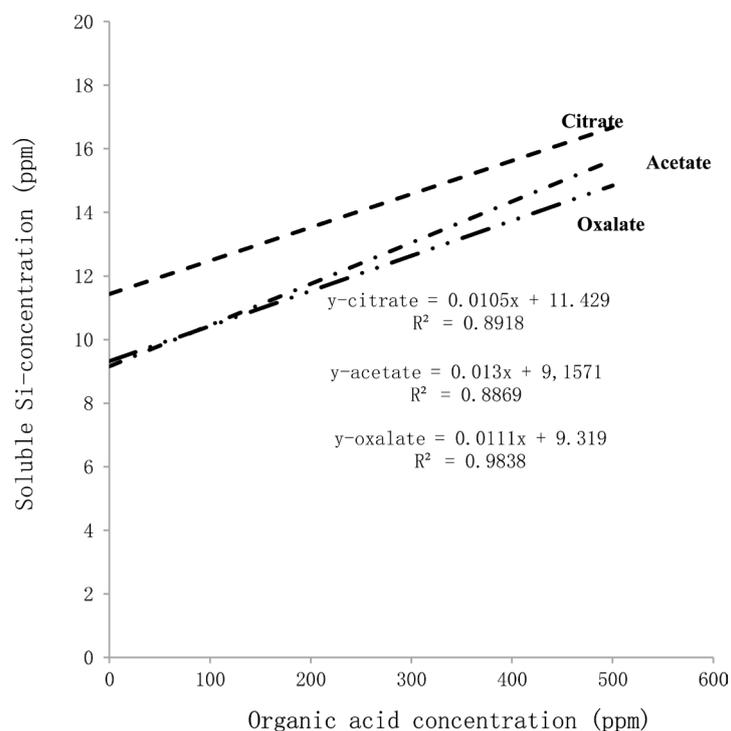


Figure 6. Relationships between selected organic acids concentrations and soluble-Si from CFA.

Table 3. Citric acid production by selected SSF isolates by using CFA as Si-source during twelve days of incubation period.

Species	Day 4	Day 8	Day 12
<i>Trichoderma sp</i>	439.0 ^{b*}	511.5 ^b	591.5 ^c
<i>T. viride</i>	399.0 ^b	469.0 ^c	536.5 ^d
<i>T. polysporum</i>	431.5 ^b	471.5 ^c	534.0 ^d
<i>T. pseudokoningii</i>	421.5 ^b	521.5 ^b	629.0 ^c
<i>A. niger strain BCCF194</i>	656.5 ^a	801.5 ^a	824.0 ^a
<i>A. niger strain Korbe 0909</i>	634.0 ^a	774.0 ^a	724.0 ^b
<i>A. niger strain A1601</i>	324.0 ^c	399.0 ^d	379.0 ^e
Control (no isolate)	296.0 ^c	334.0 ^e	321.5 ^f

*Figures followed by the same letter(s) are not significantly different according to Duncan Multiple Range Test ($P < 0.05$).

eight days and 824.0 ppm citric acid at twelve days of incubation periods which are significantly higher than the other isolates. It is also indicative from these data that production of citric acids tended to reach optimum at eight days of incubation period. The correlation analysis (Figure 7) shows that a linear relationship exists between the citric acid concentration produced by SSF isolates and soluble Si from CFA. A significant correlation ($r = 0.790 - 0.801^{**}$) during forth to twelve days of incubation period indicating that citric acid was predominant agent for solubilizing agent of Si from CFA. A relatively lower value of

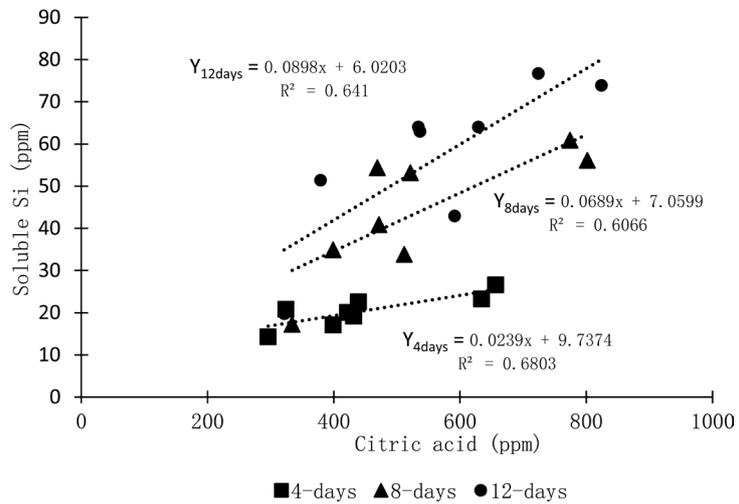


Figure 7. Correlation between citric acid produced by SSF and soluble Si from CFA at different incubation periods.

Table 4. Analytical results of CFA-derived Si fertilizer and its corresponding quality standard.

Parameter	Results of Analyses			National Quality Standard	Methods of Analyses
	Raw material	Lab-scale extraction	Scale-up extraction (120 kg-batch ⁻¹)		
pH H ₂ O	9.52	12.2	12.7	-	pH meter
Nitrogen (%)	0.02	0.01	0.01	-	Kjehdahl
P ₂ O ₅ HCl 25% (%)	0.53	0.11	0.12	-	Spectrophotometer
K ₂ O (%)	0.10	0.12	0.22	-	AAS
Sulfur (%)	0.1	0.28	0.22	-	AAS
Total SiO ₂ (%)	31.4	10.9	10.1	Min. 10	Gravimetry
Soluble Si (%)	0.008	2.5	1.6	-	Spectrophotometer
Water content	0.37	0.79	1.5	Max. 5	Gravimetry
Organic Carbon	0.49	0.24	0.25	-	Spectrophotometer
MgO (%)	1.96	0.64	0.99	-	AAS
CaO (%)	4.82	1.35	2.14	-	AAS
Al ₂ O ₃ (ppm)	28.16	8.60	8.97	-	AAS
Fe ₂ O ₃ (ppm)	20.91	4.4	7.5	-	AAS
Pb (ppm)	17.1	20.4	32.6	Max. 500	AAS
Cd (ppm)	10.5	0.9	0.8	Max. 100	AAS
As (ppm)	nd*	nd	nd	Max. 100	AAS
Hg (ppm)	Nd	nd	nd	Max. 10	AAS
Cr (ppm)	326.8	nd	6.2	<4%	AAS
Ni (ppm)	40	15.3	19.1	<0.4%	AAS

*not detected.

R² indicates that there were some other factors affecting the solubilization of Si from CFA and most likely due to acetate and/or oxalate contributions.

3.7. Quality Standard of Si Fertilizer

To be ably commercializing the product, quality of the Si fertilizer derived from CFA needs to be assessed by using authority's standard. **Table 4** shows that currently existing quality standard for Si fertilizer are based on selected chemical parameters, such as total SiO₂ content, water content, and selected heavy metals (Pb, Cd, As, Hg, Cr, and Ni) contents. Based on these characteristics the new Si-fertilizer formulated from CFA both at laboratory and scale-up production processes met the quality standard requirements set by the local authority for commercial uses.

4. Conclusion

Regardless of the current dispute regarding the use of CFA currently classified as a hazardous material for the environment, our current study revealed the potential use of CFA as Si fertilizer. Alkaline pre-treatment improved the solubility of hardly soluble Si resulting in increasing soluble Si content. A biological additional treatment by using SSF isolates proved to be beneficial in improving more the solubility of Si from CFA. Three organic acids (acetate, citrate, and oxalate) have been shown to be responsible for improved Si solubility. However, citric acid was more predominant compared to the other two. Based on the authority's quality standard, the new formulated Si fertilizer from CFA met the requirement as a commercial product.

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Conflicts of Interest

The authors declare no conflicts of interest regarding the publication of this paper.

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