Conversion of coal fly ash into advanced crystalline materials

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Abstract. In recent years, coal fly ash disposal has become one concerning environmental problems in Indonesia. Although coal fly ash is remains categorized as hazardous solid waste in several countries, it is also widely known as a valuable material used in various fields, including as a precursor for the synthesis of advanced crystalline materials such as zeolite and geopolymer. Previous studies mainly focused on the utilization of coal fly ash originated from the thermal power plant. This research done to acknowledge the potency of coal fly ash originated from the textile industry to be further converted into new advanced materials through several procedures, such as (1) modification using NaOH solution (FA-Na), (2) synthesized into geopolymer (Geo), and (3) synthesized into zeolite-A (FA-LTA). Characterization of synthesized products conducted using various techniques, i.e., X-ray Diffraction (XRD), Scanning Electron Microscopy (SEM), Fourier Transform Infrared Spectroscopy (FTIR), Brunauer-Emmett-Teller (BET), and cation exchange capacity (CEC). The results show that increasing crystallinity, specific surface area, and CEC in the samples are directly proportional to the increasing alkali concentration used. This research has proven that coal fly ash originated from the textile industry and could also synthesize zeolite and geopolymer.

1. Introduction
Various industries in Indonesia are using coal as their fuel in large quantities. For example, the textile industry, which is reported as the second-largest coal user in Indonesia, has known to use up to 4.2 million tons of coal per year [1]. High consumption of coal may potentially cause new problems to the environment because for each coal burned, 5-10% of it reportedly becoming ash. Although coal fly ash (FA) disposal has been commonly practiced for years, increasing cost of disposal and environmental concern over the leaching of toxic compounds to the soil, groundwater, and surface water has made FA utilization an attractive option [2].

FA, which is still categorized as hazardous waste in Indonesia based on Government Regulation number 101 of 2014, is widely recognized as economical material used in various fields. Novel potential applications of FA are: (1) as waste additives in waste or water treatment, (2) as valuable metal extractors
such as Al, Si, Fe, Ge, Ga, V, Ni, (3) as a land stabilizer in mining fields, (4) used to synthesis high cation exchange capacity (CEC) of zeolites, so forth. FA is predominantly composed of alumina and silica components. Thus, many studies had reported using FA as a source of alumina and silica for zeolite and geopolymer synthesis. Geopolymerization is analogous to zeolite synthesis because the elements involved are almost the same. However, the composition and chemical structure of the resulting product differ [3].

In the wastewater treatment field, FA, either remain untreated or after going through a certain synthesis process, is known to be used for dyes, heavy metals, and organic compound removal from water through the adsorption method [4–6]. This utilization is considered one breakthrough findings related to low-cost adsorbent development for activated carbon substitutes. However, depend on its origin and after-combustion treatment, direct use of FA still exhibits low adsorption capacity. Therefore, physical or chemical modification of FA is needed to increase its adsorption capacity.

FA used in previous studies were commonly originated from local power plant activities. This is based on the consideration of coal type, furnace, and combustion temperature used, affecting the overall quality of FA produced. It is rare to find literature that uses FA from industries that tend not to achieve complete combustion, such as the textile industry [3]. This research was conducted to determine structural changes and characteristics of FA from the textile industry after going through certain physical and chemical processes to become new materials and to discover their potential uses, especially in the wastewater treatment field.

2. Methodology
2.1. Materials and analytical methods
Coal fly ash (FA) used in this research was obtained from a textile industry located in Bandung, Indonesia. FA was generated from lignite-type coal combustion in an industrial boiler. To minimize pretreatment needed, only FA was collected from the cyclone unit used in this study. An EDAX micro-XRF spectrometer calculated the chemical composition of FA with an accelerating voltage of 40 kV. Deionized water was used in all solution preparations. The chemicals used in this study are sodium hydroxide (NaOH, Merck, CAS no. 1310-73-2), sodium aluminate (NaAlO2, Merck, CAS no. 11138-49-1), hydrochloric acid (HCl, Merck, CAS no. 7647-01-0), sodium silicate (Na2SiO3, Merck, CAS no. 1338443) and aluminum oxide (Al2O3, Merck, CAS no. 1344-28-1). All reagents were analytical in grade and used without further treatment or purification.

2.2. Coal fly ash preparation and conversion
FA sieved by MBT Sieveshaker AG-515 with 200 mesh size (74 µm opening) to homogenize particle size before its usage. Three kinds of FA conversion conducted in this research: (1) modification using 3 M NaOH solution (FA-Na), (2) synthesized into fly ash based-geopolymer (Geo), and (4) synthesized into fly ash based-zeolite A (FA-LTA). Modification of FA using 3 M NaOH solution (FA-Na) was done by treating FA with NaOH under one g/6 mL ratio at 60°C for 2 hours [6].

Synthesis of FA based-geopolymer (Geo) starts initially by adjusting the mole ratio of SiO2/Al2O3 into three by adding Al2O3 powder. 14 M NaOH solution and Na2SiO3 were then mixed with FA to obtain a final mole ratio of Na2O/SiO2 0.3. The liquid/solid ratio in this research was then adjusted to 0.6. The final mixture was mixed for ± 15 minutes to obtain paste texture. This paste then transferred to a polypropylene bottle (PP), set aside for several hours at room temperature, and heated at 85°C for 24 hours. Formed Geo then stored at room temperature for five days (aging) before used [3].

Before the synthesis of two-step zeolite A (FA-LTA), FA was pretreated by acid washing process, which performed by a mixture of HCl solution (10%) and FA (ratio, 25:1 mL/g) in a beaker at 80°C for 1 hour (300 r/min). Then, FA was filtered off, repeatedly washed with distilled water and dried at 100°C for 24 hours. Pretreated FA was further synthesized into FA-LTA by mixing and grounding with NaOH, under the mass ratio of 1:1.3. Then, the homogeneous mixture was heated at >590°C for 1.5 hours. The room-temperature fusion products were grounded and poured into a bottle, followed by distilled water to form a mixture. The mass ratio of the fusion products to water was 0.1725. NaAlO2 powder was added
to the mixture to obtain Si/Al ratio=1, followed by intense stirring at 25°C for 24 hours to form initial aluminosilicate gel. Then, aluminosilicate gel was poured into the specially designed autoclave at 100°C for 12 hours [4], [5]. All final products obtained in this research were filtered, washed several times with distilled water, and dried before further use.

2.3. Materials characterization

The mineralogical composition of synthesized products was determined using X-Ray Spectroscopy (XRD: Bruker D8 Advance Powder Diffractometer, USA) with diffraction angle ranging from 3 to 50° (2θ) with a 0.0205° step size using Cu Kα radiation. A Shimadzu Prestige-21 spectrometer was used to record the FTIR spectra in the range of 4000 – 400 cm⁻¹ at room temperature using KBr pelletized technique. The N₂ adsorption-desorption isotherms were determined on a Quantachrome TouchWin v1.2 instrument at 77.35 K. The pore volume was calculated using the t-plot method. In contrast, the specific surface area (SBET) was determined using the Brunauer–Emmet–Teller (BET) method. The cation exchange capacity (CEC) of the products were determined using the ammonium acetate method. Scanning Electron Microscopy (SEM) analysis using JEOL6510A could identify any morphological changes in each product.

3. Results and discussion

The chemical oxides composition of FA used in this study is shown in table 1. Commonly, FA contains SiO₂ and Al₂O₃ and other elements such as Fe, Na, K, Ca, Mg and Ti [7]. As shown in table 1, the total composition of Al₂O₃, SiO₂ and Fe₂O₃ from FA is more than 70%. Based on the American Society for Testing and Materials (ASTM) C618, FA, which contains three main components (SiO₂, Al₂O₃ dan Fe₂O₃), more than 70% is classified class-F of FA. Marking class of FA with CaO content of less than 5% [7]. These classifications are aligned with the results shown in table 1. Its reactivity characterizes Class-F of FA to alkaline materials, thus potentially chemically activated [7].

Table 1. XRF analysis of FA.

| No | Composition | %Weight |
|----|-------------|---------|
| 1  | Al₂O₃       | 23.19   |
| 2  | SiO₂        | 55.00   |
| 3  | SO₃         | 8.50    |
| 4  | CaO         | 3.27    |
| 5  | TiO₂        | 0.62    |
| 6  | V₂O₅        | 0.05    |
| 7  | Fe₂O₃       | 9.36    |

Morphological analysis of FA, FA-Na, Geo and FA-LTA are depicted in figure 1. FA from the textile industry consists of solid spherical, hollow spherical (cenosphere) particles with a size ranging from 10 to 100 µm and irregular shaped-unburned carbon. Spherical particles indicate silica, aluminum and magnesium oxides. Rougher spherical particles indicate iron crystals in the amorphous aluminum silicate phase [3]. Meanwhile, the presence of unburned carbon in FA is indicated by rougher surface particles with many pores [6]. When the FA-Na was synthesized, a marked change in surface morphology was observed. The smooth and spherical particles change into a rougher surface and full of holes, which indicate an increase of the amorphous phase in the structure [6]. Surface morphological change from FA to Geo was also shown in this research and aligned with the reference [3]. The spherical particles of FA changed into layered-surface agglomerates with a size range of 6 to 13 µm. These agglomerates are called aluminosilicate gel. As seen in figure 1, FA-LTA turns smooth and spherical FA particles into regularly and nearly uniform size cubic crystalline particles, approximately 1.6 µm.
These results are similar to this research, which indicates that all synthesis procedures were correctly done [5].

![SEM micrograph](a) FA, 1000x magnification, (b) FA-Na, 1000x magnification, (c) Geo, 1000x magnification, and (d) FA-LTA, 5000x magnification.

**Figure 1.** SEM micrograph of (a) FA, 1000x magnification, (b) FA-Na, 1000x magnification, (c) Geo, 1000x magnification, and (d) FA-LTA, 5000x magnification.

Infrared spectra analysis of FA, FA-Na, Geo and FA-LTA are shown in figure 2. As can be seen in figure 2, distinct peaks for FA are (1) 3442 cm$^{-1}$, which assigned as bending vibration of O-H bond [8]; (2) 1089 cm$^{-1}$ which indicates the presence of Si-O group; (3) 797 cm$^{-1}$ which shown stretching vibration of Si-O-Si group; and (4) 694 cm$^{-1}$ and 503 cm$^{-1}$ which indicates the presence of quartz in the structure of FA. 500-800 cm$^{-1}$ are the peak value that shows tetrahedral vibration, formed by the secondary building unit (SBU) of FA and fragments from the aluminosilicate system. These absorption bands are double ring or single ring (depends on the material structure) and/or tetrahedral bonds TO$_4$ (T=Si, Al).

As seen in figure 2, the spectra analysis of FA-Na shows similar results with FA but shifts slightly at a lower wavelength. This indicates that after the modification process, the length and angle of existing chemical groups changed [9].

FT-IR Spectra which depicted in figure 2 for Geo shows distinct peaks at (1) 3449 cm$^{-1}$ due to adsorbed molecular H$_2$O [10]; (2) 2363 cm$^{-1}$; (3) 1641 cm$^{-1}$ which assigned to H-O-H bending; (4) 1396 cm$^{-1}$ which indicates the presence of sodium carbonate, due to the reaction of residual sodium with atmospheric CO$_2$ [10]; (5) 991 cm$^{-1}$ which shown asymmetric stretching of Al-O-Al/Si-O-Si, indicating breaking and forming bonds during geopolymerization [9]; (6) 791 cm$^{-1}$; and (7) 690 cm$^{-1}$.

FT-IR spectra for FA-LTA in figure 2 shows similar results with the reference [11]. Many synthetic zeolite framework structures are reported to be detected at 200-1300 cm$^{-1}$. Distinct peaks at 465, 555, 663 and 999 cm$^{-1}$ shows internal vibration of T-O (T=Si or Al) bending; D4R bending as secondary building unit (SBU) of zeolite A; internal vibration stretch of (Si, Al)-O or symmetrical TO$_4$; and the internal vibration of TO$_4$ asymmetric stretch, respectively. Furthermore, the peaks detected at 1649 and 3442 cm$^{-1}$ are ascribed to the existence of the H$_2$O and hydroxyls, respectively [11].
XRD patterns, which describe crystallinity and the purity of materials, are depicted in figure 3. Besides some crystalline phases (quartz, mullite, hematite, so forth), FA is primarily composed of amorphous material [3]. Figure 3 shows major FA peaks at 20-30° (2θ) and lower peaks found at 35-40°, 40-45° (2θ). The peak shown in 50° (2θ) indicates the presence of quartz [12]. Similar to FA, as seen in figure 3, FA-Na shows major peaks within the range of 20-30° (2θ) and lower peaks at 35-40°, 40-45°, and 50° (2θ). However, the peaks present in FA-Na has higher intensity compared to the original material (FA). It indicates the increasing of crystallinity in FA-Na.

XRD pattern for Geo, as shown in figure 3, indicates that besides the amorphous phase, crystalline phases also exist in the synthesized geopolymer. It is seen that the crystalline phase presents in Geo samples is more than in FA and FA-Na. Geopolymerization process increases the intensity of several peaks compared to the initial peaks of FA [9]. Meanwhile, the XRD patterns of FA-LTA in figure 3 show similar results with the standard, according to the International Zeolite Association (IZA) for zeolite A. Typical peak of zeolite A are 7.18°, 10.17°, 12.46°, 16.09°, 21.64°, 23.99°, 27.09°, 29.94°, and 34.149° (2θ) [13], which aligned with the results in this study as shown in figure 3.
Tabulating Cation exchange capacity (CEC) calculation results for each sample in table 2. CEC values from lowest to highest are FA, FA-Na, Geo, and FA-LTA, respectively. CEC is a valuable property from a water or wastewater treatment perspective, particularly in the adsorption unit, when ion exchange takes place as the main mechanism involved. CEC has significantly considered if one adsorbent material has a high specific surface area [14]. Increasing specific surface area might affect the increase of surface reaction between adsorbent and adsorbate, where ion exchange process counted. The increase of CEC value from FA to FA-LTA is probably related to increasing alkali concentration used in each synthesis process. It is known that the Si-O-T bonds in the FA are attacked by OH⁻ which produces Si-O bonds. After the first bond’s rupture, these silanol groups deprotonate and might be charge-balanced by alkali cation, which in this case, Na⁺ [15].

| Samples   | CEC (meq/100g) |
|-----------|----------------|
| FA        | 5.27           |
| FA-Na     | 26.79          |
| Geo       | 82.31          |
| FA-LTA    | 151.66         |

Specific surface area (m²/g), average pore radius (nm), and total pore volume (mL/g) values for each sample using Brunauer-Emmet-Teller (BET) analysis are tabulated in table 3. It is seen that specific surface area, average pore radius, and total pore volume of the samples from lowest to highest are FA, FA-Na, FA-LTA, and Geo. Based on the International Union of Pure and Applied Chemistry (IUPAC), all samples below are categorized as mesoporous materials. For further use as adsorbent material, a sufficient specific surface area is necessary because the adsorption process mainly involves surface reactions. In most cases, a higher specific surface area results in higher adsorption capacity due to a more extensive interface [14].

| Samples   | Average pore radius (nm) | Total pore volume (mL/g) | Specific surface area (m²/g) |
|-----------|--------------------------|--------------------------|-----------------------------|
| FA        | 2.2432                   | 0.0158078                | 8.35358                     |
| FA-Na     | 2.0837                   | 0.0316794                | 18.6857                     |
| Geo       | 2.8373                   | 0.0601421                | 30.5493                     |
| FA-LTA    | 1.8468                   | 0.0333173                | 21.2108                     |

4. Conclusions
The present study shows that coal fly ash synthesis into new materials using different methods, and alkali concentration is successfully done. Structural and functional group changes were found in the new materials significant morphological change was found in the FA-LTA sample. Along with increasing alkali concentration used during the synthesis, specific surface area and cation exchange capacity (CEC) of the materials are also increased. These values are necessary for the wastewater treatment field, mainly when the ion exchange occurs as the primary mechanism involved. This research has proven the potency of coal fly ash originated from the textile industry to be further used as a precursor for advanced crystalline material syntheses such as zeolite and geopolymer.

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References
[1] Hidayat T and Santosa H 2013 Konversi 2 2252–7311
[2] Rastogi K, Sahu J N, Meikap B C and Biswas M N 2008 J. Hazard. Mater. 158 531–40
[3] Darmayanti L, Kadja G T M, Notodarmojo S and Damanhuri E 2019 J. Hazard. Mater. 377(10) 305–14
[4] Chunfeng W, Jiansheng L I, Xia S U N, Lianjun W and Xiuyun S U N 2009 J. Environ. Sci. 21 127–36
[5] Chunfeng W, Jiansheng L I, Lianjun W and Xiuyun S U N 2009 Chinese J. Chem. Eng. 17(3) 513–21
[6] Astuti W, Chafidz A, Wahyuni E T, Prasetya A, Bendiyasa I M and Abasaeed A E 2019 J. Environ. Chem. Eng. 7 1–10
[7] Belviso C 2018 Prog. Energy Combust. Sci. 65 109–35
[8] Jumaeri, Santosa S J and Kunarti E S 2014 Adv. Mater. Res. 1043 198–203
[9] Ali A, Shamsuddin M R, Ekmi N, Zul M, Man Z and Low A 2019 J. Clean. Prod. 229 232–43
[10] Novais R M, Carvalheiras J, Tobaldi D M, Seabra M P, Pullar R C and Labrincha J A 2019 J. Clean. Prod. 207 350–62
[11] Ren X, Xiao L, Qu R, Liu S, Ye D, Song H, Wu W, Zheng C, Wu X and Gao X 2018 Roy. Soc. Chem. Adv. 8 42200–09
[12] Gollakota A R K, Volli V and Shu C 2019 Sci. Total Environ. 672 951–89
[13] Matlob A S, Kamarudin R A, Jubri Z and Ramli Z 2012 Arab. J. Sci. Eng. 37(1) 27–40
[14] Zahra N L 2014 Studi Mekanisme Adsorpsi Zat Warna Tekstil Reactive Red 141 pada Tanah Liat Lokal Alami (Bandung: Institut Teknologi Bandung)
[15] Ali A, Azizi K, Man Z, Ismail L, Irfan M and Ash F 2016 Ceram. Int. 42(14) pp. 15575–84