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Experimental Synthesis of Zeolites from Pre-processed Coal Fly Ash using the Microwave Irradiation Method

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Abstract

Coal power plants contribute by an excess of 40% to the generation of electricity worldwide. Coal fly ash (CFA), being a dominating by-product of coal power generation, is unique due to its physicochemical properties such as thermal stability, chemical inertness, compressive strength, and adsorption. However, reducing the inherent impurities of CFA, which is heterogeneous, has proven to enhance its ability to be valorised into different second-generation products of high value. Pre-processing has been a successful method in eliminating impurities of CFA, and washing cycles method is the preprocessing technique used in this study. Zeolites, a second-generation product from CFA, are well known for their excellent adsorption properties due to their high surface area and porosity, being an optimal solution for wastewater treatment. Also, the microwave irradiation method has proven to be useful and rapid in synthesising zeolites. This study investigates the effect of pre-processed CFA obtained through optimised utilisation of wash cycles, compared to raw CFA, and the feasible conditions of zeolite synthesis from CFA which have undergone the wash cycle preprocessing technique. NaOH concentration and microwave irradiation power were considered as key parameters. X-ray diffraction (XRD) and Scanning Electron Microscopy (SEM) coupled with Energy Dispersive Spectroscopy (EDS) were utilised to verify the enhanced nature of CFA after pre-processing, and formation of zeolites. The results of XRD infer that Mullite ($Al_{4+2x}Si_{2-2x}O_{10-x}$) is the major crystal match for CFA obtained from the site. Also, pre-processed CFA yields a better qualitative phase analysis with Mullite than raw CFA, with the former having a peak coverage of Mullite that is approximately three-fold than the latter. Furthermore, according to the experimental results, zeolite L and zeolite Na-Y were produced from the process, having an optimal NaOH concentration of 2.5M and microwave irradiation power of 300W. These findings have been corroborated using XRD and SEM with EDS analyses, and we recommend further extension of the frontier to check the viability of zeolite formation with other critical parameters, paving way to an effective treatment of wastewater.

Keywords: Pre-processed coal fly ash; Microwave irradiation; Qualitative Phase Analysis; Zeolites

1. Introduction

Coal is the most abundant non-renewable energy source mineral that is formed naturally over several millennia [1]. As a result of its invaluable nature, power plants are created and energised through coal to generate electricity, especially in the Asian continent where the coal mines are exploited in high numbers [2]. Almost 41% of the world's electricity generation is being catered by power plants that use coal as the main resource.[3].

Coal power plants operate throughout the world and due to the process of coal combustion, Coal Combustion Residues (CCR) are generated. Among all the CCRs generated, Coal Fly Ash (CFA) occupies the majority, that is, from 65 to 95%, consisting of invaluable mineral compounds, such as Al_2O_3, SiO_2, Fe_2O_3, CaO, MgO, K_2O, TiO_2, and other heavy metal oxides in trace amounts [4]. The presence of Silica and Alumina in high quantities along with its physicochemical properties makes CFA a crucial material of interest for many scientists throughout the world since it has the potential to converted into high value-added products. Also, CFA is currently utilised mainly for cement blending work, manufacturing of bricks, backfilling, stabilising the soil, manufacturing ceramic products, wastewater treatment as an absorbent, catalyst treatment, and geopolymer production [4],[5].

On par with various applications of CFA, exposure to CFA particulate matter has the potential to cause detrimental effects such as cardiovascular and respiratory diseases, and issues in foetus development [6]. If CFA is stored improperly, the heavy metals present can easily persist and spread as pollutants, paving the way for drastic health conditions among humans and animals, upon accumulation [7]. Due to this, regular containments such as ponds, landfills and slag heaps are not an environmentally benign option to store CFA. Hence a wiser approach is required to revolutionise the byproduct CFA into a value-added material, that nullifies the aforementioned issues. Zeolites are a breakthrough material obtained from CFA, due to the possession of high Silica and Alumina content in CFA. Zeolites are microporous structured aluminosilicate materials that have extraordinary physical and chemical properties, making them key components in a wide variety of industries such as gas separation, catalysis, ion exchange, and wastewater treatment [8],[9]. Zeolites possess special micropores and honeycomb-like structures, which facilitate the adsorption of ions of organic and inorganic compounds, especially cations, due to their inherent negative charge [10].

Refining of the inherent impurities present in CFA is an important step in the process of zeolite synthesis, as studies have shown that negligence of refining could lead into hindered synthesis of zeolites [11]. Preprocessing CFA helps in that cause and, sieving, calcination, magnetic separation, washing cycles, acid treatment are key preprocessing methods utilised on CFA [12]. Washing cycles is a simple method that is cost-effective when performed optimally with the required conditions [13].

Zeolites can be synthesised using different methods, such as conventional hydrothermal, microwave-assisted hydrothermal, alkali fusion, microwave-irradiated synthesis, and ultrasonic-assisted synthesis methods [14], [15]. Among the aforementioned methods, micrfowave irradiated synthesis has proven to be the most effective and efficient method, mainly due to its quick synthesis process, reduced cost, environmental eco-friendliness, and adsorption capacities concerning its predecessor material [16]. Key parameters such as the Silica to Alumina ratio, alkali solution; Sodium Hydroxide (NaOH) to CFA ratio, reaction conditions, source of coal and synthesis method determine the nature and the properties of the synthesised zeolites [15]. Even though ample studies indicating the synthesis of zeolites from CFA using the microwave irradiation method of synthesis are available, limited discussions are present upon the possibility of zeolite synthesis using CFA that has undergone optimal washing cycle preprocessing and this study intends to demonstrate the effectiveness of pre-processed CFA (PCFA) over CFA in terms of heterogeneity, and to identify the optimal conditions (NaOH concentration and microwave irradiation time) for experimental zeolite synthesis from PCFA.

2. Materials and Methods

The key parameters examined in identifying the optimal conditions included the microwave irradiation power and the concentration of NaOH used for dissolving the zeolitic components

(Si and Al) from the CFA. The other parameters such as Si/Al ratio, pH, CFA/water ratio were kept constant.

2.1 Sample Collection and Preparation

Approximately 10 kg of CFA sample was collected from the Lakvijaya Coal Power plant directly from the silo. A representative sample of 100 g was obtained from the 10 kg bulk portion using the Coning and Quartering method to ensure homogeneity. Initial characterisation of the CFA was performed using X-ray diffraction (XRD) according to ASTM E3294-22 standards. Also, the composition of CFA was obtained through an X-ray Fluorescence (XRF), utilising the clay N method (Table 1).

2.2 Preprocessing of CFA

The 100 g CFA samples underwent a series of washing cycles. Each 100 g sample was mixed with 400 ml of distilled water (1:4) and stirred using a magnetic stirrer (AM4 from VELP) for 7.5 minutes at room temperature. The mixture was allowed to settle for 10 minutes. The water was then decanted and replaced with fresh 400 ml distilled water. This washing process was repeated five times. The final washed CFA was dried in a Teflon container at 105°C for 2-3 days [12],[13]. Following preprocessing, XRD and XRF analyses were performed on the CFA (PCFA).

2.3 Synthesis of Zeolites

Figure 1 represents the overall outline of the methodology carried out in this study.

2.3.1 Dissolution

The dissolution process involved mixing 16 g of PCFA with NaOH solution. Different concentrations of NaOH (0.5 M, 1 M, 2 M, 2.5 M) were prepared by mixing with distilled water. The mixture was stirred for one minute to ensure homogeneity.

2.3.2 Microwave Irradiation

The slurry was exposed to microwave irradiation using a Samsung TDS microwave operating at 2450 GHz. Three different microwave power levels were tested:300 W, 450 W, and 600 W.

2.3.3 Separation

Post-irradiation, the mixture was centrifuged using a HERMLE – Z 206A model centrifuge at 5000 rpm for 5 minutes, to separate the supernatant from the residue. The reason behind this is to obtain the Si and Al ions that have been dissolved into the supernatant through microwave irradiation. An alternative method involved allowing the mixture to settle for a day to study the effect of unreacted PCFA on zeolite formation.

2.3.4 Crystallisation

The supernatant was transferred to Teflon containers, covered with perforated aluminium foil, and dried in an oven at 105°C for 2-3 days to facilitate crystallisation. The resulting material was analysed for the presence of zeolitic phases using XRD (10 – 70 degrees of 2 theta diffraction angle) and SEM with EDS for morphological and elemental analysis.

2.4 Analysis of Synthesised Material

The synthesis process was carried out on an experimental basis, altering the key parameters, and successful experiments that yielded crystals were characterised through XRD and SEM with EDS to determine the optimal NaOH concentration and microwave irradiation power that facilitates the synthesis of zeolites from PCFA. The XRD profiles obtained from the XRD equipment were analysed using a unique software named ‘Match!’, which possesses an open

crystallographic database through which the crystal peaks of the unknown material were analysed and matched accordingly.

3. Results and Discussion

3.1 CFA and PCFA

The XRD analysis of both CFA and PCFA diffraction peaks matched satisfactorily with the mineral element 'Mullite,' chemical formula of $Al_{4+2x}Si_{2-2x}O_{10-x}$. The CFA consisted of a peak coverage with Mullite up to 28.17%, while there was a significant percentage of unidentified peak area, that is, almost 70% (Figure 2). The characteristic peaks were seen in the range of 25° – 30°, which agreed with various other studies reported [17], [18]. The PCFA tested under the same XRD equipment matched Mullite with a peak coverage of 41%, along with a reduced unidentified area of 49.82% (Figure 2). The comparison states an increased peak coverage for the same crystallographic material in PCFA. The XRD mineralogy formula that matched with CFA consisted of Chromium ions while the PCFA did not contain Chromium ions. Since the unidentified peak area was significant in both materials, further methods were followed. Accordingly, the mineral composition of the CFA and PCFA analysed through XRF showed a major presence of Alumina and Silica, with a slightly elevated amount of Silica and Alumina in PCFA than in CFA (Table 1).

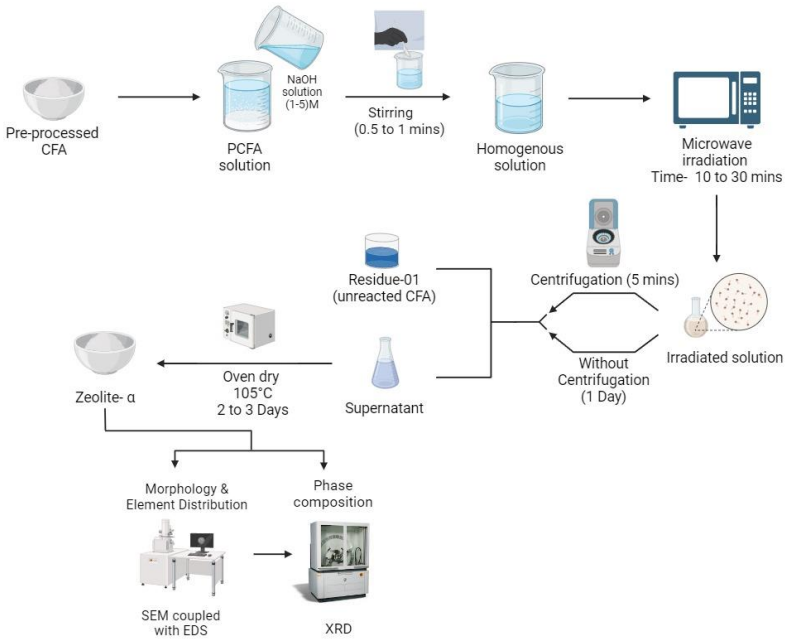

Figure 1 Pictorial representation of detailed methodology

Table 12 Composition of the studied CFA through XRF analysis

Sample label	**RAW DATA – CLAY N METHOD (XRF)**								
	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	SO_3	K_2O	Na_2O	Cl^-
PCFA	51.12	28.78	3.13	8.24	2.71	0.00	0.79	1.74	0
CFA	49.61	29.90	3.15	5.51	2.15	0.00	0.39	1.06	0

3.2 Experimentally Synthesised Material

Out of the experiments undertaken in the laboratory varying the parameters of NaOH concentration, microwave irradiation time, using both methods, that is with centrifugation and without centrifugation, five experiments yielded solidified stable crystals (Table 2). Ample experimental aspects such as the crystallisation process with alkali pretreatment, low

concentration of NaOH (0.5M) and irradiation power were promising but did not produce the desired results due to various reasons such as the method of sampling, lack of either parameter to initiate the process of zeolitisation, and solidification through crystallisation. The prime reason for the issues could be the intrusion of Ca^{2+} ions, which have proven to suppress the zeolite crystallisation process [19]. The solidified crystalline samples investigated under XRD equipment presented the presence of Zeolite-L, Zeolite Na-Y as the main types of zeolites, especially from experiments conducted using irradiation powers of 300W, 450W, and 600W, and NaOH concentrations of 1M and 2.5M. The diffraction peaks were obtained in the range of 2θ angle between 3°- 60°. During the process of reproducibility of zeolites produced in the experiments with the aforementioned parameters, zeolite-L produced in the experiment conducted using microwave irradiation power of 300 W and NaOH concentration of 2.5M showed consistency in results with approximately identical quality phase analysis values in XRD. The other experiments did not showcase consistent crystallisation during the process of reproduction, with the previously obtained results.

The crystallinity of the crystals obtained through the zeolitisation process with centrifugation, was within the range of 85-93% when assessed through XRD. A potential reason for a higher degree of crystallinity could be due to the centrifugation, through which unreacted CFA retention in the supernatant is nullified during the process of separation. On the contrary, only a single experiment yielded crystallised material from the crystals that were successfully obtained through the alternative method (without centrifugation), that is, only with a microwave irradiation power of 600W, and it demonstrated a relatively lower crystallinity percentage of 80.

The SEM with EDS analysis done on the crystallised materials shows the existence of zeolite crystals with a spread distribution of Aluminium and Silica along with Sodium (Figure 4), the composition of the zeolite, an aluminosilicate material. The shape was observed to possess a cylindrical to hexagonal framework (Figure 3) also as identified by other studies [20]. However, the 600W, 2.5M experiment that produced Zeolite-L had a slightly different structure when observed, where the hexagonal-shaped structures can be observed as a cluster rather than single crystals, which could infer that they may have clustered together due to atmospheric interaction, which could interpret as an unfavourable synthesis condition of zeolites.

Additionally, when the synthesised material was subjected to XRF analysis using fused bead (Clay N method), that is, by subjecting the material to extreme temperatures (1100°C), it was not possible to analyse the melting point of the material was higher than the temperature supplied for the analysis. It further concretes the assurance of the formation of zeolite using the aforementioned synthesis process.

3.3 Adsorption Efficiency of Zeolite

Adsorption efficiency of the synthesised material was compared with PCFA, through the adsorption of Cu^{2+} ions from a $CuSO_4$ stock solution. 10 ml of two 50 ppm solutions of $CuSO_4$ aqueous solution was taken, and similar masses of zeolite and PCFA were added to both flasks of Cu^{2+} solutions and shaken to facilitate adsorption. The Cu^{2+} concentrations of the resultant solutions were obtained using an Inductively Coupled Plasma-Mass Spectroscopy (ICP-MS). The ICP-MS test results gave concentrations of Cu^{2+} ions after adsorption using PCFA and Zeolites, as 38 ppm and 16 ppm respectively. This shows that the zeolite materials produced from CFA possess a higher adsorption character than PCFA for the same cationic concentration solution, which provides a pathway for valuable usage of CFA rather than for first-generation products.

Table 13 Experimental Setup and Parameters for Zeolite synthesis

Experiment Number	NaOH Concentration (M)	Irradiation Power (W)	Centrifugation (Yes/No)	Zeolite type
1	2.5	300	Yes	Zeolite L
2	2.5	300	No	-
3	2.5	450	Yes	Zeolite L
4	2.5	450	No	-
5	2.5	600	Yes	Zeolite L & Na-Zeolite-Y
6	2.5	600	No	Zeolite L

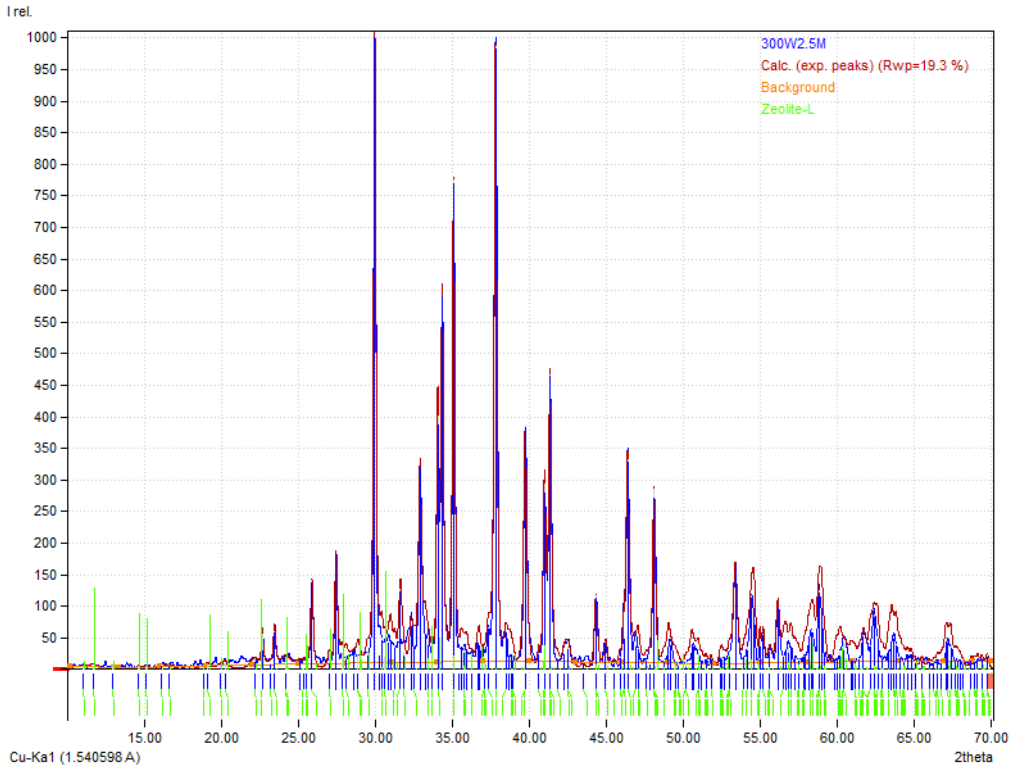

Figure 2 XRD result of the 300 W 2.5 M sample.

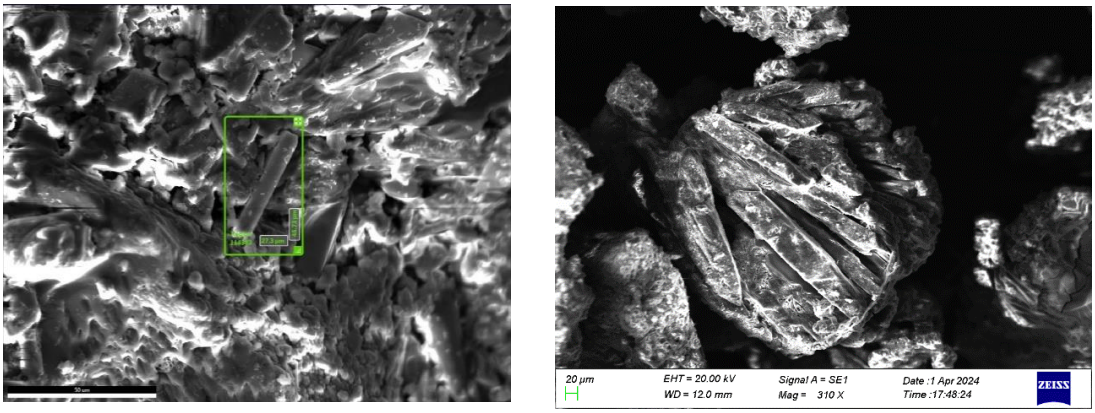

Figure 3 SEM images of the 300 W 2.5 M sample

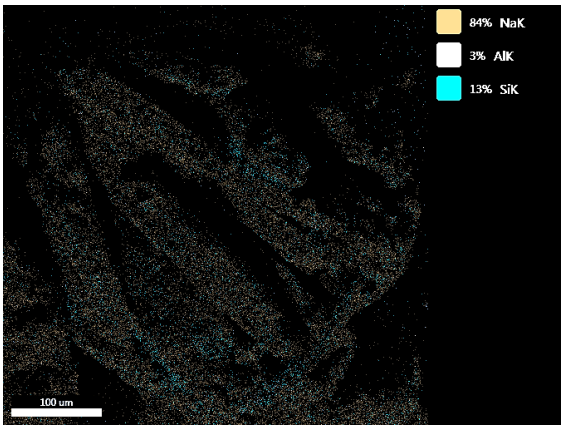

Figure 4 Element mapping from EDS of the 300 W 2.5 M sample

4. Conclusions and Recommendations

The study envisioned to explore value-added utilisation of CFA rather than its conventional first-generation uses, the suitability of preprocessing CFA using washing cycles before synthesis and optimal zeolite synthesis parameters that were considered SEM. The XRD results indicate that PCFA (41%) has a higher quality phase analysis match with the material Mullite than raw CFA (28.17%), which is seconded by the XRF analysis, increasing the Si and Al amounts facilitating the synthesis and reducing the heterogeneity present in CFA, tallying with other studies [12]. Hence it is possible to affirm that preprocessing has an impact on improving homogeneity of CFA and enhancing its viability in producing zeolites. Nevertheless, washing cycles increase the amount of Ca^{2+} ions present in the CFA, which slightly hinders the formation of zeolite crystallisation. After preprocessing CFA, five synthesis experiments yielded zeolites such as Zeolite L and Zeolite Na-Y, out of which the experiment conducted with microwave irradiation of 300W along with NaOH concentration of 2.5M delivered consistent results when observed through XRD and SEM with EDS. Furthermore, the zeolite adsorbed almost twice the amount of Cu^{2+} ions than PCFA which validates the enhanced adsorption efficiency of zeolites produced from CFA, indicating its effective utilisation in wastewater treatment. Nevertheless, the generalisability of the results contains certain limitations such as the diversity of the composition of CFA influencing the synthesis process in a varied manner. Hence it is important to perform a larger controlled experimental setup considering other significant parameters such as Si/Al ratio, pH, temperature for zeolite synthesis and subsequent adsorption efficiency of zeolite on wastewater using significant parameters such as pH of solution during adsorption, dosage of zeolite used, concentration of contaminants in synthetic wastewater samples.

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