

**“Development of fly Ash-based Geopolymer
adsorbents for Cu(II) and Mn(II) removal from
aqueous solutions”**

OTDK Thesis

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1 Introduction

In the present time, the handling of waste and preservation of water quality have become crucial concerns in human life. The proliferation of technology in urban and industrial development has led to a global rise in waste accumulation all around the world and the discharge of a large number of toxic substances including heavy metals in water streams [1]. Common hazardous heavy metals found in water include lead, mercury, manganese, cadmium, chromium, copper, and arsenic and they enter in water sources from a range of activities such as industrial processes, improper waste disposal, agriculture, and more. The buildup of heavy metals in water poses a threat to human health and animals and can even lead to fatal consequences including death [2]. As a result, it can have severe consequences on ecosystems and human populations.

Removing heavy metals from water effectively remains crucial when addressing this serious problem. Numerous technologies are capable of removing and effectively reducing the concentration level of these contaminants in water. These include chemical precipitation, ion exchange, adsorption, membrane filtration, coagulation-flocculation, floatation and electrochemical, all of which were employed in wastewater treatment.

Among these various treatments, adsorption has remained a popular and increasingly utilized approach for the removal of heavy metals because of its low cost and convenient operation. Its operational simplicity makes it adaptable for all types of treatment systems, from large industrial-scale to small community-based systems [2]. Despite these advantages, there are certain drawbacks to the adsorption process, such as the high prices of certain types of adsorbents [3].

Adsorption is a process in which contaminants adhere to the surface of a solid material. The adsorbent is the most important component of the adsorption process. Different porous materials have been investigated as heavy metals adsorbents. Activated carbon is the most extensively used adsorbent due to its high surface area, stability, and durability. However, the costly production and difficult regeneration limit its application in large-scale wastewater treatment [4]. Additionally, it failed to attain the specified adsorption capacity for heavy metal removal [5].

Many types of adsorbents, both natural and synthetic kinds, have been employed for the removal of contaminants from wastewater. However, the primary challenge lies in sourcing a material that not only proves highly effective but also demonstrates a combination of high capacity and low cost, for a particular material, to be considered very useful [6]. Therefore, the search for a highly efficient, environmentally friendly and cost-effective adsorbent is continuously expanding as a valid alternative to the existing adsorbents.

2 Overview of Geopolymers (Related Review of Literature)

A relatively new class of adsorbent materials called geopolymers which have been reported for their good adsorbent material characteristics when compared to other adsorbents, thus, have gained attention for their potential applications in environmental remediation particularly in the removal of heavy metals from water. Therefore, in this section, it aims to give a thorough introduction to the chemistry and synthesis of geopolymers, concentrate on the numerous advantages of using geopolymer materials for adsorption applications, as well as to examine and investigate previous relevant research on the use of geopolymer-based adsorbents for the removal of heavy metals.

2.1 Chemistry and Synthesis of Geopolymer

Geopolymers are porous inorganic polymer materials derived from alkali activation of aluminosilicate materials such as kaolin, metakaolin as well as industrial wastes including fly ash, granulated blast furnace slag, and water treatment sludge. In addition, the type of alkaline activator used plays a vital role for the geopolymerization process of which sodium hydroxide (NaOH) and sodium silicate (Na_2SiO_3) are the most commonly used types [7], [8], [9]. This process induces polycondensation reactions, leading to the formation of a three-dimensional aluminosilicate network as demonstrated in Figure 1. It has the structure of polymeric Si-O-Al that share all of the oxygen atoms in three dimensions and bind with alternating tetrahedral silicon and aluminum together refer Figure 2 [8]. Geopolymer can be divided into three kinds of inorganic polymers based on the Si/Al ratio, namely, single silicon aluminum (Si/Al = 1; poly-sialate (-Si-O-Al-O-)), double silicon aluminum (Si/Al = 2; poly-sialate-siloxo (-Si-O-Al-O-Si-O-)), and triple silicon aluminum (Si/Al = 3; poly-sialate-disiloxo (-Si-O-Al-O-Si-O-Si-

O)) as shown in Figure 3 [3], [9]. The resulting geopolymer materials have certain properties that make them excellent candidates for adsorption including high surface area, porosity, and stability [10].

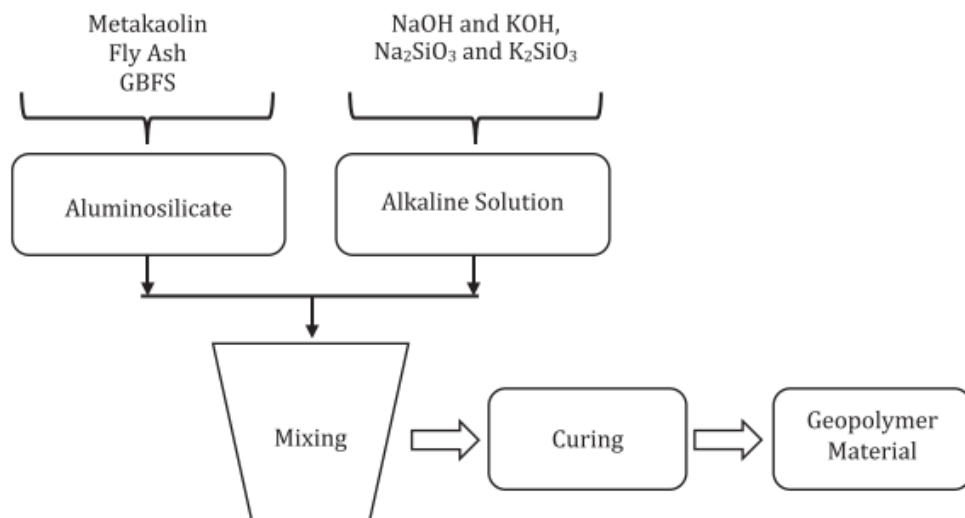


Figure 1. Synthesis of geopolymer adsorbent [2].

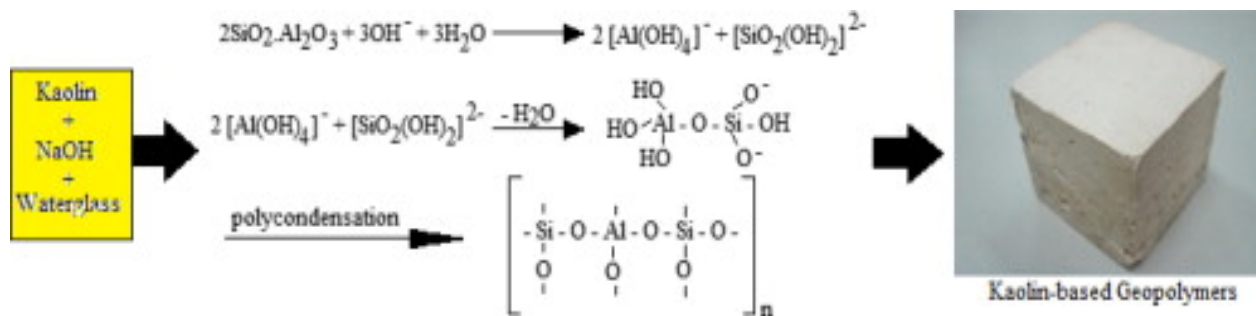


Figure 2. Production of Kaolin-based Geopolymers [8].

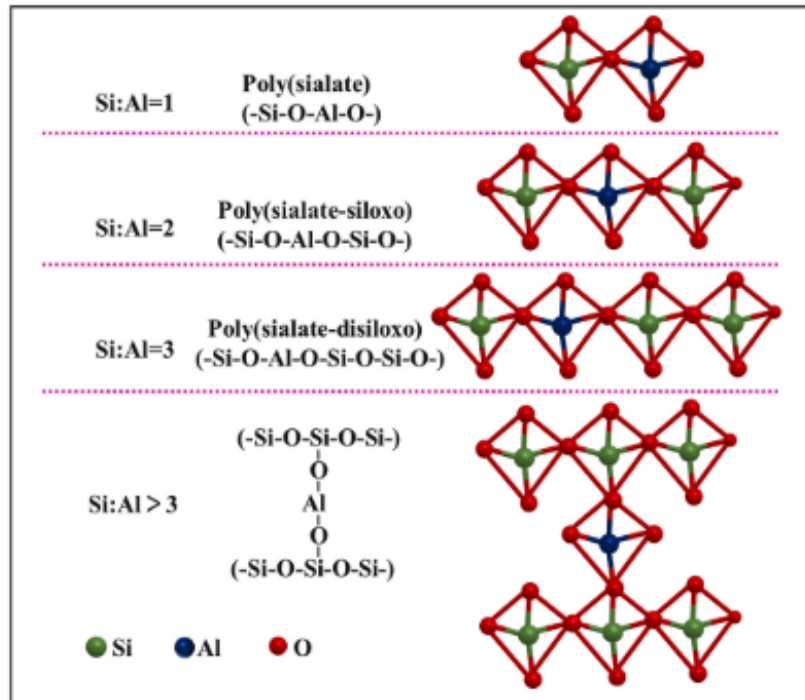


Figure 3. Structural diagrams of different Si/Al geopolymers [3].

2.2 Properties of Geopolymers

Geopolymers are a type of innovative material that can be used as an alternative to traditional Portland cement or cement in transportation infrastructures, certain constructions, and offshore builds. They are very resistant to several of the durability issues that can cause traditional concretes to crack and crumble. This is accomplished by using minimally processed natural materials or industrial byproducts. Geopolymers exhibit excellent mechanical and physical properties, such as low density, good chemical, fire and thermal resistance, high mechanical strength, and so on. Therefore, they are widely applied in numerous fields as new materials with high tech application [11], [12].

2.3 Materials for Geopolymer Production

2.3.1 Fly ash

Fly ash is a by-product of coal combustion that contains unburned carbon particles and aluminosilicate particles. It is collected by electrostatic separators before being discharged into the atmosphere. Fly ash has pozzolanic properties and the mineral components found within the

waste material include glassy phase and minor crystalline phases such as quartz, mullite, hematite, and magnetite. Moreover, fly ash is known to cause environmental pollution in the form of air and water pollution. As of right now, it has been discovered that the global fly ash production has reached an all-time high of 8,741 million tons annually [13]. In the past, landfill disposal was the common practice for handling fly ash, which causes environmental hazards. However, the utilization of fly ash can reduce the amount of coal combustion products that must be disposed of in landfills, thereby producing less harmful consequence to the environment and people's health [9], [14]. In recent years, fly ash has been used in many new areas and is widely considered to have huge potential. Because it is inexpensive, environmentally beneficial, energy efficient and allows for resource recycling, thus, alkali-activated reaction is frequently utilized as the optimal method of using fly ash to produce geopolymer. Toxic elements like Ba, Cd, Co, Cu, Nb, Ni, Pb, Sn, and U can be firmly fixed in the three-dimensional structure of fly ash-based geopolymer matrix [15].

2.3.2 Slag

More than 120 million tons of steel slag, the primary solid waste in the steel-making process, are produced in China each year. Since the majority of the steel slag was kept outside, there were potential threats to public safety and environmental protection, including the occupation of nearby land and the infiltration of heavy metal components into the soil [16]. In addition, if the steel slag is stacked in an open area or handled improperly during its treatment and transportation, a large amount of dust is generated which seriously endangers the atmospheric environment and human health. Therefore, the resource utilization of this material is highly regarded. Recently, there have been various ways to use steel slag, one of which is for wastewater treatment owing to its porous and alkaline characteristics. Moreover, steel slag contains Ca, Si, and P, as well as other plant-growth-friendly elements which can be used to manufacture fertilizer [16].

2.3.3 Metakaolin

Metakaolin is an anhydrous aluminosilicate clay mineral with the chemical composition $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$ formed by tetrahedral silica layer and one octahedral alumina layer. Several studies reported that metakaolin based geopolymer obtained by calcination about 2 to 6 hours

at ranging temperature from 500°C to 750°C. Due to its high reactivity and purity compared to other clays, metakaolin has been used and studied extensively for heavy metal ions removal such as Ni (II), Pb (II), Cd(II), Co(II) and Fe(II) from aqueous solution [17], [18].

2.4 Geopolymer Foam

Geopolymer foam refers to a lightweight and porous material created through the addition of foaming agents or air into a geopolymer matrix. As discussed above, geopolymers are inorganic, amorphous aluminosilicate materials that can be used as alternative to traditional Portland cement and can be synthesized from industrial waste or by-products like fly ash through a chemical process. When geopolymer is foamed, it results in a material with a cellular or sponge-like structure, commonly known as geopolymer foam. This foam can be used for several applications [19].

2.4.1 Geopolymer foams synthesis (Methods)

In this section, several synthesis protocols to produce geopolymer foams will be briefly discussed since several research papers have provided a detailed description. For instance, [20] discusses several geopolymer synthesis routes, including the direct foaming method, replica method, sacrificial filler method, additive manufacturing, and other methods. Each method offers unique approaches to producing porous geopolymers, and the article provides detailed insights into their respective advantages and applications.

2.4.1.1 *Direct method*

The direct foaming method is widely used technique for producing geopolymers (PGs), particularly geopolymer foams (GFs). It involves processing a suspension or liquid system without sintering and producing wet geopolymer foams. This is done by adding air or gas into a homogeneous slurry. After that, these wet foams are set by curing at specific temperatures to obtain solidified porous bodies. During curing, the geopolymerization reactions finish and produce a continuous, three-dimensional inorganic network [21].

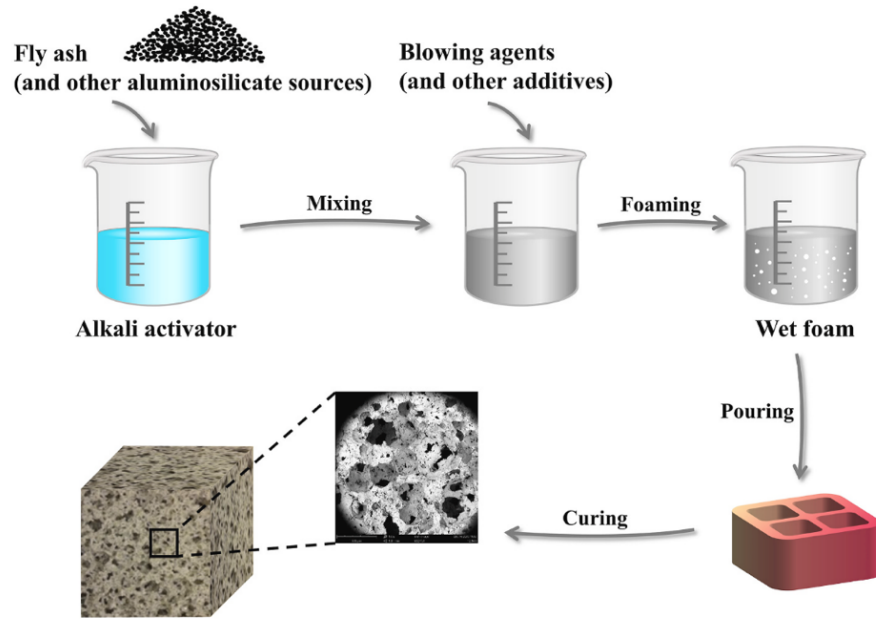


Figure 4. The process flow chart of direct foaming [21].

2.4.1.2 Replica method

The replica method for the fabrication of porous geopolymers involves retaining the cellular structure of a polymeric template, typically a polyurethane foam, and is commonly used in the industrial fabrication of ceramic foams. The process includes the polymeric template with an aqueous potassium-based geopolymer slurry, producing a geopolymer/polyurethane porous composite. After sintering at particular temperature for a certain duration, cellular geopolymers with a substantial amount of open porosity and reasonable compressive strength are obtained.

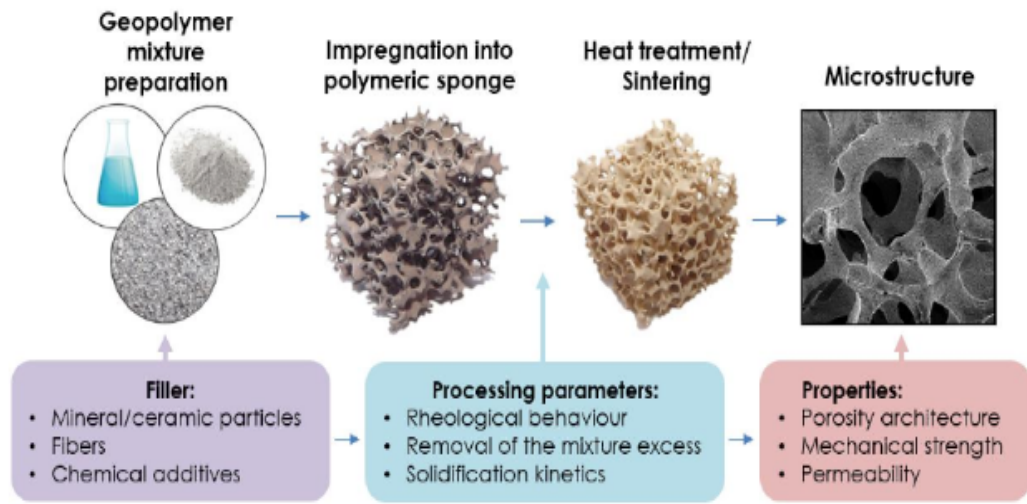


Figure 5. The process flow chart of replica method [22].

2.4.1.3 Sacrificial filler method

The sacrificial filler method is a technique for producing cellular materials with a negative replica structure of the original template, offering opposed porous structure to the positive porous structure obtained by the replica method. This method generates porosity by extracting the fillers from a dense biphasic composite, comprising a continuous geopolymer matrix and a dispersed sacrificial phase. This method facilitates the production of porous geopolymers with hierarchical pore structures and different morphologies.

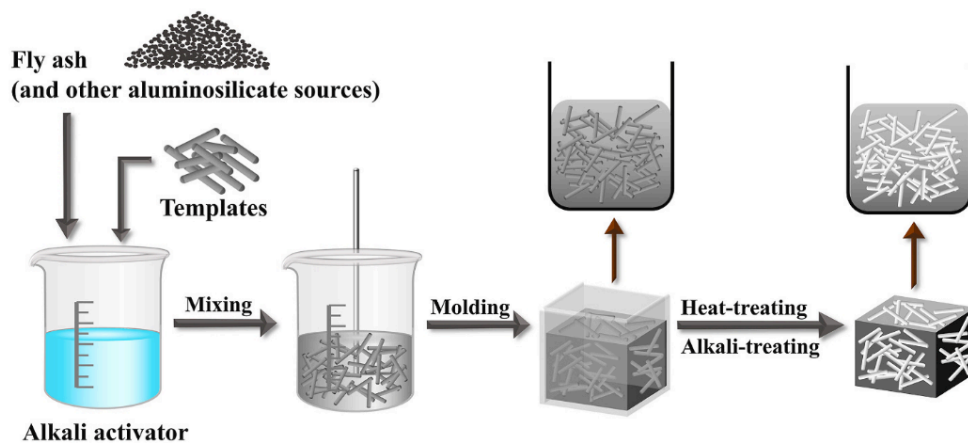


Figure 6. The process flow chart of sacrificial filler method [21]

2.4.2 Properties

Geopolymer foams are a unique class of materials that exhibit distinct properties compared to traditional foams and their properties can be tailored based on the specific formulation and processing conditions. According to [20], in their review article, they mentioned that the mechanical strength, thermal conductivity, porosity, and chemical stability of geopolymer foams are the key properties that influence their suitability for various applications. In addition, the maximum reported compression and flexural strength for porous geopolymers were around 26 MPa and 2.6 Mpa, respectively, demonstrating potential for load-bearing applications. Also, the lowest thermal conductivity reported was 0.03 W/(m K).

Porous geopolymers are known to possess low thermal conductivity and acceptable compressive strength, making them suitable for use as building materials, especially considering characteristics such as being fiber-free and retaining structural integrity during and after exposure to fire [23]. Moreover, they possess high perseverance in acidic and alkaline media. Comparatively, they are more stable under alkaline medium. No deterioration in mechanical properties when immersed in sea water (pH = 8) and sodium sulfate solution (5% Na₂SO₄) up to 360 days. On the other hand, they were severely attacked when immersed in HCL solution for long period [11].

2.4.3 Application

Geopolymers have great potential for many different kinds of application across various industries owing to their unique properties as discussed above. Due to this, it has boosted the interest in using geopolymers in environmental applications (e.g. wastewater treatment) or as energy-saving building materials (e.g. thermal and acoustic insulators).

For wastewater treatment, porous geopolymers can be considered as a new type of low-cost adsorbents to depollute industrial wastewater. They exhibit good removal efficiency and uptake capacity of different cations. [24] reported that a zinc uptake of 13.42 mg/g when using coal fly ash-based porous geopolymers. Another study, [17] investigated porous metakaolin-based geopolymer foam for dye removal. In this study, the highest methylene blue adsorption was obtained up to 90%. Maximum adsorption capacity was achieved at 2.5 mg/g for 10 mg/L dye solution in 40°C and pH = 13.

Another potential application of porous geopolymer is to act as acoustic barriers to address the increasing level of noise pollution. This is particularly relevant when considering building materials to enhance the interior acoustic comfort for inhabitants and prevent sleep disturbance associated with noise pollution. In the review article prepared by [20], reported that the raw materials (fly ash and slag) and the thickness (20 or 25 mm) of the porous geopolymer had an effect on the sound absorption coefficient. The porous geopolymer specimens a pretty good sound absorbent coefficient (0.7-1.0) in the low frequency region, ranging from 40 – 150 hz. In addition, it was also reported that the bulk density of the used specimens can influence the sound absorbent coefficient. Regardless of the frequency, the sound absorbent coefficient increased with decreasing bulk density.

Another very desirable property of building materials is their ability to withstand heat. [25] revealed that the foamed geopolymer material using copper slag and glass powder exhibited thermal conductivity in the range of 0.13 to 0.17 W/mk. They subjected the developed product to conjugate heat transfer solver in OpenFOAM where the findings of the test suggest that it can provide better thermal insulation compare to conventional materials (clay bricks), providing thermal comfort conditions indoors and can be easily maintained at reduced cost of energy consumption.

2.5 Advantages of Geopolymer Materials for Adsorption Applications

Generally, geopolymer materials are used in construction materials owing to their excellent mechanical properties; but several studies have investigated the composition and structure of geopolymer-based adsorbents for heavy metal removal. It offers several advantages for adsorption applications. One key feature is their highly porous structure which provides a substantial surface area for effective adsorption of pollutants from aqueous solutions. This characteristic is of great significant in enhancing the removal efficiency of contaminants [2], [26]. Additionally, the composition of geopolymer materials can be tailored to optimize their adsorption capacity for specific pollutants. Because of their flexibility, it can be modified according to the targeted contaminants, resulting to a more effective and concentrated removal process [27]. Moreover, the environmental sustainability of geopolymers increase their appeal and prompted researchers to do further investigations. These materials which are frequently

made from industrial by-products like fly ash, encourage sustainable development goals and eco-friendly practices by promoting waste recycling [28], [29].

2.6 Fly Ash as a Sustainable Raw Material for Geopolymerization

The rising global demand for sustainable construction materials has encouraged researchers to investigate alternative solutions that mitigate environmental impact. Fly ash is a by-product generated from coal combustion in power plants. It has emerged as an excellent candidate for geopolymerization [30] It is a waste substance that are easily to find and had been reported that could be effective for removal of heavy metals. However, it shows lower adsorption capacity unless it is treated or activated called as geopolymer [1]. In this section, it aims to explore and present various studies about fly-ash based geopolymers applications in adsorption.

Fly ash is primarily composed of fine, spherical particles that are rich in silica, alumina, and iron oxide. The chemical composition of fly ash varies depending on the coal source and combustion process. It is currently found that the amount of fly ash productions increases up to 600 million tons per year [9], [29]. Due to its pozzolanic properties, which contribute to cementitious characteristic, it makes fly ash an attractive alternative to traditional construction materials. Therefore, it is crucial to understand the composition and properties of fly ash for its effective utilization in geopolymerization refer Table 1 [31], [32].

Table 1. Chemical composition of Fly ash [50].

Chemical Composition (%)	Fly Ash
SiO ₂	48.5
Al ₂ O ₃	29.6
CaO	6.1
Fe ₂ O ₃	4.6
MgO	2.3
K ₂ O	0.9
Na ₂ O	3.68
SO ₃	0.25
MnO	0.07
TiO ₂	1.0
P ₂ O ₅	2.46

Fly ash-based geopolymerisation has been around for some time and the process parameters for their effect in geopolymer properties have been explored [33]. These fly ashes have high concentrations of toxic elements besides from trace amounts of dioxins, PAHs etc.; but these pollutants may be immobilized via geopolymerization [34], [35].

In 2019, [36] investigated the adsorption of Cu^{2+} by fly ash based geopolymer. It reported that all samples, including fly ash and geopolymers, exhibit Cu^{2+} adsorption based on Langmuir isotherm and pseudo-second order kinetic. Geopolymers, characterized by a more organized structure, establish a higher Cu^{2+} adsorption capacity, reaching up to 40 mg/g in comparison to the 7 mg/g found in the fly ash sample. The structural alteration brings about the formation of an open-framework structure with more accessible sites, facilitating increased Cu^{2+} adsorption.

In addition, Al-Harashsheh et al. [37] assessed the effectiveness of an amorphous geopolymer produced from waste fly ash in sorbing copper from aqueous solutions. In their study, the synthesized geopolymer was found to be more effective and showed better removal than the raw fly ash, especially at a pH of 6 and a temperature of 45 °C, reaching a maximum sorption capacity of 152 mg/g. The kinetic and thermodynamic characteristics of copper adsorption were also addressed in this study, emphasizing the endothermic nature of the sorption process and the advantageous and favorable adsorption at higher temperatures.

Moreover, a recent paper, [38] investigated the preparation and performance of geopolymer adsorbent derived from a mixture of metakaolin and sludge for Cu^{2+} removal. It also showed of nearly 600% increase of the number of documents published on geopolymer adsorbents in a period of ten years. So, there is an increasing demand for their use in efficient, safe, sustainable, and cost-effective remediation of wastewater contaminated by heavy metal ions.

3 Objectives and Research goal

This study plan aims to develop a scientific understanding of the properties of the resulting fly ash-based geopolymer. The following are specifics objectives and expected outcomes of this research.

1. Characterization of potential raw materials (fly ash) (particle size distribution, specific surface area (SSA), density, chemical composition, mineral composition),
2. Effect of mechanical activation on the properties of raw material (fly ash) (particle size distribution, SSA, density, FTIR measurement),
3. Geopolymer production using raw and ground fly ash with different parameters (liquid/solid ratio, NaOH molar concentration, water glass content, metakaolin addition) (In this case, it can even be tested at a given NaOH concentration and water glass content),
4. Characterization of geopolymer samples (strength, density, porosity, FTIR),
5. Geopolymer foam production using hydrogen peroxide solution. Characterization of the geopolymer foam products (strength, density, porosity, FTIR) (depends on the empirical results)
6. Adsorption tests using foamed and non-foamed geopolymers as adsorbent for heavy metal removal from aqueous solution in a batch experiment.
7. Evaluation of adsorption potential of the geopolymers.

4 Materials and Methods

4.1 Preparation of Raw Materials

The raw material used in this study was brown coal fly ash (FA). It was collected and taken from Tiszaújváros, Hungary. Before using, brown coal FA was heated by laboratory drying oven at 105°C for 24 hours to remove the moisture content, then, it was passed through a 1 mm-mesh sieve opening size to remove impurities. The chemical composition of raw coal FA was determined by X-ray Fluorescence (XRF) as reported in Table 2. The XRF Analysis of the main chemistry of the raw coal FA revealed that this material mainly contained SiO₂ (57.9%) and Al₂O₃ (23.3%), accounting for 81.2% content of the brown coal FA, which could be considered as an effective matrix for the preparation of geopolymer materials.

Table 2. Chemical Compositions of Brown Coal Fly Ash (XRF analysis) originated from Tiszaújváros, Hungary.

Composition	Fly Ash, wt. %
SiO ₂	57.9
Al ₂ O ₃	23.3
CaO	1.18
MgO	2.23
Na ₂ O	0.95
K ₂ O	1.37
Fe ₂ O ₃	5.81
MnO	0.037
TiO ₂	0.510
P ₂ O ₅	0.040
S	0.07
F	<0.3
(Total)	94.4

In addition, the physical properties of raw coal FA were also measured and summarized in Table 3. The bulk and the particle density were measured to be 0.751 g/cm³ and 1.842 g/cm³, respectively, and its moisture content was 19.50%. Moreover, the particle size distributions of the raw and mechanically activated FA were measured with HORIBA Laser Scattering Particle Size Distribution Analyzer LA-950. As shown in Figure 7, the brown coal FA had characteristic particle sizes of $x_{10} = 28.48 \mu\text{m}$, $x_{50} = 96.43 \mu\text{m}$, and $x_{80} = 157.00 \mu\text{m}$ and its specific surface area (SSA) was measured to be 1,330.15 cm²/g. Brown coal FA was not highly reactive in this state and the reactivity properties can be considerably enhanced by increasing the specific surface area and decreasing the particle size through grinding (mechanically activated) according to Mucsi et. al's research [39]. Therefore, in this study, the raw material was mechanically activated by grinding under dry conditions. The grinding experiments were carried out in a bond mill operating at 39 Hz and utilizing around 35 kg of ball grinding media with diameters ranging from 15-47 mm and two distinct grinding times: 5 minutes and 30 minutes as depicted in Figure 7.

Table 3. Physical Properties of Brown Coal FA.

	Unit	Values
Moisture Content,	%	19.498
Bulk Density	g/cm^3	0.751
Particle Density	g/cm^3	1.835
Specific Surface Area	cm^2/g	1,330.15

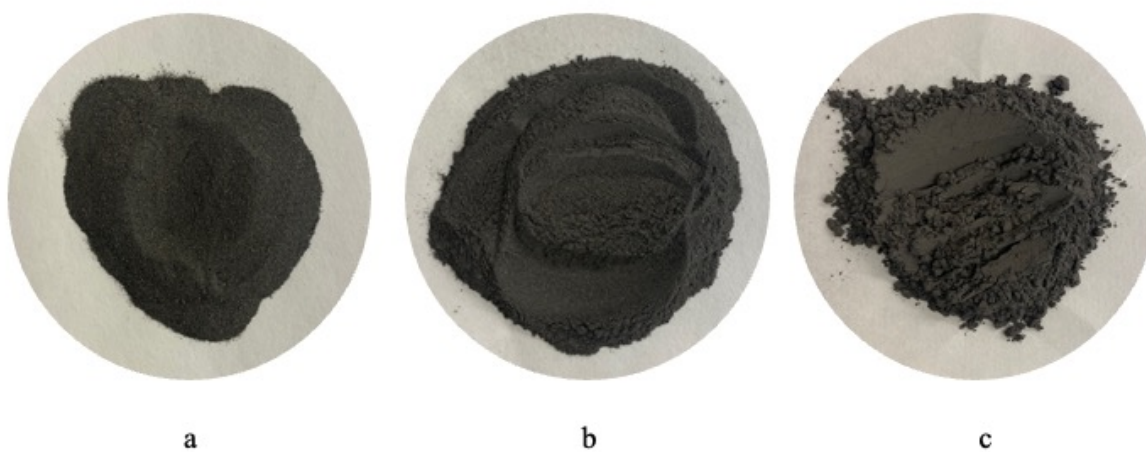


Figure 7. Mechanically activated brown coal FA at different milling time. a.) 0 minute, b.) 5 minutes, and c.) 30 minutes.

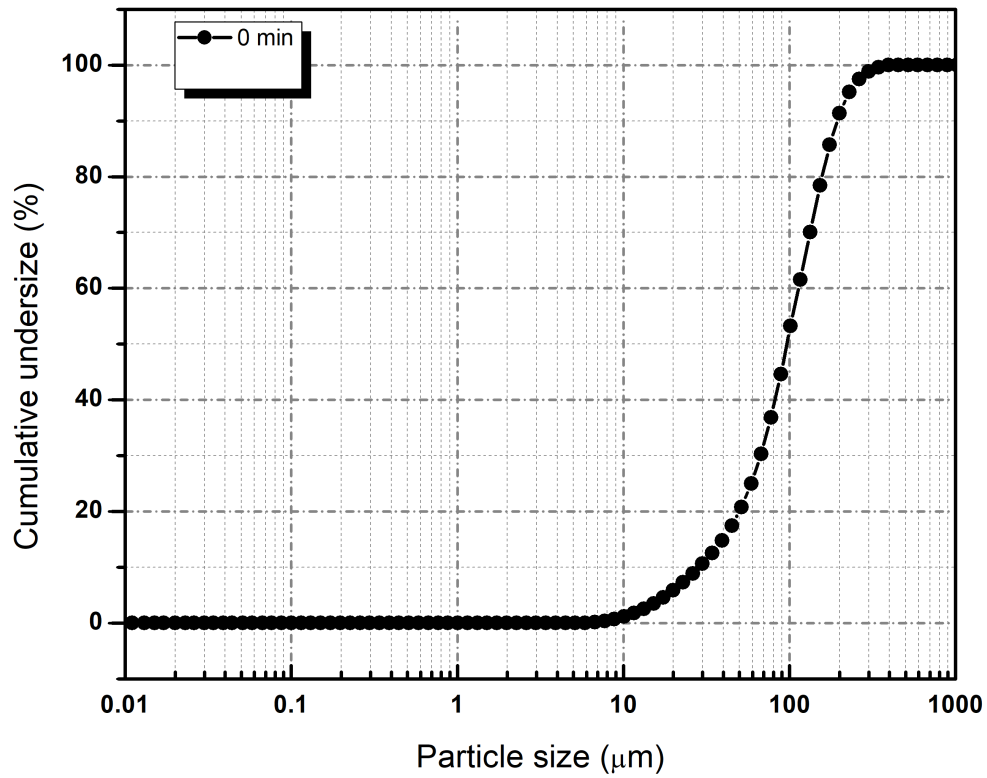


Figure 8. Particle Size Distribution of Brown Coal FA.

4.2 Methods

4.2.1 Particle size analysis

HORIBA Laser Scattering Particle Size Distribution Analyzer LA-950 was used to analyze the particle size distribution of the brown coal FA and mechanically activated FA under wet mode using distilled water as dispersing media and sodium, pyrophosphate as dispersing agent applying the Mie-theory as an evaluation method. The specific surface area (SSA) was calculated using PSD data by the laser sizer software.



Figure 9. Particle Size Distribution Analyzer.

4.2.2 Density

The bulk, particle, and material density were determined using the following equations. The liquid media used was alcohol (2-Propanol) which has a density of 0.784 g/cm³. The tests were done in three trials to measure the average density.

$$\text{Bulk density, } \rho_B = \frac{\text{Mass of dry sample}}{\text{Volume of pycnometer}} \quad \text{Equation 1}$$

$$\text{Particle density, } \rho_p = \frac{\text{Mass of solid sample}}{\text{Volume of displaced alcohol}} \quad \text{Equation 2}$$

$$\text{Material density, } \rho_M = \frac{\text{Mass of solid sample}}{\text{True solid volume}} \quad \text{Equation 3}$$

4.2.3 Moisture Content

The moisture content of the unmilled brown coal FA was measured using a laboratory drying oven at 105°C until constant mass was achieved. The drying time required to achieve constant mass varied depending on the type of the material, for example, limestone. But in this study, 24 hours drying period was employed. The tests were done in three trials to measure the average moisture content.

4.2.4 FTIR

FA of different finenesses and the fly ash-based geopolymer samples were investigated with a JASCO FT/IR-4200 type Fourier transform infrared spectrometer (FTIR) equipped with a single-reflection diamond crystal. Blank was used to characterize the functional groups' vibrations and changes before and after geopolymerization of the brown coal fly ash, as well as ball-milled fly ash and the corresponding foamed and non-foamed geopolymers in the range of $4000\text{ cm}^{-1} - 400\text{ cm}^{-1}$ wavenumber.

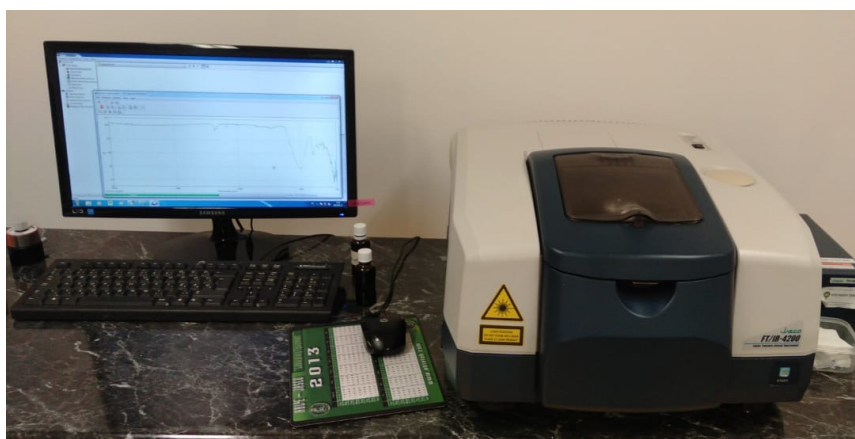


Figure 10. Fourier transform infrared spectrometer (FTIR).

4.2.5 Compressive strength

The compressive strength machine available in the university was used to evaluate the mechanical performance of the foamed and non-foamed geopolymers after seven days of aging. For each mixture, three cubic specimens were prepared and tested to determine the average compressive strength. Before the strength test, the size (diameter and height) and the weight of the specimens were measured for the determination of their density. The height was ensured to be at least 1.5x of diameter to obtain precise measurements.



Figure 11. Compressive Strength Machine.

4.2.6 Fabrication of Foamed and Non-foamed Coal fly ash-based geopolymer

Both geopolymer specimens were prepared in accordance with the design mixing ratio as shown in Table 4 and Table 5 by first mixing certain amounts of liquid reagent with the solid sample, which was subsequently manually stirred until a homogenous slurry paste was obtained. The liquid reagent is a combination of an alkaline solution (10M NaOH) , as well as the alkaline activation of aluminosilicate precursors (waste glass). The chemical foaming method was used to create the porosity in the foam structure which is known as foamed geopolymer. This method utilizes the foaming reactions in the alkaline environment (such as NaOH), as well as the alkaline activation of aluminosilicate precursors which creates gas bubbles trapped inside the slurry and consequently, forming cavities in the final foam bulk. Here, H_2O_2 as a foaming agent was added into the slurry, and mixed, and then, the mixture was poured into a mold container and cured at room temperature for 24 h. Before using the mold container, Oil was applied inside it to ensure that the hardened product would not stick to its side and could be easily removed from the mold. It was then placed in a laboratory drying oven and cured at $60^{\circ}C$ for 6 h to perform the geopolymerization process. After that, the heated product was carefully removed

from the mold and left for 7 days at room temperature to develop enough strength. On the other hand, non-foamed geopolymers were also prepared using the same method but without the addition of a foaming agent. The mechanical properties of the samples were tested by a Compression Testing Machine. Some fractured pieces were collected to be used for the other characterization techniques, i.e. material density determination.

Table 4. Design mixing proportion of the Foamed Geopolymer Matrix (mass ratio%).

	Mixture 1	Mixture 2
Liquid/Solid ratio	42.5/57.5	40/60
NaOH/Waste glass	25/75	25/75
H ₂ O ₂	3	3

Table 5. Design mixing proportion of the Non-Foamed Geopolymer Matrix (mass ratio%).

	Mixture 1	Mixture 2
Liquid/Solid ratio	42.5/57.5	40/60
NaOH/Waste glass	25/75	25/75

4.2.7 Batch Adsorption Test

4.2.7.1 Preparation of Adsorbents

First, for the mechanically activated FA, only the 30-minute milled FA was investigated since it was found out to have the highest reactivity among the three samples based on their specific surface area as tabulated in Table 3. Second, the geopolymer foams with the L/S mixing ratio of 40/60 were selected as there were not much significant difference to the other L/S mixing ratio based on their FTIR analysis results as illustrated in Figure 22. Additionally, both geopolymer specimens (foamed and non-foamed) in two L/S mixing ratio conditions also observed to have similar FTIR analysis results. Therefore, only the foamed specimens were considered in this investigation. So, three samples were investigated in this test, the 30-minute milled FA and the geopolymer foams of the L/S mixing ratio of 40/60 of the 5 and 30-minutes milling time, respectively.

The prepared geopolymer foams from section 4.2.6 were ground gently in a mortar and pestle. It was then passed through in a 200 μ m mesh sieve size to obtain a uniform particle size

material. Furthermore, the fine samples were titrated with 0.1M HCl until a pH level of 4 was obtained. Due to its alkaline nature, lowering the pH level was essential to neutralize excess alkali hydroxides, enhancing active adsorption sites. It was then sat for 1 hour to allow the fine materials to settle at the bottom of the flask. The supernatant was removed and then, was rinsed with distilled water before drying in the laboratory drying oven at 105 °C for 24 hours. The pH of this solution rose up to approximately 6.



Figure 12. The treated adsorbent samples (a) Adsorbent 1, (b) Adsorbent 2, and (c) Adsorbent 3.

4.2.7.2 Preparation of Cu^{2+} and Mn^{2+} Ion Solutions

Stock solutions of Cu(II) and Mn(II) at concentration of 1000 mg/L, respectively, were prepared by dissolving appropriate amount of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ and $\text{MnSO}_4 \cdot \text{H}_2\text{O}$ in distilled water. Required varying concentration experimental solutions (20 ppm, 50ppm, 100 ppm, 200 ppm, 400 ppm, 800 ppm and 1000 ppm) were prepared by diluting the stock solution. However, when MP-AES analyzed the prepared concentration of 1000 mg/L, it was found that the concentrations of Cu(II) and Mn(II) needed to be adjusted by a factor of 1.3 and 2, respectively. The initial pH of the solutions was measured to be around 5 – 6.5. All chemicals used were analytical grade.

4.2.7.3 Batch Adsorption Method

Adsorption of the heavy metal ions (Cu^{2+} and Mn^{2+}) were determined by adsorption experiments conducted in a batch mode. In this test, 10% of the total liquid volume (ion solution) was equivalent to the amount of the solid particles. As a result, 0.4 g of the prepared solid samples and 4 ml of the ion solution were combined in a centrifuge tube with a screw cap. The tubes containing solution of different concentrations were shaken in a mechanical shaker for 24 hours to ensure complete equilibrium. Three repetitions were performed.

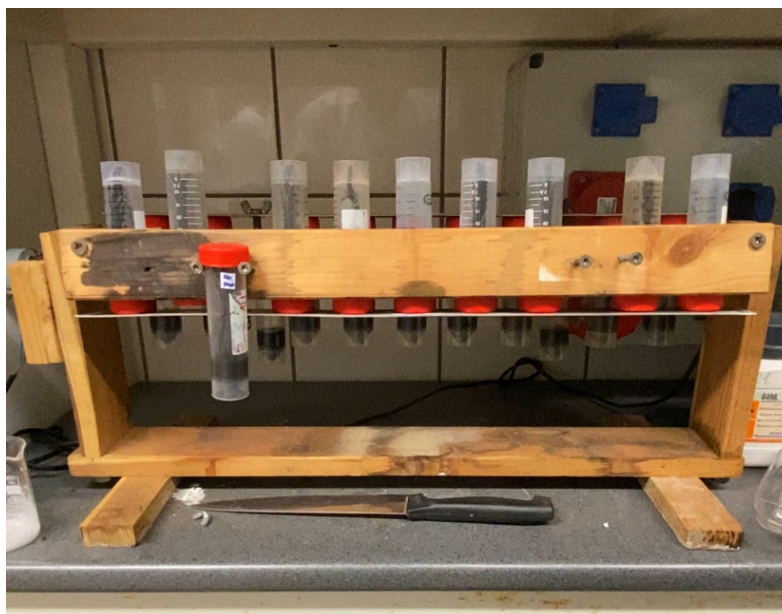


Figure 13. Centrifuge tubes with lid placed in a Mechanical Shaker.

Adsorption isotherms describe the adsorption process and how adsorbates interact with an adsorbent. It is important to establish the most acceptable correlations for the batch equilibrium data for analysis and design of adsorption systems. The most frequently used models to describe the equilibrium data of adsorption are Langmuir and Freundlich. In this study, the two models were applied in the investigation of adsorption isotherms of Cu(II) and Mn(II) .

The Langmuir model assumes that the uptake of metal ion is monolayer sorption on a homogenous surface and without any interaction between adsorbed ions [40]. The Langmuir isotherm can be described by eq.4, a nonlinear form of equation:

$$q_e = \frac{q_m k_L C_e}{1 + k_L C_e} \quad \text{Equation 4.}$$

To estimate the parameters, the Langmuir isotherm can be linearized in at least 4 different ways, as demonstrated by the following equations:

$$\frac{C_e}{q_e} = \frac{1}{q_m k_L} + \frac{C_e}{q_m} \quad \text{Equation 5.}$$

$$\frac{1}{q_e} = \frac{1}{q_m k_L} \left(\frac{1}{C_e} \right) + \frac{1}{q_m} \quad \text{Equation 6.}$$

$$q_e = q_m - \left(\frac{1}{k_L} \right) \frac{q_e}{C_e} \quad \text{Equation 7.}$$

$$\frac{q_e}{C_e} = k_L q_m - k_L q_e \quad \text{Equation 8.}$$

Where:

C_e = amount of ion concentration in the liquid phase at equilibrium, mg/L

q_e = equilibrium concentration of ion on the adsorbent, mg/g

q_m = monolayer capacity of the adsorbent, mg/g

k_L = Langmuir constants, mg/g

The Langmuir isotherm parameters q_m and k_L could be obtained by plotting specific values on the x vs. y axes, which depend on the chosen linearization method as shown in Table 6.

Table 6. Estimation of Langmuir Parameters by plot.

Equation	Plot
1	$\frac{C_e}{q_e}$ vs. C_e
2	$\frac{1}{q_e}$ vs. $\frac{1}{C_e}$
3	q_e vs. $\frac{q_e}{C_e}$
4	$\frac{q_e}{C_e}$ vs. q_e

From the graph, the straight line emerged, and the values of q_m and k_L constants were then calculated from the slopes and intercepts of the straight line using Microsoft Excel software. From the established equations, the value of q_e , which represents the capacity at specific equilibrium concentrations, is determined. This value is important for designing the column dimension for practical applications.

The Freundlich-model assumes a heterogeneous adsorption surface and active sites with different energy [41], [42]. Freundlich model is represented by the following equation:

$$q_e = k_F C_e^{1/n} \quad \text{Equation 9.}$$

The linearized logarithmic form of the equation is:

$$\log q_e = \log k_F + \frac{1}{n} \log C_e \quad \text{Equation 10.}$$

Where:

C_e = amount of ion concentration in the liquid phase at equilibrium, mg/L,

q_e = equilibrium concentration of ion on the adsorbent, mg/g,

k_F = Freundlich constant of the relative adsorption capacity of the adsorbent, mg/g.(L/mg)^(1/n),

$1/n$ = Freundlich exponent indicates adsorption intensity and surface heterogeneity, dimensionless.

Smaller value of $1/n$ implies stronger interaction between the adsorbent and heavy metal ion. When $1/n$ is greater than zero ($0 < 1/n < 1$) the adsorption is favorable, when $1/n$ is greater than 1, the adsorption process is unfavorable and it is irreversible when $1/n$ equals 1 [43]. When $1/n$ equals 1, the adsorption is linear, suggesting that the surface sites are homogeneous. The Freundlich isotherm parameters such as k_F and n could be obtained as well by plotting $\log C_e$ vs. $\log q_e$.

4.2.7.4 Analytical Method

Before analysis, the samples were centrifuged to separate the supernatant and adsorbent. The unreacted heavy metal contents of the supernatant were analyzed via MP-AES. Changes in

heavy metal concentration of the solution were represented as the removal of heavy metal by geopolymer adsorption.

The percentage removal (%RE) were calculated using equation 1.

$$\%RE = \frac{C_i - C_e}{C_i} \times 100 \quad \text{Equation 11.}$$

Where:

C_i = initial ion concentration, mg/L,

C_e = final ion concentration, mg/L.

The equilibrium uptake capacity of ion (mg-ion/g) was calculated by following equation (2);

$$q_e = \frac{(C_i - C_e)V}{1000m} \quad \text{Equation 12.}$$

Where:

C_i = initial ion concentration, mg/L,

C_e = final ion concentration, mg/L,

q_e = amount of adsorbate per unit mass of adsorbent at time t, mg/g,

V = volume of ion solution, mL,

m = mass of adsorbent, g.



Figure 14. MP-AES machine.

5 Results and discussion

5.1 Characterization of mechanically activated fly ash

Material characterization is an important stage that has to be accomplished in order to predict the potential utilization of the brown coal FA. The physical properties of the fly ash, particularly its fineness and surface area, which varies considerably all over sources, have a significant effect on how effectively the said material performs in alkali-activated materials. If all other parameters remain constant, fly ash with a higher proportion of smaller particles will typically have a higher specific surface area. Consequently, this will increase the amount of contact reaction with the alkaline medium, thus, causing a higher reaction rate and increased strength of the final material [44].

The bulk density and the specific surface area of the mechanically activated fly ash were reported in Table 7. It is apparent that the longer the milling period, the higher the resulting specific surface area. In this case, the 30-minute milling time (5,343.41 cm²/g) yielded the highest specific surface area, increasing by more than 300%. This was followed by the 5-minute milling time (2,347.49 cm²/g), and then, the 0-minute milling time (1,330.15 cm²/g). On the other hand, the lowest bulk density was measured at 0.708 g/cm³ during the 30-minute milling time. While the bulk densities of the other two samples were nearly identical at 0.751 g/cm³ and 0.757 g/cm³, respectively.

Table 7. Physical Properties of Mechanically Activated Brown Coal Fly Ash.

	Unit	Milling time		
		0 minute	5 minutes	30 minutes
Bulk Density	g/cm ³	0.751	0.757	0.708
Specific Surface Area	cm ² /g	1,330.15	2,347.49	5,343.41

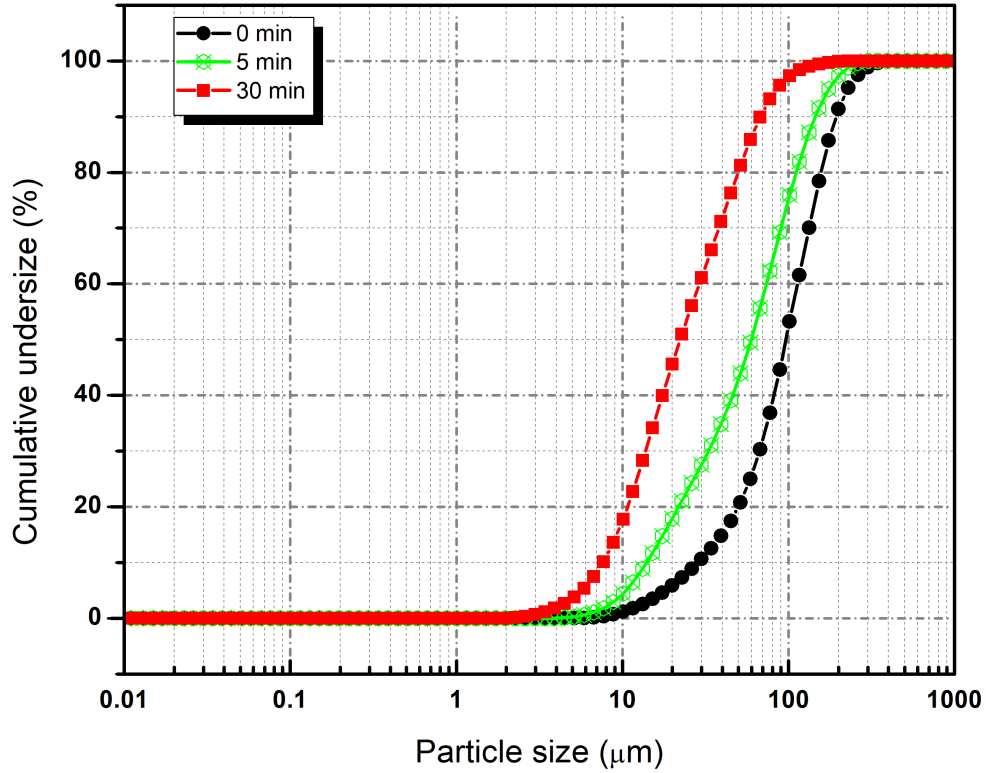


Figure 15. Particle Size Distribution of Mechanically Activated FA.

In Figure 15, the particle size distribution of raw brown coal FA and mechanically activated FAs are shown. Among the three samples, the 30-minute milling time ($x_{50} = 22.26 \mu\text{m}$) produced the lowest median particle size, followed by the 5-minute milling time ($x_{50} = 59.63 \mu\text{m}$) and 0-minute milling time ($x_{50} = 96.43 \mu\text{m}$). As a result, the finest ground product was generated in the 30-minute milling period.

5.2 Characterization of geopolymers

Figure 16 shows the relative compressive strength of the foamed and non-foamed geopolymer FA after aging for 7 days. Two different conditions of liquid/solid (L/S) mass ratio (42.5%/57.5% and 40%/60%) and two different milling times (5 mins and 30 mins) of the sample brown coal FA were studied. In these two conditions, it was observed that non-foamed geopolymer specimens have relatively higher compressive strength compared to the foamed geopolymer specimen. There are several reasons but the first factor that accounts for their substantial difference is that foamed geopolymer specimens exhibit higher porosity due to the

presence of foam bubbles as depicted in Figure 19 [45]. Porosity reduces the effective cross-sectional area available that can support weight, thereby decreasing compressive strength. Non-foamed geopolymers have lower porosity, which contributes to their higher compressive strength. In addition, the presence of foam introduces voids or air pockets into the material, reducing its overall density. Higher density is correlated with higher compressive strength because more material is present to resist deformation under applied stress. Consequently, non-foamed geopolymers are denser compared to foamed geopolymers as shown in Figure 18. Moreover, the presence of foam bubbles creates discontinuities in the material structure, which can act as stress concentrators and weaken the overall structure. As a result, non-foamed geopolymers tend to have a more homogeneous and compact microstructure which leads to better load transfer and higher compressive strength. So, the compressive strength of the foamed geopolymer specimen was affected by the addition of foaming agents.

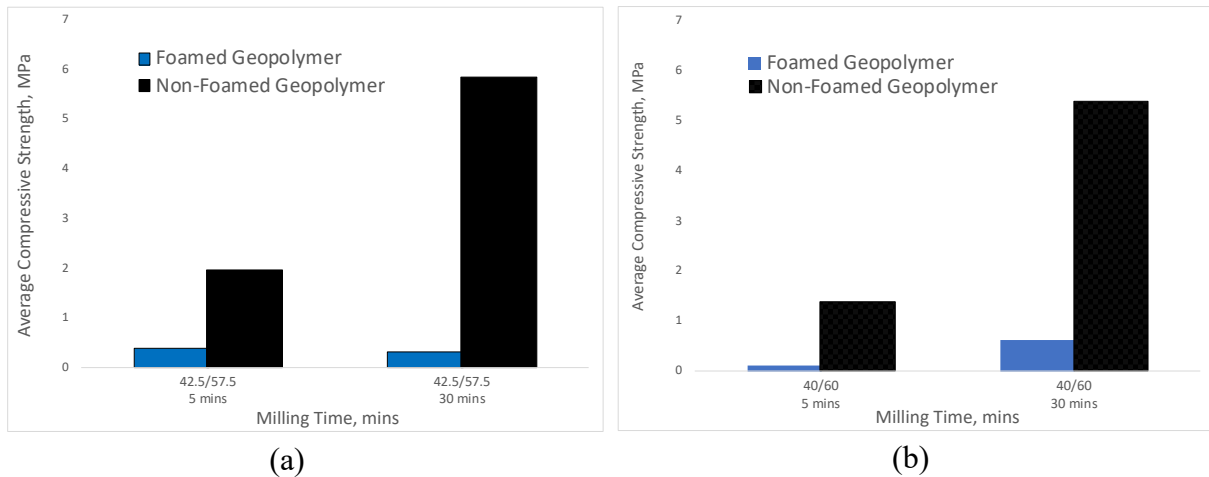


Figure 16. Variation of compressive strength of the samples milled at different time after 7 days and cured at 60 °C for 6 hours: (a) L/S (42.5/57.5) and (b) L/S (40/60).

In Figure 16a, the non-foamed geopolymer milled for 30 minutes had an average compressive strength of 5.846 MPa which was about 200% higher than that of the 5-minute milled geopolymer. However, the average compressive strength of the foamed geopolymer for both 5-minute and 30-minute milled FA was about the same – 0.404 MPa and 0.322 MPa, respectively. Meanwhile, in Figure 16b, it can be seen that the 30-minute milled non-foamed geopolymer had also a higher compressive strength of 5.382 MPa, whereas the 5-minute milled geopolymer had a compressive strength of 1.386 MPa. In contrast, the foamed geopolymer's

compressive strength for the milled FA after 30 minutes (0.623 MPa) was comparatively higher than 5 minutes (0.108 MPa), an increase of more than 400%. Overall, the compressive strength recorded for the L/S ratio of 40/60 was marginally better than the measurement for 42.5/57.5 except for the 5-minute foamed geopolymer as illustrated in Figure 11. This indicates that optimizing milling time and L/S ratio can significantly influence the structural performance of geopolymers, especially in non-foamed samples.

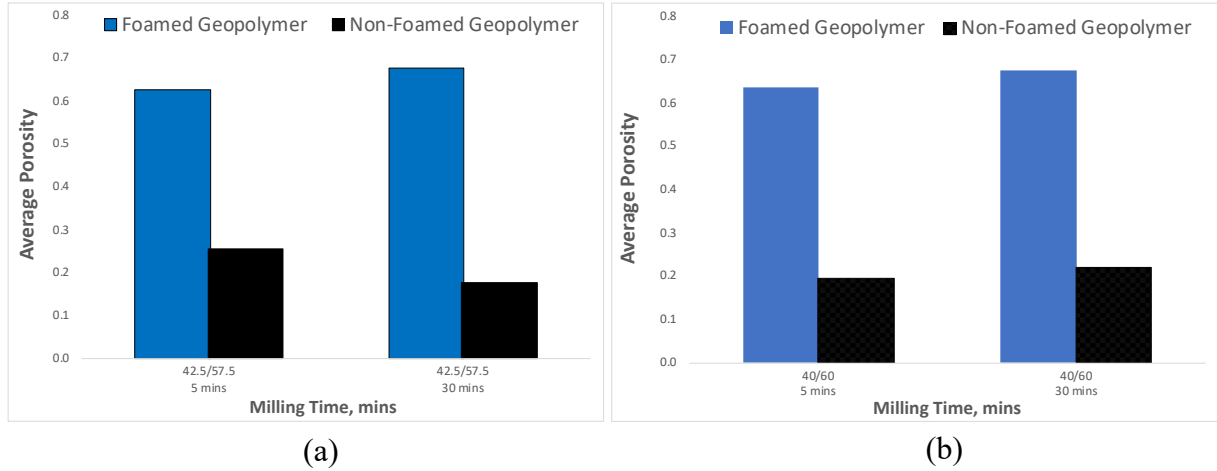


Figure 17. Average Porosity of the samples milled at different times after 7 days and cured at 60 °C for 6 hours: (a) L/S (42.5/57.5) and (b) L/S (40/60).

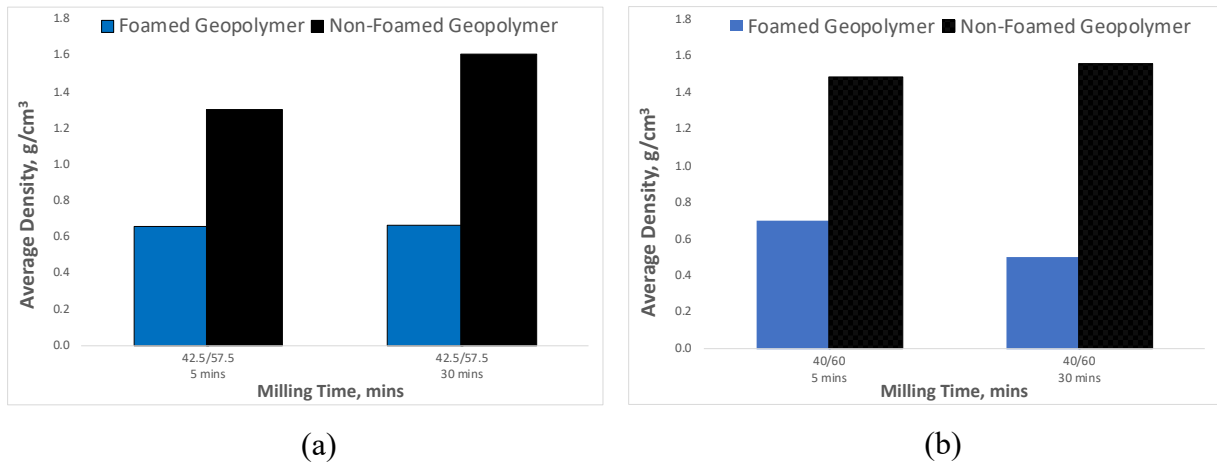


Figure 18. Average Density of the samples milled at different times after 7 days and cured at 60 °C for 6 hours: (a) L/S (42.5/57.5) and (b) L/S (40/60).



Figure 19. Geopolymer specimens after aging 7 days. (a) Foamed Geopolymer & (b) Non-foamed Geopolymer.

5.3 FTIR spectroscopy analysis

FTIR spectral analysis is useful to determine the functional groups that are present in the brown coal FA. Fly ashes are mainly composed of Silica, alumina, and ferric oxide. The presence of silica and alumina induced different linkages which have different vibration peaks for identification [46]. The FTIR spectra of the mechanically activated brown coal FA were plotted as a function of milling time as depicted in Figure 10. Based on the graph, the absorbance of each FA material (0, 5, and 30 minutes) can be observed at $1,060.66\text{ cm}^{-1}$, $1,052.94\text{ cm}^{-1}$, and $1,043.30\text{ cm}^{-1}$, respectively. These peak values represent the T-O-Si (where T = Si or Al) bonds asymmetric stretching vibration [47]. In addition, the peaks at the wavenumber of 808.99 cm^{-1} , 801.28 cm^{-1} , and 796.46 cm^{-1} indicate the presence of asymmetric stretching vibrations of Si-O-Si [39]. A slight decrease in intensity was observed for the 2-milled samples (5 and 30-minutes). Its intensity decreased with an increase in milling time. These changes were attributed to the structural modification of the sample (quartz or SiO_2) [48]. This observation is commonly observed in milled FA.

Table 8. Assignment of FTIR peaks of raw and mechanically activated FAs (0, 5, and 30 minutes milling time).

Wavenumber (cm ⁻¹)	Assignment
796.46	Si-O-Si asymmetric stretching, Al-O
801.28	Si-O-Si asymmetric stretching
808.99	Si-O-Si asymmetric stretching
1,043.30	Si-O-Si or Al-O-Si asymmetric stretching
1,052.94	Si-O-Si or Al-O-Si asymmetric stretching
1,060.66	Si-O-Si or Al-O-Si asymmetric stretching

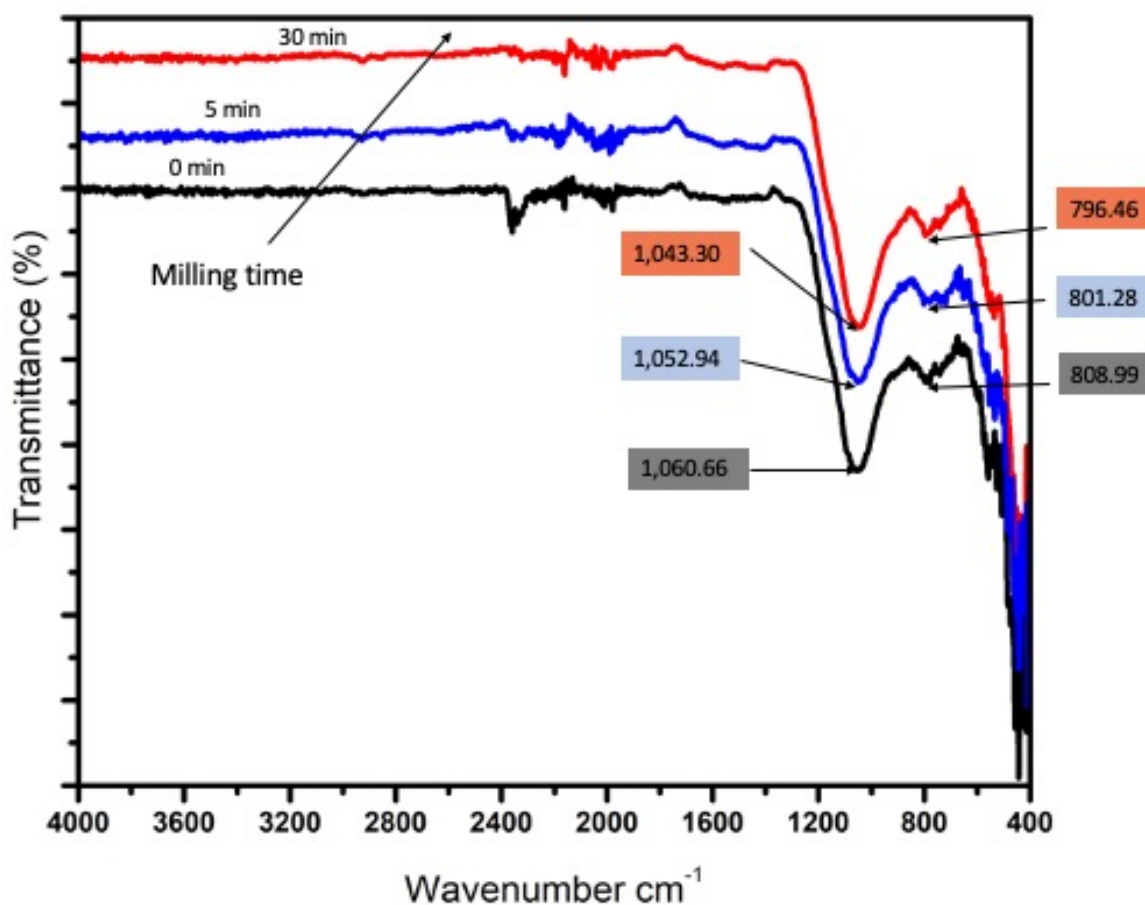


Figure 20. FTIR spectra of the brown coal FA ball milled at different times.

Table 9. Assignment of FTIR peaks of L/S ratio (42.5/57.5) for foamed and non-foamed geopolymer of mechanically activated FA (5, and 30 minutes milling time).

Wavenumber (cm ⁻¹)	Assignment
688	Si-O-Si asymmetric stretching, Al-O
714.5	Si-O-Si asymmetric stretching
728	Si-O-Si asymmetric stretching
848.53	Si-O-Si asymmetric stretching
984.48	Si-O-Si or Si-O-T (T=Al or Si)
988.34	Si-O-Si or Si-O-T (T=Al or Si)
992.2	Si-O-Si or Si-O-T (T=Al or Si)
996.03	Si-O-Si or Si-O-T (T=Al or Si)
1,394.28	Al-OH bending
1,396.21	Al-OH bending
1,453.1	Al-OH bending
1,636.3	O-H bending (water)
1,643.05	O-H bending (water)
1,644.02	O-H bending (water)
1,649.8	O-H bending (water)
3,275.5	O-H stretching (water or hydroxyl groups)
3,356.5	O-H stretching (water or hydroxyl groups)
3,379.64	O-H stretching (water or hydroxyl groups)
3,468.35	O-H stretching

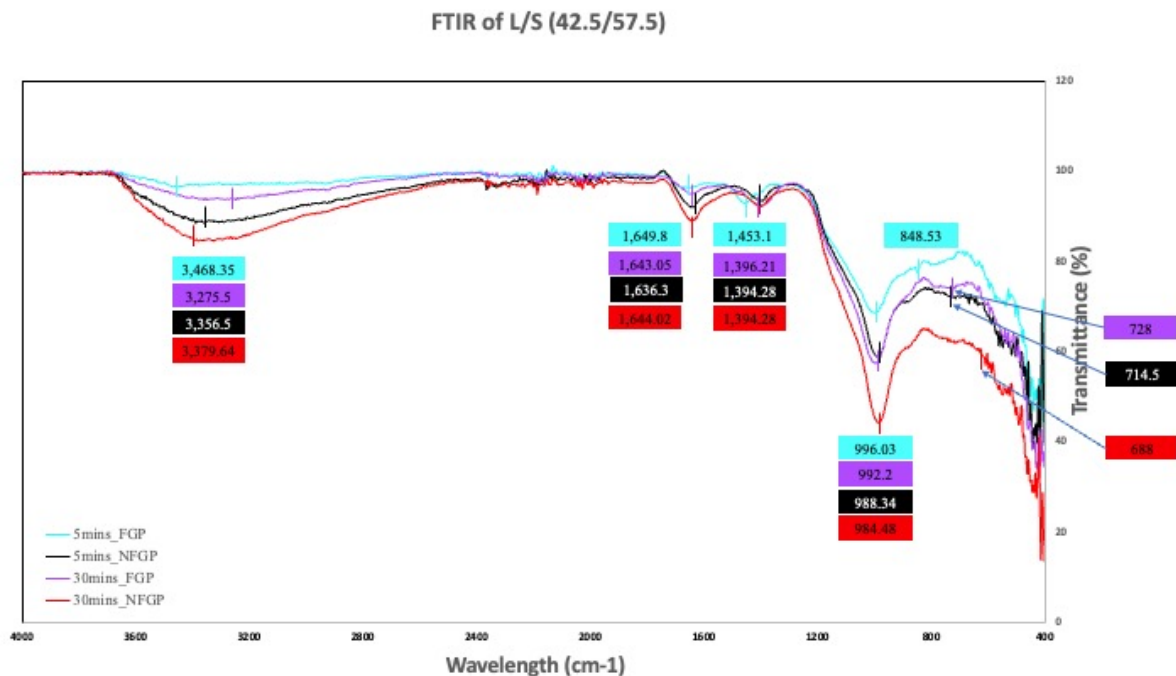


Figure 21. FTIR spectra of L/S ratio (42.4/57.5) for the Foamed and Non-foamed Geopolymer FA ball milled at different times.

The phase transformations of fly ash after geopolymerization were monitored using FTIR analysis. Figure 21 shows the FTIR spectra of L/S ratio (42.4/57.5) comparing samples of 5 - mins FGP, 5 - mins NFGP, 30 - mins FGP, and 30 - mins NFGP. There were new peaks appeared due to geopolymerization (between 3270 – 3500 cm^{-1} , 1600 – 1650 cm^{-1} , 1390 – 1460 cm^{-1} , and 850 cm^{-1}) while other peak shifted to a lower wavenumber (between 980 – 997 cm^{-1} and changed its intensity and another peak remained approximately unchanged (staying below 800 cm^{-1}). The peak between 3270 – 3500 cm^{-1} is related to - OH, HOH bonds stretching vibration, while the peak between 1600 – 1650 cm^{-1} is attributed to HOH bonds bending vibration. The peak between 1390 – 1460 cm^{-1} corresponds to the O-C-O stretching vibration. These peaks were observed across the four samples. However, a peak at 850 cm^{-1} , related to Si-O stretching and OH bending bond vibrations (Si-OH) was only detected in the 5 – mins FGP specimen. However, the peak observed between 1040 – 1060 cm^{-1} for fly ash from figure 20 shifts to a lower wavenumber (between 980 – 997 cm^{-1}) following geopolymerization, indicating the formation of a structurally organized amorphous aluminosilicate gel. This shift is attributed to the dissolution of amorphous phase of fly ash in a highly alkaline environment [39], [49].

Furthermore, no significant differences in frequency were observed between the foamed geopolymer and non-foamed geopolymer samples; both showed comparable results.

Table 10. Assignment of FTIR peaks of L/S ratio (40/60) for foamed and non-foamed geopolymer of mechanically activated FA (5, and 30 minutes milling time).

Wavenumber (cm ⁻¹)	Assignment
580.5	Si-O-Si asymmetric stretching, Al-O
778.14	Si-O-Si asymmetric stretching
771.39	Si-O-Si asymmetric stretching
778.14	Si-O-Si asymmetric stretching
986.14	Si-O-Si or Si-O-T (T=Al or Si)
991.23	Si-O-Si or Si-O-T (T=Al or Si)
997.02	Si-O-Si or Si-O-T (T=Al or Si)
1,000.87	Si-O-Si or Si-O-T (T=Al or Si)
1,398.14	Al-OH bending
1,398.14	Al-OH bending
1,400.07	Al-OH bending
1,409.71	Al-OH bending
1,637.27	O-H bending (water)
1,643.05	O-H bending (water)
1,644.98	O-H bending (water)
1,645.95	O-H bending (water)
3,341.07	O-H stretching (water or hydroxyl groups)
3,348.78	O-H stretching (water or hydroxyl groups)
3,356.5	O-H stretching (water or hydroxyl groups)
3,447.13	O-H stretching (water or hydroxyl groups)

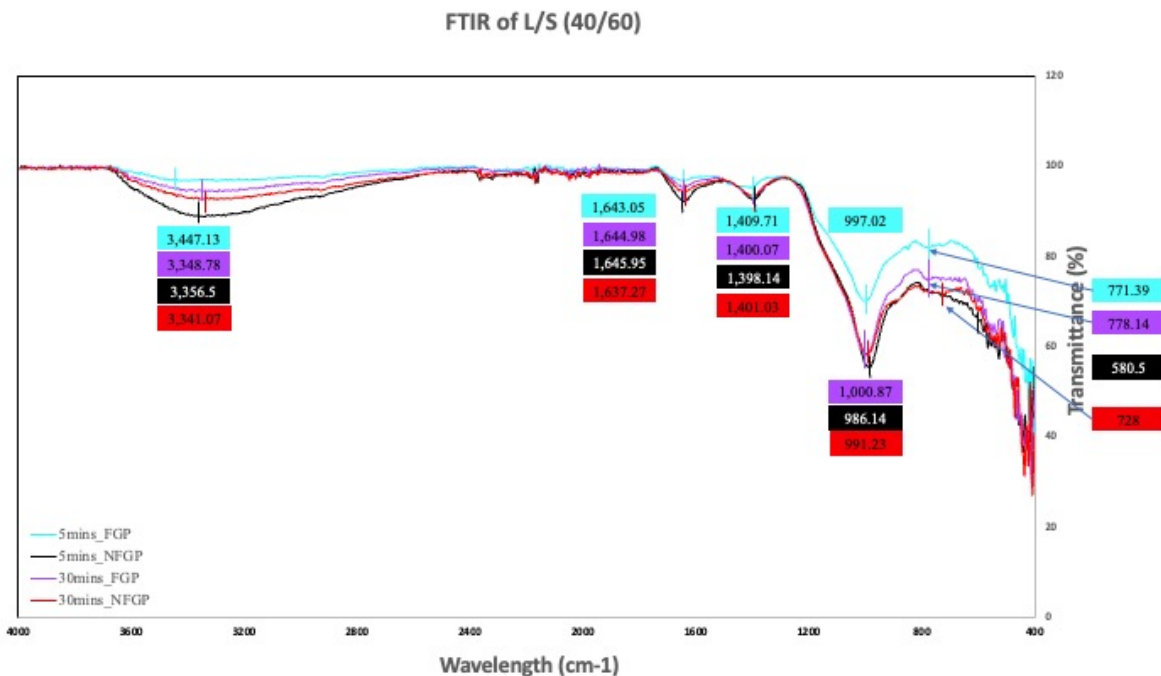


Figure 22. FTIR spectra of L/S ratio (40/60) for the Foamed and Non-foamed Geopolymer FA ball milled at different times.

On the other hand, Figure 22 shows the FTIR spectra of L/S ratio (40/60) for the 5 mins FGP, 5 mins NFGP, 30 mins FGP and 30 mins NFGP. Following geopolymerization, only three new peaks were observed (between $3340 - 3450 \text{ cm}^{-1}$, $1635 - 1650 \text{ cm}^{-1}$, and $1390 - 1410 \text{ cm}^{-1}$) across the 4 samples, while other peak shifted to a lower wavenumber (between $985 - 1000 \text{ cm}^{-1}$) and changed its intensity and another peak remained nearly the same (observed below 800 cm^{-1}). The peak between $3340 - 3450 \text{ cm}^{-1}$ is related to -OH, HOH bonds stretching vibration, whereas, the peak observed between $1635 - 1650 \text{ cm}^{-1}$ is related to the HOH bonds bending vibration. Another peak was detected between $1390 - 1410 \text{ cm}^{-1}$ is attributed to O-C-O stretching vibration. Unlike in the previous 5 minute sample condition, no peak was observed corresponding to the Si-O stretching and OH bending bond vibrations (Si-OH). Although a narrower peak range was noted, both still showed comparable results.

5.4 Batch Adsorption analysis

5.4.1 Adsorption Isotherms

Batch experiments confirmed the ability of each of the prepared adsorbents to remove a specific heavy metal ion from a synthetic solution. The results (using mean values of three replications) obtained from this investigation were interpreted by using adsorption isotherms.

5.4.1.1 Copper removal

Figure 23 illustrated the experimental equilibrium data of copper onto the prepared adsorbents that were fitted according to the linearized Langmuir (equations 4 and 5) and Freundlich (equation 9) isotherm models. Table 11 presented the estimated mean values of parameters obtained by Langmuir, and Freundlich isotherms for copper adsorption onto the three prepared samples. It is evident that each isotherm showed the preference towards the Langmuir (C_e/q_e vs C_e) as shown by the highest (closest to unity) correlation coefficients (R^2) which is a statistical parameter indicating the goodness of fit of the studied models. The estimated adsorption capacity (q_m) of the adsorbents are 8.503 mg/g (Adsorbent 3) > 7.501 mg/g (Adsorbent 2) > 4.239 mg/g (Adsorbent 1). With this information, Adsorbent 3 obtained the highest adsorption capacity for the copper removal adsorption test while Adsorbent 1 being the least effective adsorbent.

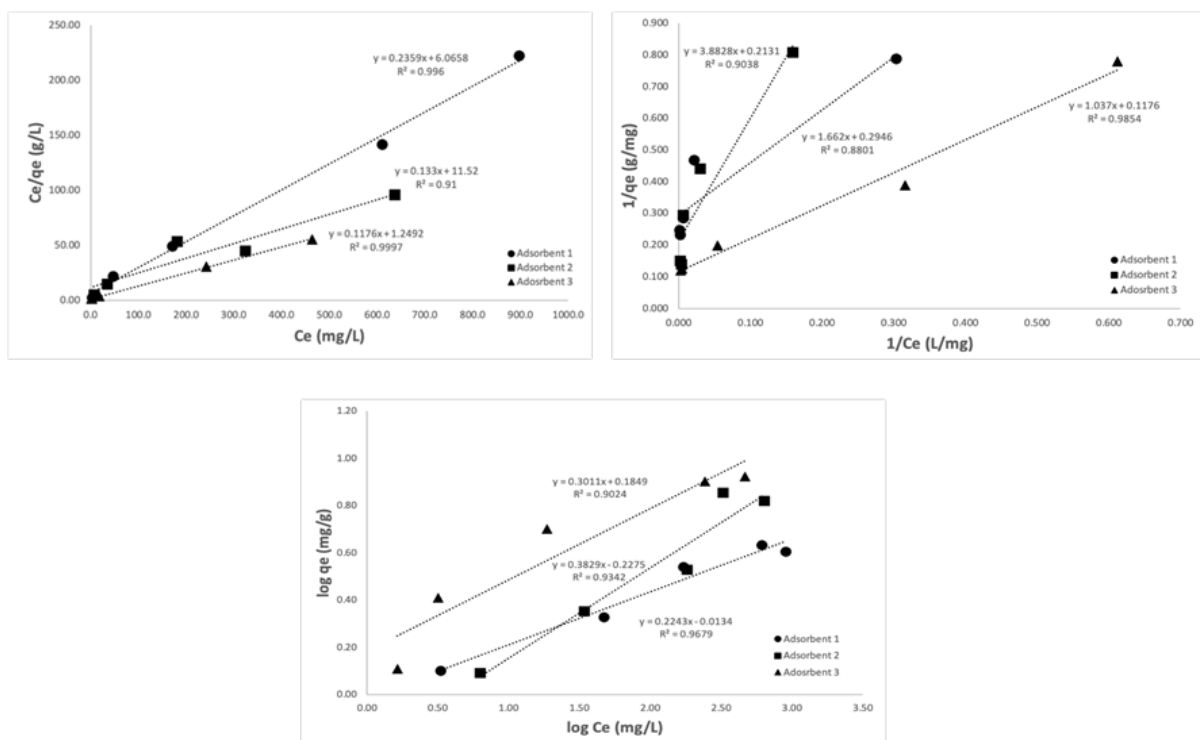


Figure 23. Experimental equilibrium data fitted according to the adsorption isotherm model for the adsorption of Cu(II) onto the prepared adsorbents: (a) Langmuir (C_e/q_e vs C_e), (b) Langmuir ($1/q_e$ vs $1/C_e$), and (c) Freundlich ($\log C_e$ vs $\log q_e$).

Table 11. Parameters of Langmuir and Freundlich isotherm for adsorption equilibrium of copper onto the prepared adsorbents.

Adsorbent	Isotherm Models	Parameters	Values	
			Cu(II)	Mn(II)
Adsorbent 1	Langmuir (C_e/q_e vs C_e)	q_m (mg/g)	4.239	3.311
		k_L (L/mg)	0.039	0.014
		R^2	0.996	0.9875
	Langmuir ($1/q_e$ vs $1/C_e$)	q_m (mg/g)	3.394	3.109
		k_L (L/mg)	0.177	0.358
		R^2	0.8801	0.958
	Freundlich ($\log C_e$ vs $\log q_e$)	k_F (mg/g)(L/mg) $^{1/n}$	0.970	0.118
		$1/n$	0.2243	0.6927
		R^2	0.9679	0.9349

Adsorbent	Isotherm Models	Parameters	Values	
			Cu(II)	Mn(II)
Adsorbent 2	Langmuir (C_e/q_e vs C_e)	q_m (mg/g)	7.519	11.587
		k_L (L/mg)	0.012	0.005
		R^2	0.91	0.9456
	Langmuir ($1/q_e$ vs $1/C_e$)	q_m (mg/g)	4.693	10.132
		k_L (L/mg)	0.055	0.006
		R^2	0.9038	0.9185
	Freundlich ($\log C_e$ vs $\log q_e$)	k_F (mg/g)(L/mg) ^{1/n}	0.592	0.311
		$1/n$	0.3829	0.5232
		R^2	0.9342	0.8658
Adsorbent 3	Langmuir (C_e/q_e vs C_e)	q_m (mg/g)	8.503	10.965
		k_L (L/mg)	0.094	0.038
		R^2	0.9997	0.997
	Langmuir ($1/q_e$ vs $1/C_e$)	q_m (mg/g)	8.503	7.605
		k_L (L/mg)	0.113	0.040
		R^2	0.9854	0.9243
	Freundlich ($\log C_e$ vs $\log q_e$)	k_F (mg/g)(L/mg) ^{1/n}	1.531	1.629
		$1/n$	0.3011	0.2867
		R^2	0.9024	0.991

5.4.1.2 Manganese removal

Meanwhile, Figure 24 depicted the experimental equilibrium data of manganese onto the prepared adsorbents which were also fitted to the same adsorption isotherm models used for the removal of copper and the values of the estimated parameters and the correlation coefficient (R^2) obtained by the isotherm models were also tabulated in the same Table 11. It can be seen from this table that each isotherm showed the preference towards the Langmuir (C_e/q_e vs C_e), same case as copper, as shown by the highest (closest to unity) correlation coefficients (R^2). The estimated adsorption capacity (q_m) of the adsorbents are 11.587 mg/g (Adsorbent 2) > 10.965 mg/g (Adsorbent 3) > 3.311 mg/g (Adsorbent 1). Therefore, Adsorbent 2 obtained the highest

adsorption capacity for the manganese removal adsorption test while Adsorbent 1 remained the least effective adsorbent.

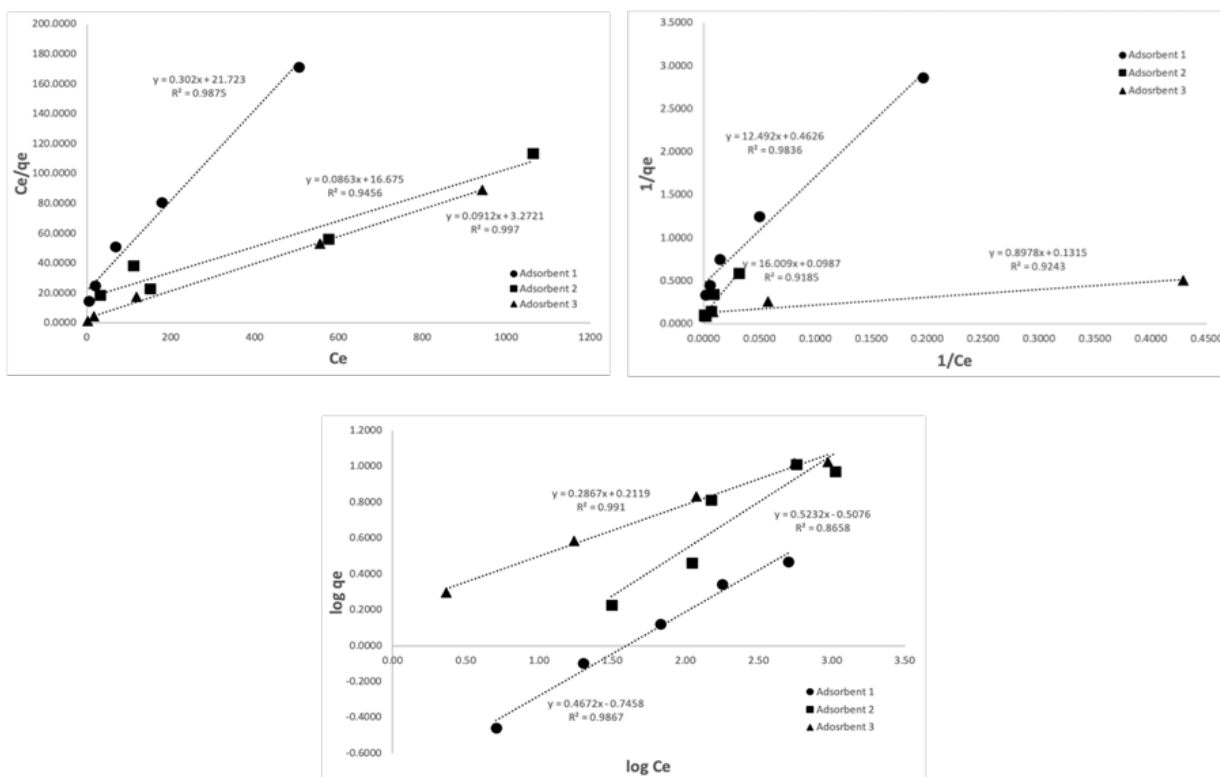


Figure 24. Experimental equilibrium data fitted according to the adsorption isotherm models for the adsorption of Mn(II) onto the prepared adsorbents: (a) Langmuir (Ce/qe vs Ce), (b) Langmuir (1/qe vs 1/Ce), and (c) Freundlich (logCe vs log qe).

5.4.2 Statistical analysis of data

In this section, the results of the statistical analysis conducted were presented to evaluate the performance of three different adsorbents in the removal of two heavy metals, copper and manganese. This analysis aims to provide an understanding of each adsorbent's effectiveness and to determine whether significant differences exist between them. Using R studio software, Two statistical methods were run. First, the one-way ANOVA was used to determine if there is a statistically significant difference among the means of three adsorbents and followed by a post hoc test, Tukey's HSD Test, only if such significant difference exists. It is to determine which specific pairs of adsorbent groups are significantly different from each other. To draw

conclusions, The F-stat value was compared with the F-critical value and the p-value was evaluated. If the F-stat value is greater than the F-critical value, the result is considered to be statistically significant. And a p-value less than 0.05 indicates statistical significance at a 5% significance level, implying that the adsorbent has a substantial effect on reducing the heavy metal concentration.

5.4.2.1 Copper

Table 12 provides the adsorption capacities for three adsorbents across three measurements (replication). As shown, the values indicate that Adsorbents 2 and 3 have higher capacities compared to Adsorbent 1.

Table 12. Langmuir adsorption capacity data.

Adsorbent capacity	Adsorbent 1 (mg/g)	Adsorbent 2 (mg/g)	Adsorbent 3 (mg/g)
qm1	3.068	8.026	8.097
qm2	4.688	6.627	8.905
qm3	3.306	7.698	8.482

Table 13. Descriptive statistics for each adsorbent group.

Adsorbent	Mean (mg/g)	Median (mg/g)	SD (mg/g)	Variance (mg/g) ²	Min (mg/g)	Max (mg/g)
Adsorbent 1	3.687	3.306	0.875	0.765	3.068	4.688
Adsorbent 2	7.450	7.698	0.732	0.535	6.627	8.026
Adsorbent 3	8.495	8.482	0.404	0.163	8.097	8.905

Table 14. Summary results of one-way ANOVA.

Source of Variation	SS (mg/g) ²	df	MS (mg/g) ²	F	P-value	F crit
Between Groups	38.357	2	19.179	39.310	0.000356	5.143
Within Groups	2.927	6	0.488			
Total	41.284	8				

Table 14 depicts the summary results of one-way ANOVA. The F-value (39.310) was much larger than the F-critical value (5.14), and the p-value was significantly below the 0.05 significance level. This implies that there was a statistically significant difference in adsorption capacities between at least two of the adsorbents. Therefore, a post hoc test was carried out. As tabulated in table 15, it was determined that the p-value (0.2384) between adsorbents 2 and 3 was higher than the 0.05 significance level, indicating no significant difference. This suggests that adsorbents 2 and 3 have similar performance levels. On the other hand, significant difference exists between the remaining group, Adsorbents 2 and 1 and Adsorbent 3 and 1.

Table 15. Tukey multiple comparisons of means 95% family-wise confidence level.

Adsorbent group	Mean diff (mg/g)	Lower (mg/g)	Upper (mg/g)	p adj	Significant?
Adsorbent 2 - Adsorbent 1	3.763	2.013	5.513	0.0014	Yes
Adsorbent 3 - Adsorbent 1	4.807	3.057	6.557	0.0003	Yes
Adsorbent 2 - Adsorbent 3	1.044	-0.706	2.794	0.2384	No

5.4.2.2 Manganese

Table 16 provides the adsorption capacities for three adsorbents across three measurements (replication). As shown, the values indicate that Adsorbents 2 and 3 have higher capacities compared to Adsorbent 1.

Table 16. Langmuir adsorption capacity data.

Adsorbent Capacity	Adsorbent 1 (mg/g)	Adsorbent 2 (mg/g)	Adsorbent 3 (mg/g)
qm1	3.282	11.429	11.574
qm2	3.028	10.163	8.511
qm3	3.549	12.953	12.270

Table 17. Descriptive statistics for each group.

Adsorbent	Mean (mg/g)	Median (mg/g)	SD (mg/g)	Variance (mg/g)	Min (mg/g)	Max (mg/g)
Adsorbent 1	3.286	3.282	0.261	0.0681	3.028	3.549
Adsorbent 2	11.515	11.429	1.401	1.96	10.163	12.953
Adsorbent 3	10.785	11.574	1.929	3.72	8.511	12.270

Table 18 provides the summary results of one-way ANOVA. The F-value (31.02) was much larger than the F-critical value (5.14), and the p-value was significantly below the 0.05 significance level. Similar to the results for copper, this implies that there was a statistically significant difference in adsorption capacities between at least two of the adsorbents. A post hoc test was also performed.

Table 18. Summary results of one-way ANOVA.

Source of Variation	SS (mg/g) ²	df	MS (mg/g) ²	F	P-value	F crit
Between Groups	124.479	2	62.240	31.012	0.00069	5.143
Within Groups	12.042	6	2.007			
Total	136.521	8				

As can be seen on Table 19, there was no significance difference between adsorbents 2 and 3 because of its p-value (0.2384) higher than the 0.05 significance level, indicating that adsorbents 2 and 3 have similar performance levels as well. On the other hand, significant difference exists between the remaining group, Adsorbents 2 and 1 and Adsorbent 3 and 1.

Table 19. Tukey multiple comparisons of means 95% family-wise confidence level.

Adsorbent group	Mean diff (mg/g)	Lower (mg/g)	Upper (mg/g)	p adj	Significant?
Adsorbent 2 - Adsorbent 1	8.229	4.680	11.777	0.0009	Yes
Adsorbent 3 - Adsorbent 1	7.500	3.950	11.047	0.0016	Yes
Adsorbent 3 - Adsorbent 2	-0.73	-4.279	2.819	0.8091	No

6 Conclusion

Based on these findings, therefore, the most important conclusions from this work are summarized as follows.

- Using ball mill, the finest FA particles were obtained with the 30-minuted milling time ($x_{50} = 22.2621 \mu\text{m}$) > 5-minute milling time ($x_{50} = 59.634 \mu\text{m}$) > 0-minute milling time ($x_{50} = 96.4297 \mu\text{m}$).
- Optimizing milling time and L/S ratio can greatly improve the structural performance of geopolymers, particularly for non-foamed samples. While increased milling time enhances compressive strength, higher porosity results in reduced structural integrity.

Therefore, the compressive strength of geopolymer specimens can be effectively controlled.

- FTIR analysis of geopolymer specimens reveals new peaks and shifts in peak position compared to the fly ash spectra. An additional peak (850 cm^{-1}) was detected in the 5-minute FGP sample with an L/S ratio of 42.5/57.5, while three new peaks (between $3270 - 3500\text{ cm}^{-1}$, $1600 - 1650\text{ cm}^{-1}$, $1390 - 1460\text{ cm}^{-1}$) were observed under each sample condition. These changes were attributed to structural changes and the formation of an amorphous aluminosilicate gel following geopolymerization. Although the peak ranges in the sample with L/S ratio of 40/60 was narrower than that of 42.5/57.6, both still showed comparable results.
- The best fit was obtained by the linear form of Langmuir isotherm model ($\frac{C_e}{q_m} = \frac{1}{q_m k_L} + \frac{C_e}{q_m}$) with coefficient correlation R^2 values nearly 1.
- For the Copper removal, Adsorbent 3 was the most effective adsorbent with an estimated mean adsorption capacity (q_m) value of 8.503 mg-Cu/g.
- For the Manganese removal, Adsorbent 2 was the most effective adsorbent with an estimated mean adsorption capacity (q_m) value of 11.587 mg-Mn/g.
- The estimated adsorption capacity (q_m) values of geopolymer adsorbents 2 and 3 were higher in Manganese removal than copper removal. Therefore, the prepared geopolymer adsorbents were more suitable for applications targeting Manganese removal.
- There was a significant improvement in the properties of coal fly ash when it underwent the geopolymerization process. The adsorption capacity is significantly higher than the raw sample. This indicates that the geopolymer material has more sorption sites for Copper and Manganese than the raw fly ash. Thus, it was proven that fly ash-based geopolymer can be appropriate adsorbents for the removal process of Copper and Manganese and appears to be technically feasible.
- According to the statistical data analysis (ANOVA and Tukey test), there was a significant difference in performance between adsorbents 1 and 2, as well as between adsorbents 1 and 3, but not between adsorbents 2 and 3 since their performance levels are comparable. Given this information, an additional 25 minutes of milling was unnecessary since in just 5 minutes of milling, the raw fly ash was sufficient for use in

geopolymerization to enhance adsorption capacity. Moreover, this approach is beneficial in terms of energy savings.

- For future studies, the researcher strongly recommends conducting FTIR analysis after the adsorption test to observe any changes in the functional groups within the adsorbent. Additionally, it is also suggested to investigate the behavior of the geopolymer adsorbents when two heavy metals are combined in the same solution.

7 Appendix

7.1 To prepare a 1000 mg/L solution of manganese ions (Mn^{2+}) from manganese(II) sulfate monohydrate ($\text{MnSO}_4 \cdot \text{H}_2\text{O}$), follow these steps:

Given:

molar mass of $\text{MnSO}_4 \cdot \text{H}_2\text{O} = 169.01 \text{ g/mol}$

molar mass of $\text{Mn}^{2+} = 54.94 \text{ g/mol}$

A concentration of 1000 mg/L of Mn^{2+} is equivalent to 1000 mg, or 1 g, of Mn^{2+} in 1 liter.

Calculate the moles of Mn needed:

$$\text{moles of Mn} = \frac{1g}{54.94 \text{ g/mol}} \approx 0.01820 \text{ mol}$$

Since 1 mole of $\text{MnSO}_4 \cdot \text{H}_2\text{O}$ contains 1 mole of Mn:

$$\text{Mass of } \text{MnSO}_4 \cdot \text{H}_2\text{O} = \frac{0.01820 \text{ mol}}{169.03 \frac{\text{g}}{\text{mol}}} \approx 3.08 \text{ g}$$

Thus, to prepare a 1000 mg/L solution of manganese ions, you need to dissolve approximately 3.08 grams of $\text{MnSO}_4 \cdot \text{H}_2\text{O}$ in 1 liter of water.

7.2 To prepare a 1000 mg/L solution of manganese ions (Cu^{2+}) from copper(II) sulfate tetrahydrate ($\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$), follow these steps:

Given:

molar mass of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O} = 249.72 \text{ g/mol}$

molar mass of $\text{Mn}^{2+} = 63.55 \text{ g/mol}$

A concentration of 1000 mg/L of Cu^{2+} is equivalent to 1000 mg, or 1 g, of Cu^{2+} in 1 liter.

Calculate the moles of Cu needed:

$$\text{moles of Mn} = \frac{1g}{63.55 \text{ g/mol}} \approx 0.01574 \text{ mol}$$

Since 1 mole of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ contains 1 mole of Cu:

$$\text{Mass of } \text{CuSO}_4 \cdot 5\text{H}_2\text{O} = \frac{0.01574 \text{ mol}}{249.72 \frac{\text{g}}{\text{mol}}} \approx 3.93 \text{ g}$$

Thus, to prepare a 1000 mg/L solution of manganese ions, you need to dissolve approximately 3.08 grams of $\text{MnSO}_4 \cdot \text{H}_2\text{O}$ in 1 liter of water.

7.3 Experimental Data

7.3.1 Cu(II) analysis results

Table 20. Experimental data of Cu(II) removal at varying concentrations.

Co, mg/L	Adsorbent 1				Adsorbent 2				Adsorbent 3			
	Ce, mg/L				Ce, mg/L				Ce, mg/L			
	T1	T2	T3	Mean	T1	T2	T3	Mean	T1	T2	T3	Mean
130	4	3.3	2.6	3.3	6.6	6	6.3	6.3	1.4	1.8	1.7	1.6
260	43.9	36	61.1	47	32.5	35.3	33.8	33.9	3.1	3.1	3.9	3.2
520	171	149	194	171.3	146	199	199	181.3	18	18	18	18.7
1,040	510	520	800	610	370	300	300	323.3	264	221	264	241.7
1,300	1,010	860	820	896.7	590	700	620	636.7	461	426	461	464.0

7.3.2 Mn(II) analysis results

Table 21. Experimental data of Mn(II) removal at varying concentrations.

Co, mg/L	Adsorbent 1				Adsorbent 2				Adsorbent 3			
	Ce, mg/L				Ce, mg/L				Ce, mg/L			
	T1	T2	T3	Mean	T1	T2	T3	Mean	T1	T2	T3	Mean
40	5.6	5.4	4.3	5.1	-	-	-	-	-	-	-	-

100	18.3	20.5	21.4	20.1	-	-	-	-	-	-	-	-
200	62	66	75	67.7	32	28	34	31.3	2	2	3	2.3
400	172	156	209	179	100	119	115	111.3	17	18	17	17.3
800	506	527	483	505.3	131	126	193	150	119	123	114	118.7
1600	740	850	720	773.3	430	760	540	576.7	547	543	577	555.7
2000	980	870	890	913.3	1050	1120	1020	1063.3	880	1180	770	943.3

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