



Faculty of Sciences
Department of Chemistry and Forensic Sciences

**Synthesis of Highly Porous Geopolymeric Materials from Fly Ash
Obtained from Morupule Power Station in Botswana for the
Adsorption of Cationic and Anionic Dyes**

by

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A Dissertation/Thesis Submitted to the Faculty of Sciences in Partial Fulfilment of the
Requirements for the Award of the Degree of Master of Science in Chemistry of BIUST

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December 2022

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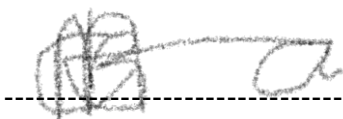
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CERTIFICATION

This dissertation/thesis entitled **“Synthesis of Highly Porous Geopolymeric Materials from Fly Ash Obtained from Morupule Power Station in Botswana for the Adsorption of Cationic and Anionic Dyes”** was compiled by Christopher Mbochwa and submitted as a fulfillment of the requirement for a degree of Master of Science in Chemistry at Botswana International University of Science and Technology.

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ACKNOWLEDGEMENTS

I would like to thank my supervisors Dr. Stephen Majoni and Prof. Foster Mbaiwa for all the help and guidance they did for me during my research. They were patient with me throughout my research. Thanks to BIUST for providing a financial assistance to complete my study. Thanks to BIUST for the Research Initiation Grant (grant #00129) REF: DVC/RDI/2/7 IV (72).

I would also like to thank and appreciate my chemistry colleagues for helping me when I needed them. Their input has helped me to complete my research and call it a thesis. A very big thanks to the chemistry technicians for always being there for me when I needed help with operating instruments and requesting materials. Thanks to the BIUST sign language interpreters who helped by translating language for me. A big thanks to Botswana Society For the Deaf for playing a part in providing an interpreter for me during presentations.

Finally, thanks to my family and friends for the support, my children for motivation and Sedilame Manyepedza and Sekgabo Maruping for always being there for me. Thanks to my housemate Mrs Eniah Serame for always encouraging me to work hard and always helping me at home. Thanks to Robert Gembo, Lesego Musutlha, Moreetsi Manake and Obakeng Makabi for helping me where I needed them. Above all, glory to God.

DEDICATION

This thesis is dedicated to my late sister Kadzana Mbochwa, and my kids Mofenyi Ryan Elias, Unashe Dodo Manyepedza and Baoliki Mpho Mbochwa.

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LIST OF ABBREVIATIONS

FA – Fly Ash

CR – Congo Red

MB – Methylene blue

XRD – X-ray diffractometer

XRF – X-ray fluorescence spectroscopy

SEM – Scanning Election Microscopy

FTIR – Fourier transform infrared

TPS – Thermal Power station

TGA – Thermogravimetric analysis

ICP – MS Inductively coupled plasma mass spectrometry

LOI – loss on ignition

ABSTRACT

As the world population grows, factories such as textile, paper, food colouring, and leather industries are using large amounts of dyes. Small amounts of dyes can pollute large sources of water used for domestic consumption and agricultural sectors. If the dyes are not treated before being discharged, they can cause harm to the human body and the environment. Various approaches such as chemical, physical, and biological techniques, have been studied in connection with the removal of dyes from wastewater. The adsorption method has been favored in the removal of dyes since it is eco-friendly, low-cost, has high efficiency, and is easy to operate. In this research, geopolymers synthesized from fly ash (FA) from the Morupule thermal power station were used in the adsorption of cationic and anionic dyes which are pollutants found in wastewater. Fly ash is a fine waste product produced by burning coal and its high in silica and alumina. The main aim of this study was to synthesize fly ash-based geopolymers which were employed in the removal of cationic and anionic dyes which have serious environmental consequences such as pollution of water and thus are a great health hazard. Four geopolymers were synthesized using Na_2SiO_3 and H_2O_2 which were then studied for the adsorption of methylene blue (cationic dye) and Congo red dyes (anionic dye). Factors that affect the adsorption capacity and removal efficiencies such as time, concentration, dosage, and pH were investigated to find the most active geopolymers. The morphology, crystallography, and identification of major chemical components of fly ash were performed by scanning electron microscope (SEM), X-ray diffractometer (XRD), and X-ray fluorescence spectrometer (XRF), respectively. The Uv-visible spectroscopy was used to monitor the adsorption process while thermogravimetric analysis (TGA) techniques were used to study the thermal degradation of fly ash. The Brunauer-Emmett Teller (BET) analysis was used to calculate pore size distributions, pore volume, and surface area. Fourier transform infrared (FTIR) spectra were obtained and showed the presence of OH, Si-O-Si and S-O-Al bands. Four prepared geopolymers (12-M- Na_2SiO_3 , 10-M- Na_2SiO_3 , 12-M- H_2O_2 and 10-M- H_2O_2) and raw fly ash at the mass of 3 g adsorbents and 0.3 L of dyes were studied to determine the adsorption isotherms and adsorption kinetic models. The Langmuir isotherm, and pseudo-second-order model were favoured as they show high correlation coefficient values, R^2 , and the calculated Q_m values are close to experimental values. The maximum adsorption capacity of methylene

blue (MB) using Na_2SiO_3 -geopolymer was 17.7 mg/g which was nearly identical to the experimental value (16.3 mg/g), while Congo red (CR) achieved 3.8 mg/g using Na_2SiO_3 -geopolymer compared to 4 mg/g experimental value. The highest removal efficiency of MB using Na_2SiO_3 -geopolymer was 90 % and 84 % using H_2O_2 -geopolymer. The Q_e of CR based on both geopolymers displayed a low removal efficiency, but high removal efficiency using raw FA (94 %).

CHAPTER 1

1.0 Introduction

1.1 Background of the study

With the advancement of technology all over the world, coal waste materials have become an important source of economic growth, generating electricity ([Tiwari et al. 2016](#)). Coal is an organic rock enriched in carbon and with minor concentrations of hydrogen, oxygen, sulphur, nitrogen, and water ([Vassilev and Tascón 2003](#)). Burning coal produces hazardous solid wastes such as fly ash and gaseous wastes such as NO_x, CO₂, and SO₂ which are toxic to the environment ([Means 2021](#)). Coal is a non-renewable source of energy. There are four major types of coal which are bituminous (high-heating coal), sub-bituminous (low-heating coal), lignite (low-grade coal), and anthracite (hard coal), ([Rasheed et al. 2015](#)). Coal-fired thermal plants are the world's largest in power generation ([Temuujin et al. 2011](#)). Coal-fired power plants' by-products' annual disposal estimate went high up to 600-750 million tons worldwide ([Ferrarini et al. 2016](#), [Ahmaruzzaman 2010](#)). Every year, tons of fly ash are produced worldwide. Toward 2019, the world had reached 800 tons of fly ash produced ([Das and Rout 2021](#), [Helong et al. 2020](#)). It has been revealed that coal fly ash from coal-fired power stations is the most important waste of electricity production ([Harja et al. 2009](#)). Waste disposal can be environmentally unfriendly ([Jha and Badhamagar 2012](#)), and pose a serious threat to people, land, and water resources ([Sumathi et. al., 2010](#), [Khan., 2014](#)).

Fly ash (FA) is a fine powdered waste product generated from thermal power stations (TPS) burning coal, or biomass or co-combustion ([Seslija et al., 2016](#), [Stanislav and Vassilev 2005](#)). As a residue of TPS, fly ash is known as problematic solid waste all over the world because it contains heavy metals and the current disposal methods of the waste are not environmentally friendly. ([Dwivedi, and Jain. 2014](#), [Uzbas and Aydin 2019](#)). Enormous quantities of fly ash are produced in many industries which use pulverized coal as a fuel source ([Tiwari et al., 2016](#), [Liu et al. 2019](#)). Fly Ash has an

excellent particle size, porosity, and specific surface area, making it suitable for use as low-cost sorbent material (Ge et al. 2018). Fly ash also contains siliceous materials (Wattimena et al. 2017, Hower et al. 2017) and can form cement in the presence of water. Fly ash is classified into two classes, which are class C fly ash and class F fly ash (Zerfu and Ekaputri., 2015). Class F fly ash contains low calcium, and class C fly ash contains high calcium content (Franus et.al. 2014, Widayanti et al. 2018). FA can again be classified as wet fly ash or dry fly ash. Class F fly ash is produced mainly from anthracite and bituminous coal types while class C fly ash is produced by burning lignite or sub-bituminous coal types (Tiwari et al., 2016).

Previous research (Tiwari et al., 2016., Harja et al., 2009) stated the benefits of FA utilization as opposed to disposal in ash dumps and pits. FA is mostly used at cement industries as pozzolanic material (Siddique., 2004) for manufacturing Portland Pozzolana Cement (PPC). It is also used in the ceramic industry, road base stabilization, soil stabilization, concrete manufacturing, pavement, and wastewater treatment (Rishi et al., 2012, Pandey., 2020). Doing this research, would aid in recycling waste fly ash by removing cationic and anionic dyes from wastewater using fly ash and fly ash based geopolymer.

The expansion of manufacturing industries has resulted in an increase in the production and use of dyes. Dyes are among the most concerning pollutants in wastewater pollution (Zalfika et al. 2017). If the dye wastewater is not treated immediately, it may be harmful to human health and environment because it is a source of water and air pollution (Taufi et al. 2018, Zhou. et al. 2020, Li. et al. 2019, Shaban et al. 2018). Classification of dyes is based on chemical structures and charges such as cationic, anionic, and non-ionic (Kandisa et al. 2016, Yagub et al. 2004). Dyes are used to produce colour for products in industries such as printing, textiles, cosmetics, foods, and paper industries (Mall. 2005). Manufacturing industries such as the printing and textiles industries produce dyes with a high concentration that leads to toxic wastewater and an unhealthy environment. Since dyes are water-soluble, it produces intense colour in water which causes environmental problems (Li. et al. 2006). The

uses of dyes can be harmful to the environment because they decrease light penetration, which in-turn affects photosynthesis process and has an adverse effect on the entire ecosystem ([Lellis et. al 2019](#)). Dyes can make people sick as they evaporate in the air since it can get absorbed through the skin or be breathed and cause major respiratory issues ([Kant 2021, Lellis et al. 2019](#)). Methylene blue solution is a cationic dye solution used in different industries such as textiles, paper, plastic manufacturers, and leather ([Alouani et al. 2019](#)).

Our research involves the characterization of FA and the production and characterization of geopolymers. The current study goal is to identify the potential uses of the FA such as producing adsorbent materials, that reduce the amount of fly ash that ends up the ash dump at Morupule thermal power station, which we will use to remove cationic and anionic dyes from synthetic water.

1.2 Problem statement

Fly ash disposal from coal combustion has become an area of greater concern as fly ash is environmentally unfriendly and could be a major risk to land and water resources ([Temuujin et al., 2011, Yao et al., 2015](#)). On the other hand, industries produce lots of dyes which cause water contamination that pose danger to human health and the environment. List below are research questions.

- i. What are the chemical and physical characteristics of fly ash?
- ii. What are the effects of system parameters on the synthesis of geopolymers?
- iii. What are the adsorption properties of geopolymers synthesized via different methods?

1.3 Objective

The main objective of the research is to identify the potential uses of the FA materials as opposed to the current disposal methods of ash dumps at Morupule power station,

Botswana. The FA will be used to synthesize FA-based geopolymers which will be employed to remove cationic and anionic dyes which have serious environmental consequences such as water pollution and a great health hazard. The specific objectives include to:

- i. Characterize fly ash
- ii. Prepare geopolymers using fly ash
- iii. Characterize prepared geopolymers in terms of crystallinity using x-ray diffraction (XRD), morphology using a scanning electron microscope (SEM), chemical composition (XRF), and chemical properties such as organic and inorganic groups (FTIR).

1.4 Justification of the study

As the world population increases, manufacturing factories' demands become high. Manufacturing factories play a big part in the development of the economy and employment worldwide. This has resulted in an increase in textile and paper-making factories which produce and use a high number of dyes. When the dye wastes are not disposed of properly that can endanger human health and the environment. On the other hand, electricity demand is growing worldwide. As more coal is used, it produces millions of tons of waste materials that are unfriendly to the environment. Although fly ash is used in Portland Cement Concrete (PCC) and roads, large amounts remain unutilized. As the amount of coal fly ash increases, some of the fly ash is dumped in landfills ([Jaturapitakkul 2004](#)) causing diseases such as cancer. With more research carried out, it was discovered that fly ash can be used as a low-cost materials for the adsorption of dyes from wastewater and gases in the atmosphere ([Ahmaruzzaman 2010](#)), compared to the previous methods of disposal which is a risk to public health and the environment ([Lemly 2017](#)).

This work involves the use of fly ash in the environmental remediation as opposed to dumping in landfills and ash dumps. It also contributes to the knowledge of the synthesis of highly porous geopolymers, formulation strategies for different foamed

highly porous geopolymers and the effects of parameters on geopolymers synthesis. With this research, the synthesis of highly porous polymeric materials from fly ash is investigated and used in the process of adsorption of cation and anionic dyes, contributing to a clean environment by the removal of dyes in wastewater. When trace elements are high in fly ash, it poses a threat to the environment and human health ([Dai and Finkelman 2017](#)).

CHAPTER 2

2.0 Literature Review

2.1 Dyes

A dye is a colour substance mainly used in different factories such as textiles, foods, printing, and cosmetics (Kandisa et al. 2016, Mall. 2005). Dyes are useful in many manufacturing industries as they produce colour. It is critical that the dye in wastewater be treated before it can be disposed of because it will harm the environment. Not only will it harm the environment when left untreated, but it can also cause harmful effects on humans as it causes diseases such as cancer, difficulty in breathing and allergic reactions (Rehman et al. 2018). With the advancement of technology such as textiles, food processing, plastics, etc., it is estimated that more than 7×10^5 tons of dyes are produced worldwide each year (Rehman et. al 2018). To date, over 100,000 different types of dyes have been produced from various industries and classified as cationic dyes, non-ionic dyes, reactive dyes, and anionic dyes (Taufiq et al. 2018, Li et al. 2019). Dyes are also classified based on their uses, chemical structure, and application (Gurses et al. 2016). Dyes have become a major source of water pollution. Table 1 shows examples of textile dyes that are commonly discharged in wastewater.

Table 1. Major types of dyes ([Liu et al. 2019](#), [Benkhaya et. al 2020](#))

Types of dye	Background
Direct dye	• Applied in celluloses, leather, nylon • It's neutral • Can be soluble in water
Reactive dye	• Applied in silk, wool, printing, nylon • Requires high temperature
Vat dye	• More expensive • Water-insoluble • Used in hemp fabrics, cotton
Disperse dye	• Low solubility in water • Used in acetate, cotton, papers
Acid	• Neutral and good water-soluble • Applied on paper, silk, wool, inks
Basic	• Applied on polyester, paper, inks • Dissolves in water • It's a cheap dye

2.2 Wastewater

Industrial growth has become a major source of water contamination as industries release many pollutants, including dyes into the environment. Water pollution has become a significant threat to both humans and the environment. To protect humans and the environment, wastewaters need treatment before disposal. There are various major sources of pollutants in wastewater such as heavy metals, dyes, pesticides, and surfactants ([Al-husseiny and Ebrahim., 2021](#)).

Removal of dyes from wastewater have been investigated using techniques such as physical, biological, and chemical. Different methods such as aerobic/anaerobic

treatment, membrane separation, ozonation, flocculation, chemical oxidation, coagulation, and photocatalytic degradation, and adsorption have been investigated for dye removal from wastewater ([Azari et al., 2020](#), [Mor et al., 2018](#), [Ling et al., 2019](#), [Qu et al. 2021](#)). The most promising method in wastewater remediation emerged as adsorption because of its low cost, high efficiency, ease of use, low energy requirements and environmental friendliness ([Azari et al., 2020](#), [Siyal et al., 2020](#)). Activated carbon (AC) is the most commonly used adsorbent for dye removal even though it is expensive and difficult to use ([Zhou et al., 2020](#)). Low-cost adsorbents have been investigated for the removal of dyes from wastewater. The most studied low-cost adsorbents for the removal of wastewater are fly ash, husk ash, and biomass-based materials ([Bulgariu et al. 2019](#), [Daudi et al., 2021](#), [Fitrian et al., 2020](#)). Table 2. presents various methods for wastewater treatment that make use of low-cost, readily available adsorbents.

Table 2. Methods of treatment of dye-polluted water as reported in the literature.

Methods	Description
Physical methods	In comparison to other methods such as biological and chemical methods, physical methods prove to be the least expensive method for removing pollutants from wastewater. Physical methods include adsorption, floatation, coagulation, and flocculation (Ge et al. 2018).
Chemical methods	Chemical treatment methods are the most used common methods in wastewater treatment. Chemical methods include electrochemical treatment methods, chemical precipitation, and ionic change (Salgot et al. 2018). Although removal of pollutants from wastewater is highly efficient (Mushtaq 2018), there is a disadvantage as a larger amount of chemicals are used in the process of treating wastewater leading to an excessive amount of chemicals in the environment and it also can be a high-cost method (Gembo et al. 2021).
Biological methods	Biological methods degrade wastewater through natural cellular process that relies on bacteria and other small organisms. Since biological methods involve the use of bacteria, algae, fungi, and yeast, it makes it economically feasible and environmentally friendly (Karthik et al. 2014 , Bhatia 2017). Although, biological methods are both environmentally friendly and economically feasible, they have low removal efficiency (Gembo et al. 2021).

2.2.1 Adsorption process

Adsorption can be a physical and chemical process ([Qayoom et al. 2017](#)), a typical phase transfer process for removing substances from fluid phases. Adsorption is a high-quality wastewater treatment method for removing dissolved organic pollutants such as dyes. Adsorption is a popular technique because of its low cost, simplicity, and efficiency and the use of materials from agricultural, natural sources and industrial waste ([Kandisa et al. 2016](#), [Said et al. 2014](#), [Shaban et al. 2018](#), [Shi 2019](#)). Factors affecting adsorption are temperature, solution pH, adsorbate dose, contact time, initial dye concentration, surface area, ratio, and particle size of adsorbate ([Azari et al. 2020](#), [Yagub et al. 2014](#)).

Adsorption equilibrium studies provide information about the adsorbent's capacity. Adsorption equilibrium isotherm models like Langmuir, Freundlich, Temkin, and Dubinin-Radushkevich are investigated to study adsorption isotherms. The isotherm's shape is determined by the adsorption mechanism and associated sorption energy. Linear regression is the most common method for determining the best-fit isotherm model and calculating associated parameters ([Emenike et al. 2016](#), [Han et al. 2005](#), [Kandisa et al. 2016](#)). Adsorption kinetic studies describe the process of determining the rate of solute uptake. Several kinetic models such as pseudo-first order, pseudo-second order, and intraparticle diffusion models are used for studying adsorption kinetics ([Yagub et al. 2014](#), [Nandi et al. 2009](#)). The effects of parameters were studied by different authors and listed in Table 3 while Table 4 compares adsorption capacity.

Table 3. Effect of parameter on adsorption study

Parameter	Finding	References
Time	Efficiency removal increase as time increase then continue to rise slowly until equilibrium is attained. Q_t increases as time increases	Novais et al. 2019
pH	The increase in pH decreases efficiency removal in adsorption of anionic surfactants.	Siyal et al. 2019
Concentration	A decrease in concentration of analytes leads to an increase in removal efficiency. An increase in concentration leads to an increase in Q_e .	Shaban et al. 2018 Kaewmee et al. 2020
Dosage	The dosage effect depends on the concentration. Increase in dosage led to decrease in efficiency removal at high concentrations.	Buema et al. 2021

Table 4. Comparison of different reported literature on adsorption capacity.

Dye	Adsorption capacity (Q _e) (mg/g)	References
Methylene blue	15	(Novais et al., 2018)
Methylene blue	15.4	(Novais et al., 2019)
Methylene blue	37	(Novais et al., 2018)
Methylene blue	43.5	(Alouani et al., 2018)
Methylene blue	79.9	(Alouani et al., 2018)
Methylene blue	36.9	(Shaban et. al., 2018)
Methylene blue	50.7	Liu et al., 2018
Congo red	14.5	Shaban et. al., 2018

2.3 Geopolymers

Geopolymer is a three-dimensional material ([Anggarini and Sukmana 2016](#)) that is composed of a polymeric Si-O-Al framework with SiO₄ and AlO₄ tetrahedral framework ([Alehyen et. al. 2017.](#), [Strydom 2002](#); [Wattimena et al., 2017](#)). The term “geopolymers” was first introduced by Joseph Davidovits as the mineral polymer, resulting from geosynthetic or geochemistry ([Wattimena et al., 2017](#); [Swanepoel and Strydom. 2002](#)). Geopolymers are materials with high-temperature resistance, are non-polluting to the environment and have low gas emissions during processing ([Sindhusha and Rao., 2017](#), [Hamidi et. al., 2016](#)). Geopolymers that have good mechanical properties like Portland cement have attracted many researchers as they are believed to be less costly and environmentally friendly ([Roviello et. al., 2013](#)). Geopolymers can be synthesized using materials such as fly ash, red mud, biomass-based fly ash, Kaolin, and metakaolin ([Fitriani et. al 2020](#)). The synthesis of geopolymers is done using NaOH or any other alkaline activator at a low temperature.

Synthesis of geopolymers is affected by several parameters such as the mass-to-volume ratio, the ratio of fly ash to sodium silicate, reaction time, temperature,

concentrations, pH, dosage, foaming agents and amount of sodium silicate, which need to be monitored during synthesis ([Anggarini and Sukmana 2006.](#), [Darmayanti et al. 2019](#); [Jha and Budhamagar 2012](#)). The potential applications of geopolymers include as a replacement for Portland cement, for advanced high-tech composites and as an immobilization system for heavy-metal containment ([Jha and Budhamagar 2012](#)).

2.3.1 Synthesis of porous geopolymers

Geopolymers are synthesized in three steps at room temperature. The first step in the geopolymer process is the preparation of activation agents. Step 2: Mixing fly ash with activation agents in a specific ratio to achieve good homogenization. Step 3 entails moulding and curing prior to use ([Novas et al. 2017](#), [Feng et al. 2014](#), [Kioupis et al. 2018 and das 2021](#)). Placing samples in the oven is important because it allows the sample to completely dry and sieves it into small particles, resulting in a larger pore size ([Siyal et al. 2019](#), [Alouani et al. 2019](#)). A high temperature was used in the synthesis of geopolymer, which resulted in a large surface area and pore volume. Low temperatures boost the strength of geopolymers ([Das and Rout 2021](#)). The mineralogical composition of raw materials influences structure and properties of geopolymers ([Kioups et al. 2018](#)).

CHAPTER 3

3.0 Materials and Methods

3.1 Introduction

This study was conducted at Botswana International University of Science & Technology (BIUST) while samples of fly ash (raw material) were obtained from Morupule Power station, in Palapye, Botswana. FA was used as an aluminosilicate source in the synthesis of geopolymers. Instruments used to analyze properties such as the particle size, specific area and chemical and mineralogical composition of FA samples includes XRD, XRF, FTIR, SEM, TGA, and Uv-Visible spectroscopy. This chapter also discusses the materials and methods used in the experiment. The synthesis of geopolymers is discussed in this chapter as well as the adsorption tests.

3.2 Chemicals and Materials

The chemicals used in this experiment were analytical-grade reagents and are listed below:

- Sigma Aldrich: Methylene blue ($C_{16}H_{18}ClN_3S$, 98%), Sodium Hydroxide (NaOH, 98%), 0.45 μm pore sized Whatman filter papers, Congo red ($C_{32}H_{22}N_6Na_2O_6S_2$), Sodium silicate (Na_2SiO_3)
- Rochelle chemical : Sodium Nitrate ($NaNO_3$, 99.8%)
- ACE: hydrogen Chloride (HCl, 32%)
- SAAR: Hydrogen peroxide (H_2O_2 34.01%)

3.3 Instruments used in characterization

X-Ray Diffraction (D8 advanced Bruker, Germany) was used to determine the mineralogy composition in the Fly ash and geopolymers while Portable X-Ray Fluorimeter (Olympus Delta) was used to determine the chemical composition present in fly ash. A software named Match! was also used to determine the percentage of chemical composition from XRD data. Fourier Transform Infrared Spectroscopy

(Bruker Vertex 70V) was used in the research to understand the surface groups found in fly ash and geopolymers. The FTIR spectra were collected at the wavelength between 4000 cm^{-1} and 400 cm^{-1} , resolution of 4 cm^{-1} with a sample scan at 64 scans. A thermogravimetric analysis instrument was run to determine the thermal degradation profile of fly ash. UV-Visible spectroscopy (UV201, Japan) was used to measure the residual concentration of the dyes. Scanning Electronic Microscopy (Carl Zeiss FEGSEM Gemini 500) helped with the analysis of the surface morphology of fly ash and fly ash-based geopolymers. The Surface area, pore volume and pore size distributions were measured using Brunauer-Emmett Teller (Micromeritics 3Flex 3500 Chem-TCD Loop).

3.4 Leaching and characterization of fly ash

Leaching of fly ash was done using NaOH solution prepared from NaOH pellets. Different concentrations of 8, 10 and 12 M of NaOH solution were prepared. The leaching study was done to determine the amount of reactive aluminium (Al) and Silicon (Si) that would be available for geopolymer synthesis. Quantification of leached Al and Si indicates the amounts that are available for reaction. A given NaOH concentration was mixed with a given mass of raw FA in a flask (250 mL). The mixture was then stirred at a constant speed for 24 hrs at room temperature. The solution was then filtered using $0.45\text{ }\mu\text{m}$ filter paper to separate residues. The filtrate was heated in an oven at a constant temperature of $40\text{ }^{\circ}\text{C}$ for 2 hrs to allow it to dry up. After the heating process, it was allowed to stand at room temperature to completely dry. Once it had completely dried up, the white crystals formed were analyzed for the presence of Si and Al. The analysis was done using XRD and XRF to determine mineralogy and ICP-MS helped with the amount of Al and Si present in fly ash.

3.5 Preparation of synthetic wastewater

3.5.1 Methylene Blue

A methylene blue dye (MW 319.85, $C_{16}H_{18}ClN_3S$) was used in the adsorption experiments. A 1 g sample of methylene blue powder was added to 1000 mL of Deionized (DI) water in a volumetric flask to make a 1000 mg/L stock solution. From the prepared 1000 mg/L solution, different concentrations were prepared by diluting 1000 mg/L and used in the experiment. Methylene blue dye appears brown as a solid powder, but it is blue when dissolved in water with a wavelength of maximum absorbance of 661 nm.

3.5.2 Congo Red

Congo Red (MW 696.665 g/mol, $C_{32}H_{22}N_6Na_2O_6S_2$) is an azo dye. It's a red powder that dissolves in water. To prepare a stock solution, 1 g powder was dissolved in 1000 mL DI water. The solution was then used to prepare different concentrations assigned to the experiment. Congo red has a wavelength of maximum absorbance of 498 nm.

3.6 Synthesis of Geopolymers

The geopolymers were synthesized using sodium hydroxide (NaOH) and sodium silicate (Na_2SiO_3). NaOH was used to prepare the alkaline activator (10 and 12 M solution NaOH). Alkaline activator was prepared by mixing NaOH solution with Na_2SiO_3 and foaming agent hydrogen peroxide (H_2O_2). The synthesis of porous geopolymer was carried out at room temperature. The fly ash used in this project came from the Morupule coal power station. To remove moisture, 90 g of raw fly ash was dried in an oven at 105 °C for 2 hours. It was then allowed to cool for 24 hours at room temperature. 20 g of heated fly ash was weighed and placed in a yoghurt container (replacing mould plastic). The FA was then treated with 12.5 mL of DI water and 11.5 mL of 12 M NaOH solution and then stirred for 2 minutes to give a complete homogenization. 11.5 mL of Na_2SiO_3 solution was added to the mixture and continually stirred for 1 minute (Na_2SiO_3 -geopolymer). It was labelled 12-M- Na_2SiO_3 . The same

procedure was repeated using 10 M Na_2SiO_3 and labelled 10-M- Na_2SiO_3 . The same procedure was repeated by replacing Na_2SiO_3 with 5 mL of 3% H_2O_2 (H_2O_2 -geopolymer) and the mixtures labelled 12-M- H_2O_2 and 10-M- H_2O_2 respectively. The mixtures were then allowed to stand at ambient temperature and pressure for 24 hours to allow them to cure. The samples were then placed in an oven at 55 °C for 24 hours to allow them to dry. It was then cured at room temperature for 21 days before analysis and the adsorption test.

3.7 Adsorption Test

Adsorption tests were carried out to study the effect of dosage, contact time, initial concentration, and pH. The adsorption of methylene blue and Congo red using FA-based geopolymers and raw FA were done at room temperature using five clean 1000 mL beakers. A volume of 300 mL of 50 mg/L – 300 mg/L concentration of Methylene blue dye was added to a flask with weighed geopolymers of 3 g each. The flasks were labeled 12-M- Na_2SiO_3 -MB, 10-M- Na_2SiO_3 -MB, 12-M- H_2O_2 -MB, 10-M- H_2O_2 -MB, and Raw FA-MB. A shaker (Stuart orbital shaker SSL1) was used for shaking the mixture at a constant speed of 180 rpm for 90 minutes to attain equilibrium. A small portion of the mixture (3 mL) was extracted at a given time from 5 minutes to 90 minutes and centrifuged at 2500 rpm for 10 mins to separate the solid phase from the liquid phase. Following centrifugation, the supernatant was withdrawn using a syringe and analyzed on a Uv-visible spectrometer to determine the amount of dye adsorbed. The same procedure was repeated using Congo red and samples labelled 12-M- Na_2SiO_3 -CR, 10-M- Na_2SiO_3 -CR, 12-M- H_2O_2 -CR, 10-M- H_2O_2 -CR, and Raw FA-CR.

CHAPTER 4

4.0 Results and Discussion

4.1 X-Ray diffraction

An XRD powder D8 Advanced X-Ray Diffractometer was used to determine the mineralogical composition for both raw FA and the synthesized geopolymers and the results are shown in Fig. 1 and 2. The XRD was operated at a voltage of 40kV and current of 40mA and Cu K α ($\lambda = 1.54439$). The main crystalline phase found in fly ash were quartz (SiO $_2$), mullite (3Al $_2$ O $_3$.2SiO $_2$), Calcite (CaCO $_3$) and Gypsum (CaSO $_4$.2H $_2$ O). A shift of the baseline from zero may be indicative of amorphous phase [Qiu et. al \(2017\)](#). There is no significant difference in the XRD patterns of raw fly ash and H $_2$ O $_2$ -geopolymers. Much of the quartz is the melting quartz residue left over from the burning of coal, and its crystal structure is still in a low-temperature state. Mullite is the product of in-situ disintegration and phase transition of clay minerals such as kaolinite during the burning of coal. Strong quartz, calcite, and gypsum characteristic peaks and a small amount of mullite characteristic peaks can be detected in the spectra of the prepared materials. The appearance of the CaCO $_3$ characteristic peaks is caused by the addition of limestone during the desulfurization process. Fig. 3 shows the XRD pattern after leaching which indicate that leaching did not change the crystal structure of the materials because the position of the diffraction peaks did not change, but only reduction in intensity. It can be seen in 8M NaOH that the peaks increased compared to 10M NaOH and 50 mL H $_2$ O. This could be due to dissolution and recrystallization which affects the crystallinity of the materials depending on the leaching agent.

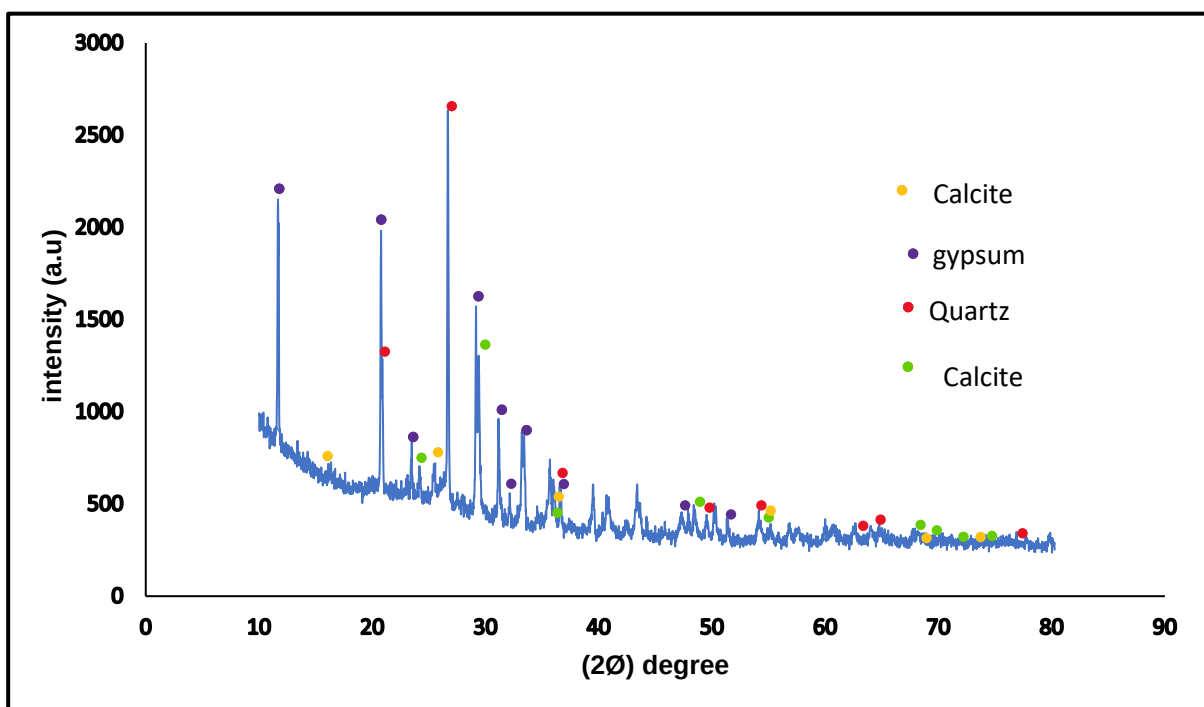


Figure 1. XRD patterns of raw fly ash

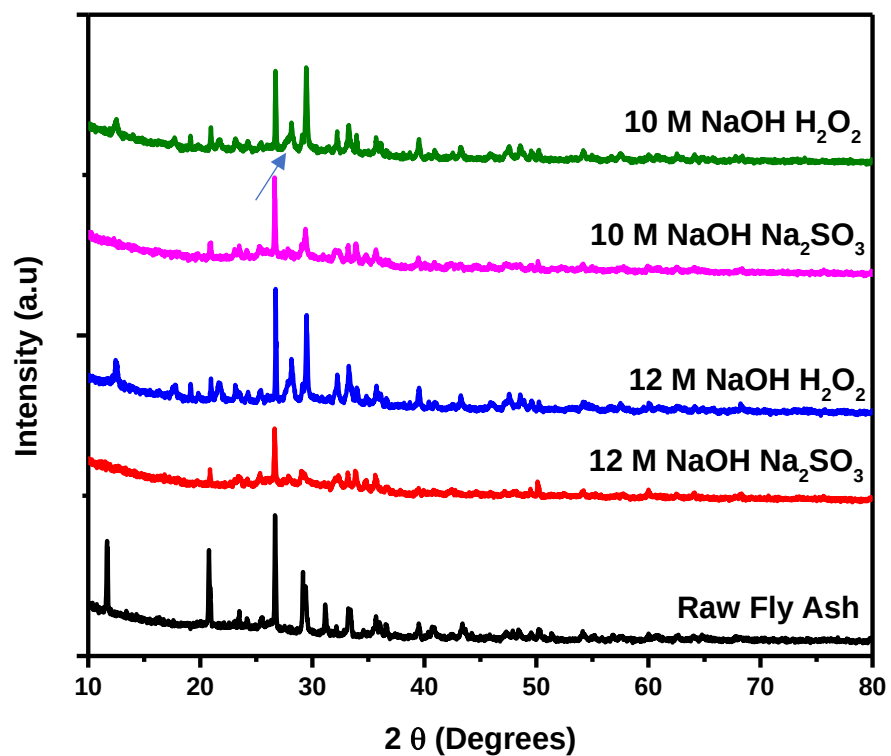


Figure 2. XRD patterns of raw fly ash and fly ash based geopolymers

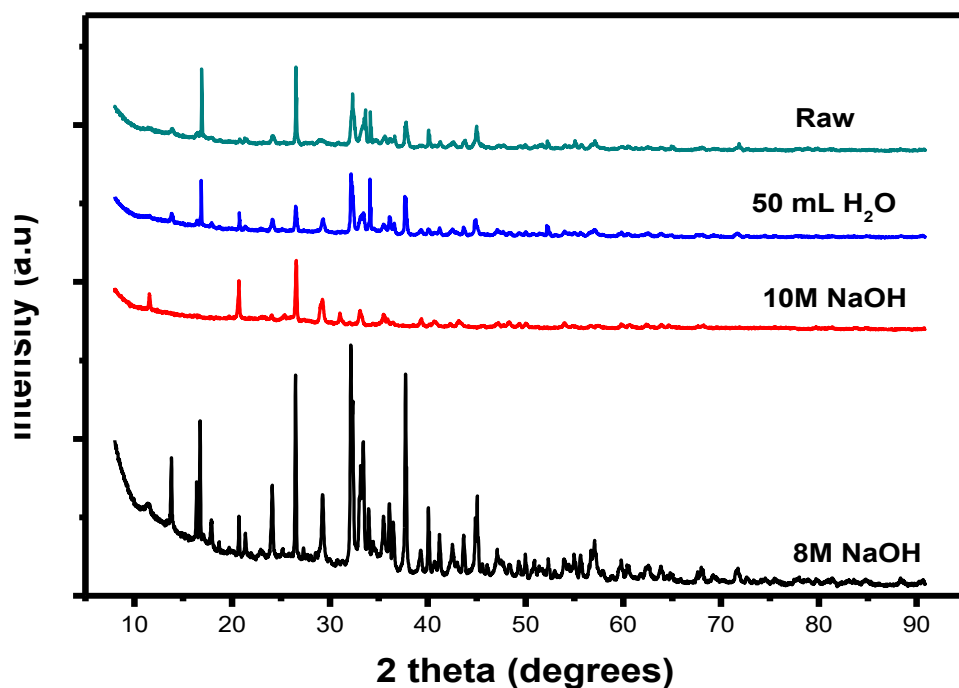


Figure 3. XRD patterns of leached fly ash

4.2 X-Ray Fluorimetry (XRF)

The chemical composition of fly ash and geopolymers were analyzed using X-Ray Fluorimeter (XRF). Some of major components presented in fly ash are silica (SiO_2), alumina (Al_2O_3), Sodium Oxide (Na_2O) and Calcium Oxide (CaO). Some of the minor elements found in fly ash and geopolymers are Al, Si, S, Fe, and Ca. XRD was also used to confirm the presence of silica and alumina which showed crystalline phases such as mullite, quartz, and calcite. The loss on ignition (LOI) values were high in 10-M- Na_2SiO_3 compared to 12-M- Na_2SiO_3 and higher in 10-M- H_2O_2 compared to 12-M- H_2O_2 and the fly ash raw show low LOI compared to geopolymers. Table 5 shows chemical composition of fly ash and fly ash based geopolymers while trace elements of fly ash and fly ash based geopolymers are presented in Table 6.

Table 5. Chemical composition of raw fly ash and geopolymers

	Samples (%)				
Major elements	Raw FA	12-M-Na ₂ SiO ₃	10-M-Na ₂ SiO ₃	12-M-H ₂ O ₂	10-M-H ₂ O ₂
SiO₂	33.500	28.5	27.2	24.6	16.8
Na₂O	0.440	13.7	15.5	15.5	9.36
Al₂O₃	20.5	9.560	9.33	15.1	10.7
CaO	10.780	5.42	5.0	8.36	5.48
Fe₂O₃	6.394	3.161	3.039	4.965	3.273
SO₃	6.010	2.87	3.090	4.92	3.130
MgO	1.560	0.783	0.778	1.21	0.835
TiO₂	1.310	0.586	0.558	0.975	0.633
K₂O	0.277	0.215	0.147	0.297	0.157
MnO	0.114	0.046	0.05	0.090	0.051
Cl	0.043	0.043	0.046	0.058	0.035
SrO	0.055	0.027	0.023	0.041	0.026
ZrO₂	0.043	0.028	0.05	0.059	0.056
Sb₂O₃	-	-	0.014	0.026	0.017
LOI (%)	19.23	35.080	35.137	23.786	49.455

Table 6: Trace and minor elements present in fly ash and geopolymers

	samples				
Metal present (%)	Raw FA	10-M-Na ₂ SiO ₃	12-M-Na ₂ SiO ₃	10-M-H ₂ O ₂	12-M-H ₂ O ₂
Al	3.27	1.55	1.35	1.87	1.81
Si	5.9	5.6	3.38	3.97	3.42
S	1.5451	0.7131	0.8236	0.7973	0.5428
K	0.1193	0.074	0.0621	0.088	0.0728
Ca	9.21	4.54	4.16	4.58	4.54
Cr	-	0.017	0.011	0.025	0.035
Mn	0.0637	0.056	0.037	0.77	0.075
Fe	4.1433	2.43	2.0	2.39	2.1
Zn	0.0027	0.0031	0.0031	0.0021	-
Rb	0.0016	0.0009	0.001	0.0008	0.0008
Sr	0.0485	0.0252	0.0246	0.0256	0.0199
Y	0.0044	0.0023	0.0022	0.0022	0.0017
Zr	0.0328	0.0191	0.017	0.0157	0.0128
Nb	0.002	0.0012	0.0011	0.0009	0.0008
Ba	0.073	0.0317	0.0356	0.0236	0.0167
Ta	0.0051	0.0037	0.003	0.0032	-
Pb	0.0058	0.0032	0.0023	0.0024	0.0016
Th	0.0027	0.0016	0.0014	0.0014	0.001

4.3 Thermogravimetric analysis (TGA)

TGA is a thermal technology that helps with determining the mass change of samples over time and temperature. It can be described by chemical phenomena and physical phenomena. Fig. 4 shows the TGA analysis results of mass loss and loss on ignition (LOI). The curve line shows that the weight loss has three steps of mass loss. The first step takes place between 0 – 160 °C where dehydration takes place due to removal of water from fly ash while the second step takes place between 160 – 700 °C and it is where the burning of organic matter takes place as the crystallization water takes place breakage of polymeric structure groups. The last step that took place from 700 – 800 °C is where the decomposition of the sample happened as the weight loss of materials reached equilibrium due to the carbonation structure as polymer chain break down.

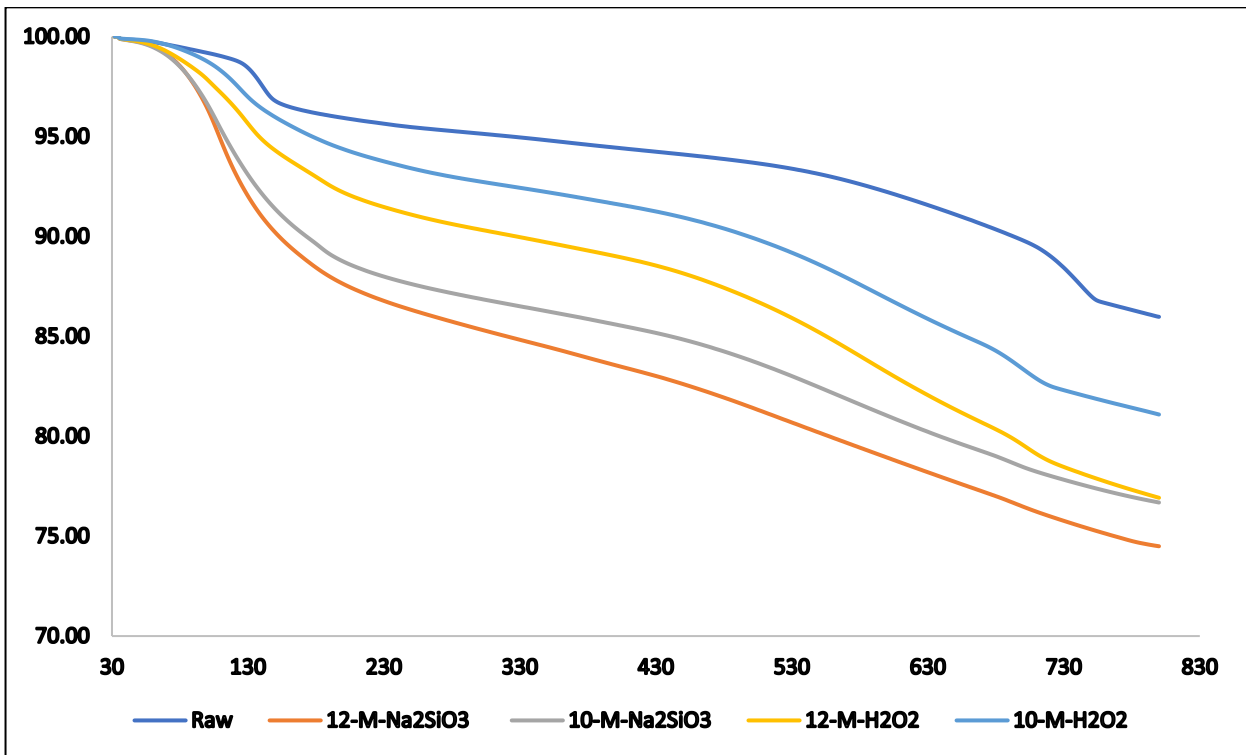


Figure 4. TGA analysis of fly ash and geopolymers

4.4 Fourier transform infrared spectroscopy

Figures 5 a and b show the FTIR spectra of fly ash leached in 10 M NaOH and distilled water respectively. The spectra were collected from 500 cm^{-1} to 4000 cm^{-1} to identify functional groups in fly ash. There were differences in bands between samples leached in NaOH and leached in water, in water leaching new bands were formed at 948 cm^{-1} (Si-O) from 1114 cm^{-1} (Si-O-Si). The presence of bending vibration Si-O-Al was evidenced by the peaks around 750 cm^{-1} and 1050 cm^{-1} for the sample in 10 M NaOH leaching while leached in water showed the presence of Si-O-Al at peaks of 620 cm^{-1} and 1260 cm^{-1} due to increased active ion leaching from low-calcium fly ash occurs as a result of NaOH activation compared to H_2O . A broad band was observed around 3500 cm^{-1} in fly ash leached in 10 M NaOH and a weak peak from leaching in water due to the stretching vibrations of hydrogen-bonded OH group in fly ash, this may be due to adsorbed water in FA leached in NaOH.

Figure 6 shows the FTIR spectra of raw fly ash and geopolymers. The spectra were collected between 4000 cm^{-1} and 400 cm^{-1} . The peaks of fly ash and geopolymers had bands at the same positions. The presence of OH was shown by a little peak of 3500 cm^{-1} (Liu et al. 2019). The bands appearing between 950 cm^{-1} and 1050 cm^{-1} indicated the symmetric bend on Si-O-Si and S-O-Al bands. The band of fly ash appeared at 1037 cm^{-1} indicates bending vibration of Si-O and new bands formed at 950 cm^{-1} indicates stretching vibration group Al-O which confirms the formation of a new product during geopolymers, similar finding by Qiu et al. (2017) and Petrus et al. (2019) in their research. The vibrational bands above indicate bending vibrations of O-Si-O and Si-O-Si confirming the presence of quartz, mullite, Calcite and Gypsum (Fauzi et al. 2016, Alaouani et al. 2018) which agrees with XRD results.

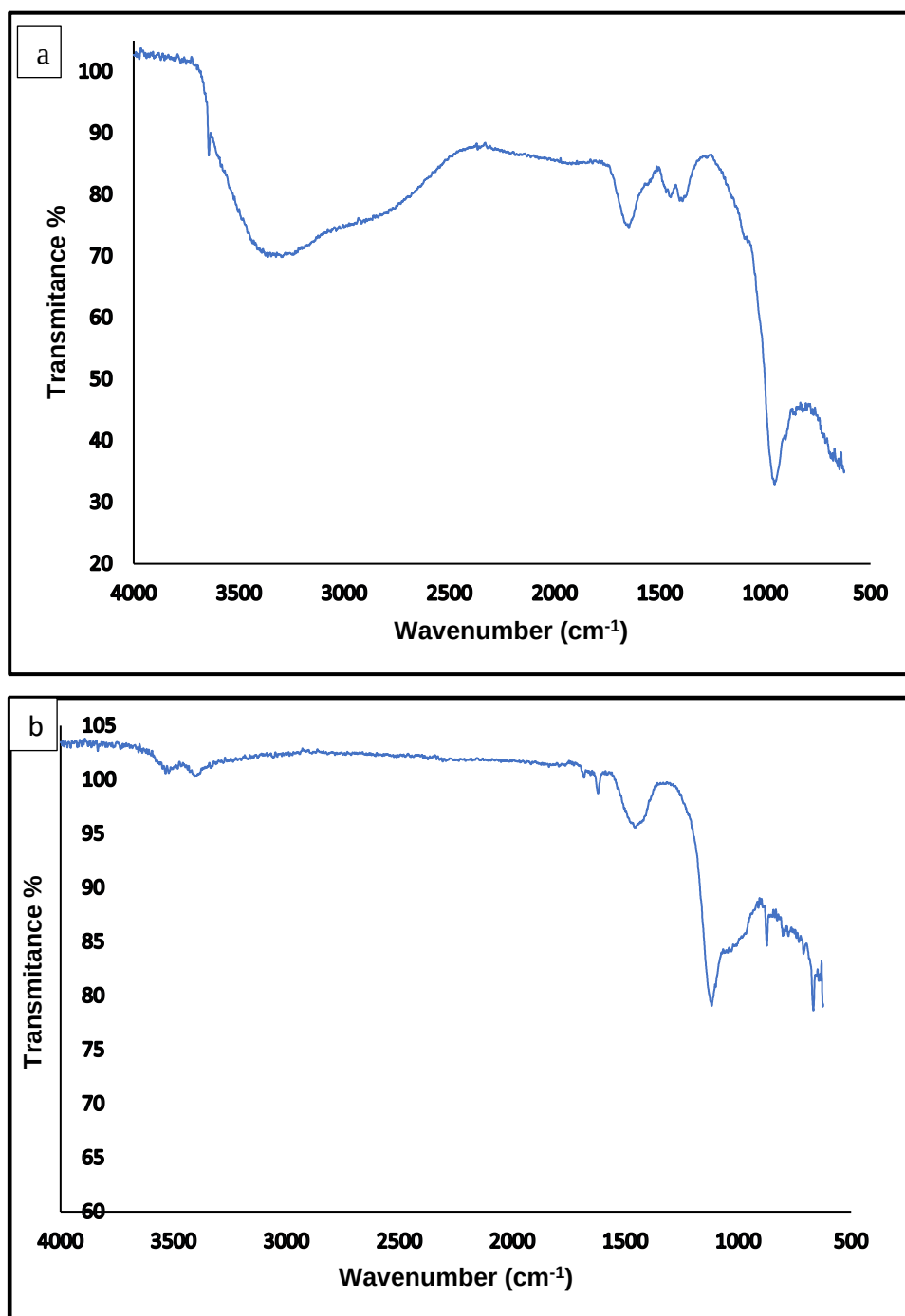


Figure 5. FTIR spectra of FA. (a) leached in 10M NaOH, (b) leached in distilled water

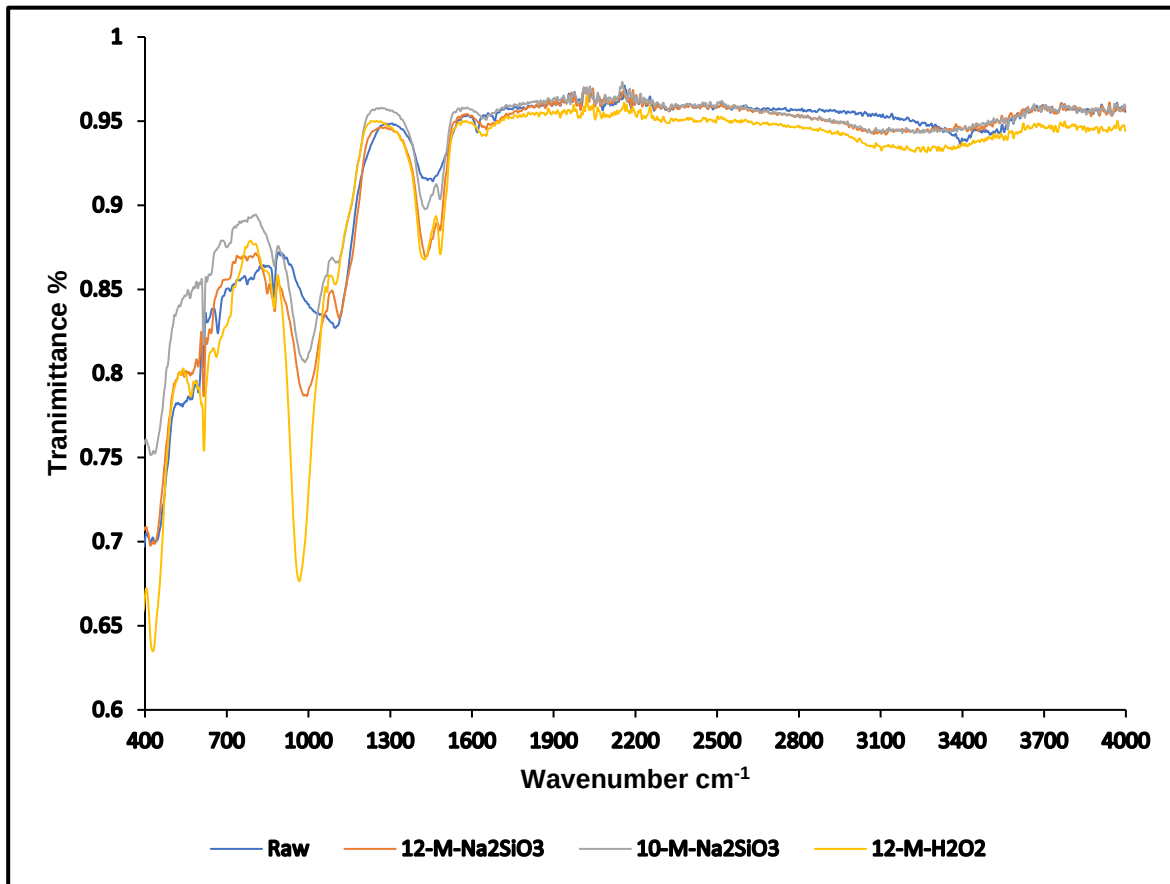


Figure 6. FTIR spectra of raw fly ash powder and geopolymers FA powder

4.5 Scanning Electron Microscopy

Scanning Electron Microscope (SEM) is a primary testing tool for in-depth micro area investigation. Its advantages include high resolution, wide depth of field, high magnification, and powerful stereoscopic vision. SEM photos are obtained at higher magnifications (5X - 1000000X) and with more clarity than those taken with optical microscopy (10X – 100X) (Wen et al., 2021). The SEM technique has been widely used in variety of fields. It is a useful method in the analysis of organic and inorganic materials on a nanometre to micrometre (μm) scale. SEM operates at a high magnifications of up to 300,000x and even 1000000 producing extremely precise images of a wide range of materials (Mohammed & Abdullah, 2018). In this study, SEM was used to examine the morphology of FA and FA-based geopolymers and

the results are displayed in Fig. 7. Fig. 7a shows that fly ash has irregular flakes shaped like broken glass and smooth rods microstructure which represent the crystalline phase. The micrograph shows some scattered pores on the surface of raw FA. After geopolymerisation the samples dimensions did not have homogeneous distribution with no certain shape as shown in Fig. 7b and c. Fig. 7d show low porosity due to a high reactive silica in geopolymers and H_2O_2 which is similar to findings by Oz et al. (2021).

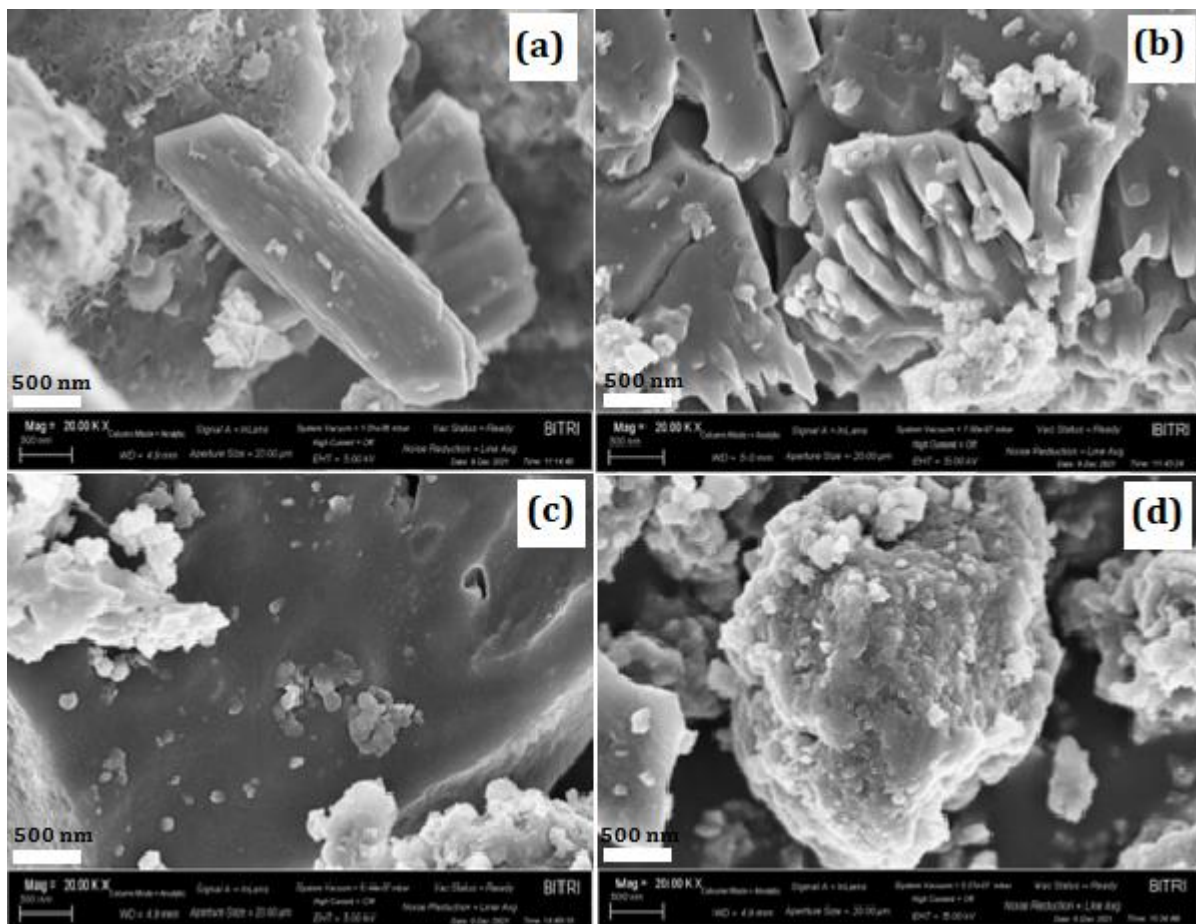


Figure 7. SEM images of raw fly ash (a), 10-M-Na₂SiO₃ (b), 12-M-Na₂SiO₃ (c), and 12-M-H₂O₂ (d).

4.6 Brunauer-Emmett-Teller (BET)

The BET surface area (S_{BET}) and the pores sizes of the synthesized FA-based geopolymer materials were determined by Micrometrics 3Flex 3500 Chem-TCD Loop instrument. The linearized form of the BET as shown in [equation 1](#) was applied to determine the surface area ([Naderi, 2015](#), [Zhou et al., 2019](#)):

$$\frac{P/P^0}{V_{ads}(1-P/P^0)} = \frac{1}{V_{m1} \cdot C_{BET}} + \frac{C_{BET}-1}{V_{m1} \cdot C_{BET}} \cdot \frac{P}{P^0} \quad 1$$

where P/P^0 , V_{ads} , V_{m1} , and C_{BET} are relative pressure, quantity adsorbed, adsorbed monolayer volume and constant, respectively. Fig. 8 displays corresponding N_2 isotherms for the synthesized materials.

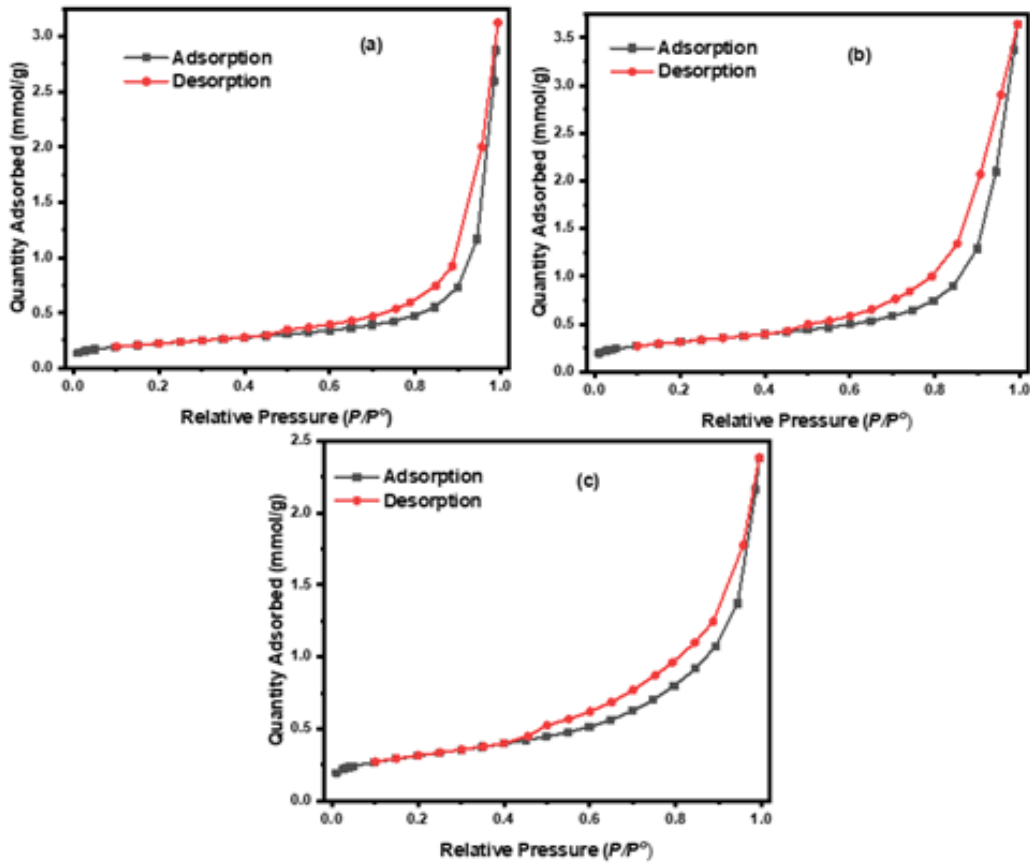


Figure 8. N_2 adsorption/desorption isotherms of 10-M- Na_2SiO_3 (a), 12-M- Na_2SiO_3 (b), and 12-M- H_2O_2 .

The performance of the sorbents is widely influenced by the pore structure and surface area. There are three classifications of pores in solids. Micropores are smaller than 2 nm, mesopores are between 2 – 50 nm and macropores are larger 50 nm (Buema et. al. 2021). The isotherms shown in Fig. 8a-c are of type-IV based on Brunauer, Deming, Deming, and Teller (BDDT) IUPAC classification. The materials display type H3 hysteresis loops at P/P^0 of 0.5 to 1.0 showing the presence of mesopores. The shape of the loops is linked with the pores slit-shaped within the material microstructures (Sing et al., 1985).

The BET surface area, pore volume, micropore area, and pore size of the prepared samples are shown in Table 7. Observing pore size and pore volumes, raw FA shows that low pore sizes have high pore volume. NaOH improves the porosity of materials hence increase in surface area. The BET surface area of 12-M-H₂O₂ is high and supported by the higher micropore volume and smaller pore size. After the fly ash was treated with Na₂SiO₃ and H₂O₂, it appears from SEM images that some freshly generated pits have formed on the surface of the material. This suggests that the Na₂SiO₃ and H₂O₂ have opened micropores on the surface, increasing micropore area and BET surface area.

Table 7. The BET surface area, pore volume, micropore area, and pore size of the prepared samples.

Sample ID	BET surface area (m ² /g)	Micropore area (m ² /g)	Pore size (nm)	Pore volume (cm ³ /g)
10-M-Na ₂ SiO ₃	17.5553	2.3719	25.5216	0.001062
12-M-Na ₂ SiO ₃	24.8808	3.0700	19.2165	0.001341
12-M-H ₂ O ₂	25.1804	3.2378	13.3701	0.001273
Raw FA	6.43639	-	4.7366	0.007621

4.7 Adsorption Efficiency and adsorption capacity

The adsorption efficiency of dyes (methylene blue and Congo red) was done using four fly ash based geopolymer samples (12-M-H₂O₂, 10-M-H₂O₂, 12-M-Na₂SiO₃ and 10-M-Na₂SiO₃) and raw FA. This was done in order to find the optimized time, pH, and dosage for the best active geopolymers by testing different parameters (time, dosage, concentration and pH). Concentration ranged from 50 mg/L to 300 mg/L for the adsorption of Congo red and 50 mg/L to 500 mg/L for the adsorption of MB with a time ranging from 30 minutes to 27 hrs. A dosage of raw fly ash and fly ash based geopolymers that ranged between 0.1 g and 4 g was investigated at pH 4 for methylene blue and pH 3 for Congo red. From the investigated results, the optimised dosage ranged from 0.5 g to 1.0 g for both dyes within a time of 5 Hrs. Fig. 9 shows the % efficiency for adsorption of CR using fly ash based geopolymers. It shows that H₂O₂-geopolymers perform better at adsorbing Congo red compared to Na₂SiO₃-geopolymers which have higher efficiency in the adsorption of MB. H₂O₂ generates pores in geopolymers hence the H₂O₂ geopolymer is characterized as having low sizes and a high surface area considering the BET results, which show that reduced pore sizes boost the adsorption capacity. The minimum % efficiency removal of MB using Na₂SiO₃-geopolymers was 70% and the maximum was 90% with 10-M-Na₂SiO₃ as the highest one. The H₂O₂-geopolymers attained low % removal efficiency with a minimum of 14% and a maximum of 42%. Adsorption of Congo red using raw fly ash produced a high % removal efficiency as the minimum was 92 % while the maximum was 94%. This could be due to a more positive charge density on the FA surface as observed from point of zero charge analysis resulting in more attraction of anionic dyes. Anionic dyes and more activity in H₂O₂-geopolymers while cationic dyes are more active in Na₂SiO₃-geopolymers. In light of the BET results in cation dyes, which demonstrate that larger pores increase adsorption capacity compared to the anion dye. The Na₂SiO₃ geopolymer is described as having high pore size and low surface area. High dye concentrations displayed low % efficiency but a high adsorption capacity (Q_e). Figures 10 shows the % efficiency for different concentrations for adsorption of MB using fly ash based geopolymers. The results show low concentration having high % efficiency removal than high concentration at the same contact time and same amount of dose add. At high concentrations there are more dye particles than the active sites for

adsorption and only small fractions of the dye are adsorbed onto the surface. A table of calculated value for adsorption capacity and equilibrium dye concentration is found at the appendix. The removal efficiency of the dyes was calculated using [equation 2](#).

$$\% \text{ removal} = \frac{(C_o - C_e)}{C_o} \times 100 \quad (2)$$

Where C_o is the initial dye concentration in (mg/L) and C_e is the remaining equilibrium dye concentration (mg/L).

The adsorption capacity was obtained using equation (3)

$$Q_e = \frac{(C_o - C_e)}{w} \times V \quad (3)$$

Where Q_e is the amount of dye adsorbed by geopolymer (mg/g), w is the mass of the given geopolymer (g) and V is the given volume of dye (L).

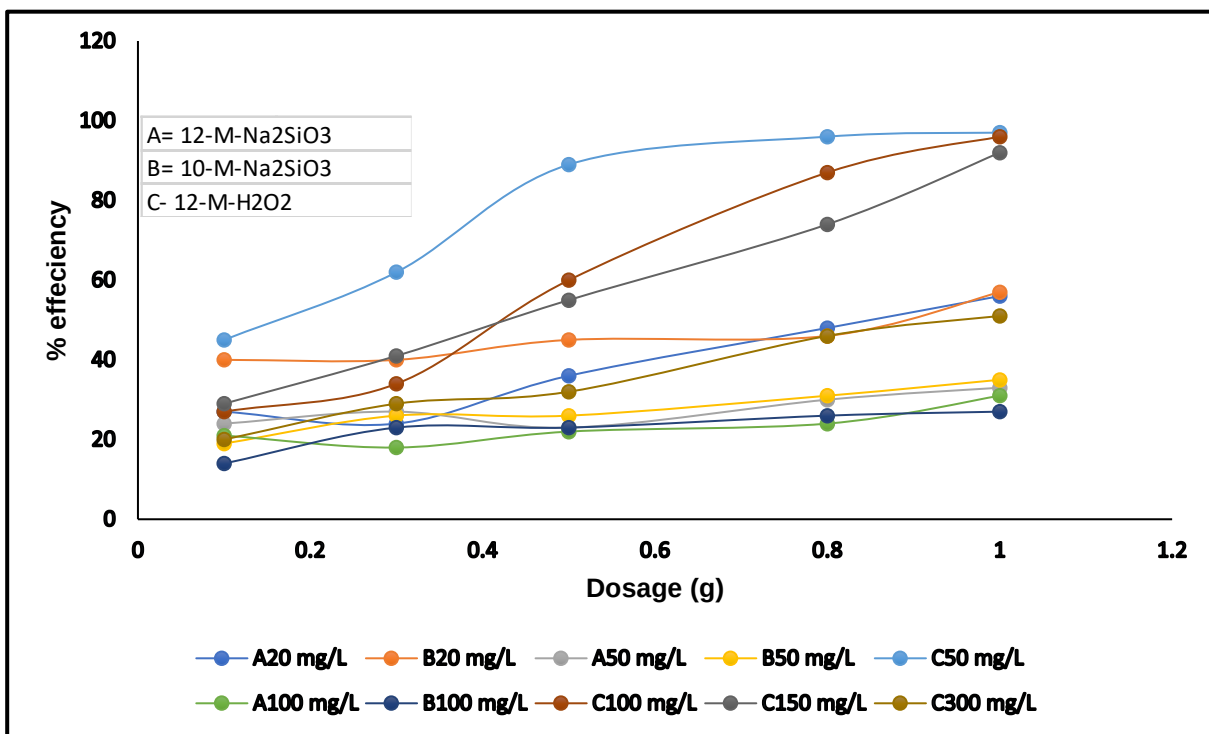


Figure 9. The effects of dosage and concentration on the adsorption of Congo red on fly ash based geopolymers

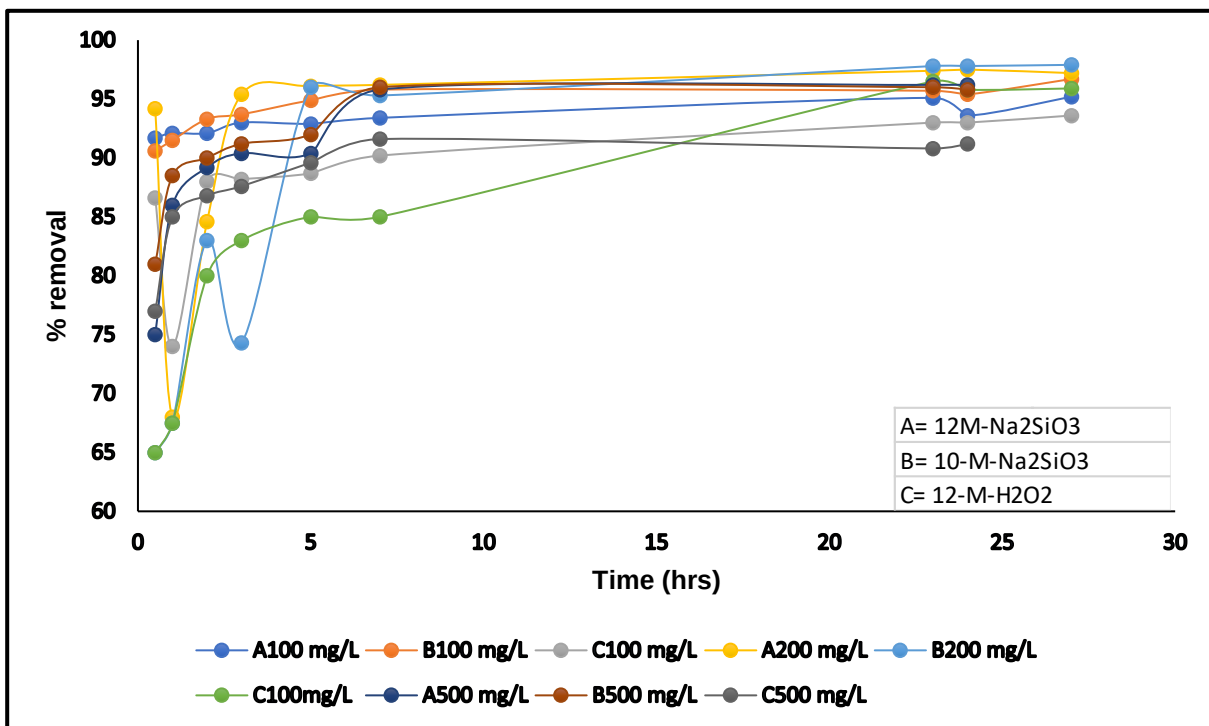


Figure 10. The effects of contact time and concentration on the adsorption of MB on fly ash based geopolymer

4.7.1 Optimization of time

The effect of contact time on the removal of dyes using geopolymers was investigated at room temperature using different masses of fly ash and geopolymers with dye concentrations of methylene blue and Congo red ranging from 50 mg/L - 300 mg/L. The experiment was carried out over time range from 5 minutes up to 90 minutes in order to determine the equilibrium concentration. The adsorption of methylene blue in four fly ash based geopolymers increases as time increases. Fig. 11 – Fig. 14 show removal % for different fly ash based geopolymers and concentrations of both dyes. The maximum % removal of methylene blue reached 98% in 10-M- Na_2SiO_3 geopolymer and 96% for Congo red in 12-M- H_2O_2 . Fig. 11 show that with the same mass and contact time, low concentration gives high % efficiency removal compared to high concentration as concentration increase, % efficiency decrease. Fig. 12 show unexpected rises for 300 g/mL at 45 minutes then lowered down as time increase. The trending was fluctuation for both concentrations with low % efficiency removal. Fig. 13-14 show % removal increase as time increase. The 90 mins was not enough to reach equilibrium stages. The unexpected fluctuation was caused by the reaction which mean at 90 mins the reaction was still taking places.

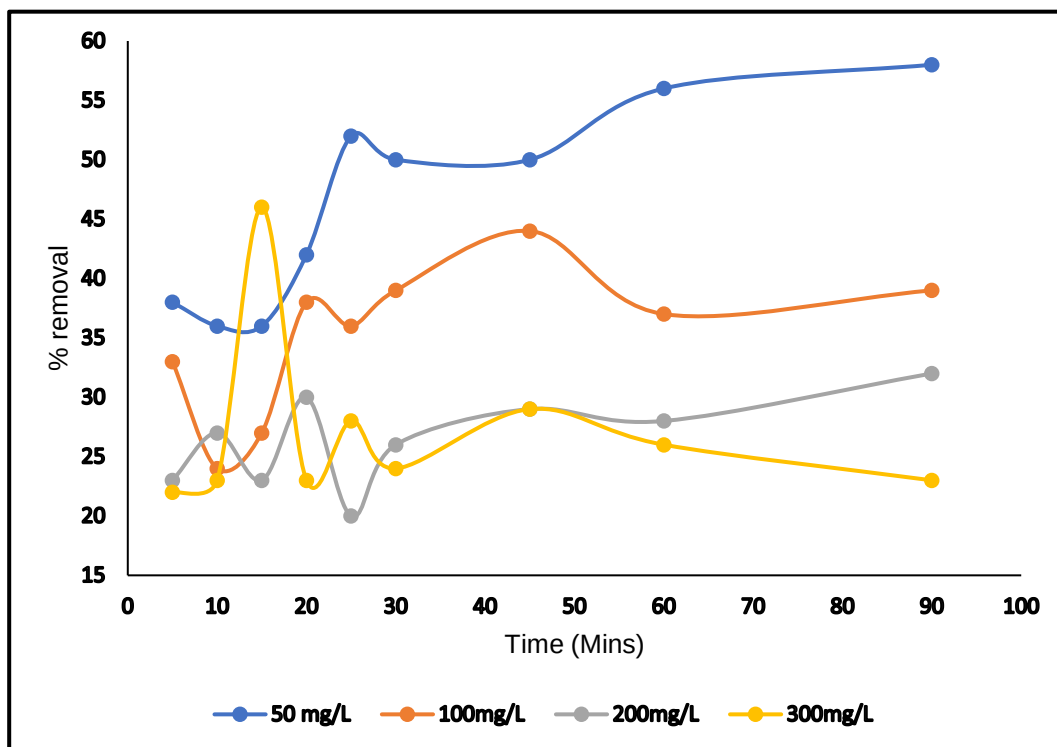


Figure 11. % Removal of Congo red on 12-M-H₂O₂

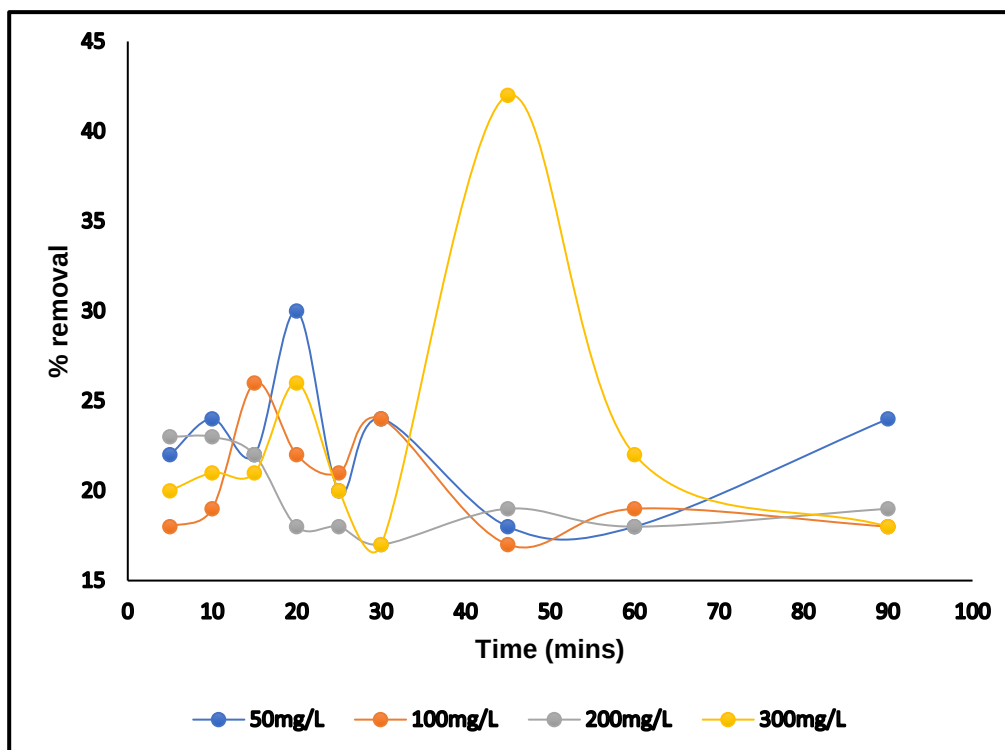


Figure 12. % Removal of Congo red on 12-M-Na₂SiO₃

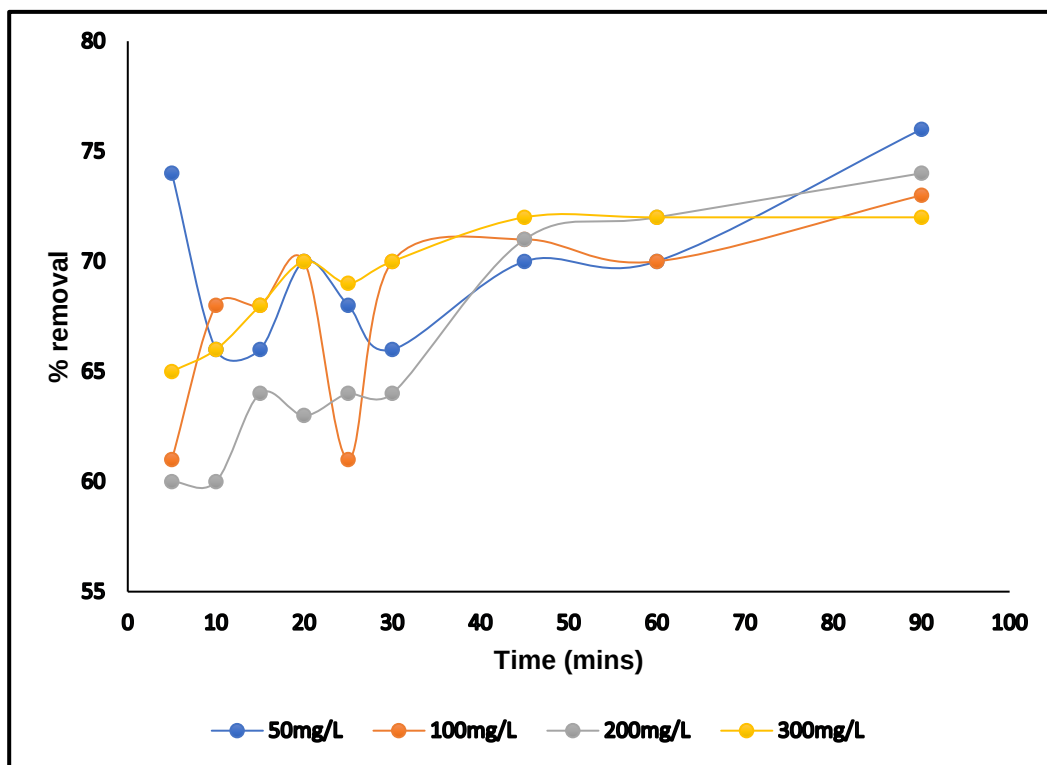


Figure 13. % Removal of methylene blue on 12-M-H₂O₂

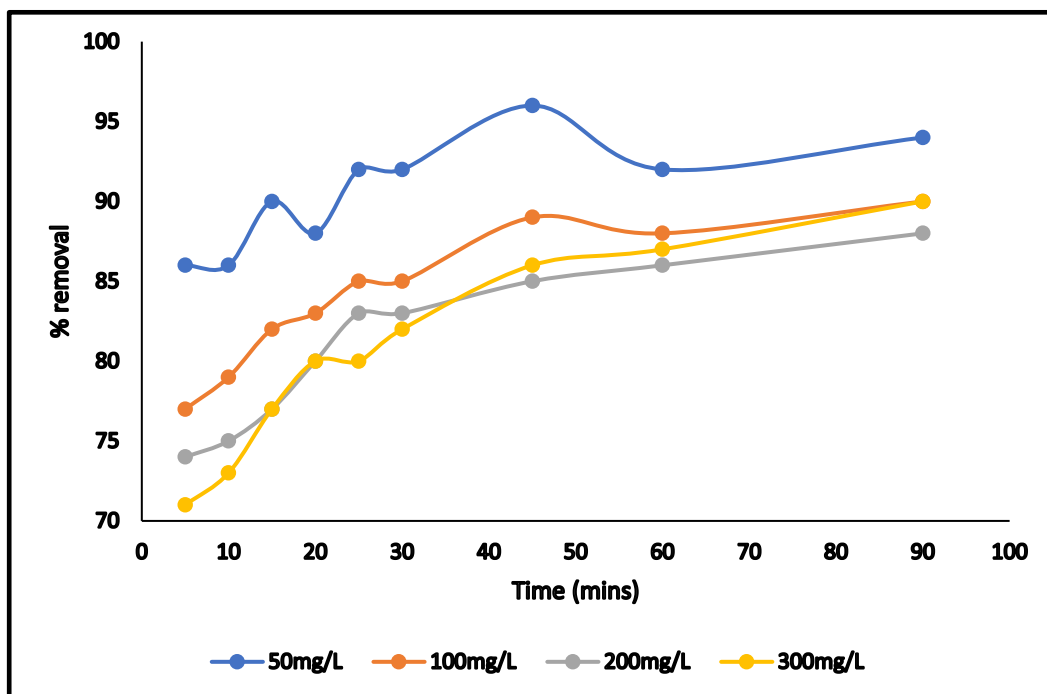


Figure 14. % Removal of methylene blue on 10-M-Na₂SiO₃

4.7.2 Optimization of dosage

To obtain optimum mass, a 40 mL solution of different concentration ranging between 20 mg/L and 300 mg/L (Methylene blue and Congo red) was used in the experiment as both dyes has shown interesting % removal in low concentration, 20 mg/L was used as lowest concentration with fly ash based geopolymers mass range of 0.1 g – 1.0 g. Prepared fly ash based geopolymers (12-M-Na₂SiO₃, 10-M-Na₂SiO₃ and 12-M-H₂O₂) and raw fly ash were used in the study to look into the effects of dosage on the adsorption of dyes on geopolymers. Fig. 15 shows the adsorption capacity (Q_e) of dyes obtained for different dosages of fly ash based geopolymers. Q_e range from 0 to 24 mg/g was used to determine the optimum mass ranging between 0.1 and 1 g which was then used for the kinetic study. [Mor et al. \(2018\)](#) stated that the formation of monolayer results in a decrease in Q_e as mass increases. This is because as mass is added, more adsorption sites are created while the amount of adsorbate remains constant. 0.1 g was the optimum dosage for all concentration.

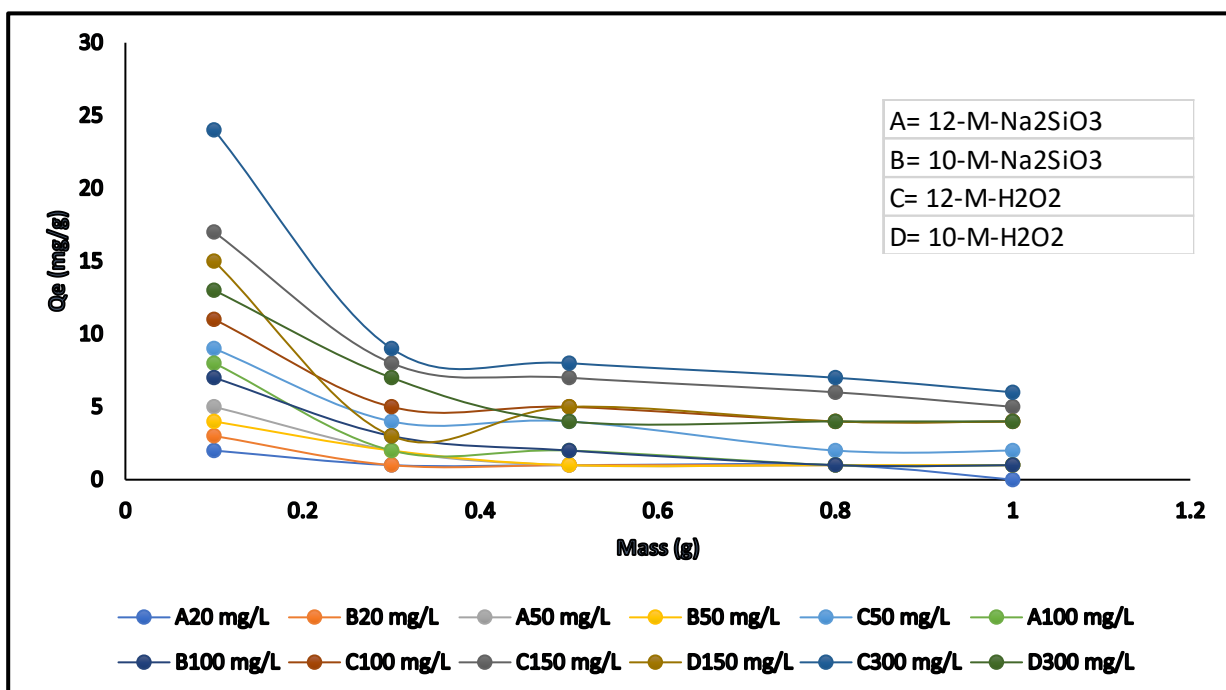


Figure 15. The effect of dosage and concentration on the adsorption capacity of dye on geopolymers

4.7.3 Points of zero charge

Points of zero charge (PZC) values were determined in 0.1 M NaNO₃ solution at room temperature. The procedure and methods used in this article were adapted from [Gembo et al \(2021\)](#). The pH of the solution was adjusted to initial pH values of 2 - 11 using 0.1 M NaOH or 0.1 M HCl. The pH was measured using Orion star pH meter model A111. 10, 0.2 g geopolymer samples were weighed and added to 40 mL of 0.1 M NaNO₃ solutions in different flasks and at different pH values. Each flask was placed on a shaker (Stuart orbital shaker SSL1) at a constant speed of 180 rpm for 24 hrs. A final pH was measured after 24hrs and recorded. The difference between final and initial pH was calculated as ΔpH and a graph of ΔpH vs initial pH was plotted and the pH_{pzc} was taken where ΔpH is zero.

Fig 16. shows results for zero points of charge for raw fly ash, 12-M-Na₂SiO₃, 10-M-Na₂SiO₃ 12-M-H₂O₂ and 10-M-H₂O₂. The results obtained Fig. 16 show that pH at points of zero charges (PZC) values of geopolymers were found between 7.4 and 8.5. PZC means the fly ash and geopolymers have no net surface charge at those pH values. When the solution pH value is below pH_{PZC} , the material carries a net positive charge and repels cations. When the pH of solution exceeds pH_{pzc} the surface becomes negatively charged and attracts cations ([Alaouani et al. 2018](#), [Herman et al. 2021](#)). This allows the determination of solution pH for adsorption of cations or anions.

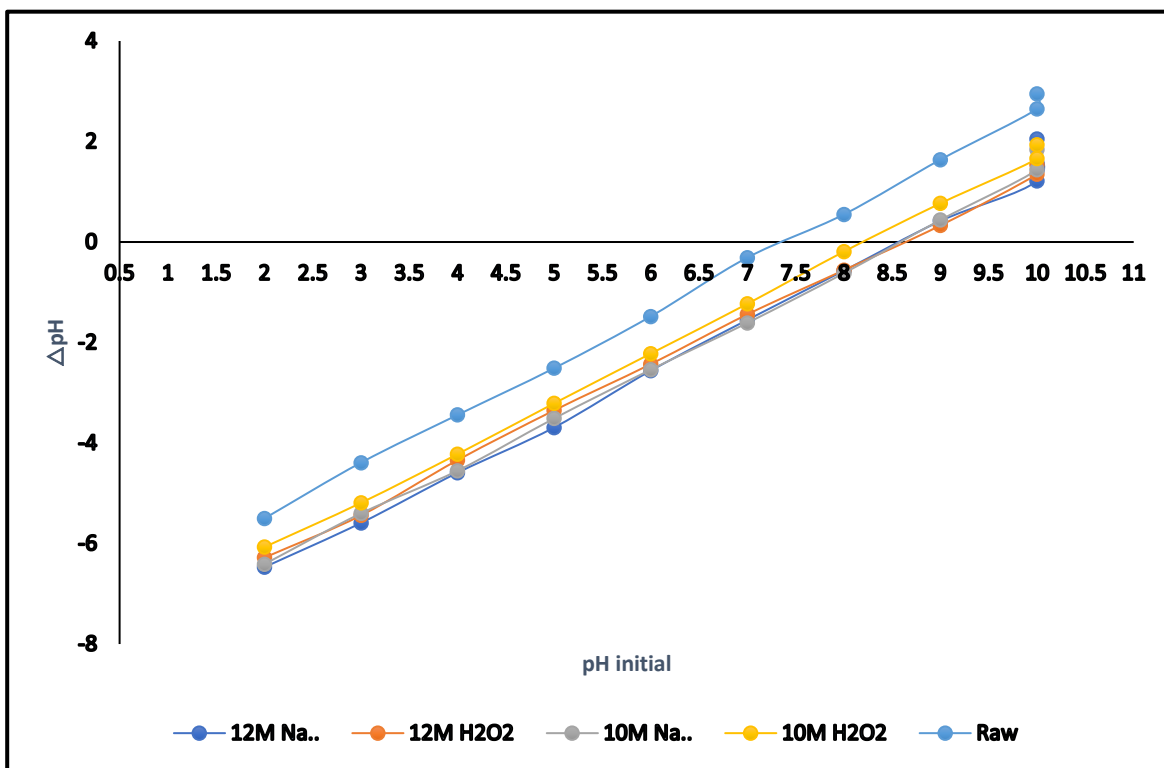


Figure 16. Points of zero charge of raw fly ash and fly ash based geopolymers

4.7.4 Optimization of pH

The influence of pH on the adsorption of methylene blue and Congo red was studied at room temperature with constant mass and stirring for 24 hr. The initial concentration was 100 mg/L of the given dye with 0.2 g of each fly ash based geopolymer sample. Fig. 17 shows the percentage removal of MB dye while Fig. 18 shows the efficiency removal of Congo red using fly ash based geopolymers. The pH ranged from 2 to 12. The optimum pH of methylene blue adsorption was 4 and Congo red pH was 3. The removal efficiency is more favourable in acidic than basic for both dyes. The percent reduces as the pH increases and all fly ash based geopolymers had the same percentage at pH 4 (99.5%) for MB. Figs. 17 and 18 show that the adsorption efficiency increases from 33% to 97% before it decreases. The maximum adsorption efficiency occurred at pH 3 for Congo red before its gradual decrease. At high pH, the surface charge of the adsorbent is negatively charged which leads to weak electrostatic

repulsion between both dyes and geopolymers and results in low removal efficiency (Rahman et al. 2018, Qu et al. 2021).

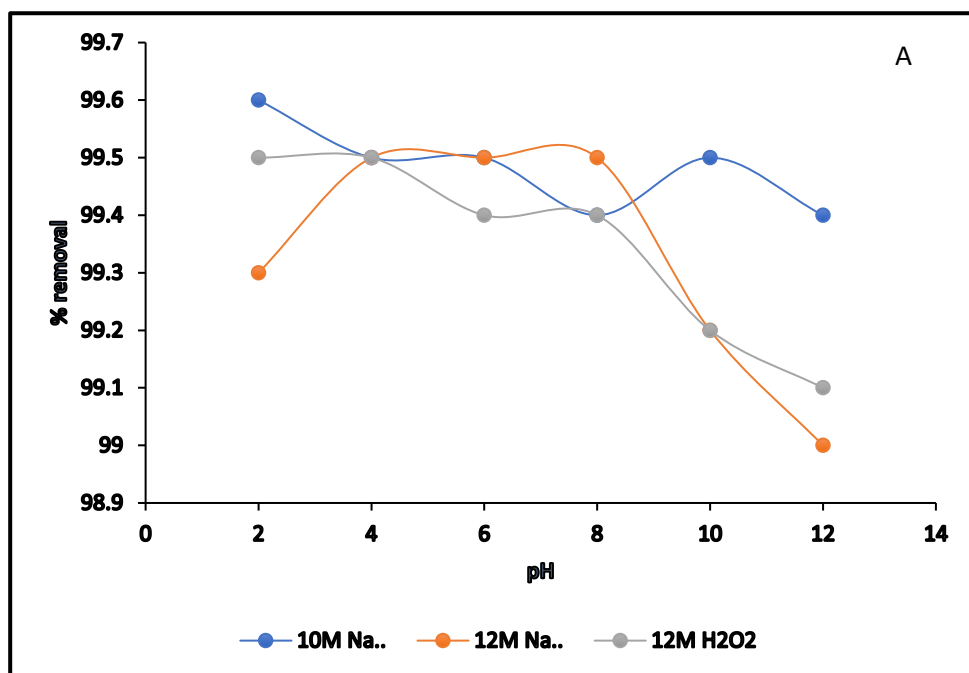


Figure 17. Effect of pH on the removal efficiency of Methylene Blue

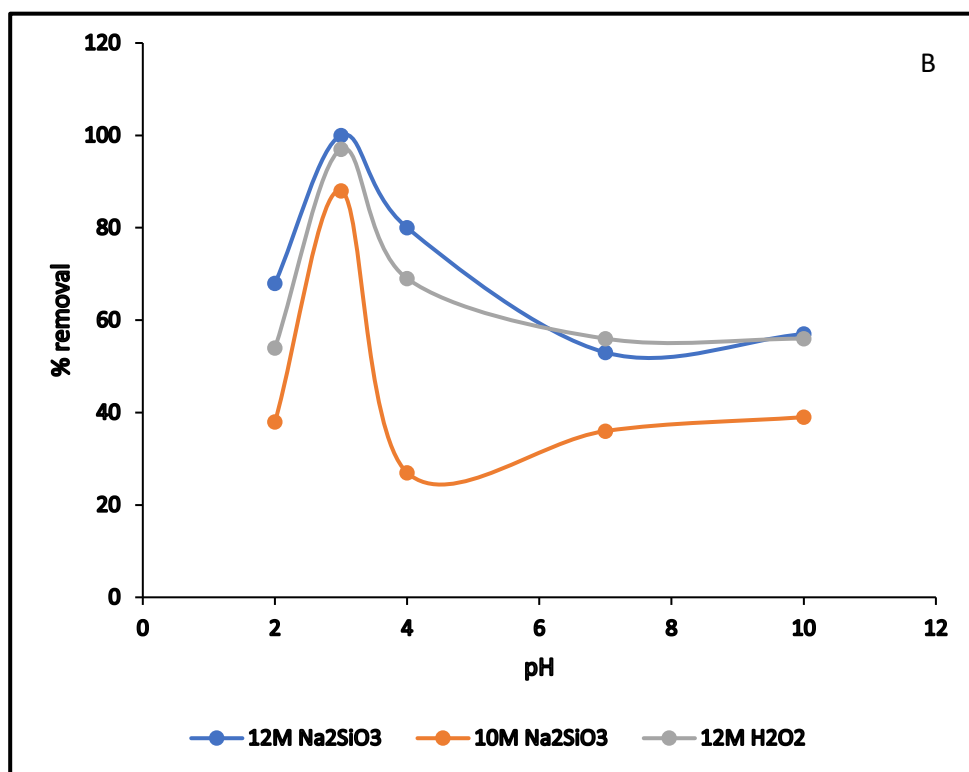


Figure 18. Effect of pH on the removal efficiency of Congo red using Based geopolymers

4.7.5 Effects of dye concentrations

The effects of initial dye concentration on the adsorption of methylene blue and Congo red were studied at the same time as the effects of time. In the study, both MB and CR concentrations ranging from 5 to 500 mg/L were investigated in dosage ranges from 0.1 g to 1.0 g. This study was done to determine the isotherms and hence the mechanism of adsorption. The analysis of initial dye concentration demonstrates the significance of dosage to concentration is important in the adsorption process because the low dosage cannot adsorb dyes at high concentrations. Also, concentration was investigated with all four geopolymers and they displayed different effects. The concentrations ranging from 50 to 300 mg/L was studied for the adsorption test and it showed high removal efficiency with 50 - 200 mg/L as suitable for all the four geopolymers. The maximum % removal reached 98% for 10-M-Na₂SiO₃ in methylene blue and 96% for 12-M-H₂O₂ in Congo red. As the concentration of dyes increase,

adsorption capacity increases while % removal decreases. Fig. 19 show the adsorption capacity obtained from different concentration in the adsorption of CR using 12-M- H_2O_2 . The finding shows that the increase of concentration leads to increase of adsorption capacity. At the same contact time (90 mins), concentration of 300 mg/L was 5 mg/g while 50 mg/L was 1.8 mg/L. Fig. 20 displays the Q_e of MB using 12-M- H_2O_2 . The increase of concentration lead to increase of adsorption capacity. Concentration of 50 mg/L gave 3.8 mg/L adsorption capacity compared to 21.7 mg/g adsorption for 300 mg/L.

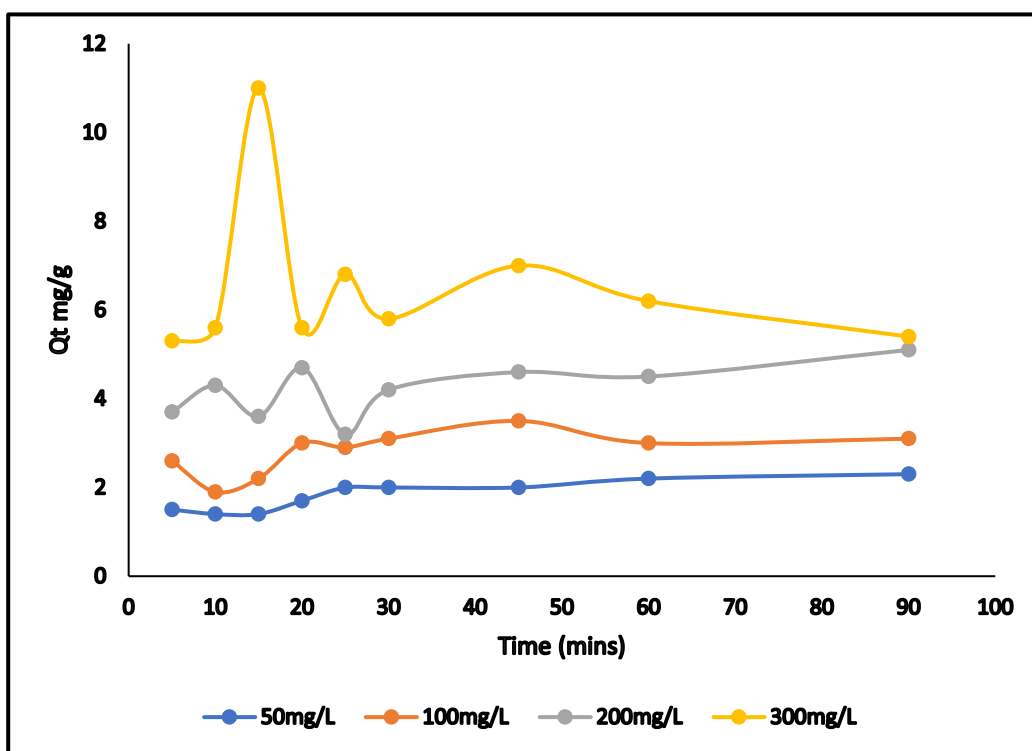


Figure 19. The adsorption capacity of CR on 12-M- H_2O_2

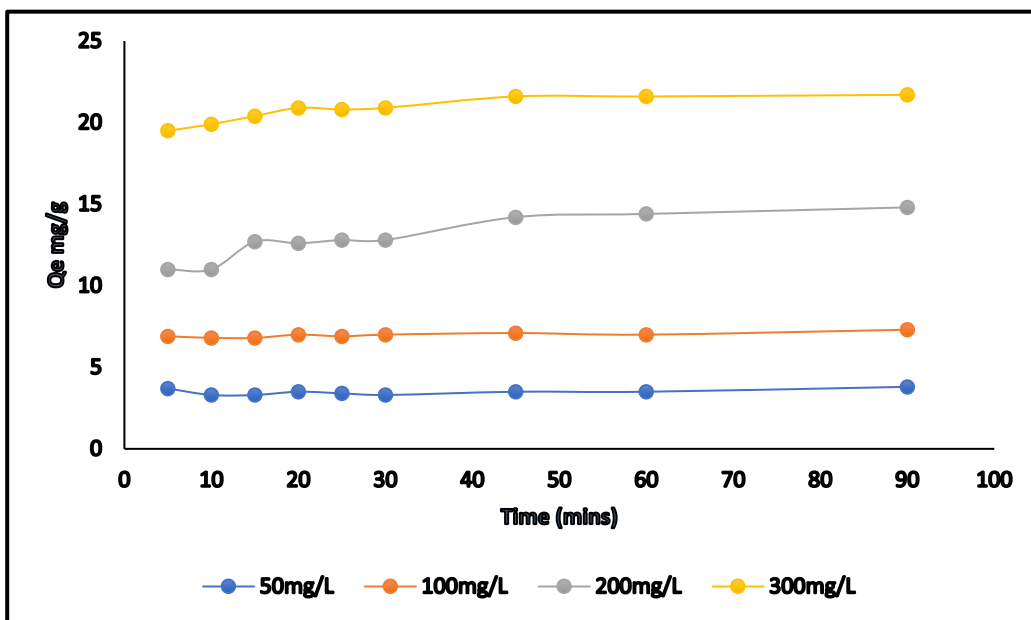


Figure 20. The adsorption capacity of MB using 12-M-H₂O₂

4.7.6 The effects of the syringe

This experiment was carried out to determine the effects of the syringe on the adsorption of dyes using geopolymers. Two experiments were run in parallel, with the first experiment running using an injection syringe for filtering while the second one ran without an injection syringe for a filter. The centrifuge was used in both samples to separate fly ash from the solution. Once done with a centrifuge, an injection syringe was used in experiment 1 before running Uv-Vis while experiment 2 was analyzed with Uv-Vis without using an injection syringe. An injection syringe has shown a high percentage of removal compared to a non-injection syringe. With the injection syringe, there was some challenge as the lambda max for MB changed from 661 nm to 514 nm. The lambda max of methylene blue was 661 nm which remained the same for experiment 2 without an injection syringe. With the injection syringe, the dye that was left from the adsorption of dye was also left in the filter making it hard to know how much concentration of dye was adsorbed and the adsorption capacity. This led to the injection syringe being ruled out in the adsorption studies of geopolymers. Fig. 21a-b show % removal of 12-M-Na₂SiO₃ using an injection syringe and non-injection syringe

using 50 mg/L as constant concentration for dye with different dose of geopolymer. As dose increase, the % removal decrease on time. Syringe displayed a high % removal comparing to non-syringe experiment. This explains that the adsorption didn't take place as the dyes adsorbed left in syringe before it could be analyzed with Uv-Vis. Fig. 22a-b show results for 10-Na₂SiO₃ obtained using an injection syringe and non-injection syringe. Both displayed high % removal as dose decrease with time but with injection syringe the % removal was higher than non-syringe. Using syringe led to removal of some of the dye that was left after adsorption.

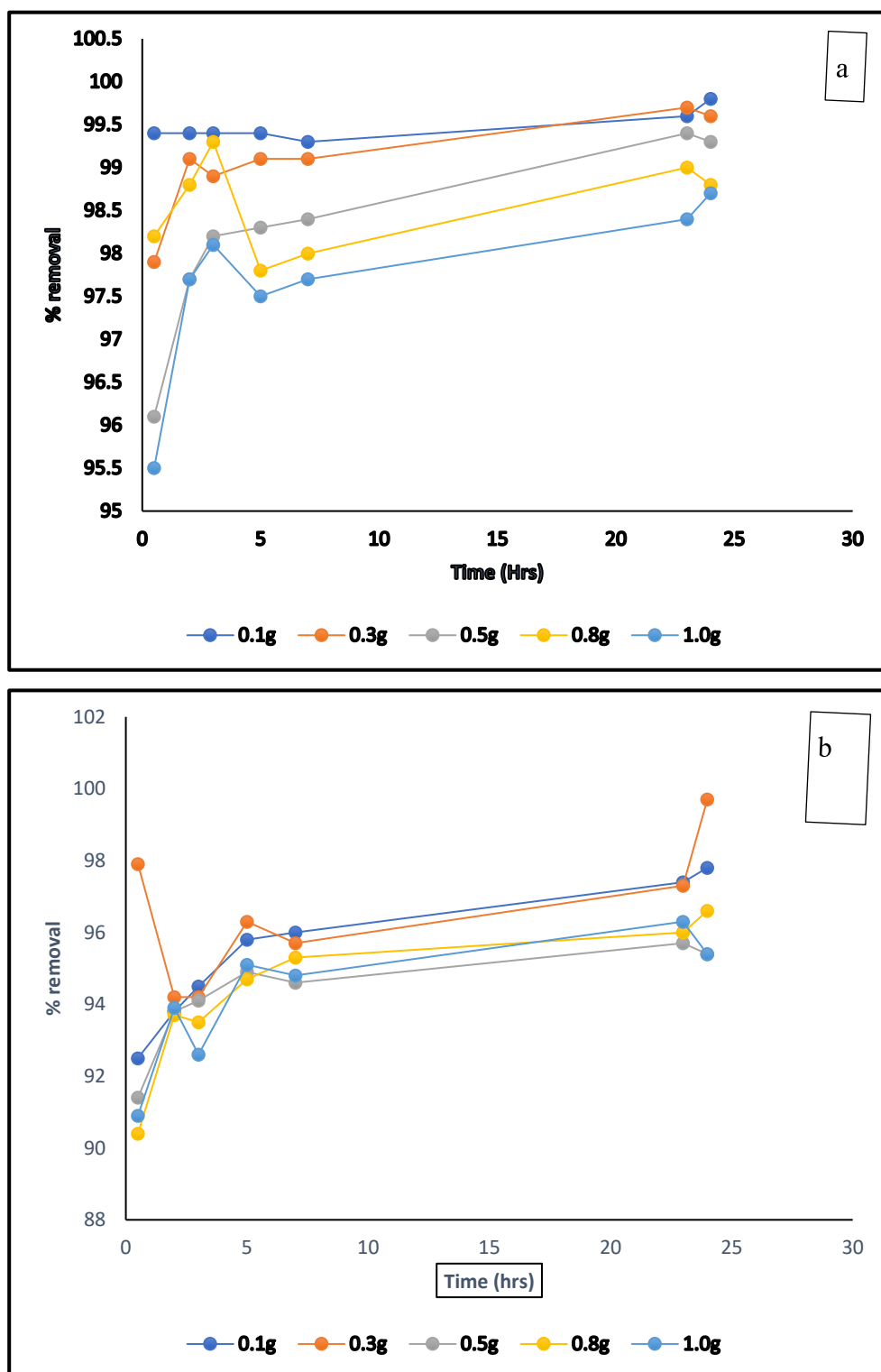


Figure 21. The effects of injection syringe on adsorption of methylene Blue.
 (a) 12-M-Na₂SiO₃ with filter. (b) 12-M-Na₂SiO₃ with no filter.

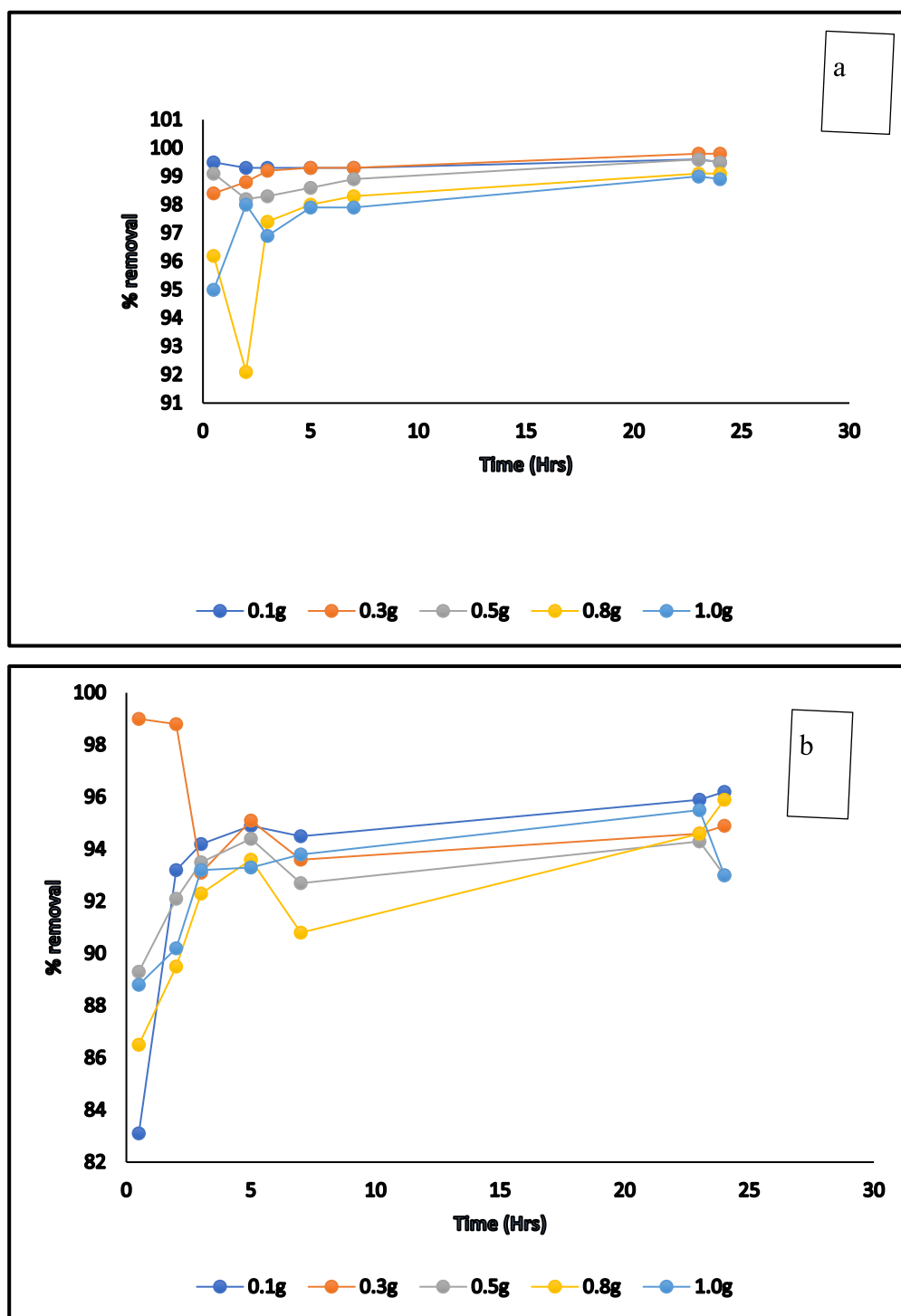


Figure 22. The effects of injection syringe on adsorption of methylene blue.
 (a) 10-M-Na₂SiO₃ filter, (b) 10-M-Na₂SiO₃ with no filter

4.8 Adsorption isotherms

4.8.1 Langmuir isotherm

The Langmuir isotherm model was used to describe the equilibrium of the adsorbent and adsorbate phases. It defines monolayer coverage in the sample and the subsequent monolayer adsorption capacity. For the dye adsorption by fly ash and fly ash-based geopolymers, data fitted to the Langmuir isotherm are shown in Figs. 23a–i. Na_2SiO_3 -geopolymers adsorption of MB and CR is shown in Figs. 23a through 23c. The R^2 value ranges between 0.7186 to 0.9958 for Na_2SiO_3 -geopolymers in MB and CR. H_2O_2 -geopolymer MB and CR dyes is shown in Figs. 23d–g. In contrast to 12-M- H_2O_2 -CR, 10-M- H_2O_2 -MB, and 10-M- H_2O_2 -CR, 12-M- H_2O_2 -MB had the greatest R^2 , which was 0.9922. R^2 for unprocessed fly ash in MB and CR is depicted in Figs. 23h–i. R^2 of 0.6474 for raw FA-MB versus 0.8 for raw FA-CR. While H_2O_2 -geopolymers give high R^2 in 12-M- H_2O_2 -MB, Na_2SiO_3 -geopolymers give high R^2 in 12-M- Na_2SiO_3 -CR overall. The highest maximum monolayer adsorption capacity obtained was 85.47 mg/g for MB in 12- H_2O_2 -MB and 34.36 for CR in 10-M- H_2O_2 -CR. Table 8 shows Langmuir isotherm parameters for the adsorption of dyes using fly ash based geopolymer. Dimensionless separate factor (R_L) determines the favorability of the Langmuir isotherms where $R_L=1$ indicate that isotherm is linear, $0 < R_L < 1$ indicates favourable, $R_L > 1$ is unfavourable, while $R_L = 0$ is irreversible. The convenience of the Langmuir isotherm is determined by comparing the R^2 values with those of the other isotherms. A Langmuir isotherm can be given by the following equations 4 and 5.

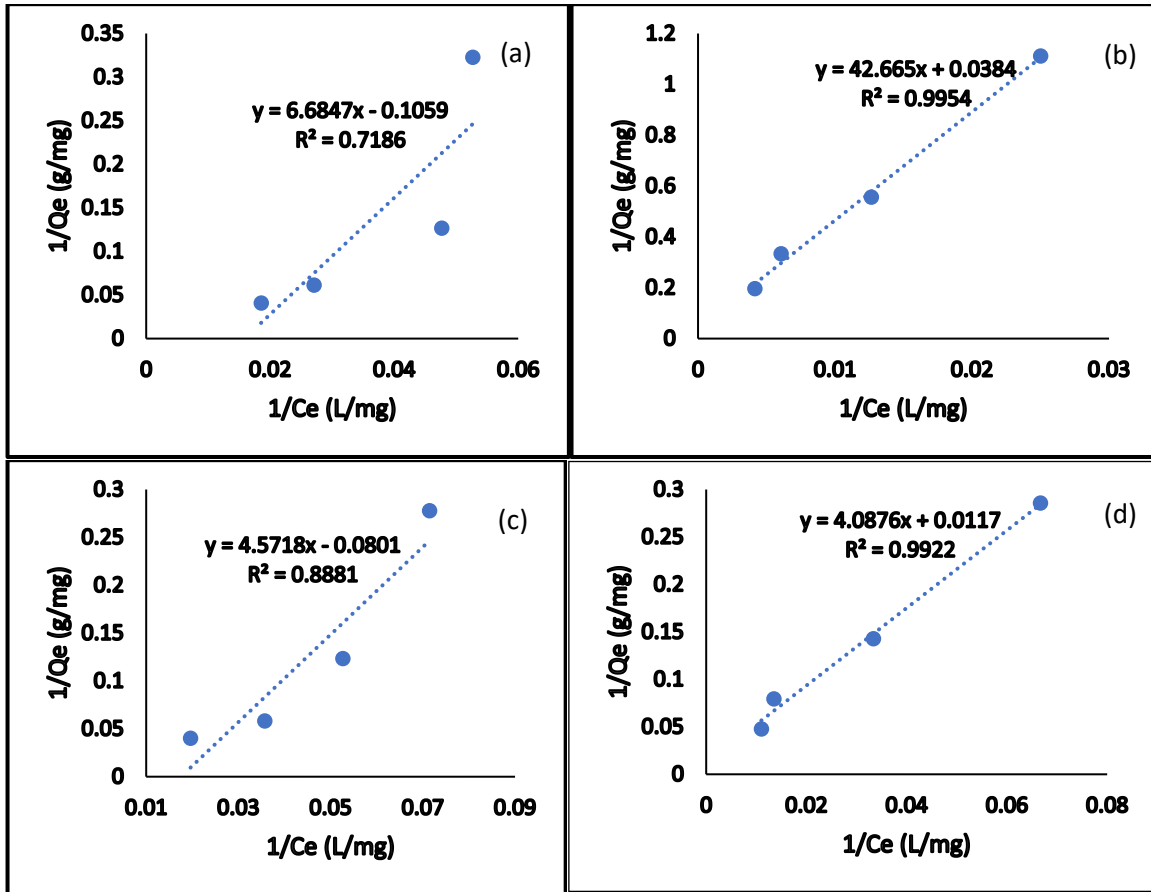
Linear equation:

$$\frac{1}{Q_e} = \left(\frac{1}{K_L Q_{max}} \right) \times \frac{1}{C_e} + \frac{1}{Q_{max}} \quad (4)$$

Nonlinear equation:

$$Q_e = \frac{Q_{max} K_L C_e}{1 + K_L C_e} \quad (5)$$

Where Q_e is the amount of dye adsorbed on the adsorbents at equilibrium (mg/g). C_e is the solute equilibrium concentration (mg/L); Q_{max} is the maximum monolayer capacity of dye adsorption onto the adsorbents (mg/g); while K_L is the Langmuir constant of adsorption (mg/L).



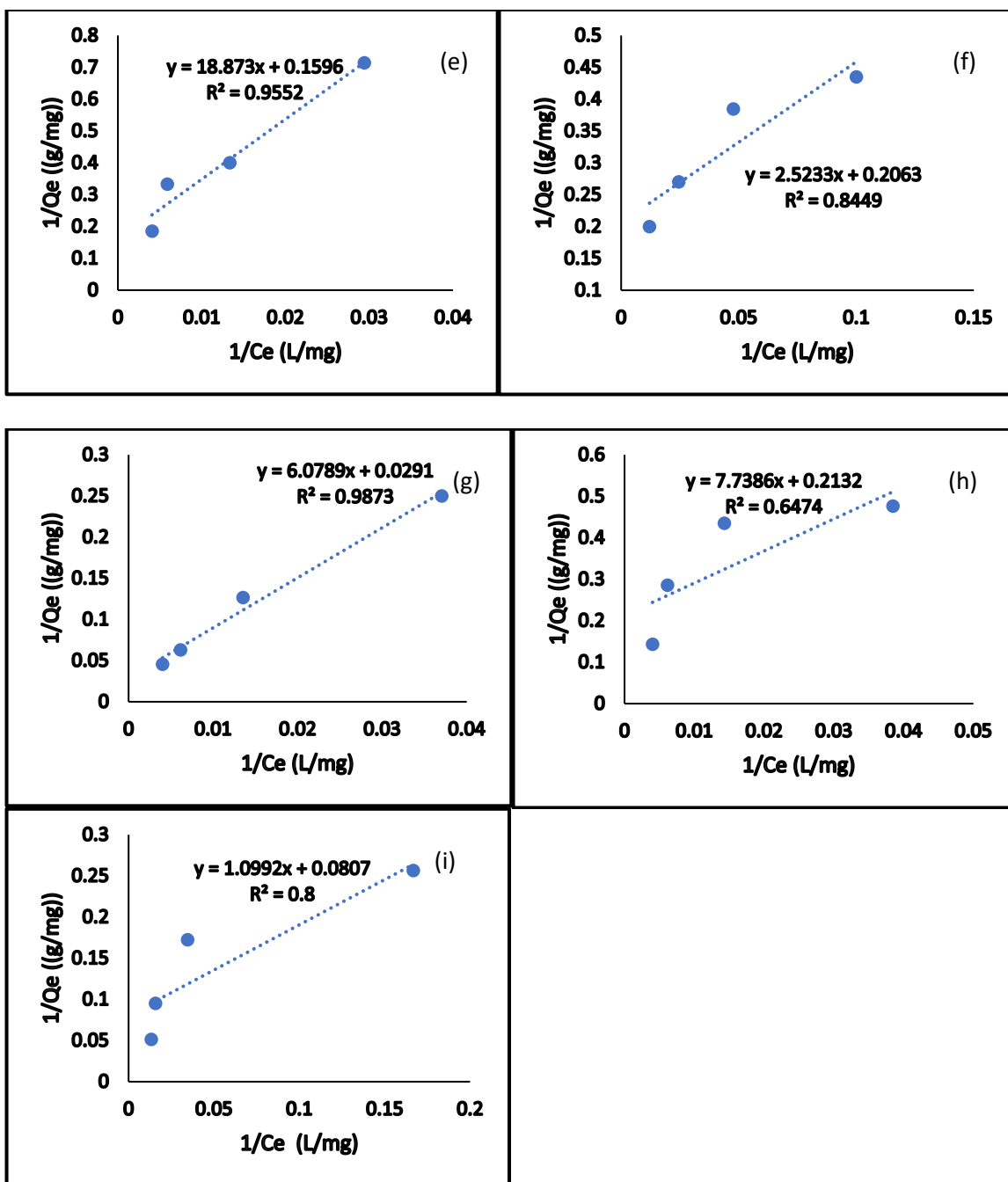


Figure 23. Linear regression langmuir isotherm for adsorption of dyes; (a). 12-M- Na_2SiO_3 -MB, (b) 12-M- Na_2SiO_3 -CR, (c) 10-M- Na_2SiO_3 -MB, (d) 12-M- H_2O_2 -MB, (e) 12-M- H_2O_2 -CR, (f) 10-M- H_2O_2 -MB, (g) 10-M- H_2O_2 -CR, (h) Raw FA-MB, (i) Raw FA-CR.

Table 8: Langmuir isotherm parameter for adsorption of dyes; (a). 12-M-Na₂SiO₃-MB, (b) 12-M-Na₂SiO₃-CR, (c) 10-M-Na₂SiO₃-MB, (d) 12-M-H₂O₂-MB, (e) 12-M-H₂O₂-CR, (f) 10-M-H₂O₂-MB, (g) 10-M-H₂O₂-CR, (h) Raw FA-MB, (i) Raw FA-CR.

		Linear			
Adsorbent	Dye	Q _{max} (mg/g)	K _L (L/mg)	R _L	R ²
12-M-Na ₂ SiO ₃	MB	-9.44	-0.016	-0.461	0.7186
12-M-Na ₂ SiO ₃	CR	26.04	0.0009	0.957	0.9954
10-M-Na ₂ SiO ₃	MB	-12.48	-0.018	-0.0004	0.8881
10-M-Na ₂ SiO ₃	CR	-	-	-	-
12-M-H ₂ O ₂	MB	85.47	0.003	0.875	0.9922
12-M-H ₂ O ₂	CR	18.87	0.053	0.003	0.9552
10-M-H ₂ O ₂	MB	4.85	0.197	0.082	0.8449
10-M-H ₂ O ₂	CR	34.36	0.005	0.807	0.9873
Raw FA	MB	4.69	0.606	0.032	0.6474
Raw FA	CR	12.39	0.073	0.214	0.8

4.8.2 Freundlich isotherm

Freundlich isotherm model is used to explain multilayer adsorption on adsorbents. The results fitted to the Freundlich isotherm for the dye adsorption by fly ash and fly ash-based geopolymers are displayed in Figs. 24a–i. Figs. 24h-i show R² for raw fly ash in MB and CR adsorption. Table 9 shows the Freundlich isotherm parameter for the adsorption of dyes onto fly ash and fly ash-based geopolymers. Freundlich was expressed using the [equations 6 and 7](#):

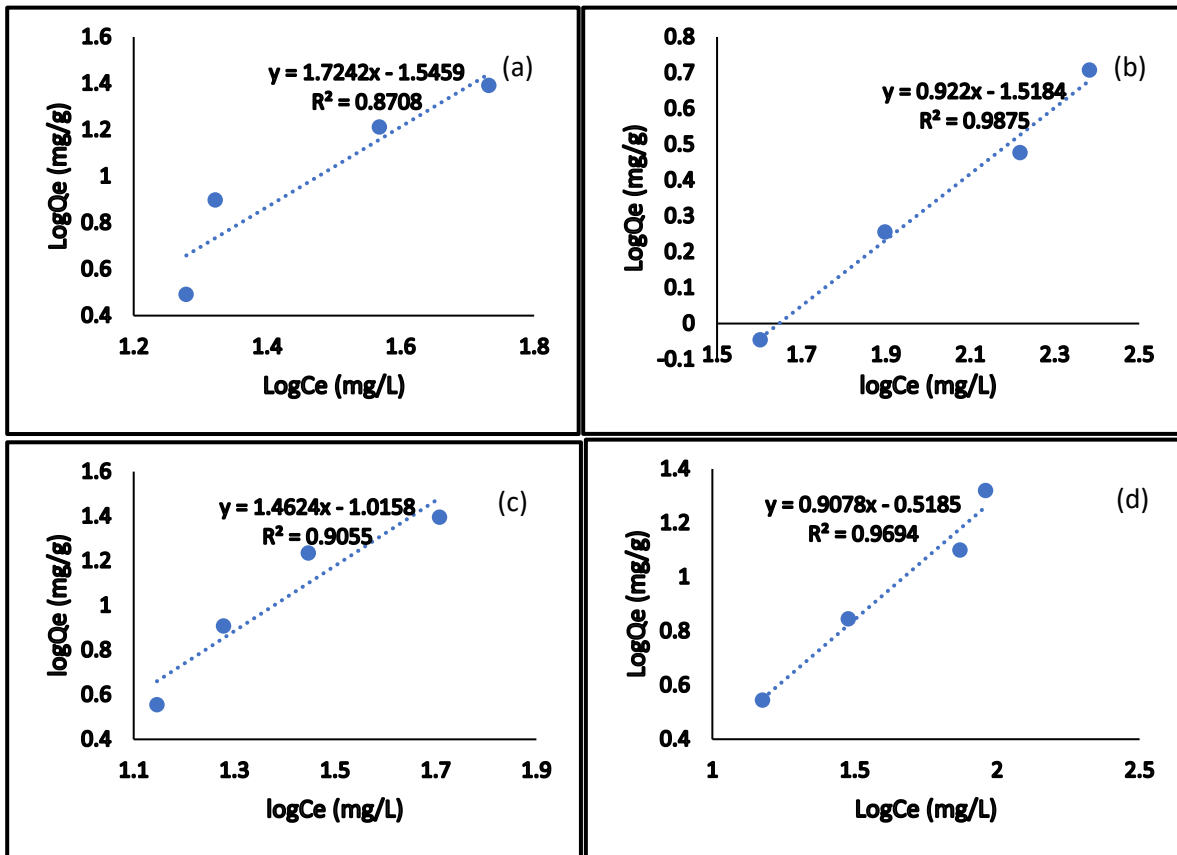
Linear equation:

$$\text{Log}Q_e = \text{Log}K_F + \frac{1}{n}\text{Log}C_e \quad (6)$$

Nonlinear equation:

$$Q_e = K_F C_e^{\frac{1}{n}} \quad (7)$$

Where Q_e is the amount of dye adsorbed on the adsorbents at equilibrium (mg/g); C_e is the solute equilibrium concentration (mg/L); K_F is the adsorption capacity while $1/n$ value represents adsorption intensity.



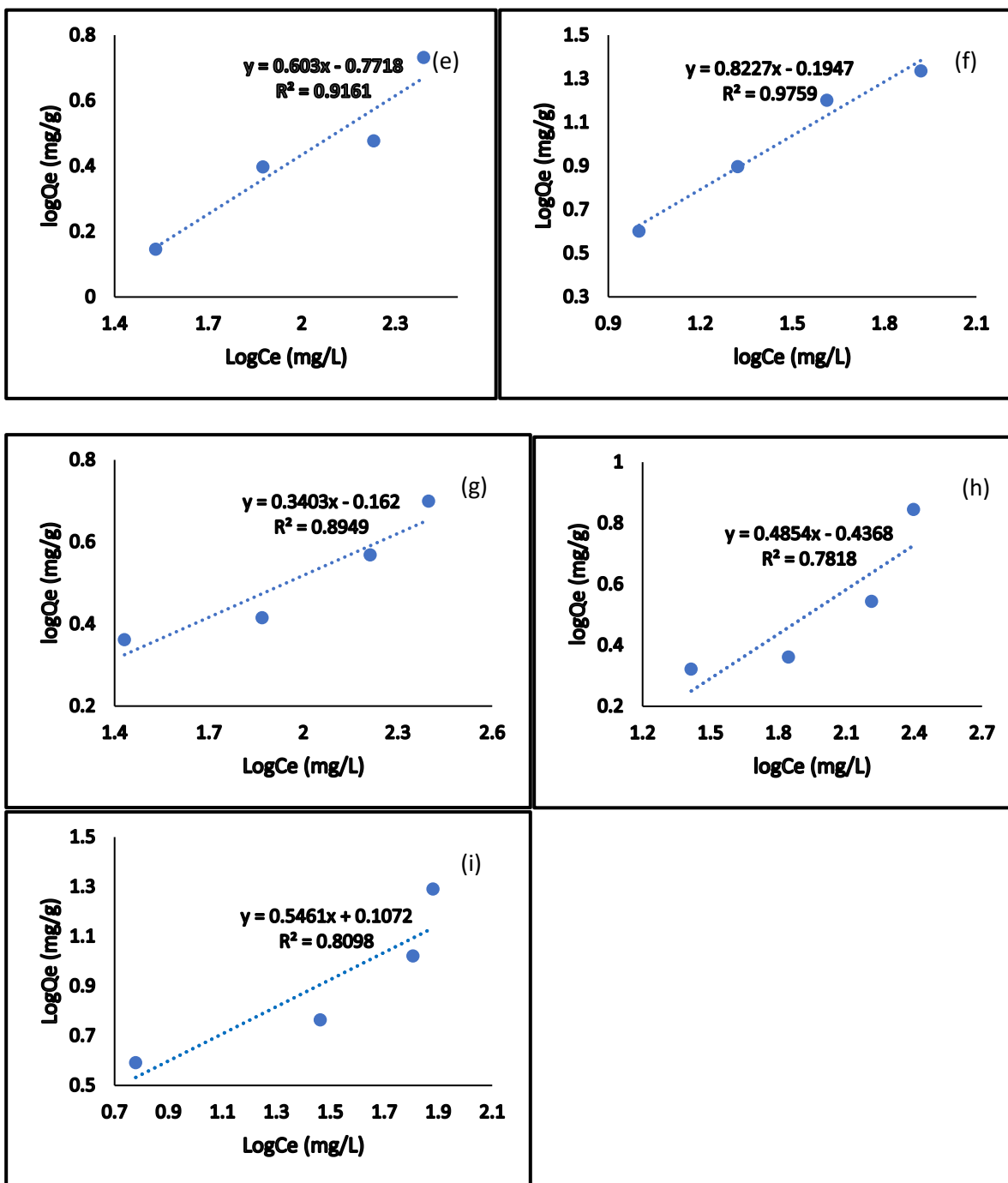


Figure 24. Linear regression Freundlich isotherm for adsorption of dyes; (a). 12-M- Na_2SiO_3 -MB, (b) 12-M- Na_2SiO_3 -CR, (c) 10-M- Na_2SiO_3 -MB, (d) 12-M- H_2O_2 -MB, (e) 12-M- H_2O_2 -CR, (f) 10-M- H_2O_2 -MB, (g) 10-M- H_2O_2 -CR, (h) Raw FA-MB, (i) Raw FA-CR.

Table 9: Freundlich isotherm parameter for adsorption of dyes; (a). 12-M-Na₂SiO₃-MB, (b) 12-M-Na₂SiO₃-CR, (c) 10-M-Na₂SiO₃-MB, (d) 12-M-H₂O₂-MB, (e) 12-M-H₂O₂-CR, (f) 10-M-H₂O₂-MB, (g) 10-M-H₂O₂-CR, (h) Raw FA-MB, (i) Raw FA-CR.

Adsorbent	Dyes	Linear		
		K _F (mg/g)	1/n	R ²
12-M-Na ₂ SiO ₃	MB	0.028	1.7242	0.8708
12-M-Na ₂ SiO ₃	CR	0.030	0.922	0.9875
10-M-Na ₂ SiO ₃	MB	0.096	1.4624	0.9055
10-M-Na ₂ SiO ₃	CR	-	-	-
12-M-H ₂ O ₂	MB	0.303	0.9078	0.9694
12-M-H ₂ O ₂	CR	0.169	0.603	0.9161
10-M-H ₂ O ₂	MB	0.639	0.8227	0.9759
10-M-H ₂ O ₂	CR	0.689	0.3403	0.8949
Raw FA	MB	0.3657	0.4854	0.7818
Raw FA	CR		0.5461	0.8098

4.8.3 Temkin Isotherm

The Temkin isotherm model predicts that rather than decreasing logarithmically with coverage, the rate of adsorption of all molecules decreases gradually ([Mor et. al. 2018](#), [Quayoom et al. 2017](#)). Figs. 25a-i show the results for dye adsorption by fly ash and fly ash-based geopolymers that were fitted to the Temkin isotherm. Figs. 24a–c show Na₂SiO₃–geopolymers in MB and CR. R² values for raw fly ash in MB and CR adsorption are shown in Figs. 24h-i. Table 10 presents Temkin isotherm model parameters for the adsorption of the dyes. The model can be given by the following [equations 8 and 9](#).

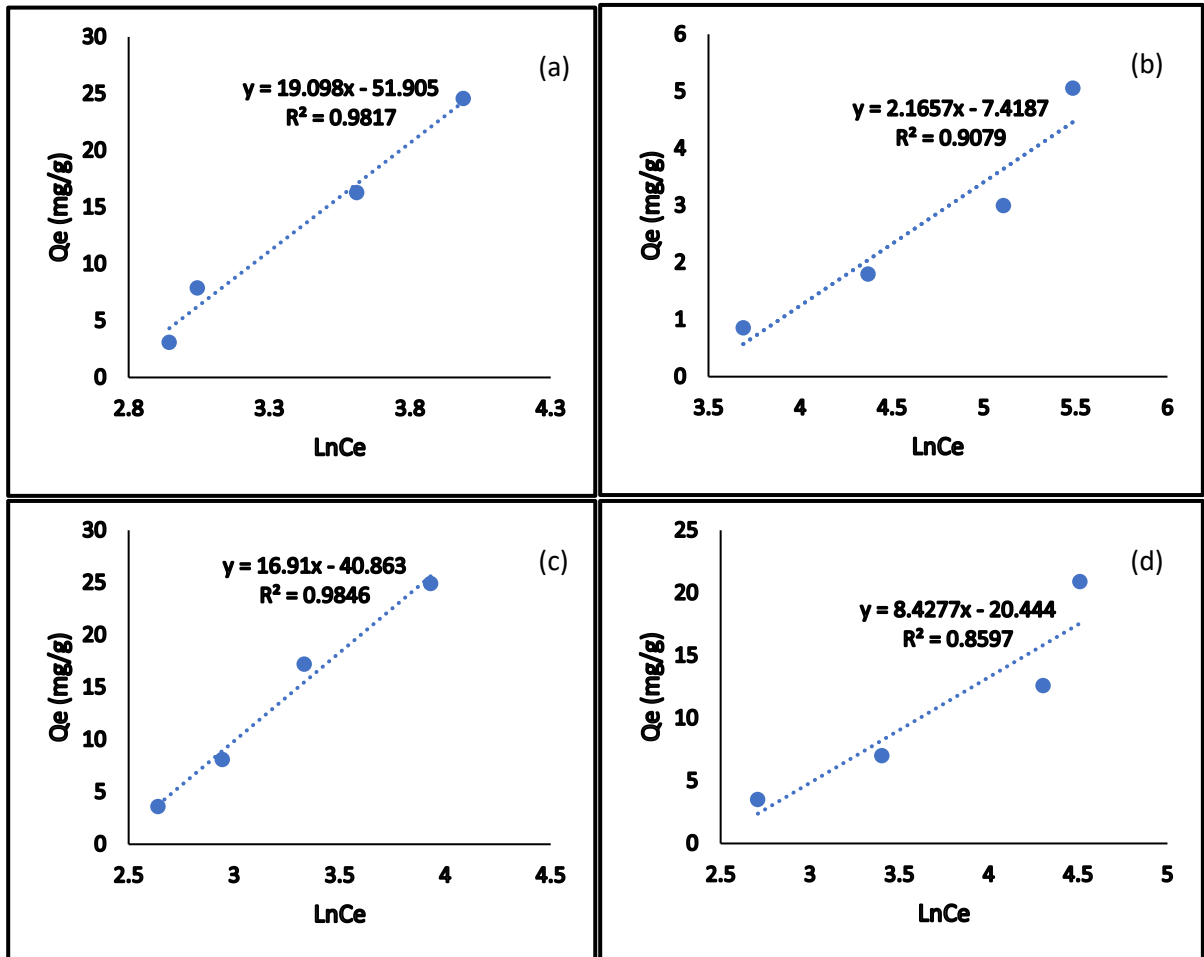
Linear equation:

$$Q_e = B_T \ln A_T + B_T \ln C_e \quad (8)$$

Non Linear equation:

$$Q_e = \frac{RT}{B \ln(A_T C_e)} \quad (9)$$

Whereas A_T is the Temkin isotherm energy constant (L/g); B_T is the constant related to heat of sorption (J/mol); T is temperature (K); R is molar gas constant ($\text{J} \cdot \text{mol}^{-1} \text{K}^{-1}$);



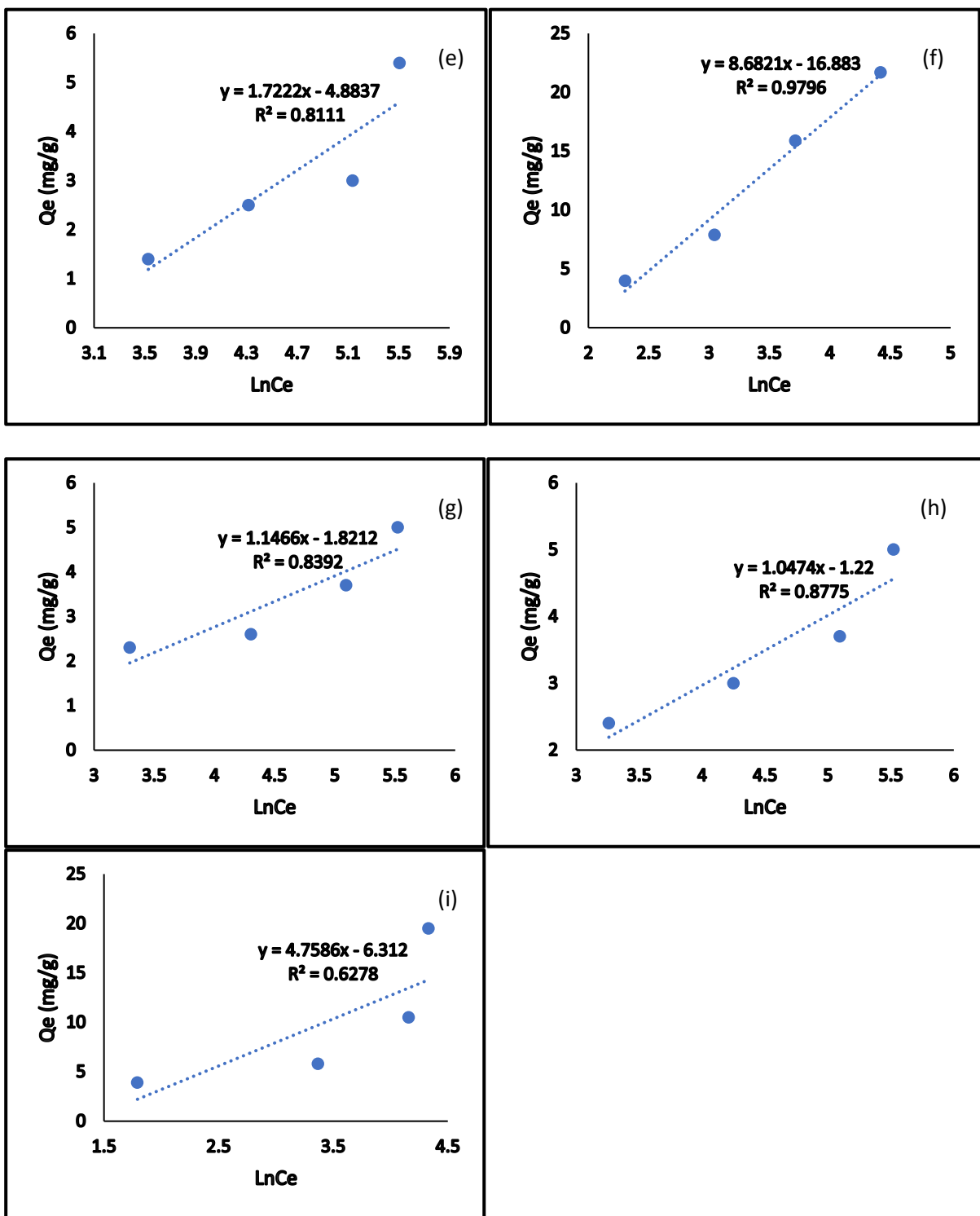


Figure 25. Linear regression Temkin isotherm for adsorption of dyes; (a). 12-M- Na_2SiO_3 -MB, (b) 12-M- Na_2SiO_3 -CR, (c) 10-M- Na_2SiO_3 -MB, (d) 12-M- H_2O_2 -MB, (e) 12-M- H_2O_2 -CR, (f) 10-M- H_2O_2 -MB, (g) 10-M- H_2O_2 -CR, (h) Raw FA-MB, (i) Raw FA-CR.

Table 10: Temkin isotherm parameter for adsorption of dyes; (a). 12-M-Na₂SiO₃-MB, (b) 12-M-Na₂SiO₃-CR, (c) 10-M-Na₂SiO₃-MB, (d) 12-M-H₂O₂-MB, (e) 12-M-H₂O₂-CR, (f) 10-M-H₂O₂-MB, (g) 10-M-H₂O₂-CR, (h) Raw FA-MB, (I) Raw FA-CR.

Adsorbent	Dyes	Linear		
		A _T (L/g)	B _T	R ²
12-M-Na ₂ SiO ₃	MB	0.066	19.098	0.9817
12-M-Na ₂ SiO ₃	CR	0.032	2.1657	0.9079
10-M-Na ₂ SiO ₃	MB	0.091	16.91	0.9846
10-M-Na ₂ SiO ₃	CR	-	-	-
12-M-H ₂ O ₂	MB	0.088	8.4287	0.8597
12-M-H ₂ O ₂	CR	0.058	1.722	0.8111
10-M-H ₂ O ₂	MB	0.143	8.682	0.9796
10-M-H ₂ O ₂	CR	0.204	1.147	0.8392
Raw FA	MB	0.312	1.0474	0.8775
Raw FA	CR	0.265	4.7586	0.6278

4.8.4 Dubinin-radushkevich (D-R) isotherm

Dubinin-Radushkevich isotherm model describes the nature of adsorption in both heterogenous and homogenous. It is also similar to the Langmuir isotherm model (Quayoom et al. 2017) and it is usually applied to express the types of adsorption such as chemical and physical. Figs. 26 (a – i) show linear of D-R isotherms for the adsorption of dyes. Table 11 represents the D-R isotherm parameter for the adsorption of dyes. D-R isotherm can be expressed by equations 10-12

$$\ln Q_e = \ln(Q_{max}) - K\varepsilon^2 \quad (10)$$

Where K is the constant sorption of the energy (mol²/kJ²); ε is the polanyi potential which is given by the equation:

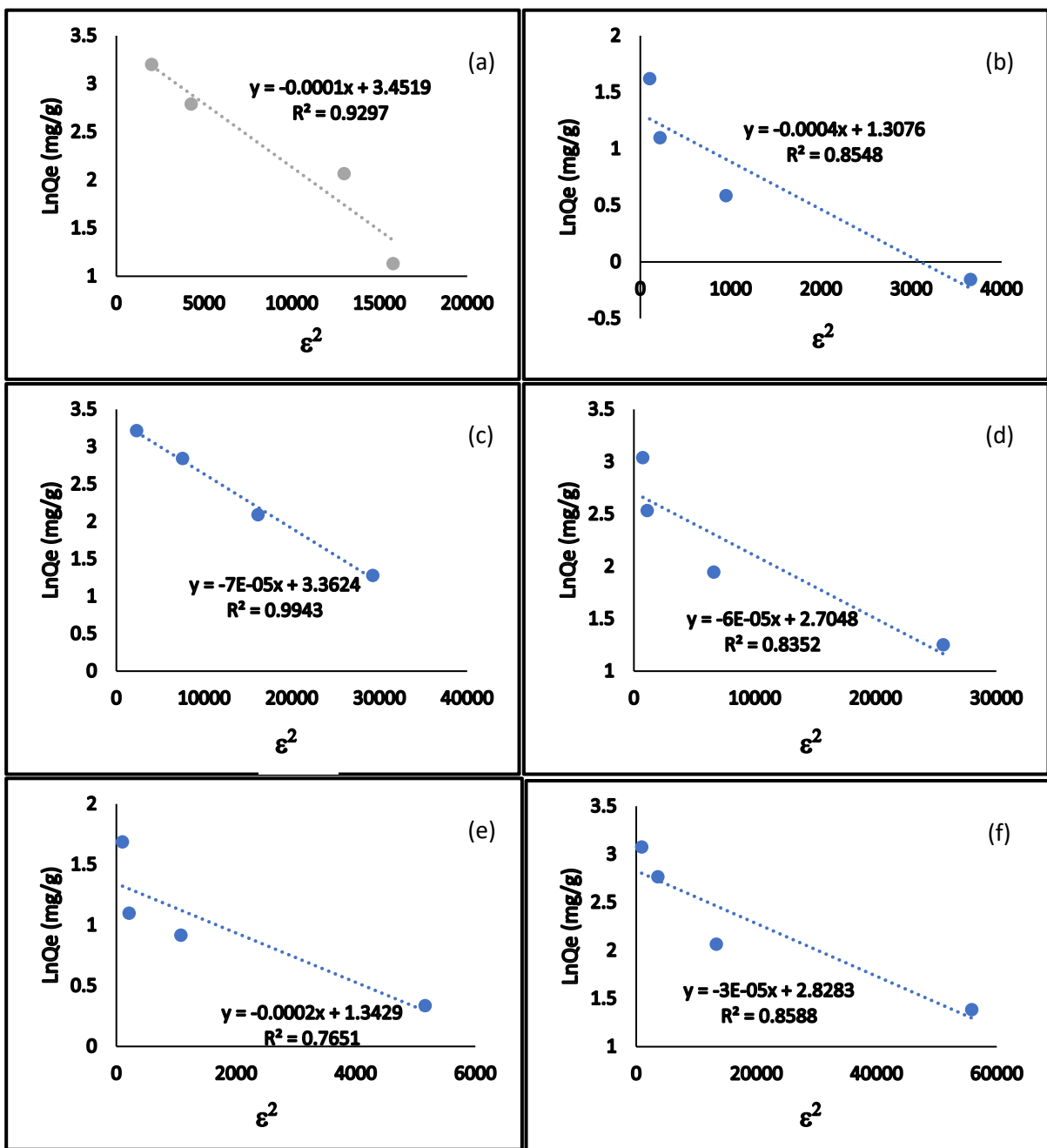
$$\varepsilon = RT \ln(1 + \frac{1}{C_e}) \quad (11)$$

Where R is the universal gas constant (8.314 J.mol⁻¹ K⁻¹); T is the temperature (K); C_e is the equilibrium concentration of dye (mg/L), and Q_{max} is the maximum adsorption capacity.

The value means of energy of sorption, E (kJ/mol) can be calculated from the equation below:

$$E = \frac{1}{\sqrt{2K}} \quad (12)$$

The value of E provides useful information about the adsorption mechanism. Physical adsorption occurs when E is less than 8 kJ/mol; chemisorption occurs when E is between 8 and 16 kJ/mol. Particle diffusion is in charge of regulating adsorption if E is more than 16 kJ/mol.



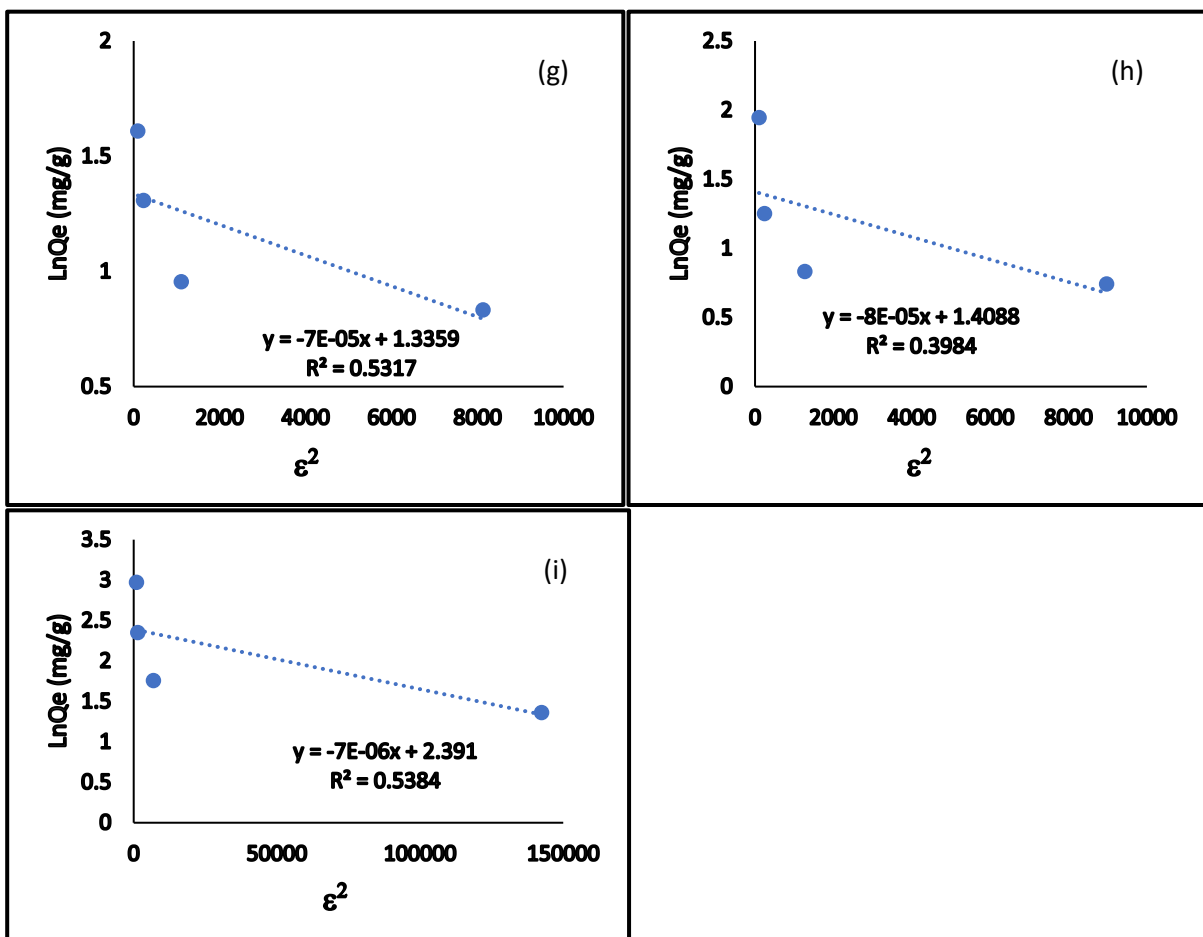


Figure 26. Linear regression D-R isotherm for adsorption of dyes; (a). 12-M- Na_2SiO_3 -MB, (b) 12-M- Na_2SiO_3 -CR, (c) 10-M- Na_2SiO_3 -MB, (d) 12-M- H_2O_2 -MB, (e) 12-M- H_2O_2 -CR, (f) 10-M- H_2O_2 -MB, (g) 10-M- H_2O_2 -CR, (h) Raw FA-MB, (i) Raw FA-CR.

Table 11: D-R isotherm parameter for adsorption of dyes; (a). 12-M-Na₂SiO₃-MB, (b) 12-M-Na₂SiO₃-CR, (c) 10-M-Na₂SiO₃-MB, (d) 12-M-H₂O₂-MB, (e) 12-M-H₂O₂-CR, (f) 10-M-H₂O₂-MB, (g) 10-M-H₂O₂-CR, (h) Raw FA-MB, (i) Raw FA-CR.

Adsorbent	Dyes	Linear		
		Q _{max} (mg/g)	E (Kj/mol)	R ²
12-M-Na ₂ SiO ₃	MB	31.56	70.71	0.9297
12-M-Na ₂ SiO ₃	CR	3.697	35.355	0.8548
10-M-Na ₂ SiO ₃	MB	28.85	84.515	0.9943
10-M-Na ₂ SiO ₃	CR	-	-	-
12-M-H ₂ O ₂	MB	14.95	91.287	0.8352
12-M-H ₂ O ₂	CR	3.83	50	0.7651
10-M-H ₂ O ₂	MB	16.92	129.01	0.8588
10-M-H ₂ O ₂	CR	3.80	84.51	0.5317
Raw FA	MB	4.09	79.06	0.3984
Raw FA	CR	10.92	267.3	0.5384

In this research, 4 isotherm models namely Langmuir, Freundlich, Temkin and the Dubinin-Radushkevich were investigated in order to fit the experimental data. The comparison of parameters and the value of the correlation coefficients (R²) were investigated to identify the best-fit isotherm model for the adsorption process. This investigation was done on raw FA and 4 prepared fly ash based geopolymers (12-M-Na₂SiO₃, 10-M-Na₂SiO₃, 12-M-H₂O₂, 10-M-H₂O₂) for adsorption of different dyes (MB and CR). Linear regression method was applied to determine correlation coefficients. [Novas et al. \(2019\)](#) stated that Langmuir was applicable in high concentrations while Freundlich fit well in low concentrations. [Mor et. al \(2018\)](#) showed that adsorbents favoured Langmuir at a temperature of 40 °C which explains that temperature affects adsorption isotherm. The obtained results show that the maximum value of R² obtained from Langmuir isotherm linear equation (0.9954 for 12-M-Na₂SiO₃-MB), Freundlich isotherm linear equation (0.9875 for 12-M-Na₂SiO₃-CR), Temkin isotherm linear equation (0.9846 for 10-M-Na₂SiO₃-MB), Dubinin-Radushkevich isotherm linear equation (0.9943 for 10-M-Na₂SiO₃-MB). The results show that the Langmuir isotherm fit best for the adsorption of MB and CR using 12-M-Na₂SiO₃ and 12-M-H₂O₂ while

Temkin fit in both 10-M-Na₂SiO₃ and 10-M-H₂O₂. The adsorption on CR using raw fly ash showed a high R² (0.9996) using linear regression methods compared to the adsorption of MB using raw FA which gave R² (0.9604). The maximum adsorption capacity for the adsorption of MB was 17.7 mg/g calculated value of 16.3 mg/g experimental value while CR was 3.4 mg/g compared to 4 mg/g. The separation factor R_L confirms that the adsorption of MB and CR on fly ash based geopolymers is favourable as R_L value ranged between 0.002 and 0.957. The R_L value obtained, showed that two geopolymers (12-M-Na₂SiO₃-MB and 10-M-Na₂SiO₃-MB) did not fit the Langmuir model as they had negative adsorption constant (K_L).

4.9 Adsorption kinetic studies

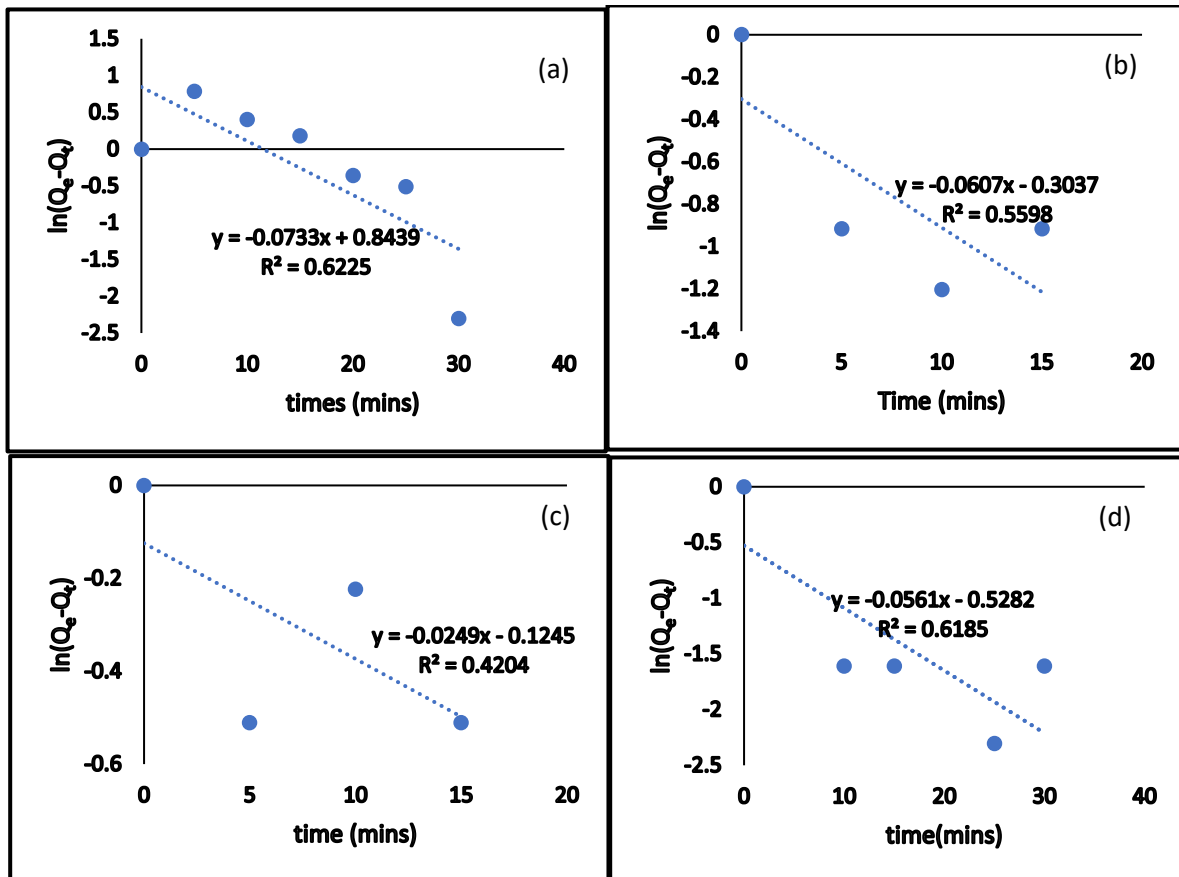
Adsorption kinetic models are employed to analyze the adsorbent's performance and investigate the mechanisms of adsorption kinetics. The physical meanings of the kinetic models and the methods for solving them are not well understood (Wang and Guo, 2020). The adsorption kinetic model determines the rate of adsorption, which determines how long it takes for the adsorption process to reach equilibrium (Sahoo and Prelot, 2020). Pseudo-first order, pseudo-second order and Weber and Morris intraparticle diffusion models were used to assess the kinetic data of the study. In this process, 10-M-H₂O₂ geopolymer was not used as it was shown to have no adsorption activity, the test was repeated twice.

4.9.1 Pseudo-first order model

The pseudo-first order model was first introduced by Lagergren (1898). The pseudo-first-order model is used to determine whether the reaction mechanism is a physical adsorption process or not. The pseudo-first-order kinetic model is expressed by equation 13. A plot of $\ln(Q_e - Q_t)$ vs t was plotted in Figs. 27a-h. In Figs 27a-h it can be seen that the R² was poor as it was low and with the aid of table 12, none of the Q_e calculated value was close to Q_{exp} value. This mean the adsorption cannot be described by pseudo-first order model. Table 12 shows the summary of the pseudo-first-order parameter.

$$\ln(Q_e - Q_t) = \ln Q_e - k_1 t \quad (13)$$

Where Q_e is the adsorption capacity at equilibrium (mg/g); Q_t is the adsorption capacity at time t (mg/g); t is the time (minutes); k_1 is the pseudo-first-order rate constant (1/min).



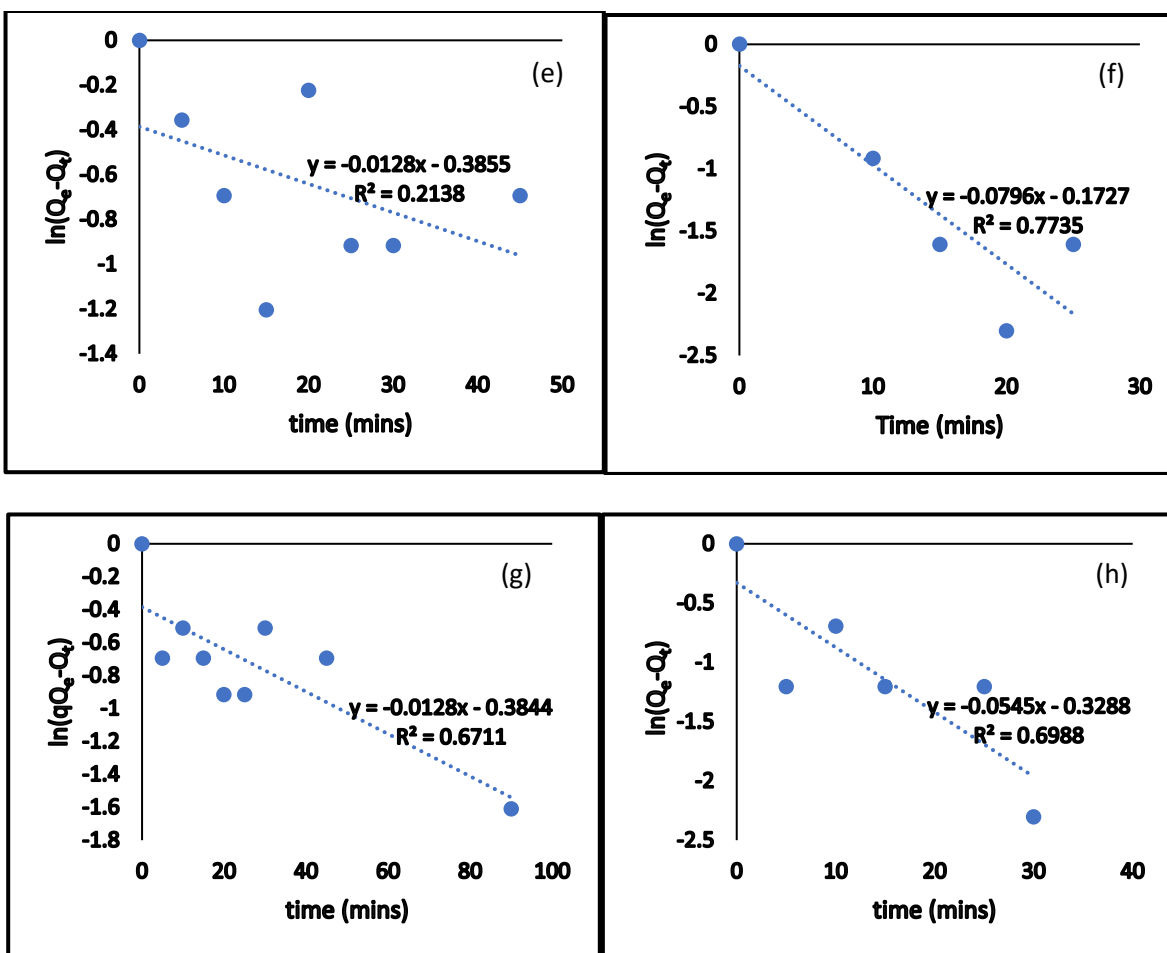


Figure 27. Linear regression of pseudo-first-order kinetic model for adsorption of dye; (a). 12-M- Na_2SiO_3 -MB, (b) 12-M- Na_2SiO_3 -CR, (c) 10-M- Na_2SiO_3 -MB, (d) 12-M- H_2O_2 -MB, (e) 12-M- H_2O_2 -CR, (f) 10-M- H_2O_2 -MB, (g) 10-M- H_2O_2 -CR, (h) Raw FA-MB,

Table 12: Pseudo-first-order kinetic model parameter for adsorption of dye; (a). 12-M-Na₂SiO₃-MB, (b) 12-M-Na₂SiO₃-CR, (c) 10-M-Na₂SiO₃-MB, (d) 12-M-H₂O₂-MB, (e) 12-M-H₂O₂-CR, (f) 10-M-H₂O₂-MB, (g) 10-M-H₂O₂-CR, (h) Raw FA-MB,

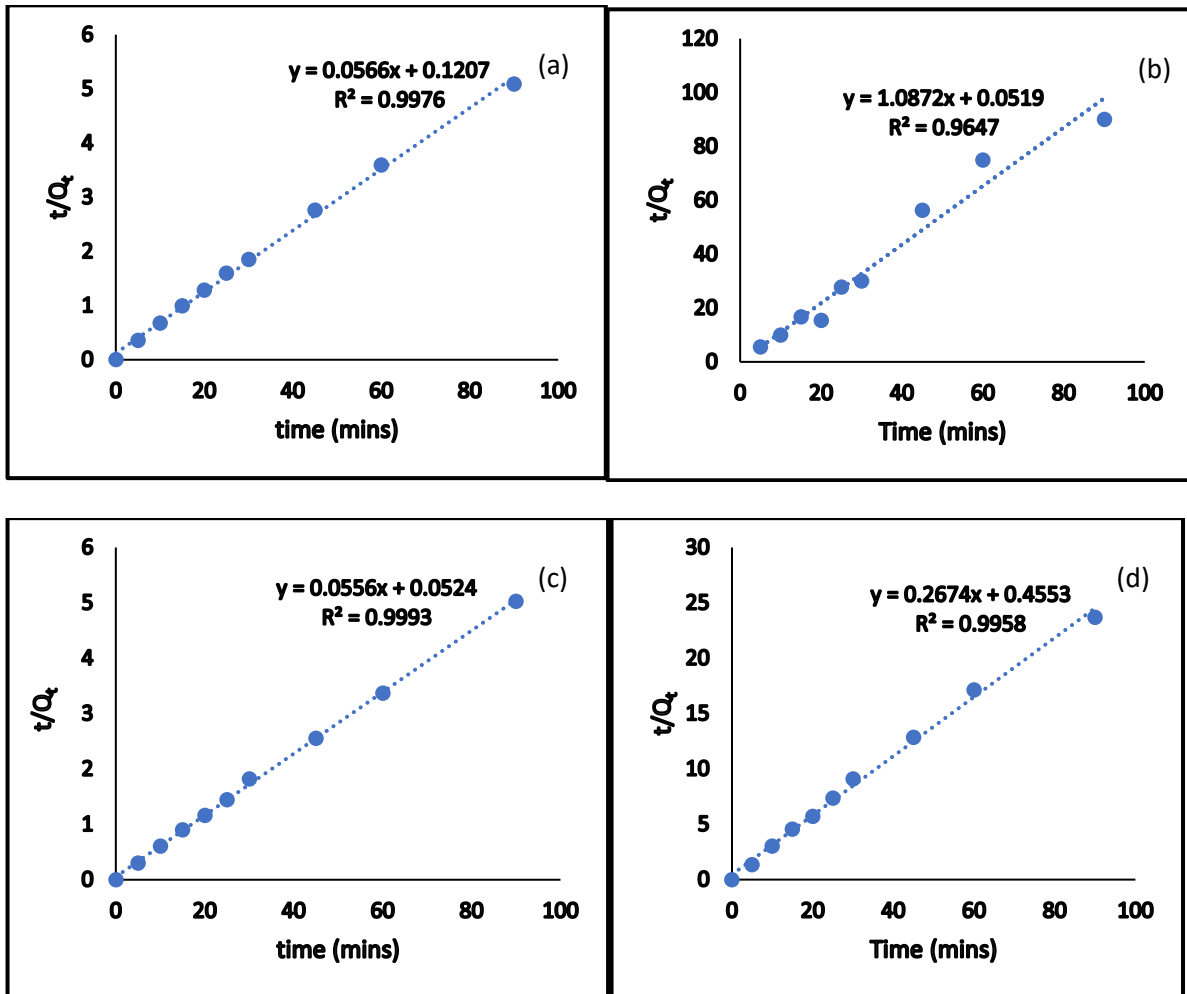
Adsorbent	Dyes	Linear			
		Q _{exp}	Q _e (mg/g)	k ₁	R ²
12-M-Na ₂ SiO ₃	MB	3.1	2.3	-0.002	0.6225
12-M-Na ₂ SiO ₃	CR	1.3	0.73	0.0007	0.5598
10-M-Na ₂ SiO ₃	MB	3.6	0.88	-0.002	0.4204
10-M-Na ₂ SiO ₃	CR	-	-	-	-
12-M-H ₂ O ₂	MB	3.5	0.589	-0.002	0.6185
12-M-H ₂ O ₂	CR	1.4	0.680	-0.0003	0.2138
10-M-H ₂ O ₂	MB	4	0.84	-0.007	0.7735
10-M-H ₂ O ₂	CR	2.3	0.68	-0.0001	0.6711
Raw FA	MB	2.4	0.72	-0.002	0.6988
Raw FA	CR	3.8	-	-	-

4.9.2 Pseudo-second order model

The pseudo-second order kinetic model assumes that chemical sorption or chemisorption is the rate-limiting phase and predicts behavior across the whole range of adsorption. (Sahoo and Prelot, 2020). Figs. 28a-i show plots of t/Q_t vs t . The R^2 ranges between 0.9604 to 0.9995 with good agreement between Q_e calculated value and Q_{exp} experimental value. Table 13 shows summary of the pseudo second-order parameters. The pseudo-second order kinetic model is expressed by equation 14.

$$\frac{1}{Qt} = \frac{1}{k_2 Q_e^2} + \frac{1}{Q_e} \quad (14)$$

Where Q_e is the amount of dye adsorbed (mg/g); t is time (mins); k_2 is the pseudo second-order rate constant ($\text{g.mg}^{-1}\text{min}^{-1}$).



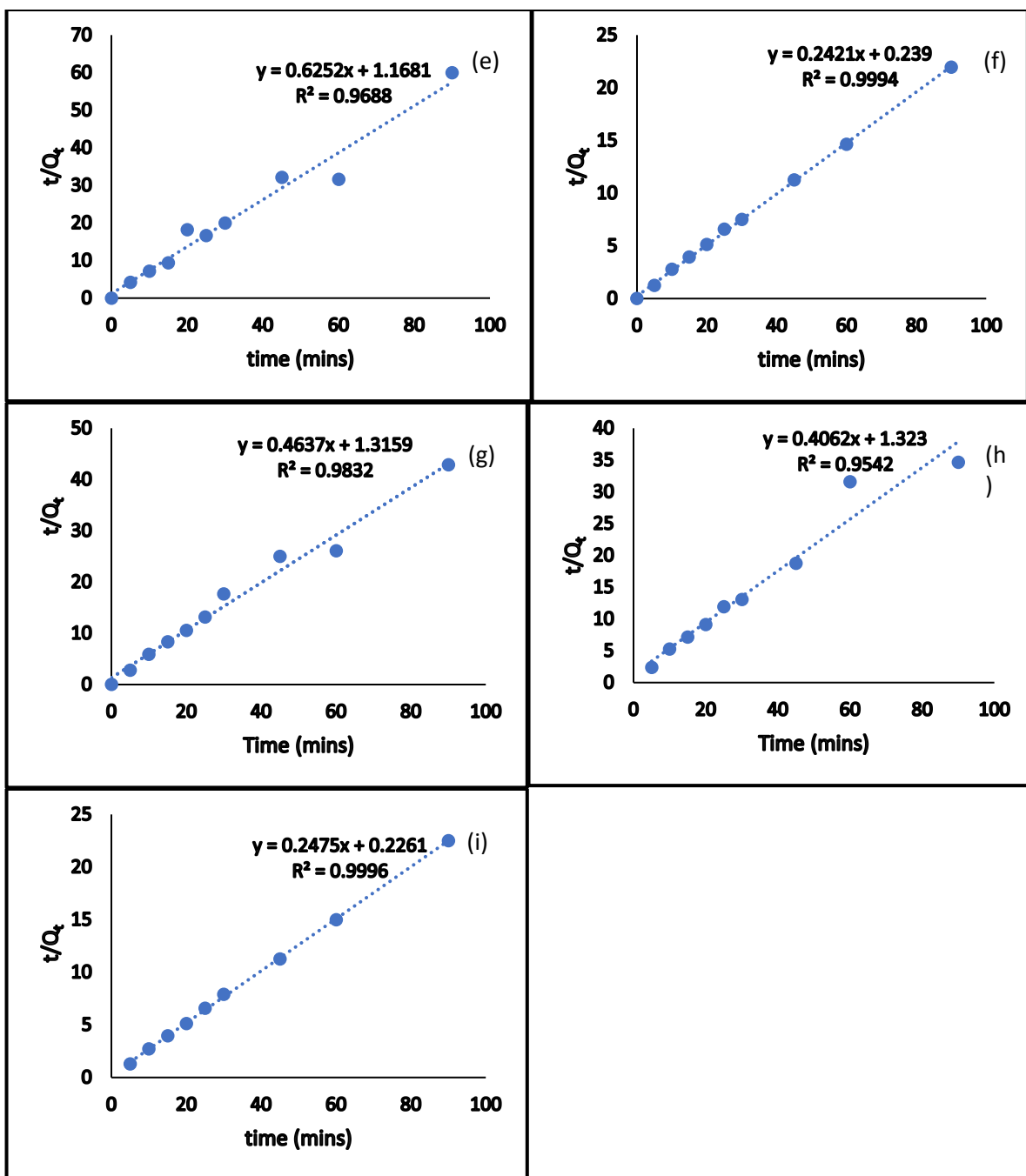


Figure 28. Linear regression of pseudo-second-order kinetic model for adsorption of dyes; (a). 12-M- Na_2SiO_3 -MB, (b) 12-M- Na_2SiO_3 -CR, (c) 10-M- Na_2SiO_3 -MB, (d) 12-M- H_2O_2 -MB, (e) 12-M- H_2O_2 -CR, (f) 10-M- H_2O_2 -MB, (g) 10-M- H_2O_2 -CR, (h) Raw FA-MB, (i) Raw FA-CR.

Table 13: pseudo-second-order kinetic model parameter for adsorption of dyes; (a). 12-M-Na₂SiO₃-MB, (b) 12-M-Na₂SiO₃-CR, (c) 10-M-Na₂SiO₃-MB, (d) 12-M-H₂O₂-MB, (e) 12-M-H₂O₂-CR, (f) 10-M-H₂O₂-MB, (g) 10-M-H₂O₂-CR, (h) Raw FA-MB, (i) Raw FA-CR.

Adsorbent	Dyes	Linear			
		Q _{exp}	Q _e (mg/g)	K ₂ (g min ⁻¹ mg ⁻¹)	R ²
12-M-Na ₂ SiO ₃	MB	16.3	17.8	0.0265	0.9976
12-M-Na ₂ SiO ₃	CR	1.3	0.92	22.77	0.9649
10-M-Na ₂ SiO ₃	MB	17.2	17.9	0.059	0.9993
10-M-Na ₂ SiO ₃	CR	-	-	-	-
12-M-H ₂ O ₂	MB	3.5	3.7	0.1570	0.9958
12-M-H ₂ O ₂	CR	1.4	1.6	0.3346	0.9688
10-M-H ₂ O ₂	MB	4	4.1	0.2452	0.9994
10-M-H ₂ O ₂	CR	2.3	2.2	0.1762	0.9832
Raw FA	MB	2.4	2.4	0.1662	0.9604
Raw FA	CR	3.8	4	0.2709	0.9996

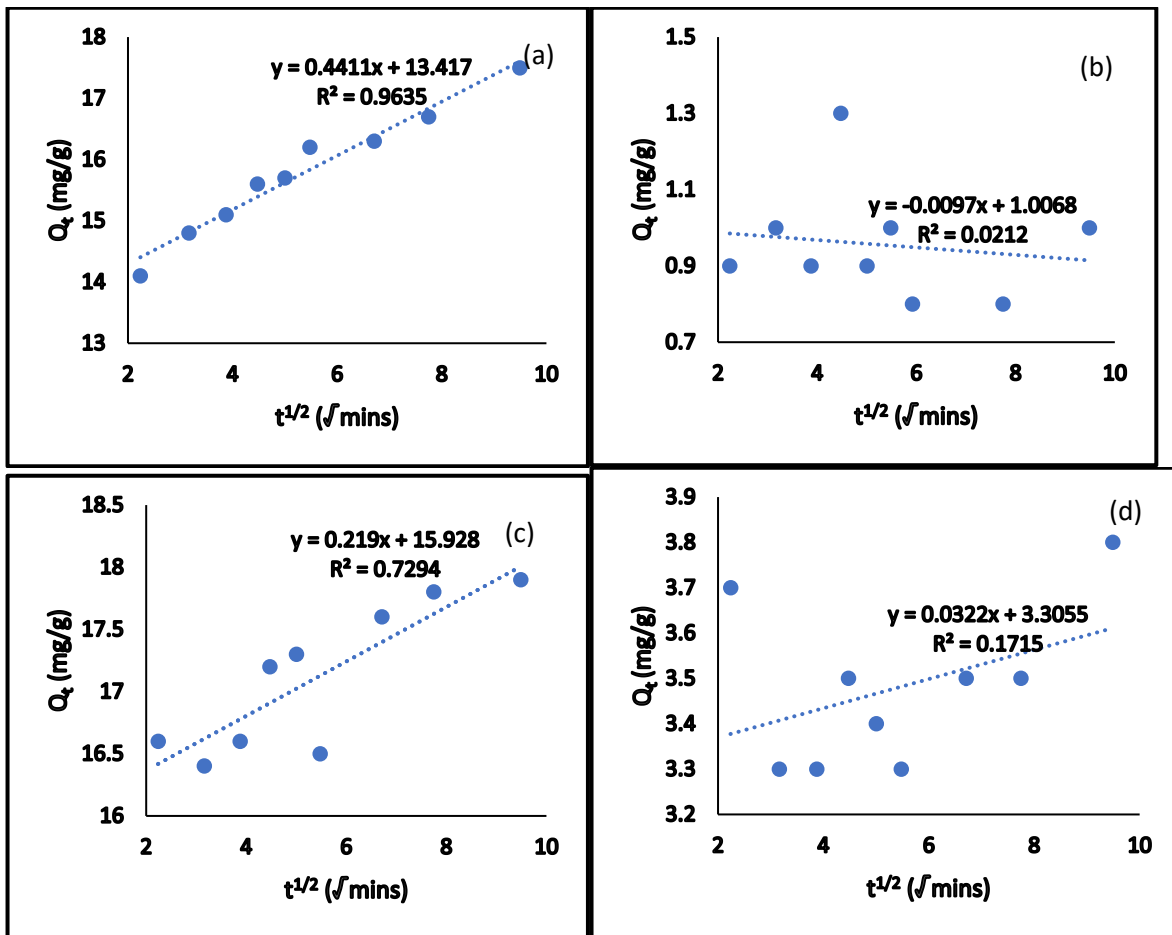
4.9.3 Intraparticle diffusion model

Weber and Morris Interparticle diffusion model was developed and proposed by [Weber and Morris \(1963\)](#). The intraparticle diffusion is used to evaluate diffusion as the adsorption rate-controlling step. Intra-particle diffusion model is the rate controlling step if the Weber-Morris plot the most linear. Figs. 29a-c show plots graph of Q_t vs t^{1/2}.

Table 14 shows summary of intraparticle diffusion parameters. The intraparticle diffusion kinetic model is expressed by the equation 15

$$Q_t = k_1 t^{1/2} + C \quad (15)$$

Where t is the time (mins); Q_t is the adsorption capacity at time (mg/g); k_1 is intraparticle diffusion rate constant (mg/(gmin^{1/2})); C represents the intercept (mg/g).



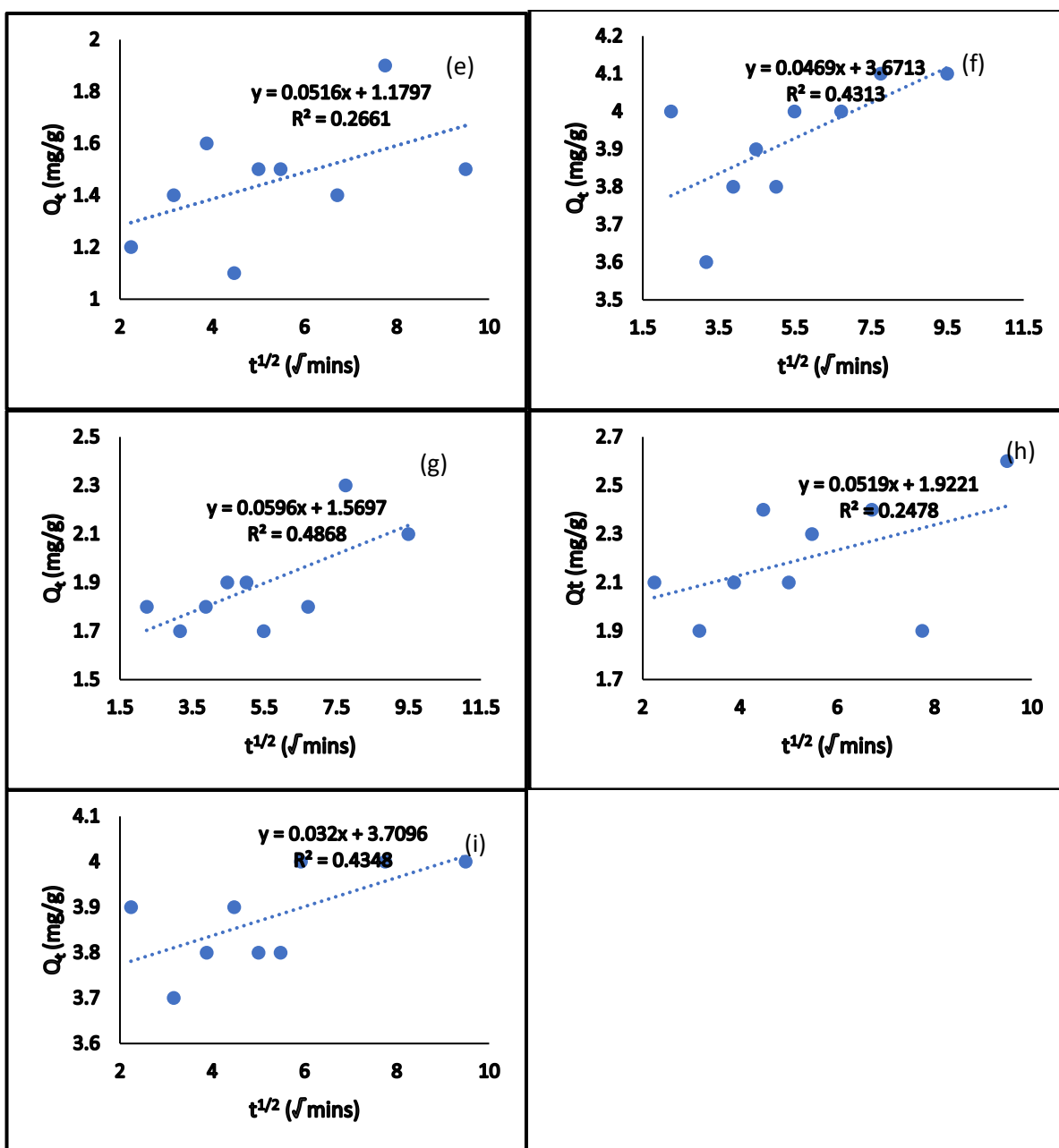


Figure 29. Linear regression of Intraparticle diffusion model for adsorption of dyes; (a). 12-M- Na_2SiO_3 -MB, (b) 12-M- Na_2SiO_3 -CR, (c) 10-M- Na_2SiO_3 -MB, (d) 12-M- H_2O_2 -MB, (e) 12-M- H_2O_2 -CR, (f) 10-M- H_2O_2 -MB, (g) 10-M- H_2O_2 -CR, (h) Raw FA-MB, (i) Raw FA-CR.

Table 14: Intraparticle diffusion model parameter for adsorption of dyes; (a). 12-M-Na₂SiO₃-MB, (b) 12-M-Na₂SiO₃-CR, (c) 10-M-Na₂SiO₃-MB, (d) 12-M-H₂O₂-MB, (e) 12-M-H₂O₂-CR, (f) 10-M-H₂O₂-MB, (g) 10-M-H₂O₂-CR, (h) Raw FA-MB, (i) Raw FA-CR.

Adsorbent	Dyes	Linear		
		C (mg/g)	K _{id} (mg/gmins ^{1/2})	R ²
12-M-Na ₂ SiO ₃	MB	13.4	0.4411	0.9635
12-M-Na ₂ SiO ₃	CR	1.01	-0.01	0.0212
10-M-Na ₂ SiO ₃	MB	15.9	0.219	0.7294
10-M-Na ₂ SiO ₃	CR	-	-	-
12-M-H ₂ O ₂	MB	3.306	0.033	0.1735
12-M-H ₂ O ₂	CR	1.18	0.05	0.2661
10-M-H ₂ O ₂	MB	3.67	0.0469	0.4313
10-M-H ₂ O ₂	CR	1.57	0.0596	0.4868
Raw FA	MB	0.99	0.052	0.2478
Raw FA	CR	3.71	0.052	0.4347

In this study, three different kinetic models were applied to describe the adsorption process in the adsorption of dyes (MB and CR) using geopolymers (12-M-Na₂SiO₃, 10-M-Na₂SiO₃, 12-M-H₂O₂, 10-M-H₂O₂) and raw FA. The models applied were pseudo-first order, pseudo-second order and Intraparticle diffusion (Weber and Morris 1963). From obtained results, the maximum linear regression correlation coefficients (R²) of pseudo-first order is 0.7735 (10-M-H₂O₂-MB), pseudo-second-order is 0.9994 (10-M-H₂O₂-MB) and intraparticle diffusion is 0.9734 (12-M-Na₂SiO₃-MB). Based on the R² obtained for all geopolymers, the pseudo-second order rate (0.9994) fit best on the adsorption of MB using 10-M-Na₂SiO₃ and 10-M-H₂O₂. The maximum R² for pseudo-second order displayed Q_{exp} (4 mg/g) close to Q_e (4.1 mg/g) which explains that when compared to the pseudo-first order and intraparticle diffusion models, the pseudo-second-order model accurately describes the adsorption process. Pseudo-second order also fit best in the CR adsorption using raw FA as it gave R² (0.9996) and calculated adsorption capacity of (3.8 mg/g) compared to the experimental value (4 mg/g). Pseudo-second order model indicated

that the chemisorption process controls the adsorption process. The similar result was obtained in the previous research by [Alaouani et al. \(2018a, 2019b\)](#). Pseudo-first order could not describe the adsorption behaviour as it has a low R^2 (0.7735 as maximum) and there was a big different value between the calculated adsorption capacity (0.73 mg/g) and experimental value (1.3 mg/g). A similar theory was mentioned by different researchers such as [Gao et al. \(2016\)](#) [Attari et al. \(2017\)](#), and [Qiu et al. \(2017\)](#). [Zhou et.al \(2021\)](#) and [Siyal et al. \(2020\)](#) also stated that if the kinetic model has a low R^2 value it means that the kinetic model did not fit the adsorption data. All this research agreed with pseudo-second-order which also applies to our research finding as the R^2 ranged between 0.9604 – 0.9996 for all geopolymers and raw fly ash. Also, all the calculated Q_e were close to or the same as the experimental value as it confirmed that the process followed adsorption reaction kinetic model of pseudo second order.

CHAPTER 5

5.1 Conclusion

The results show that the geopolymers are excellent adsorbents for anionic and cationic contaminants in wastewater. Several factors such as pH, contact time, dose, and concentration were investigated at room temperature throughout the investigation to assist in the discovery of the active geopolymers. Morphology, chemical composition, and crystallinity were studied using a variety of techniques such as XRD, XRF, FTIR, TGA, and SEM. Adsorption isotherm models such as Langmuir, Freundlich, Temkin, and D-R are frequently used to assess the adsorption capacity of the different adsorbents. The Langmuir isotherm model emerged as the best isotherm for estimating equilibrium parameters as it showed a value of $Q_{\max}$ calculated value close to Q_e of experimental data. The pseudo-second-order model was used to describe adsorption kinetics instead of the pseudo-first-order model and intraparticle diffusion with the R^2 values for the pseudo second order model ranging from 0.9604 to 0.9994. The outcomes of the experimental results showed the maximum adsorption capacity of methylene blue was 16.3 mg/g using Na_2SiO_3 -geopolymers, while the maximum adsorption capacity of Congo Red was 3.8 mg/g using Na_2SiO_3 -geopolymers. The removal efficiency reached 90% for 10-M- Na_2SiO_3 and 82% for 10-M- H_2O_2 . Adsorption for methylene blue and Congo red dyes was high at low pH, which was 3 and 4 respectively. As the dye concentration increased, the removal percentage decreased while the adsorption capacity increased. In conclusion, Na_2SiO_3 -geopolymers had high activity at low dosages of geopolymer while H_2O_2 had high activity at high dosages. The percentage removal of Congo red using Na_2SiO_3 -geopolymer was very low compared to H_2O_2 -geopolymers. It shows that Congo red has more activity in H_2O_2 geopolymers while methylene blue has more activity in Na_2SiO_3 -based geopolymers. Raw fly ash has also shown a high removal efficiency and adsorption capacity for Congo red, which was higher than most geopolymers. The maximum removal efficiency of Congo red using raw FA was 94% compared to all fly ash based geopolymers which maybe due to the high surface charge of raw fly ash since Congo red is anionic.

5.2 Recommendation

In this study, parameters were investigated at a constant temperature of 25 °C. Parameters such as concentration, time, and dosages were tested. The results obtained have shown that parameters play important roles in the adsorption of geopolymers. Therefore, we recommend that temperature effect be investigated to enable investigation of adsorption thermodynamics. In this study, the adsorption of Congo red using raw fly ash had greater removal efficiency, therefore we recommend that raw fly ash be investigated with different dyes, especially anionic dyes. The geopolymers showed a lot of fluctuations in adsorption studies, optimization of synthesis process need to be investigated for cleaner materials that allows further studies of temperature effects allowing for determination of thermodynamic parameters and adoption for dye removal in industrial waste waters.

REFERENCES:

- Ahmaruzzaman M.; (2010). A review on the utilization of fly ash. *Progress in energy and combustion science* 36(2010) 327-363.
- Al-husseiny R.A., and Ebrahim S.E., (2021). Synthesis of geopolymer for the removal of hazardous waste: a review *IOP con. Series: Earth and Environmental science* 779 (2021) 012102.
- Alehyen S.; Achouri M. E.L.; & Taibi.; (2017). Characterization, microstructure, and properties of fly ash-based geopolymer. *Jmes*, 2017 vol. 8, issue 5 page 1783-1796.
- Alouani M.E., Alehyen S., Achouri M.E., and Taibi M., (2018). Adsorption of caution dye onto fly ash-based geopolymer: batch and fixed bed column studies. *MATEC web of conf.* 149, 0288 (2018).
- Alouani M.E.; Alehyen S.; Achouri M.E.; & Taibi.; (2019). Preparation, characterization, and application of metakaolin-based geopolymer for removal of methylene blue from aqueous solution. *Journal of Chemistry*, Volume 2019.
- Anggarini U.; & Sukmana N. C.; (2006). Synthesis and characterization of geopolymers from bottom ash and rice hulk ash. *Material science engineering.* 107 (2016) 012022.
- Attari M., Bukhari S.S., Kazemian H., and Rohani S., (2017). A low-cost adsorbent from coal fly ash for mercury removal from industrial wastewater. *Journal of Environmental Chemical Engineering* 5 (2017) 391-399.
- Azari A., Nabizadeh R., Nasser S., Mahui A.H and Mesdaghinia A.R. (2020). Comprehensive systematic review and metal-analysis of dyes adsorption by carbon-based adsorbent materials: classification and analysis of last decade studies. *Chemosphere* 250 (2020) 126238.
- Benkhaya S., rabet S., Harfi A., (2020). A review on classification, recent synthesis and applications of textile dyes. *Inorganic Chemistry Communication* 115 (2020) 107891.

- Bhandari R.B.; Pathak A.; & Jha V.K.; (2012). A laboratory-scale synthesis of geopolymers from locally available coal fly ash from the brick industry. J. Nepal chem. Soc., vol. 29, 2012.
- Bhatia D, Sharma N.R, Singh J and Kanwar R, (2017) Biological methods for textile dye removal from wastewater. A review. Critical Reviews in environmental Science and Technology.
- Buema G., Harja M., Lupu N., Chiriac H., Forminte L., Ciobanu G., Bucur D., and Bucur R.D, (2021). Adsorption performance of modified fly ash for copper ion removal from aqueous solution. Water 2021, 13, 207.
- Bulgariu L., Escudero L.B., Bello O.S, Iqbal M., Nisar J., Adegoke K.A., Alakhras F., Kornaros M., Anastopoulos L., (2019). The utilization of leaf-based adsorbents for dyes removal: A review. Journal of Molecular Liquids, Vol 276, pages 728-747.
- Dai S., and Finkelman R.B., (2017). Coal as a promising source of critical elements: Progress and future prospects. International Journal of coal Geology. 186, 155-164.
- Darmayanti L.; Notodarmojo S.; Damanhuri.; Kadja G.T.M.; & Mukti R.R.; (2019). Preparation of alkali-activated fly ash-based geopolymer and their application in the adsorption of copper (II) and Zinc (II) ions. MATEC web of con. 267,06012 (2019).
- Das D., and Rout P., (2021). Synthesis, Characterization and Properties of fly ash based geopolymers materials. Journal of Materials Engineering and Performance. 10.1007/s11665-021-05647-x
- Das D., and Rout P.K., (2021). Synthesis and characterization of fly ash and GBFS Based geopolymer materials. Biointerface research in applied chemistry. Vol. 11, issues 6, 2021, 14506-14519.
- Daud N.A.A., Shamsuddin M.R., and Pradanawati S.A., (2020). Synthesis and characterization of fly ash based geopolymer membrane for methylene blue dye removal. IOP con. Series: Earth and Environmental science 765 (2021) 012081.
- Dwivedi A.; & Jain M. K.; (2014). Fly ash- waste management and overview: A review. Recent Research in Science and Technology. Vol. 100, No. 12.

- Dzoujo T. Hermann, Sylvain Tome, Victor O. Shikuku, Jean T. Tchuigwa, Alex SpeiB, Christoph Janiak, Marie Annie Etoh and David Dina. (2021). Enhanced performance of hydrogen peroxide modified pozzolan-based geopolymers for abatement of methylene blue from aqueous medium.
- Emenike P.C., Omole D.O., Ngene B.U., and Tenebe I.T., (2016). Potentiality of agricultural adsorbent for the sequestering of metal ions from wastewater. *Global J. Environ. Sci. Manage.*, 2(4): 441-442.
- Fauzi A. Nuruddin M. F, Malkawi A. B, Abdullah M. M. A. B, (2016). Study of fly ash characterization as a cementitious material. *Procedia Engineering* 148 (2016) 487-493.
- Feng, J., Zhang, R., Gong, L., Li, Y., Cao, W., & Cheng, X. (2015). Development of porous fly ash-based geopolymer with low thermal conductivity. *Materials & Design* (1980-2015), 65, 529–533.
- Ferrarini F. S.; Cardoso M. A.; Paprocki A.; & Pires M.; (2016). Integrated Synthesis of Zeolites using coal fly ash: Element Distribution in the products, washing waters, and effluent. Vol. 27, No. 11, 2034-2045, 2016.
- Fitrian E., and Purbasari A., (2020). Application of low-cost mesoporous geopolymers for dye waste removal. *IOP conf. series: material science and engineering*. 1053 (2021) 012020.
- Franus W.; Wdowin M.; & Franus M.; (2014). Synthesis and characterization of zeolite prepared from industry fly ash. *Environ Monit asses* (2014) 186: 5721-5729.
- Gao X., Dai Y., Zhang Y., Zhai X., and Fu F., (2016). Effective dye removal from wastewater using novel low-cost NaOH-Modified fly ash. *Clays and Clay minerals*, Vol. 64, No.6, 695-705, 2016.
- Ge J.C.; Yoon S.K.; & Choi N.J.; (2018). Application of fly ash as adsorption for removal of air and water pollutants. *Appl. Sci.* 2018, 8, 1116.
- Gembo R. O, Aoyi O, Majoni S, Etale A, Odistse S and King'ondeu C. K, (2021). Synthesis of bismuth oxyhalide ($\text{BiOBr}_{z\text{I}(1-z)}$) solid solutions for photodegradation of methylene dye. *AAS Open research*.
- Gurses A, Acikyildiz M, Gunes K., and Gurses M. A. (2016). Dye and Pigments: Their structure and properties. *Dyes and pigments*, 13-29.

- Guyu S., (2019). Fly ash-based geopolymer as innovative material for environmental application. Environmental Engineering Commons. 1778.
- Hamid R.M.; man Z. & Azizli K.A.; (2016). Concentration of NaOH and the effect on properties of fly ash-based geopolymer. Procedia Engineering 148(2016) 189-193.
- Han R., Zhang J., Zou W., Shi J., and Liu H., (2005). Equilibrium biosorption isotherm for lead ion on chaff. Journal of Hazardous materials. Vol. 125, issues 1-1, pages 266-271.
- Harja M.; Barbuta M.; & Garvrescu M.; (2009). Utilization of coal fly ash from power plants II. Geopolymer obtaining: Environmental engineering and management. Journal, vol. 8, No. 3, 513-520.
- Hower, J. C., Groppo, J. G., Graham, U. M., Ward, C. R., Kostova, I. J., Maroto-Valer, M. M, & Dai, S. (2017). Coal-Derived unburned carbons in fly ash: A review. International Journal of Coal geology, 179, 11-27.
- Jaturapitakkul C., (2004). A study of disposed fly ash from landfill to replace Portland cement. Waste management 24 (7): 701-9.
- Jha V.K., & Budhamagar G.P., (2012). Synthesis of geopolymers from coal fly ash. J. Nepal chem. Soc., vol. 30, 2012.
- Kaewmee P., Song M., Iwanami M., Tsutsumi H., and Takashi F., (2020). Porous and reusable potassium-activated geopolymer adsorbent with high compressive strength fabricated from coal fly ash wastes. Journal cleaner production 272 (2020) 122617.
- Karthik V., Saravanan K., Bharathi P., and Meiaraj C., (2014). An overview of treatments for the removal of textile dyes. Journal of Chemical and Pharmaceutical Sciences. 7(4):301-307.
- Khan M.I., Azizli K., Sufian S., Siya A.A., Man Z., & Ullah H., (2014). Sodium silicate free geopolymer as coating materials: adhesion to steel.
- Kioupis D., Kavakakis C., Tsivilis S., and Kakali G., (2018). Synthesis and characterization of porous fly ash-based geopolymers using Si as foaming agents. Advances in materials science and Engineering, 2018, 1-11.

- Lemly A.D, (2017). Environmental hazard assessment of coal ash disposal at proposed Rampal power plant. Human and Ecological Assessment: An international Journal. ISSN: 1080-7039.
- Li B, and Lin X., (2019). Adsorption of congo red from aqueous solution using La/MFA composite as adsorbent. Materials science forum. ISSN: 1662-9752, vol. 944, pp 1117-1122.
- Li L., Wang S. and Zhu Z., (2006). Geopolymeric adsorbents from fly ash for dye removal from aqueous solution. Journal of colloid and interface science 300 (2006) 2-59.
- Mall I.D., Srivastava V.C.S., Agarwal N.K., and Mishra I.M., (2005). Removal of congo red from aqueous solution by bagasse fly ash and activated carbon: kinetic study and equilibrium isotherm analyses. Chemosphere 61 (2005) 492-501.
- Means T., (2021). What is coal ash and how dangerous is it? Environment Pollution.
- Mohammedi A. and Abdullah A., (2018). Scanning Electron microscopy (SEM): A review. Proceeding of 2018 international Conference on Hydraulics and Pneumatics-HERVEX. ISSN 1454-8003.
- Mor S., Chhvi M.K., Sushil K.K., and Ravinda K., (2018). Assessment of hydrothermally modified fly ash for the treatment of methylene blue dye in the textile industry wastewater. Environ Dev Sustain (2018) 20:625-639.
- Mustaq F., Zahid M., Bhatti I.A., Nasir S., and Hussain T., (2018). Possible application of coal fly ash in wastewater treatment. Journal of environment management 240 (2019) 27-46.
- Naderi M., (2015). Surface Area: Brunauer – Emmett – Teller (BET). Progress in Filtration and Separation, 585–608.
- Nandi B., Goswami A., and Purkait M., (2019). Removal of cationic dyes from aqueous solutions by kaolin: Kinetic and equilibrium studies. Applied class science, 42 (3-3), 583-590.
- Novais R.M., Ascensao G., Tobaldi D.M., Seabra M.P., and Labrinch J.A., (2017). Biomass fly ash geopolymer monoliths for effective removal of methylene blue from wastewaters. Journal of cleaner production. 2017.10.078.

- Novais R.M., Carvalheiras J., Tobaldi D.M., Seabra M.P., Pullar R.C., and Labrincha J.A., (2018). Synthesis of porous Biomass fly ash-based geopolymer spheres for effective removal of methylene blue from wastewaters. *Journal of cleaner production*. 2018.09.265.
- Nyale S. M., et al. (2013). Synthesis and characterization of coal fly ash-based foam geopolymers. *Procedia environmental science* 18 (2013) 722-730.
- Oz H.O., Glamtimur N.G.D., Bilgil A., Tamer A. and Gunaydin K., (2021). Process Development of fly ash-based geopolymers mortars in view of the mechanical characteristics. *Material* 2021, 14, 2935.
- Pandey V.C., (2020). Opportunities and challenge in fly ash-aided paddy agriculture. *Phytomanagement of fly ash*, 103-139.
- Petrus H.T.M., Adelizar A.S., Widiyatmoko A., Olvianas M., Suprpta W., Perdana I., Prasetya A., and Astuti W., (2019). Kinetics of fly ash geopolymerization using semi quantitative fourier-transform infrared spectroscopy (FTIR); *Corr Data. Mater. Sci. Eng.* 532 012001.
- Qayoom A., Kazmi S.A. and S. Ali S.N, (2017). Equilibrium modelling for adsorption of aqueous Cd(II) onto Turmeric: Linear versus Nonlinear regression analysis. *Mor. J. Chem.* 5 N°2 (2017) 362-370.
- Qu Y., Yan D., Su R., Hu W., and Dai Y., (2021). Study on adsorption of dye wastewater by modified fly ash. *Web of conferences* 267, 02020 (2021).
- Qui J., Zhao Y., Xing J., and Sun X., (2017). Fly as-based geopolymer as a potential adsorbent for Cr(VI) removal. *Desalination and Water treatment* 70 (2017) 201-209.
- Rasheed M.A., Rao P.L.L., Hasan S.Z., Patel A., Velani V., & Patel K., (2015). Geochemical characterization of coals using proximate an ultimate analysis of tadkeshwar coal, Gujarat. *Geoscience* 5(4): 113-119.
- Rehman R., Manzoor I., and Mitu L., (2018). Isothermal study of Congo red dye biosorptive removal from water by solanum tuberosum and Pisum sativum peels in economical way. *Bull. Chem. Soc. Ethiop.* 2018, 32(2), 213-223.

- Roviello G., Ricciotti L., Ferone C., Colangelo F., Cioffi R., & Tarallo., (2013). Synthesis and characterization of novel epoxy geopolymer hybrid composite. *Material* 2013, 6.
- Sahoo T.R., and Prelot B., (2020). Chapter 7- adsorption process for the removal of contaminants from wastewater: the perspective role of nanomaterial and nano technology. *Micro and Nano Technologies 2020*, page 161-222.
- Said A, Hakim M.S and Rohyami Y., (2014). The effect of contact time and pH on Methylene Blue removal by Volcanic Ash. (ICCBES' 14).
- Salgot M., and Folch (2018). Wastewater treatment and water reuse. *Current Opinion in Environmental Science & health* 2012, 2:64-74
- Seslija M., Rosic A., Vasic M., Dogo M., & Jotic M., (2016). Properties of fly ash and slag from the power plants. *Geologia croatica. Journal of Croatian Geological survey and the Croatian Geological Society*, 69/3 317-324.
- Shaban M., Abukhadra M.R., Khan A.A.P., and Jibali B.M.,(2018). Removal of Congo Red, Methylene blue and Cr(VI) ions from using natural serpentine. *Journal of the Taiwan Institute of Chemical Engineers (Elsevier)-Vol. 82*, pp 102-116.
- Siddique R., (2004). Performance characteristics of high-volume class F fly ash concrete. *Cement and concrete research* 34 (2004) 487-493.
- Sindhusa C.H., and Rao V.R., (2017). Study on behavior of alkali-activated fly ash-based geopolymer concrete. *IJCIEF. Vol. 8, issue 1 January 2017*, pp 728-733.
- Sing K.S.W., Everett D.H., Haul R.A.W., Moscou L., Pierotti R.A., Rouquero J., (1985). Reporting Physisorption Data for Gas/Solid Systems with Special Reference to the Determination of Surface Area and Porosity. *Pure and Applied Chemistry*, 57(4), 603–619.
- Siyal A.A, Shamsuddin M.R, Robat N.E, Zulfiqar M., Man Z. and Low A. (2019). Fly ash based geopolymer for the adsorption of anionic surfactant from aqueous solution. *Journal of cleaner production* 22(2019)323-243.
- Siyal A.A., Shamsuddin M.R., Low A. (2020). Fly ash geopolymers for the adsorption of cationic and nonionic surfactants from aqueous solution. A feasibility study. *Material letters* 282 (2021) 128758.

- Song H., Fan H., Gao H., Liu J., and Mou H., (2020). Improving fly ash brightness with carbon and iron oxide removal. *Recycling* 2020, 5,5
- Stanislav V.V., and Vassileva C.G., (2005). Methods of characterization of composition of fly ash from coal-fired power stations: a critical overview. *Energy & fuels*, vol. 19, No 3, 2005.
- Sumathi S., Bhatia S., Lee T.K., and Mohamed A.R., (2010). Selection of best impregnated palm shell activated carbon (PSAC) for simultaneous removal of SO₂ and NO_x. *Journal of hazardous material* 176 (2010) 1093-1096.
- Swanepoel J.C., and Strydom C. A., (2002). Utilization of fly ash in a Geopolymeric material. *Applied Geochemistry*. Published by Elsevier Science Ltd PII: S0883-2927 (02) 00005-7.
- Taufiq A., Hidayat P. and Hidayat A. (2018). Modified coal fly ash as low-cost adsorbent of removal reactive dyes from batik industry. *MATEC web of conferences* 154, 01037 (2018)
- Taufiq A., Hidayat P., Hidayat A., (2018). Modified coal fly ash as low-cost adsorbent for removal reactive dyes from batik industry. *MATEC Web of Conferences* 154, 01037 (2018).
- Temuujin J., Minjigmaa A., Davaabal B., Ochirbat Z., (2011). Characterization of fly ashes from 4th Thermal Power Station of Ulaanbaatar City and its applicability for a zeolite synthesis. *Mongolian Journal of chemistry*. Vol. 12, No. 38.
- Tiwari M. K., Bajpai S., Dewangan U. K., (2016). Fly ash utilization: A Brief review in Indian context. *International Research Journal of Engineering and technology*. Volume: 03 Issue: 04.
- Uzbas B., and Aydin A.C, (2019). Analysis of fly ash concrete with scanning electronic microscopy and X-ray diffraction. *Advances in science and technology research journal* vol. 13(4), 2019.
- Vassilev V.S., and Tascón J.M.D., (2003). Methods for characterization of inorganic and mineral matter in coal. A critical overview. 272 *Energy & fuels*, Vol. 17, No. 2, 2003.

- Vital R.K., Narayana S.K.V., Khasim B.S., and Gopinath R., (2016). Dye removal by adsorption: A review. *Bioremediation and Biodegradation*. 7:6 10.4172/2155-6199.1000371.
- Wang X., Jiang C., Hou B., Wang Y., Hao C., and Wu J., (2018). Carbon composite lignin-based adsorbents for the adsorption of dyes. *Chemosphere* 206 (2018) 387e596.
- Wattimena O.K., Antoni., and Hardjito D., (2017). A review on the effect of fly ash characteristics and their variations on the synthesis of fly ash based on Geopolymer. *Green Construction and engineering education for a sustainable future*.
- Wen S., Liu, J., and Deng J., (2021). Methods for the detection and composition study of fluid inclusions. In *Fluid Inclusion Effect in Flotation of Sulfide Minerals*.
- Widayanti A., Soemitro R.A.A., Suprayitno H., and Ekaputri J.J. (2018). Characterization and compressive strength of fly ash based-geopolymers paste. *Matec web of conferences* 195, 01023 (2018).
- Yagub M.T., Sen T.K., Afroze S., Ang H.S., (2014). Dye and its removal from aqueous solution by adsorption: a review *Advances in Colloid and interface science* 12433.
- Yao Z.T.; Sarker P.K.; Tang J.H.; Ge L.Q.; Xia M.S.; Xi Y.Q.; (2015). A comprehensive review on the application of coal fly ash. *Earth science reviews* 141(2015) 105-121.
- Yunxia L., Zeng F., Sun B., Jia P., andbGraham I.T., (2019). Structural characterizations of aluminosilicates in two types of fly ash aamples from Shanxi Province, North China. *Minerals* 9, no. 6: 358.
- Zerfu K., and Ekaputri J.J., (2010). Review on alkali-activated fly ash-based Geopolymer concrete. *Material science forum* vol. 841.
- Zhou J., Xia K., Lin X., Fang L., Du H., Zhang X,. (2020). Utilization of cationic polymer-modified fly ash for dye wastewater treatment. *Clean technologies and environmental policy* (2021) 23: 12731282.

- Zhou S., Zhang D., Wang H., and Li X., (2019). A modified BET equation to investigate supercritical methane adsorption mechanisms in shale. *Marine and Petroleum Geology*, 105(March), 284–292.
- Zulfika H.B.Z.M et.al (2017). Effects of pH, dosage and concentration of adsorption of congo red onto untreated and treated aluminum. *Dors. IOP conf. ser.; mater. Sci. Eng.* 205 012026.

APPENDIX

Appendix I

Standard Calibration curve

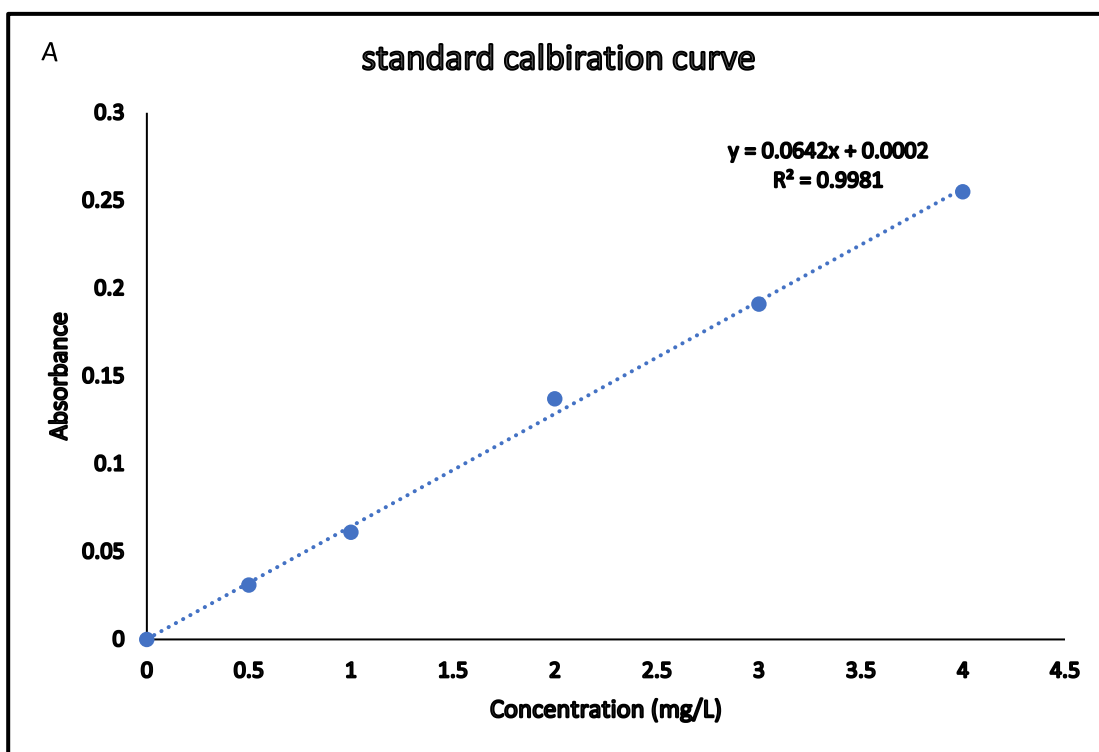


Figure A. calibration standard curve of Methylene Blue

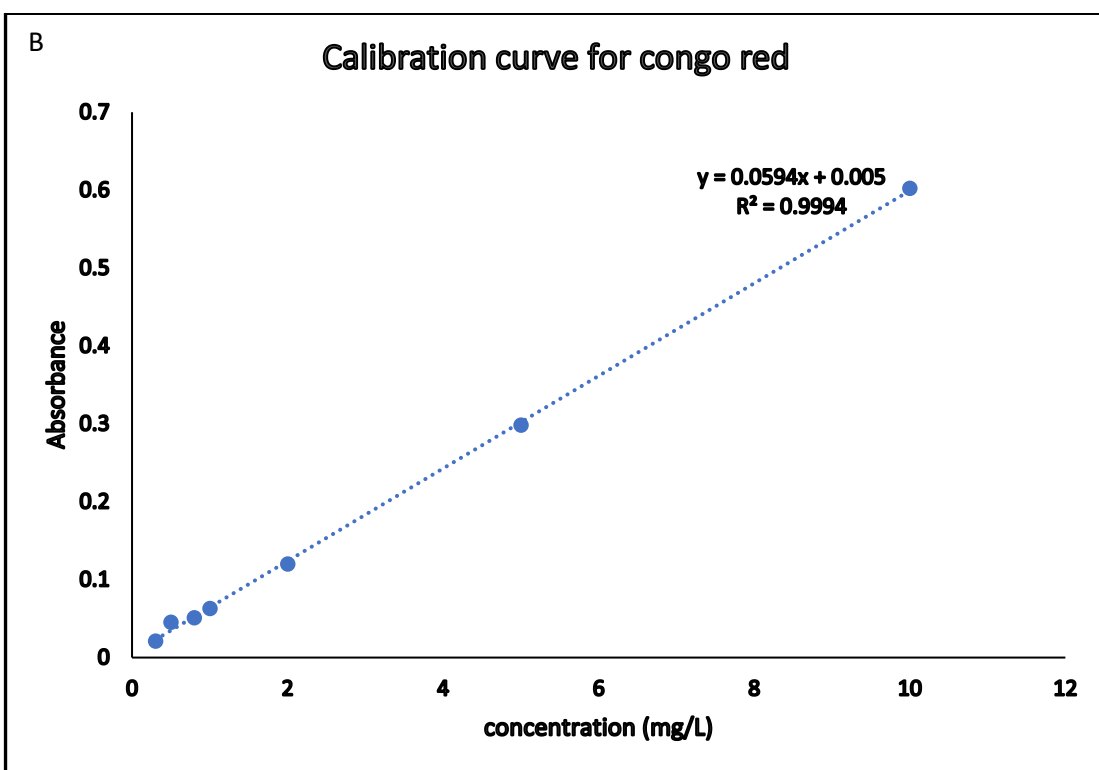


Figure B. Standard calibration curve of Congo red dye

Appendix II

Adsorption Isotherm

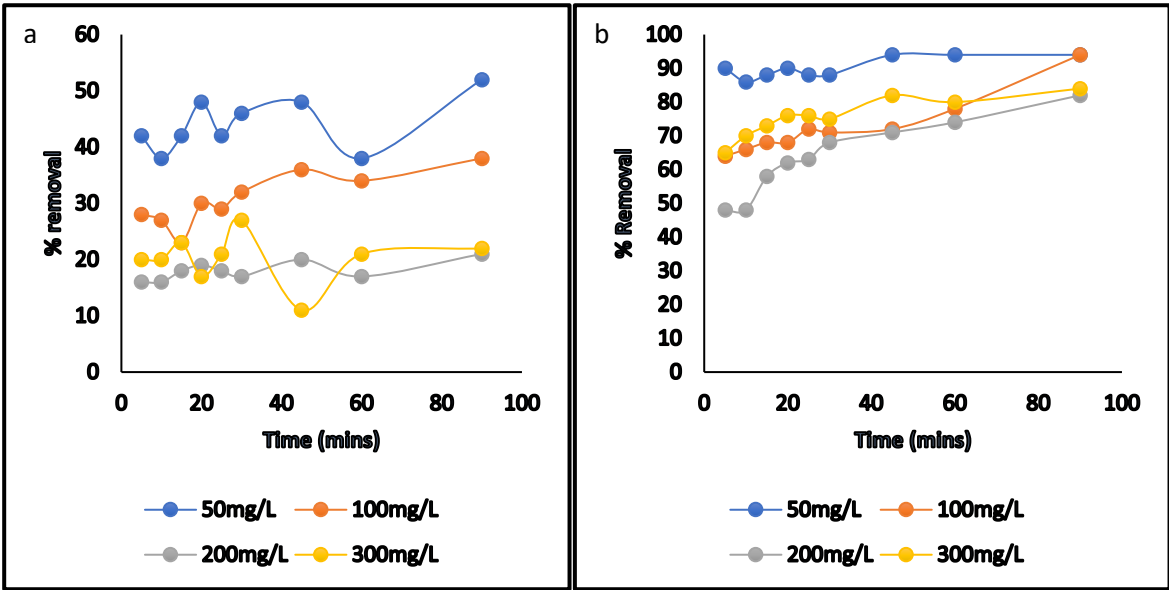


Figure C. Raw fly ash: (a) efficiency removal in MB (b) efficiency removal in CR

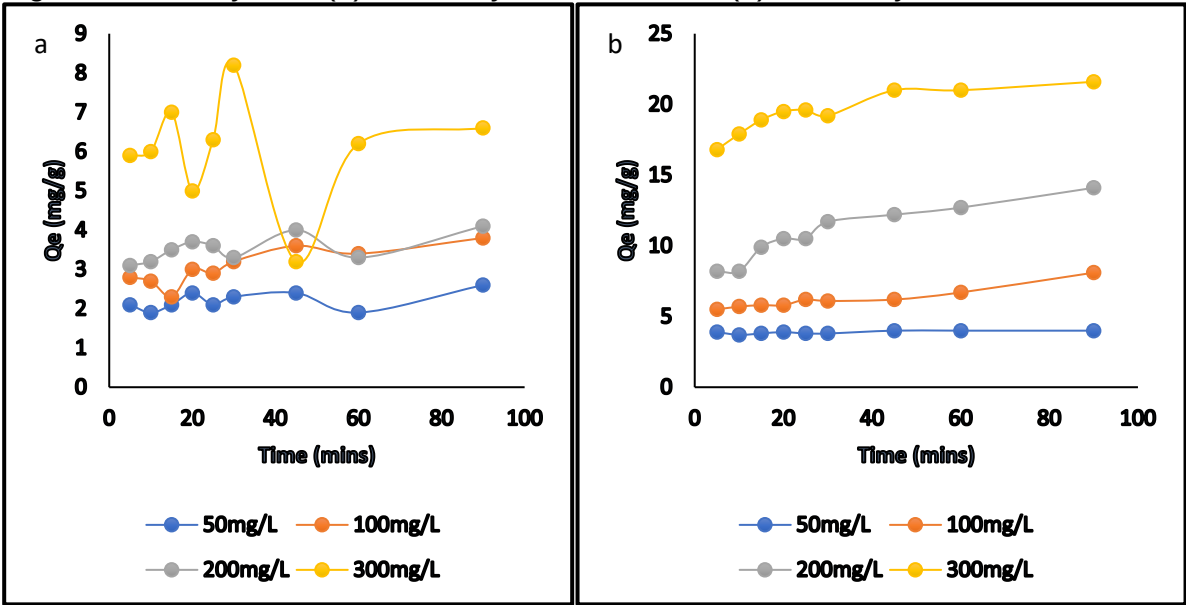


Figure D. Raw fly ash: (a) adsorption capacity in MB (b) adsorption capacity in CR

SEM micrographs

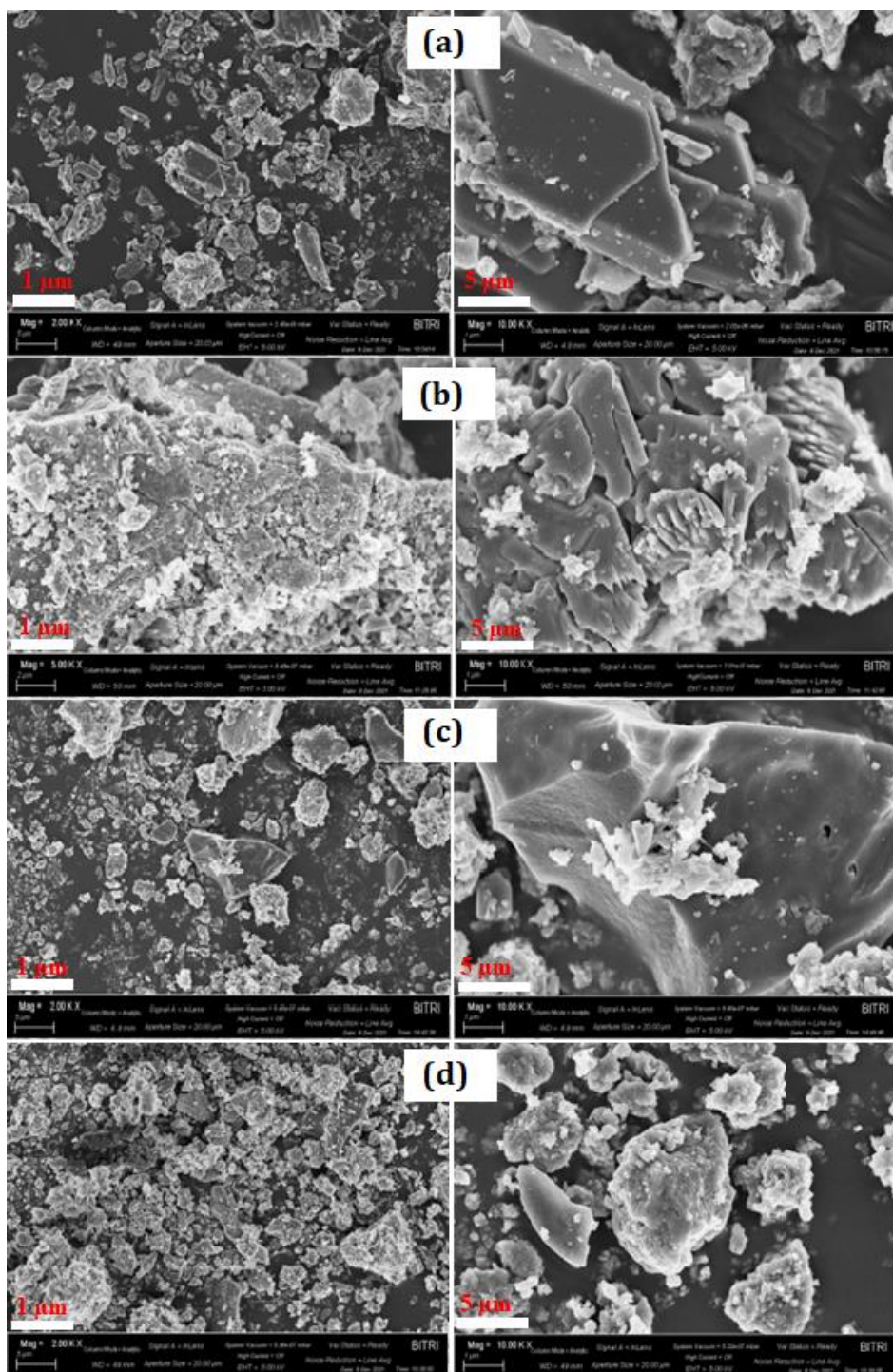


Figure E: SEM images of raw fly ash (a), 10-M- Na_2SiO_3 (b), 12-M- Na_2SiO_3 (c), and 12-M- H_2O_2 (d).

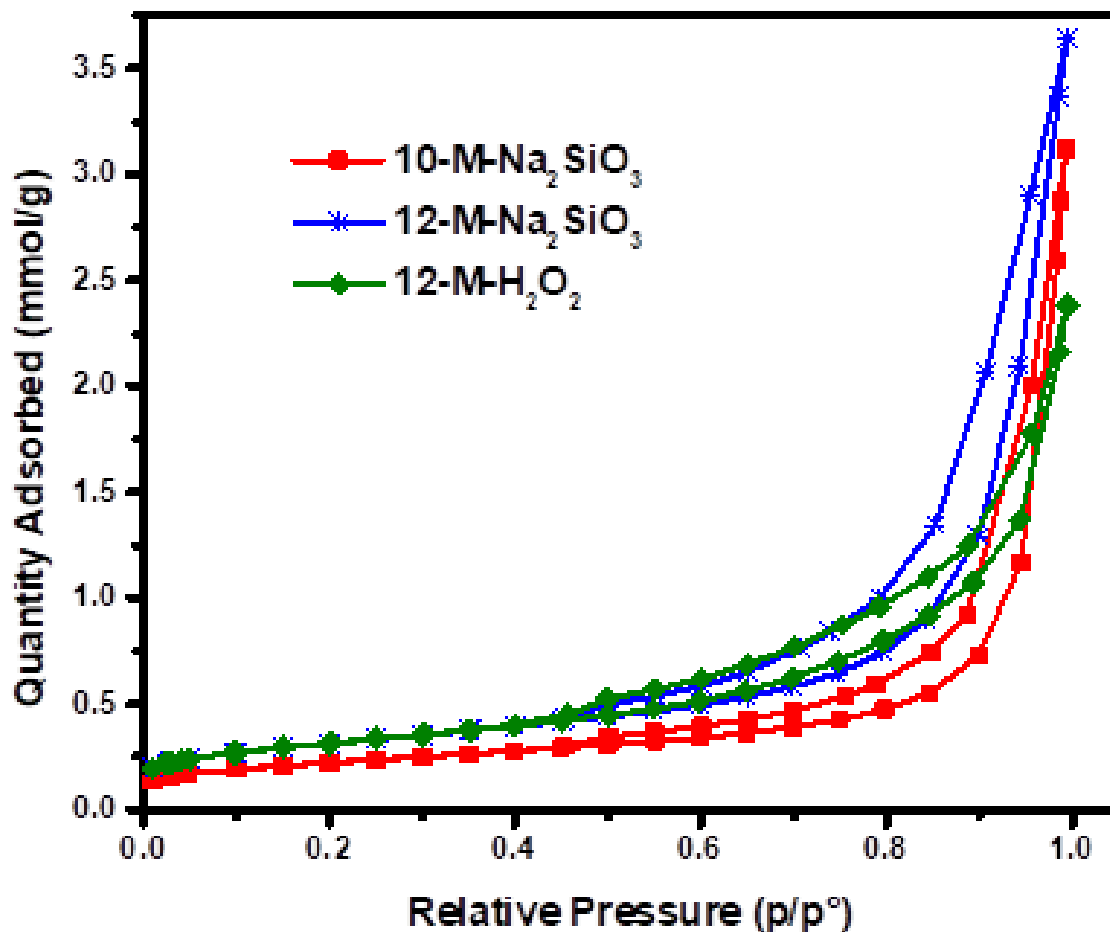


Figure F. N₂ adsorption/desorption isotherms of the samples

Appendix II

Adsorption capacity and equilibrium concentration

Table A: C_e and Q_e value

Adsorbent	Dyes	C _i (mg/L)	C _e (mg/g)	Q _e (mg/g)
12-M-Na ₂ SiO ₃	MB	200	37	16.3
12-M-Na ₂ SiO ₃	CR	50	35	1.3
10-M-Na ₂ SiO ₃	MB	200	28	17.2
10-M-Na ₂ SiO ₃	CR	-	-	-
12-M-H ₂ O ₂	MB	50	15	3.5
12-M-H ₂ O ₂	CR	50	34	1.4
10-M-H ₂ O ₂	MB	50	10	4
10-M-H ₂ O ₂	CR	50	27	2.3
Raw FA	MB	50	26	2.4
Raw FA	CR	50	6	3.9