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REMOVAL OF COPPER (II) FROM AQUEOUS SOLUTION USING DOLOMITE AS NEW GEOPOLYMER ADSORBENT BASED ALKALI ACTIVATED MATERIAL

This study evaluates the effectiveness of dolomite as the primary material in geopolymer adsorbent for removing copper ions from aqueous solutions. Dolomite is an alkali-activated material (AAM) known for its ability to adsorb harmful elements like copper ions in wastewater, thanks to its distinctive composition and structure. This material is considered a cost-effective adsorbent due to its abundance and global availability. However, there is limited research on using dolomite as an adsorbent to eliminate heavy metals from wastewater, and no studies have explored producing dolomite as the primary material for geopolymer adsorbents. The aim of this study is to assess the effectiveness and capabilities of dolomite in producing a high-quality geopolymer adsorbent based AAM for adsorbing copper ions. Otherwise, this material was examined for characterization techniques using X-ray diffraction (XRD), Scanning electron microscopy (SEM), and Fourier transform infrared (FTIR) to analyse the structural and morphological changes for synthesizes geopolymer. Various parameters, such as the solid-to-liquid ratio (2, 2.5, 3) and the alkali activator ratio (1.5, 2, 2.5, 3), influenced the removal efficiency. The results showed that dolomite based geopolymer adsorbent demonstrated superior removal performance compared to raw dolomite. The highest copper ion removal efficiency was achieved with a solid-to-liquid (S:L) ratio of 2.5 and an alkali activator ratio of 2.5, resulting in a removal efficiency of 46.92% and an adsorption capacity of 181.33 mg/g. The Langmuir isotherm provided a more accurate fit than the Freundlich isotherm, indicating a monolayer adsorption on the surface. The results showed that dolomite may effectively be used as a geopolymer adsorbent to remove copper ions from wastewater. *Keywords:* Dolomite; Alkali activated materials; Geopolymer, Adsorption; Copper ions

1. Introduction

Environmental pollution, especially from heavy metals in wastewater, is the biggest problem in Malaysia [1,2]. Heavy metal pollution from the aquatic environment is a worldwide issue since these metals are durable and, at high concentration, have detrimental effects on living creatures. Otherwise, the rapid development of an industrial society has led to a significant increase in the demand for water that is free of contaminants [3]. However, industrial wastewater has tremendously harmful effects on the environment. Heavy metals usually produced from various activities such as mineral extraction, water treatment, metal casting, metal coating, battery manufacturing, nuclear industry, and nuclear power generation [4]. In addition, when heavy metals enter the food chain on a large scale, it can make heavy metals accumulate in the human body. Even in low con-

centrations, heavy metals have dangerous effects on health [5,6]. Common toxic heavy metals in wastewater include arsenic (As), lead (Pb), copper (Cu), mercury (Hg), cadmium (Cd), and iron (Fe). Therefore, all of these toxic heavy metals must be removed from wastewater to ensure clean water and safe pollution for human society.

In response to the environmental concerns produced by contamination of water, some researchers have dedicated themselves to the creation of wastewater treatment technologies. So far, a lot of efficient technologies have been studied for the elimination of heavy metals, including chemical precipitation, ion exchange, reverse osmosis, electrodialysis, ultrafiltration, nanofiltration, coagulation flocculation, and many more [7-12]. However, these methods have several drawbacks, such as high reagent requirements, unpredictable removal of metal ions, generation of toxic sludge, and complicated procedure [13,14]. The adsorp-

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tion process, considered highly straightforward, affordable, and efficient, has shown to be the most favoured approach for eliminating harmful pollutants from wastewater [15,16]. As supported by Rashid et al. [7] pointed out that adsorption process is a very straightforward production, environmentally friendly, inexpensive and beneficial to the environment that is different from other existing procedures for wastewater treatment. However, high performance of adsorption process mainly depend on the effective adsorbent including small size of the adsorbent, large area of surface, and uniform pore size [17].

Adsorbents can be made from minerals, shellfish, starch, tree bark, industrial and agricultural wastes. However, the production of some adsorbents is complicated, expensive, and not suitable for large-scale production use [18-20]. In addition, there are some problems, such as high environmental requirements, limited application of the adsorbent and poor selectivity in practical application [14,21,22]. Therefore, materials with low price, abundant raw materials and simple preparation are very competitive for widespread use as adsorbent. Hence, a few interesting and outstanding materials have been investigated lately namely geopolymer production. Although the most research on geopolymer focuses on the topic of concrete-based application, presently they are regarded as a feasible alternative for adsorption use in aqueous solutions. Researchers have explored a relatively new material composed of alkali-activated materials (AAMs) also known as geopolymer because it has exceptional properties for the removal of pollutants by adsorption processes [23-25]. Besides, geopolymer adsorbent can be considered as an environmentally friendly substance as it can be synthesized using recyclable materials and by products [26].

Geopolymer is an inorganic polymeric substance made of aluminosilicate network structure, and its effectiveness for eliminating contaminants from wastewater has been revealed lately. Geopolymer is reported to be efficient to eliminate contaminants from effluent by adsorption process, in which the pollutants are trapped onto the surface of geopolymer [27]. Furthermore,

geopolymers have several other advantages such as excellent toughness, acid and alkaline resistance, thermal stability, and effective solidification of toxic waste [28]. Various types of aluminosilicate materials are commonly used as raw materials for the geopolymers that is rich in silica and alumina contents includes metakaolin, fly ash, blast furnace slag, red mud and perlite which ultimately achieve a different performance of adsorption. Fig. 1 illustrates the adsorption process using geopolymer materials to remove various pollutants. Cheng et al. [28] examined the adsorption of several heavy metals such as Pb²⁺, Cu²⁺, Cr²⁺, and Cd²⁺ under discrete experimental conditions in recent years. The following adsorption capacities were achieved: $Pb^{2+} = 86.2 \text{ mg/g}$, $Cu^{2+} = 40.9 \text{ mg/g}$, $Cr^{2+} = 9.8 \text{ mg/g}$, and $Cd^{2+} = 68.9 \text{ mg/g}$ with the optimal pH at 5. Wang et al. [29] investigated a fly ash-based geopolymer for Cu²⁺ removal from an aqueous solution. The adsorption capacity was 92 mg/g, which is significantly greater compared to the natural fly ash and natural zeolite. It has been proven that geopolymer adsorbents outperform raw materials in terms of removal efficiency of heavy metals.

There are many different adsorbents from diverse natures can be employed either in unmodified or modified form to eliminate hazardous heavy metal ions from wastewater [31-34]. The selection of precursor material for the development of low-cost AAMs adsorbents depends on numerous aspects. The precursor material must be publicly available, affordable, and non-toxic [35-37]. Adsorbents made from carbonate minerals for the elimination of contaminants such as heavy metals have been the goal of numerous study in the development of cheaper and simpler removal technologies [3,38,39]. In the past few years, researchers have identified that dolomite is one of the carbonate materials group, and an affordable natural mineral, has an excellent capacity for adsorption of boron [40], arsenic [41,42], phosphate [43-46], and lead [47]. Dolomite is relatively common minerals may be found over the world especially in Indonesia, Canada, Switzerland, Mexico and Spain. In general, dolomite is lightweight and can be effortlessly crushed into finer

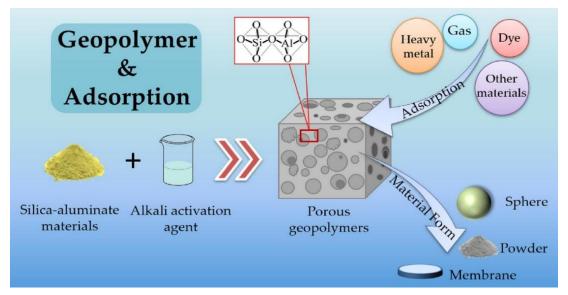


Fig. 1. The process of adsorption using geopolymer materials to remove various pollutants in different material form [30]

particles, making it a simple and cheap material to obtain [48,49]. In addition, dolomite mineral can be used as a raw material for geopolymer composites due to their chemical composition and unique structure [50]. However, the use of dolomite as a main precursor material in the geopolymer field is still new and at an early stage of research, and only few researchers have conducted studies on the suitability of dolomite for use in geopolymers in term of mechanical strength [51-56]. Therefore, this paper aims to discover the effectiveness and capabilities of dolomite as the main precursor of geopolymer adsorbents based on alkali activated materials to remove copper ions from wastewater by adsorption process. In addition, dolomite was characterized in its raw state, before and after geopolymerization by using X-ray diffraction (XRD), Scanning electron microscope (SEM) and Fourier transform infrared (FTIR). Besides that, behaviour of the adsorption process under different conditions, including the solid-to-liquid ratio and the alkali activator ratio, was studied. Both Langmuir and Freundlich models were applied to evaluate the adsorption isotherm of copper ions in the prepared geopolymer.

2. Materials and methods

2.1. Materials

Dolomite samples were supplied by Perlis Dolomite Industries (PDI) Sdn Bhd, Padang Besar, Perlis, Malaysia. Dolomite is usually soft and can be easily crushed into fine particles, making it a simple and inexpensive material. At the first stage, the dolomite samples are dried in the oven at 100°C about 24 hours in order to eliminate the amount of moisture. Then, the raw material is sieved through 300 micrometres (μm) to obtain fine particles and then used to prepare the synthesis of geopolymer [57]. Furthermore, some chemical reagent used for the entirely of the experiment for alkali activator solution are sodium hydroxide (NaOH) and sodium silicate (Na₂SiO₃) while Cu²⁺ sulphate pentahydrate (CuSO₄-5H₂O) is used for copper stock solution.

2.2. Instrumentation

The phase identification of geopolymer was investigated using the Brucker D2 phaser X-ray Diffractor (XRD). The analytical apparatus was installed at 49 kV and 35 mA. The phase was detected at a 2θ value from 10° to 90° with a scan speed of 0.01° /s. The obtained sample was analyzed using X'pert Highscore Plus software to ascertain the phase of the geopolymer samples. The microstructure and surface elements distribution of geopolymer materials adsorbents before and after adsorption was examined using a Scanning Electron Microscope (SEM) JEOL JSM-6460LA connected with an energy-dispersive detector at an acceleration energy of 15 keV. Sputter-coater Q150R S was applied for covering the element by conductive substance made from gold about one minute in order to prevent the electron

charge during analysis in SEM. The copper ions concentration fluctuations were assessed using Atomic Absorption Spectroscopy (AAS) with a Perkin Elmer Analyst 800 model. The acquired data were used to assess the efficiency of removing copper ions.

2.3. Preparation of copper ions solution

Stock solution of copper can be produced by dissolving 3930 mg of Cu^{2+} sulphate pentahydrate ($CuSO_4$ - $5H_2O$) in 1000ml of pure water in a 1000 ml beaker to produce 1000 ppm copper stock solution [58]. Then, the copper stock solution is dilute with distilled water to produce 500 ppm for initial copper concentration.

2.4. Synthesis of dolomite

According to theory, any of the alkali can be employed in polymerization reactions; nevertheless, numerous studies have concentrate on the impact of sodium (Na⁺) ion [57]. Sodium ions, especially in the form of NaOH and Na₂SiO₃, are crucial elements that impact the reactivity, alkalinity, compressive strength, and overall rate of the polymerization process [56]. Their presence and concentration significantly influence the characteristics and performance of geopolymers. For this reason, both NaOH and Na₂SiO₃ are utilized in this research for geopolymer production. A defined amount of dolomite sample was mixed with a strong alkali activator solution which are NaOH and Na₂SiO₃ to produce a geopolymer synthesis based on alkali activated materials. For this study, the alkali activator was prepared as a liquid part using 10 M NaOH and Na₂SiO₃ with a different modulus ratio of Na₂SiO₃:NaOH as a variable parameter of mix design. The alkali activator was applied and combined uniformly with the precursor to produce an aluminosilicate geopolymer adsorbent paste according to the prescription in TABLE 1. TABLE 1 displayed the values of parameter used during synthesize dolomite as geopolymer adsorbents in term of S:L ratio and alkali activator ratio.

Next, the obtained product was cured in the oven at constant temperature for 2 days at $80^{\circ} C$ [57,58]. Then, the cured geopolymer paste was crushed with a porcelain mortar and washed three times with distilled water with the pH of the wash water was 7.0±0.5. After washed, powder was passed through sieving to get particles with a diameter of <300 μm , which is then suitable for the process of sorption.

TABLE 1
The value of mix design use to produce geopolymer adsorbent

Raw material	Na ₂ SiO ₃ :NaOH	S:L
Dolomite	1.5 2.0 2.5 3.0	2.0 2.5 3.0

2.5. Batch adsorption

For the batch adsorption experiment, a constant amount of the geopolymer adsorbent was mixed with 100 ml of the prepared copper solution and shaken at 220 rpm for 1 hr. Finally, the adsorption efficiency of the geopolymer adsorbent was compared with the reference sample prepared before process of adsorption. Copper concentration in the obtained solution was measured by AAS and the removal percentage and the uptake capacity were calculated. The percentage removal efficiency (*RE*) was calculated using the following equation [59]:

$$RE = \frac{C_0 - C_e}{C_0} \times 100\% \tag{1}$$

where C_0 is the initial concentration of copper (ppm) and C_e is the remaining equilibrium copper concentration (ppm).

The quantity of copper ion uptake by the geopolymer was determined as [59]:

$$q = \frac{\left(C_o - C_e\right) \times V}{m} \tag{2}$$

where q is the quantity of copper ion uptake by geopolymer phase (mg (metal)/g (geopolymer)), V is the volume of the solution (L) and m is the mass of the adsorbent (g).

3. Results and discussion

3.1. XRD phase analysis

Dolomite with the chemical formula CaMg(CO₃)₂ belongs to the group of carbonate minerals. This mineral is in the form of trigonal, rhombohedral crystals, which may be fine or microcrystalline. Dolomites can occur in different colour ranges from white, grey, light brown, red, green to black [60,61]. In this study, the colour of the dolomite sample is greyish white.

The XRD pattern of both dolomite and synthesized geopolymer sample is shown in Fig. 2. The XRD scan shows the sharpest diffractions for the dolomite phase and mention the chemical compositions. The characterizations of dolomite are analyzed according to different types, including raw dolomite, and synthesized dolomite as geopolymer before and after adsorption process. It was found that raw dolomite (before geopolymerization process) indicates the presence of calcite (CaCO₃) and quartz (SiO₂) as main minerals due to its high peak intensity observed at 31.04°. The loss of ignition values means that dolomite has less carbonaceous components and a higher content of mineral components [62,63]. Most of the dolomite samples have an amorphous structure, which makes dolomite a reactive material [64]. After geopolymerization process, it was found that dolomite based on geopolymers (before adsorption) contained additional minerals, namely halite (NaCI), quartz (SiO₂) and hematite (Fe₂O₃). This result shows that the geopolymer successfully reacted to dolomite because the amount of silica and sodium was distributed at the edge of the crystal particles. Azimi et al [60] pointed out that the higher the content of silica and alumina, the greater the effectiveness of the geopolymer. Thus, it can be said that these identified minerals supported the geopolymer structure on dolomite.

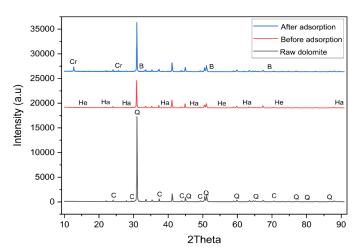


Fig. 2. XRD pattern of raw dolomite and dolomite synthesized geopolymer before and after adsorption (C-calcite, Q-quartz, He-Hematite, Ha-Halite, Cr-corundum, B-bornite)

Unfortunately, changes in the structure and composition of the dolomite samples were observed after the adsorption process. The changes in the physicochemical properties of dolomite are due to the influence of impurities of the sorbent. As a result of adsorbed copper ions (II), the colour of dolomite changed from grey to blue, and the spatial structure of this sorbent became more uniform. The colour change can be attributed to the formation of copper (II) complexes on the surface of the dolomite or changes in the crystal structure of the sorbent. In dolomite-based geopolymers, the presence of corundum (Al₂O₃) was detected after adsorption, since dolomite is one of the metamorphic rocks, and presence of copper ion sulphide (Cu₅FeS₄) proves the existence of copper ions on the adsorbent dolomite. In conclusion, the presence of other elements in the structure of natural dolomite proves the presence of impurities on the surface of the adsorbent caused by repeated processing, extraction and good adsorption properties [65].

3.2. SEM analysis

Scanning electron microscope (SEM) was used to observe the surface features of powdered dolomite rock. The SEM analysis of the dolomite as a raw material, dolomite based geopolymer before and after adsorption process also were evaluated in this study as shown in Fig. 3. From the image, it can be seen that raw dolomite structure (Fig. 3(a)) is composed of a crystalline form and its complex and porous surface texture. Also, the surface morphology of dolomite was found to be rough and irregular. The surface of dolomite has also many porosities which provide good trapping places for copper ions. According to Tamjidi et al. [66] have found that adsorbents with larger and wider porous

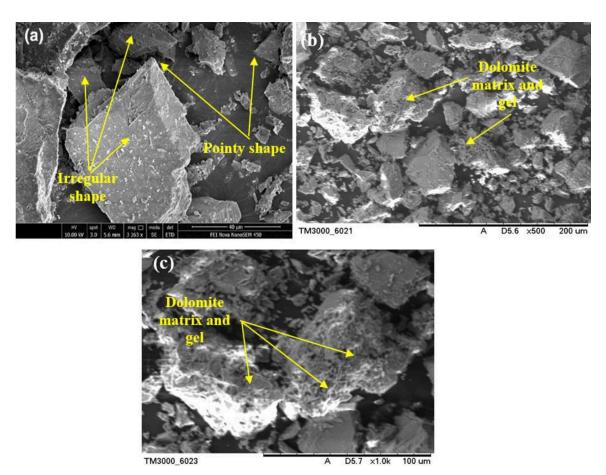


Fig. 3. SEM results of dolomite as a a) raw material b) before adsorption process based geopolymer and c) after adsorption process based geopolymer

surfaces have a greater capacity to collect heavy metal ions, hence increasing the material's potential for sorption. In addition, the microstructure of dolomite based geopolymer is shown in Fig. 3(b). When dolomite is incorporated into geopolymers, the alkaline activation process can alter its surface morphology. The geopolymerization process involves the dissolution of aluminosilicate precursors in an alkaline environment, followed by the reorganization of the dissolved species into a three-dimensional network structure. From the Fig. 3(b), it can be seen that most of the particles in the geopolymer were surrounded by the geopolymer gel.

In addition, based on microscopic dolomite images after adsorption as shown in Fig. 3(c), showed that dolomite particles changed into aggregates after the adsorption process, and a reduction in the porosity surface was observed. The findings indicate that the dolomite particles undergone shape changes as a result of the adsorption process, possibly as a result of the production of adsorbate layers or the occlusion of pores. Furthermore, the surface roughness of dolomite based geopolymer as can be seen in figure can influence the wettability and, consequently, the adsorption behaviour of the geopolymer. A rougher surface can increase the contact area between the adsorbent and the adsorbate, improving the efficiency of the adsorption process [67]. Besides that, there are limited research on the dolomite as geopolymer adsorbent that the surface morphology may be compared and examined. As a conclusion, copper ions are ef-

ficiently removed from aqueous solutions by dolomite based geopolymer which can be employ as a low-cost and excellent alternative of adsorbent for wastewater treatment.

3.3. FTIR analysis

FTIR spectral analysis is used to analyse adsorbents and identifies their functional groups therefore expected interactions between the functional groups of adsorbents and the heavy metal ions. In order to examine the mechanism of Cu adsorption, the infrared spectra of natural dolomite based geopolymer adsorbent before and after of adsorption were collected and results are displayed in Fig. 4. The functional groups were determined by using FTIR at a wavelength range of 600-4000 cm⁻¹. As can be observed from the Fig. 4, spectra of dolomite based geopolymer before and after adsorption exhibits significant changes that revealed the metal-binding process occurred at the surface of dolomite as geopolymer adsorbent during adsorption process which lastly effect the functional group.

From the Fig. 4, it can be seen that several peaks which are attributed to the carbonate group were seen at (2169 cm⁻¹, 2008 cm⁻¹,1421 cm⁻¹, and 867 cm⁻¹) for dolomite before adsorption and changed after adsorption (2168 cm⁻¹, 2008 cm⁻¹, 1439 cm⁻¹, and 868 cm⁻¹). The changes of peaks intensity after adsorption of copper ions implying that the metal binding pro-

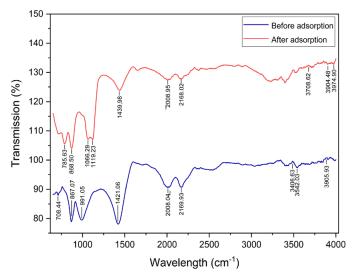


Fig. 4. FTIR spectra of the dolomite as geopolymer adsorbent before and after adsorption

cess occurred at the active sites of dolomite during adsorption process [68]. In term of dolomite sample after adsorption process demonstrated that the peak wavenumbers seen at 3708 cm⁻¹ were related to the present of hydroxyl groups (OH) stretching in water. Similar with dolomite before adsorption procedure, the peak at 3500 cm⁻¹ further substantiated the existence of hydroxyl groups. This band is expressing the stretching and deformation vibration of OH and H-O-H groups, respectively, from the weakly-bound water molecules that were adsorbed on the surface or trapped in the huge voids between the rings of the geopolymer products. This is due to the dolomite is a double salt, therefore it includes of double salt (CaMg(CO₃)₂), which dissolving and hydration phenomenon will occur in interaction with H₂O [68]. Other than that, these findings demonstrated that Cu adsorption onto dolomite based geopolymer may include complexing with OH group in the adsorbent structure. However, in order to clarify the mechanism of complexation in detail, it would be more useful to analyse the region of metal-ametal bonds in depth for dolomite structure. The major variations in the adsorption peak frequencies may be related to the binding of the metal ions that produce a variation in adsorption frequencies. The variations in absorbance represent that there were metal-binding reactions taking place on the active sites of the adsorbents. Below than 1000 cm⁻¹ spectra indicate that certain functional group bands are shifting. The shifts occurred after heavy metal ions uptake, implying that the process of metal-binding happened on the active sites during the adsorption process. The ionizable functional groups which are shown in FTIR spectra analysis can interact with cations; this demonstrates that these functional groups may be useful in the removal of positively charged copper ions from solution. This statement also were supported by past study of Darweesh et al. [69]. To conclude, the FTIR image of the dolomite showed a diminish in peak intensity after interaction with metal ions. As mentioned by Khoshraftar et al. [68], this might be due to the interaction between species of metal ions and the functional groups of dolomite.

3.4. Effect of S:L ratio and alkali activator ratio

The removal efficiency of copper ions for natural dolomite and dolomite-based geopolymer adsorbent was examined under the following conditions: pH (5), 500 ppm as the initial Cu²⁺ concentration, 60 min contact time, and 0.15 g adsorbent dosage. The experiment's findings demonstrated that the production of dolomite-based geopolymers has a greater capacity to adsorb copper ions compared to raw dolomite. From the result, the removal efficiency of raw dolomite is lower at 14.53%, with an adsorption capacity of 56.17 mg/g. Al-Zboon et al. [70] evaluated the performance of a crystalline geopolymer produced from fly ash, which exhibited higher removal efficiency of copper ions versus pure fly ash. The synthesized fly ash achieved high removal efficiency up to 99%. Similarly, in a study, Kara et al. [71] investigated the performance of metakaolin-based geopolymers for the removal of manganese and cobalt ions, which were eventually removed up to 75% successfully.

Fig. 5 shows the removal efficiency of copper ions by different solid-to-liquid (S:L) ratios and alkali activator ratios. From the graph, it can be seen that the adsorbent efficiency increases linearly with increasing S:L ratio and alkali activator ratio. To explain, increasing dolomite content by increasing S:L ratio at 2.5 improved the reaction between the alkali activator and the aluminosilicate materials which enhanced the geopolymerization process [72]. Other than that, uses an ideal S:L ratio can produce better strength due to increase in workability of the alkali activated mixer [73,74]. However, when the S:L ratio and alkali activator ratio reaches 2.5, the removal efficiency starts to decrease. This may be due to the fact that the solid precursors do not dissolve properly because of the higher S:L ratio due to the lack of alkali solution in the matrix, resulting in inefficient hydrolysis reactions and gel formation [75]. Furthermore, higher alkali molarities resulted in mitigating drying shrinkage which at

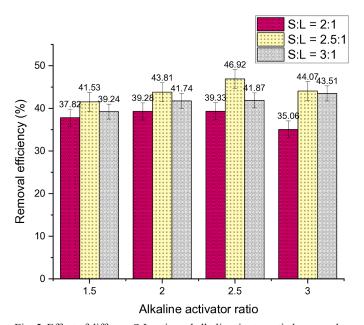


Fig. 5. Effect of different S:L ratio and alkali activator ratio by geopolymer adsorbent on copper ions removal efficiency

the end will affect the performance of adsorption [76]. The finding of the study determines that the optimum mix design for dolomite as geopolymer adsorbent is achieved at S:L ratio 2.5 and alkali activator ratio 2.5. The highest removal is achieved at 46.92% with an adsorption capacity of 181.33 mg/g. Therefore, it is expected that dolomite based geopolymer adsorbent reveal high removal efficiency copper ions compared to raw dolomite. This result may be assigned to transformation from crystalline structure of dolomite material into amorphous one leading to production of more porous structure favouring adsorption of copper ions [65,68].

3.5. Sorption isotherms

Sorption isotherms are necessary in order to investigate the nature of the relationship between metal ion and the synthesized geopolymer and are beneficial in improving its application as a sorbent. Two isotherm models were applied in this study to determine the sorption capacity of the synthesized geopolymer.

3.5.1. Langmuir isotherm

Langmuir isotherm is one of the most widely used models to investigate the adsorption mechanism. The assumptions of this model include: the adsorbent surface is in contact with the adsorbate present in solution, the surface of the adsorbent contains a number of active sites on which the adsorbate adsorbed, and, lastly, the adsorption involves the attachment of only one molecular monolayer on adsorbate surface [34]. The most common variant of this model is given by the following equation accordingly by Bany-Aiesh et al [77]:

$$\frac{C_e}{Q_e} = \frac{1}{Q_{\text{max}}b} + \frac{C_e}{Q_{\text{max}}}$$
 (3)

where C_e is the equilibrium concentration (mg/L), Q_e is the equilibrium adsorption capacity (mg/g), $Q_{\rm max}$ is represent maximum monolayer capacity of the adsorbent, while b is the Langmuir adsorption constant. As mentioned by Benjelloun et al. [78], this equation called as Lineweaver-Burk is one of the four linear forms of the Langmuir model.

According to the aforementioned equation, a plot of C_e/Q_e versus C_e will provide a straight line with a positive slope of $(1/(Q_{\rm max}))$ and an intercept of $(1/Q_{\rm max}b)$. Other than that, Langmuir model was evaluated at varied S:L ratio of 2, 2.5 and 3. Otherwise, the importance of this isotherm is to explain the adsorption process by proven the value of correlation coefficient R^2 . It was discovered that the adsorption data fits the Langmuir model with correlation coefficients between 0.99728 and 0.9989 for the tested mix design of geopolymer as shown in TABLE 2 and Fig. 6. As both S:L ratio and alkali activator ratio increase, the adsorption capacity increase reaching the greatest value of 75.53 mg/g at a S:L ratio 2.5 and alkali activator ratio 3. It is acknowledged that a high solid to liquid

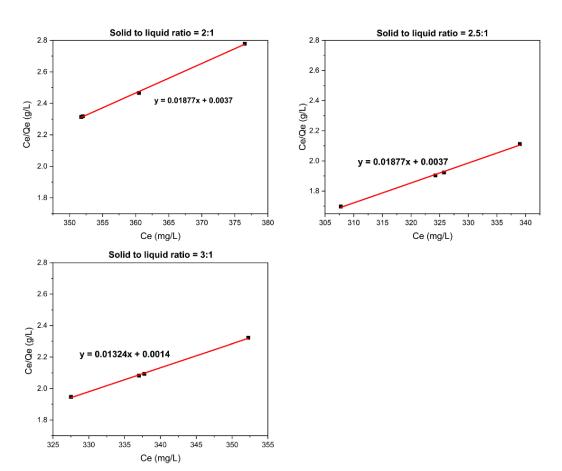


Fig. 6. Experimental isotherm for removal Cu (II) by geopolymer adsorbent using Langmuir isotherm plots

content and alkali activator solution in geopolymer adsorbent will raise the pore intrinsic characteristics which at the end will enhance the potential of the metal being adsorbed onto the sorbent and lastly improve the capacity for adsorption [79]. As indicated by Liu et al. [80] established that geopolymer has the same adsorption processes as zeolite and faujasite block materials. These findings suggests that geopolymer manufacture can be energy-saving, low-cost and environmentally benign technique in adsorbent manufacturing. The characteristics of the Langmuir isotherm can be expressed in terms of a dimensionless equilibrium parameter (R_L) which is defined by:

$$R_L = \frac{1}{1 + bCi} \tag{4}$$

where Ci is the initial concentration of metal ions (mg/L) and b is Langmuir constant (L/mg). R_L number represents the nature of adsorption system as unfavourable ($R_L > 1$), linear ($R_L = 1$), favourable ($0 < R_L < 1$) and irreversible ($R_L = 0$). The results obtained for the values of R_L were found to be 0 for each S:L ratio of 2, 2.5 and 3. The separation factor (R_L) is assumed as 0 and reflects an irreversible adsorption. This result explains the chemical bonds between adsorbate and surface of adsorbent. As validated by Khoshraftar et al. [68] stated that heavy metal adsorption using dolomite usually takes place by chemical adsorption by monolayer uniform sorption which indicates the adsorption mechanism is followed by a Langmuir isotherm. Usually, this chemisorption between dolomite and Cu^{2+} required high temperature and activation energy to be adsorbed.

Langmuir Model							
S:L	Q _{max} (mg/g)	b	R^2	R_L			
2	53.28	5.0730	0.9989	0			
2.5	53.28	5.0730	0.9973	0			
3	75.53	9.4571	0.9983	0			

Langmuir isotherms for adsorption of Cu (II) onto dolomite as geopolymer adsorbent

3.5.2. Freundlich isotherm

The Freundlich isotherm is an empirical model used to describe the adsorption in aqueous systems. It consists of a heterogeneous adsorption surface and active sites with various energies. The numerical expression of this theory is shown in the following equation [81]:

$$\log Q_e = \log kf + \frac{1}{n} \log C_e \tag{5}$$

where kf and n are the Freundlich constant which represent the relative sorption capacity and sorption intensity accordingly. The plot of $\log Q_e$ against $\log C_e$ as shown in Fig. 7 produces straight lines with intercept kf, related to the adsorption capacity and a slope of 1/n. Similar to Langmuir model, Freundlich isotherm was investigated for S:L of 2, 2.5 and 3. The obtained value of parameter in Freundlich isotherm are given in TABLE 3. The R^2 values varied between 0.9928 and 0.9987 which suggests

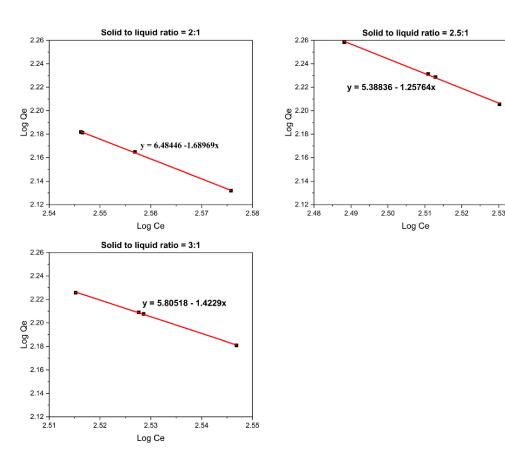


Fig. 7. Experimental isotherm for removal Cu (II) by geopolymer adsorbent using Freundlich isotherm plots

that Freundlich model is also adequate to describe the adsorption of Cu^{2+} on the geopolymer adsorbent. However, the slope from the plotted graph was found to be negative, showing that the adsorption behaviour of the studied system does not follow the theory on which the Freundlich technique is based. Furthermore, the n value reflects the degree of non-linearity over solution concentration and adsorption as follow: If n = 1, then adsorption is linear; if n < 1, then adsorption is a chemical process; and if n > 1, then adsorption is a physical process. For this research, the n values were obtained are -0.59, -0.80 and -0.70 with S:L ratio 2, 2.5 and 3, respectively. To be assume as n value is less than 1, the process demonstrates the chemical adsorption. To conclude, for the two research isotherms, Langmuir adsorption isotherm model revealed more substantial correlation ($R^2 = 0.9982$) than Freundlich isotherm model ($R^2 = 0.9965$) which represent monolayer adsorption.

TABLE 3
Freundlich isotherms for adsorption of Cu (II) onto dolomite
as geopolymer adsorbent

Freundlich Model						
S:L	n	kf	R^2			
2	-0.59	3.05×10^6	0.9993			
2.5	-0.80	2.44×10 ⁵	0.9978			
3	-0.70	6.39×10 ⁵	0.9987			

4. Conclusions

This research was focused on the synthesis of dolomite based geopolymer and its adsorption characteristics toward copper ions elimination. The resulting geopolymer was found to be very amorphous. It was also revealed that the adsorption capacity of the synthesized dolomite as geopolymer is high compared to that raw dolomite. From the economic and ecological point of view, this application provides an effective technique to handle the problem of accumulation of dolomite as waste material. Dolomite, a natural substance, may be regenerated, recycled, and reused as an adsorbent, making it suitable for the circular economy. The study conducted by El Messaoudi et al. [82] indicated that the regeneration process of adsorbents made from natural materials involves the removal of adsorbed substances using certain eluents. This technique enables the adsorbents to be used for several cycles, hence improving their sustainability. Hydrochloric acid, methanol, and Fenton's reagent are employed as desorbing agents throughout the regeneration process to effectively eliminate contaminants. The regeneration procedure often entails subjecting the adsorbents to elevated temperatures in an inert atmosphere or employing microwave heating techniques. These approaches facilitate the release of volatile chemicals and restore the adsorbents for subsequent utilization. To sum up, dolomite-based adsorbents provide a cost-efficient and eco-friendly remedy for water purification. By implementing precise desorption processes, these adsorbents can be efficiently recycled, hence promoting sustainable environmental practices. Therefore, it is widely recommended to be a suitable alternative adsorbent compared to many other sorbents given its unique structure. The sorption properties of copper ions from aqueous solutions were investigated under different conditions utilizing batch method. It is concluded that the synthesized dolomite as geopolymer in this study can be used as a novel sorbent for removal of copper ions from aqueous solutions. The influence of S:L ratio and alkali activator ratio on copper ions metal ions absorption demonstrated that the adsorption efficiency rises as the synthesized geopolymer dose increases. To conclude, the best sorption efficiency was attained at S:L ratio 2.5 and alkali activator ratio 2.5 under experimental conditions (contact time: 60 min, agitation speed: 220 rpm and adsorbent dosage: 0.15 g). From the findings of kinetic investigations, it was established that the adsorption process followed by Langmuir isotherm fit perfect for the adsorption of copper ions utilizing dolomite as geopolymer adsorbent. Maximum adsorption capacity determined by the Langmuir isotherm model was found to be 75.53 mg/g. Correlation plot data revealed a strong correlation coefficient of 0.9982, indicating that the solid-solution suitable for adsorption process prediction.

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