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ADSORPTIVE STUDY OF COPPER (CU^{2+})IN AQUEOUS SAMPLES USING EFFERVESCENCE AMINO-ZEOLITE

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Abstract

Heavy metals, the non-degradable elements of the earth's crust, have many adverse effects on the human body. Their presence in the water environment poses serious health risks to other living organisms as well. Industrial wastewater also contains large amounts of copper ions, which migrate through soil and aquatic streams into the atmosphere and ultimately accumulate along the food chain, causing human beings to face health risks. Excessive human intake of copper ions contributes to severe mucosal irritation and corrosion, hepatic and renal damage, widespread capillary damage, severe gastrointestinal irritation, central nervous system irritation, and potential liver and kidney necrotic changes. Therefore, Cu2+ions are considered for removal. Several products have been used to control sorption contaminants, including granulated activated carbon, EFF-APTES-zeolite, montmorillonite, peat, and compost. The main objective of the current study was to synthesize and characterize EFF-APTES-zeolite using different techniques. The removal of Cu2+ ions was investigated using synthetic solutions at different ion concentrations, contact time, EFF-APTES-zeolite dosage, temperature, and sample pH. The findings of the current study have shown that EFFAPTES-zeolite has been successfully synthesized and characterized by FT-IR, FESEM and BET methods. The results of the current study also showed that the optimal dose for Cu2+ removal was 20 mg with 99.21%, while the optimum concentration was 100 ppm with 99.20%. Similarly, the pH of 4 is the optimum value for EFF-APTES zeolite to extract 99.99% of Cu2+ metal ions from aqueous water. In the meantime, the contact time of 15 min was the optimum period for the successful removal of Cu2+ from aqueous samples. Lastly, 30℃ was noted to be the best temperature for EFF APTES-zeolite to efficiently remove Cu2+ ions (99.69%) from aqueous water. The adsorption kinetics analysis demonstrated a pseudo-first-order and pseudo-second order adsorption model for Cu2+ ions using EFF-APTES-zeolite. This suggests that the adsorption can be regulated by chemical adsorption. Both the Langmuir and Freundlich ii models match the balance data well, suggesting the presence of a monolayer adsorption with a high adsorption potential for Cu2+ at different concentrations.

Keywords: Adsorption, Effervescence, Heavy Metals, Zeolite

Introduction

Water is an inorganic, tasteless, odorless, and a colorless chemical substance, which considered the main constituent of the earth and is very important in our daily life. Water

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offers no calories or organic nutrients; nevertheless, it counted a critical fluid for all types of living organisms. Water pollution can be defined as the contamination of water bodies, occurs when harmful particles that lack of treatment discharged into the water bodies. This contamination can be categorized into pointandnon-pointresources.[1,2,3] The point source is a particular and identifiable cause of water pollution, including discharge pipe of factories and sewage treatment plants. On the other hand, non-point sources of water pollution are the effects that occur over a large area of the water bodies and not specified to a particular source. Furthermore, thepointsourceofwaterpollutionscanbeclassifiedinto chemical (organic andinorganic) and biological pollutants.[4] Such compounds like heavy metals, sulfates, nitrates, phosphates, oxalates, fluorides, and chlorides possess harmful effects on human health, whereas, heavy metals are trace metals and categorized belong to the inorganic pollution of water were documented as an extremely deleterious and carcinogenic. Heavy metals are non-degradable and naturally occurring compounds of the earth's crust that can be consumed and entered a human body through drinking water and food. Some heavy metals are useful for human and animal health in a minute amounts, such as copper (Cu^{2+}), lead (Pb^{2+}), and zinc (Zn^{2+}), however, they can be harmful and poisonous at a large doses.[5,6]

Copper (Cu^{2+}) considered an essential trace element beside zinc and iron. It is needed in a minute amount, play an important role in heme synthesis and iron absorption in human and animal. However, it is associated with many health problems, including gastrointestinal disorders, diarrhea, stomatitis, tremor, vomiting, paralysis, depression and pneumonia.[7]The concentration of serum copper in healthy persons ranged up to 1.5 mg/L. On the other hand, the high concentration of Cu^{2+}may cause many health problems including liver, kidney, stomach and intestinal diseases.[8,9] Many techniques have been applied in order to remove the heavy metal ions specifically $Cu^{2+}$and those techniques includes but not limited to, reverse osmosis, chemical precipitation, ion exchange, ultrafiltration and adsorption.[10] Among those techniques, adsorption is considered the most preferable technique due to it is economically advantageous, highly efficient, and applicable. In the current study, 3-aminopropyltriethoxysilane(APTES) was employed to eliminate Cu^{2+} aqueous solution and particularly water bodies. The exchange ability of the amino-zeolite ions to eradicate the Cu^{2+} ions was reported by Shaaran.[11]

Materials and Methods

[Second order headings should be bold, font size 12, bold and centered]

Preparation of Cu^{2+} stocksolution

The standard solution of copper has been prepared from Cu^{2+} solid powder. A standard solution of 1000 ppm for Cu^{2+} was prepared by dissolving 1 g of Cu^{2+} in 1000 mL distilled water. Afterward, different concentrations of Cu^{2+} standard solution were prepared by diluting the Cu^{2+} standard solution with distilled water to get the final concentration of 50 ppm, 100 ppm, and 150 ppm.

Synthesis ofeffervescence-APTES-zeolite

Synthesis of APTES-zeolite

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APTES-zeoliteused in the study was synthesized asdescribedbyNik*etal*.(2011).[12] Briefly, 2 g of dried zeolite powder was added into 100 mL ethanol and stirred in a roundbottomflaskfor1hat80℃.Then,8mLofAPTES(4mLaminosaline/gzeolite) as a grafting agent was added to the mixture by syringe under stirring. Post 24h,thesolutionwascooleddown,filtered,andwashedusingethanol. Finally, the grafted zeolites was dried in a vacuum oven at 100℃ for 24 h.

Preparation of effervescence-APTES-zeolite(EFF-APTES-zeolite)

A 300 mg of sodium dihydrogen phosphate dihydrate and 150 mg of anhydrous sodium carbonate was desiccated separately in an oven at 90℃ for 5 h then mixed together. Subsequently, 10, 20, 30, 40, and 50 mg of APTES-zeolite were added and grounded into a fine powder using glass mortar.

Characterization of zeolite, APTES-zeolite, andEFF-APTES-zeolite

In order to characterize the zeolites,APTES-zeolite,andEFF-APTES-zeolite, the spectroscopic and microscopic examination was employed.Fourier transformed infrared spectroscopy (FTIR) was used for thespectroscopymethod, while Field emission scanning electronmicroscopy (FESEM) used for the microscopic technique. The overall surface area and weight loss of zeolites, APTES-zeolite, and EFF-APTES-zeolite were evaluated through the BET technique and thermal gravimetric analysis (TGA).

Adsorptionstudy

Batch adsorption tests were performed through intermingling the sample solution containing the fixed size of adsorption with different parameters, including the initial concentration of heavy metals ions, adsorbent dosage, samples' pH, contact time and temperature. It permits the relationship between adsorbent and adsorbates in the sample solution until it attains equilibrium. The trials were conducted by differing one of the parameters while keeping other parameters fixed. After the adsorption procedure, the sample solutions were sent to the inductively coupled plasma - optical emission spectrometry (ICP-OES) to analyze the ultimate concentration of the solution. Then, the adsorption capacity and percentage removal of heavy metal ions have analyzed using the following formula described by Garba *et al.* (2016).[13] The percentage removal of heavy metal ions is described as bellow:

$$\% \text{ removal} = \left(\frac{Co - Ce}{Co}\right) \times 100 \qquad (1)$$

Where $C_o$istheinitialconcentrationofasamplesolution(mg/L),and$C_e$isthefinalconcentration of a sample (mg/L). Effervescence ATPES occurred due to chemical interaction between base and acid with APTES-zeolite, which effectively remove the heavy metal ions from thesamples.Thepresenceofaluminamakesthezeolitehasanegativechargeframework, whichwouldbeinequilibriumwithpositivecationsofCu^{+2},formingastrongelectrostatic stateontheinternalsurfaces.Thosecationscouldexchangetomodifytheporesizeorthe adsorbent properties. The adjusted pH and negative charge of the Eff-APTES-zeolite surface preferring good adsorption of cationic molecules of Cu^{+2}ion.

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Optimization of adsorptionstudy

The sorption tests were conducted on solutions holding Cu^{2+} ions with the EFF- APTES-zeolite in batch and column procedures, as described by Ismail *et al.* (2014).[14]The batches and experiments of the study were carried out asfellow:

Effect of initial concentrations of Cu^{2+}solutions

The effect of initial concentrations of Cu^{2+} ion solutions on the sorption procedure has beenexaminedwithfivedifferentinitialconcentrationsoftheionsolutions,whichare50, 100, 150, 200, and 250 mg/L. 0.2 g of EFF-APTES-zeolite was added into 25 mLoftheionsamplesolution.Thecontactedtimeusedwere5,15,25,35,and45minand the adsorption process was carried out at room temperature. After the adsorption process, the sample was filtered through a sterile syringe filter and sent to ICP-OES to determine removalpercentage.

Effect of Mass ofAdsorbent

Different doses of adsorbents were used in this study, including 10, 20, 30, 40, and 50 mg. The adsorbents were immersed in the sample solution with 25 mL of 100-ppm solution at room temperature. The contact times used were 5, 15, 25, 35, and 45 min and the adsorption process was carried out at room temperature. After the adsorption process, the sample was filtered through a sterile syringe filter and sent to ICP-OES to determine removal percentage.

Effect of Sample pH

The pH significantly affects the sorption of both Cu^{2+} ions in the solution utilizing EFF-APTES-zeolite. A series of 25 mL test tubes, comprising 0.2 g of EFF- APTES-zeolite were spiked with five different initial concentrations of the ion solutions: 50, 100, 150, 200, and 250 mg/L of Cu^{2+} ions. The pH level has been adjusted at 3, 4, 5, 6, and 7 using a 0.1M of hydrochloric acid (HCL).[15] Initial examinations indicated the sorption procedure of each studied ion was accomplished in 15 min. The acquired suspension was filtered to isolate thesolids from the liquid phase. The filtered liquid phases were sent to ICP-OES for the determination of removalpercentage.

Effect of Contact Time

A series of25mLtesttubes,comprising0.2 gofEFF-APTES-zeolite,were spiked with five different initial concentrations of the ion solutions, which are 50, 100, 150,200,and250mg/LofCu^{2++}ions.Thecontacttimebetweenadsorbentandadsorbates during the adsorption process was 5, 15, 25, 35, and 45 min. The adsorbents were immersedinasamplesolutionwith25mLof100ppmsolutionatroomtemperature.

WhileotherconditionssuchasinitialconcentrationsofCu^{2+}ions,themassofadsorbents, pH, and temperature remainedpersistent.

Effect of Temperature

Theimpactsofdifferenttemperatures(30,40,50,and60℃)ontheadsorption process was examined in the currentstudy. A series of 25 mL test tubes, comprising 0.2 g of EFF- APTES-zeolite were spiked with five different initial concentrations of the ion solutions: 50,100,150,200,and250mg/LofCu^{2+}ions.Theadsorbentswereimmersedinasample solution with a 25 mL 100 ppm solution, kept at 30, 40, 50, and 60℃ to permit the adsorption process.

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While the incubation temperatures were varied, all the other conditions remainedconstant.

AdsorptionKinetics

The kinetic batch examinations were conducted at a stable concentration of initial metalionsof100mg/Lemployingat roomtemperaturesforCu^{2+} ionssorptiononEFF-APTES-zeolite.Firstly,0.2gofEFF-APTES-zeolitewereadded in a 25 mL solution of 100 ppm metal ion solution concentration. Besides, the samples were processed in different contact times at 5, 15, 25, 35, and 45 min. Subsequently, the solutionwasfilteredthroughasterilesyringefiltertoisolatetheliquidphase'ssolids phase. The acquired clear phase was sent to ICP-OES for the determination of removalpercentage. The adsorption mechanism and rate of adsorption was further analyzed by using pseudo-first and second order models. The rate constant of adsorption was determined from the pseudo-first-order equation:

$$Log\ (qe - qt) = logqe - k1t / 2.303 \quad (2)$$

Where *qe* and *qt* (mg/g) are the amount of adsorbed (mg/g) at equilibrium and at time t (min), respectively. While *k1t* is the adsorption rate constant (min^{-1}). The pseudo-second-order equation based on the equilibrium adsorption is described below:

$$t / qt = 1 / k^2 qe^2 + t / qe \quad (3)$$

Where k^2 (g/mg·min) is the rate constant of second-order adsorption. It found that the modified zeolite is a good potential as an adsorbent for heavy metal ions with a pseudo-second-order model. Therefore, this model is the potential to represent the completely experimental range of heavy metal adsorption better than the pseudo-first-order model. Furthermore,thecorrelationcoefficientswereclosedtounityforthepseudo-second-order model. Thus, the removal of heavy metal is quite described by the pseudo-second-order model.

AdsorptionIsotherms

In the tests of sorption isotherm assessments, 25 mL of each Cu^{2+} ions solution of initial concentration (50, 100, 150, 200, and 250 ppm) were added with 0.2 g of EFF-APTES-zeolite. Following the establishment of contact time, the aliquot of supernatants was drawn, and the degree of the metal ion held in the EFF- APTES-zeolite (mg/g),evaluated utilizing the below equation; this equation was statedbefore.

$$\%\ of\ removal = (Ci - Ce / Ci) \times 100 \quad (4)$$

Where *Ci*and *Ce*are the initial and equilibrium concentrations of the metal ion in the solution (mg/L). The effect of initial concentration of Cu2+ ions was further analyzed by using adsorption isotherm models, Langmuir isotherm and Freundlich isotherm.

TheLangmuirmodelwasadoptedtoassumetheabsorptionofmetal ions occurred on a homogeneous surface between adsorbed ions and the sorption sites. The equation for this model isbelow:

$$Ce / qe = (1 / K1\ Qm) + (Ce / Qm) \quad (5)$$

Where Ce/qevs. Ce confirms the validation of the Langmuir with correlation coefficients (R^2) closed to unity, and Kl is a constant of free energy of adsorption.

Freundlich isotherm explained the relationship between the concentration of adsorbate molecules on the surface of adsorbent in the aqueous solution when they contacted. The equation for this model is below:

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$$\text{Log } q_e = \log k + (1/n) \log C_e \qquad (6)$$

Where k is a Freunglich constant that related to the temperature, n is a characteristic constant of Freundlich for the adsorption system, C_e (mg/L) is the equilibrium concentration and q_e (mg/g) is the amount of adsorbate adsorbed per unit weight of adsorbent.

Cu^{2+} Ions of Aqueous WaterSamples

Two kinds of aqueous samples have been employed to examine the removal of Cu^{2+} ions through EFF-APTES-zeolite, including Lake 1, Lake 2. The initial ion concentrations of two aqueous water samples were measured through ICP-OES. Optimum conditions includingroomtemperature,pH4,100-ppminitialconcentration,0.02gofEFF-APTES- zeolite have been provided to permit efficient removal of Cu^{2+} ions in the aqueous water samples by determining the adsorption capacity (mg/g) and percentage exclusion of Cu^{2+} ions. The EFF-APTES-zeolite with a 0.02 g dose has been immersed in aqueous water samples. Finally, the last concentration was calculated by utilizing ICP-OES. It complies with the method described by Ismail.[14]

Results and Discussion

Characterization

FTIR Characterization of Zeolite, APTES-zeolites, and EFF-APTES-zeolite

FTIRanalysisistypicallyutilizedtoexplorethesamplechemicalstructure,recognizethe materials, degree of reactions, and determine the composition of the mixtures.[16] The surface structures of functional groups in the modified zeolites significantly affect the metal sorption limit.[17]In the current study, FTIR spectroscopy was executed to analyze the adsorbent zeolite, APTES-zeolite, and EFF-APTES-zeolite. Thus, the functional groups of zeolite, APTES-zeolite, and EFF- APTES-zeolite adsorbents were characterized and their FTIR spectra are shown in Figure 1. Table 1 presented the wavelength of the leading functional group in the zeolite,APTES-zeolite,andEFF-APTES-zeolitewiththeirintensityandtypeofvibration.

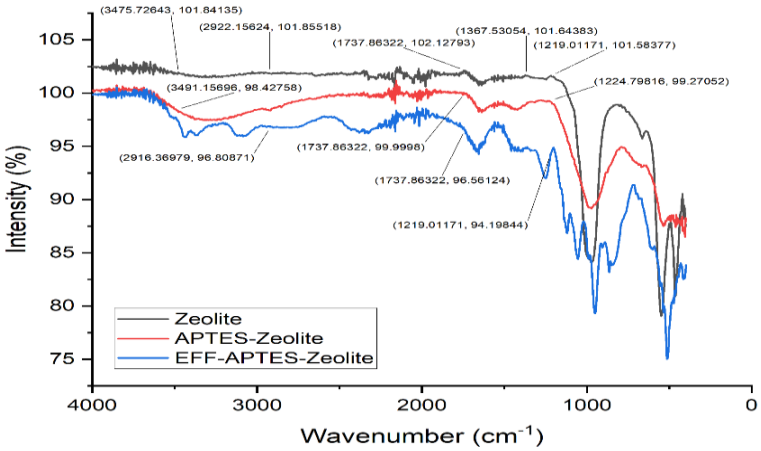

Figure 1. FTIR spectra of Zeolite, APTES-zeolite, and AFF-APTES-zeolite at different ratios.

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Table 1. The wavelength of the leading functional group in the Zeolite, APTES-zeolites, and EFF-APTES-zeolite with their intensity and type of vibration.

Zeolite Type	Wavelength (cm^{-1})	Functional Group	Vibration, Intensity
Zeolite	1219.01	C – O	Stretching, Strong
	1367.53	C – H	Bending, Medium
	1737.86	C = O	Stretching, Strong
	2922.16	C – H	Stretching, Medium
	3475.73	O – H	Broad, Strong
APTES – Zeolite	1224.80	C – O	Stretching, Strong
	1369.46	C – H	Bending, Medium
	1664.57	C = O	Stretching, Strong
	1737.86	C – H	Stretching, Medium
	3491.16	O – H	Broad, Strong
EFF – APTES – Zeolite	1219.01	C – O	Stretching, Strong
	1367.53	C – H	Bending, Medium
	1670.35	C = O	Stretching, Strong
	1737.86	C – H	Stretching, Medium
	2916.37	O – H	Broad, Strong

FTIR spectra of zeolite in Figure1 displays three significant ester groups at 1737.86 cm^{-1} for zeolite, 1664.57 cm^{-1} for APTES-zeolite and 1670.35 cm^{-1} for EFF-zeolite (C=O ester). The broad and strong peak at 3475.73 cm^{-1} characterizes the −OH peak strength of zeolite. For APTES-zeolite, the spectrum pattern was slightly different from the zeolite. The broad peak of the hydrogen bond of −OH groups is detected at 3491.16 cm^{-1}, weaker than the zeolite peak. The APTES-zeolite also exhibits a weak peak of C=C at 500 cm^{-1} because C=C's vibrational modes of C=C after casting. Similarly, the EFF-APTES-zeolite shows −OH band at 2916.37 cm^{-1}. The presence of the NH_2 group in APTES- Zeolite, EFF-zeolite at 3491 cm^{-1} directly relates to corresponding structure because of the addition of amino silane. The natural zeolite doesn't contain an amino group band. The stretching of the amino group at 3300- 3500 cm^{-1} is almost the same stretching pattern as the OH group. The presence of phosphate group in EFF-zeolite at 2500 cm^{-1} and the absence of this strong band in APTES-zeolite and natural zeolite confirms the structure of EFF- zeolite. The dissimilarities in the spectrum patterns represent the successful casting of EFF-APTES- zeolite compared to APTES-zeolite and the zeolite. The results were comparable to the results reported by Yakout *et al.*.[17]

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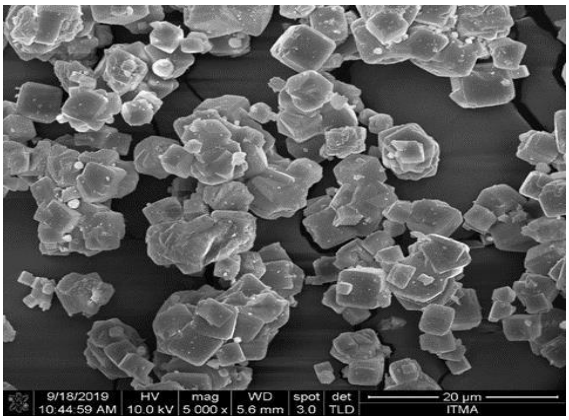
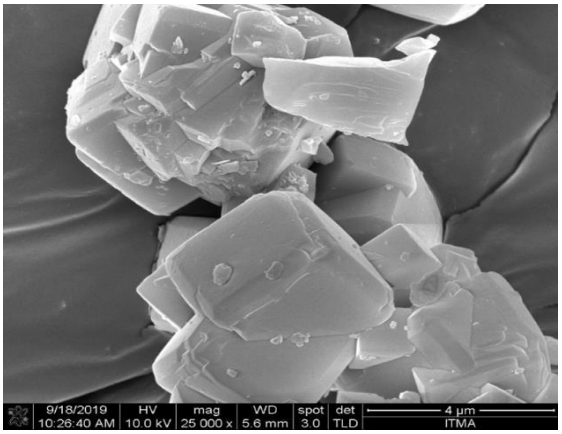
Field Emission Scanning Electron Microscopy Characterization of Zeolite, APTES-zeolite, andEFF-APTES-zeolite

In the current study, morphologies of zeolite, APTES-zeolite, and EFF-APTES-zeolite were observed using JEOL JSM-7600F FESEM. These zeolites were coated with platinum to avoid charging effect during analysis. The micrographs of Zeolite, APTES-zeolite, and EFF-APTES-zeolite are presented in Figure 2. It demonstrated a significant difference between Zeolite, APTES-zeolite, and EFF-APTES-zeolite in terms of particles' size and shape. The FESEM images revealed that the three zeolites appeared to have a relatively non-uniform surface, uneven pore morphology, and the different particlesizes.Thezeoliteparticleswerecube-shaped,havingaparticlesizeof20µm.The APTES-zeoliteparticleswerealsocubed-shapedbutsmallerinsize(4µm).Ontheother hand, the EFF-APTES-zeolite particles were flakes or spherical-shaped, having the particlesizeof20µm.ThehomogeneousstructureofEFF-APTES-zeolitepresentingthat EFF-APTES-zeolite has the aptitude to be effectively utilized as an adsorbent for the exclusion of Cu^{2+} ions from aqueous watersamples.



A



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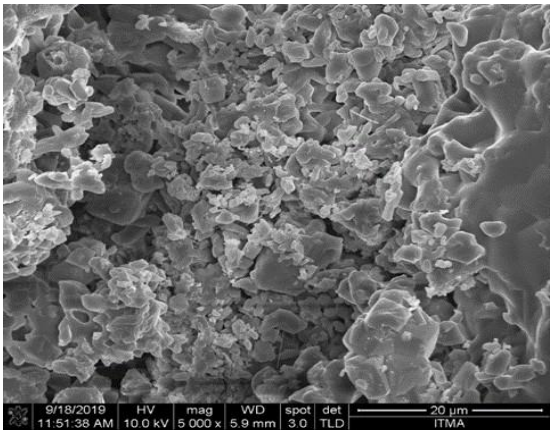

C

Figure 2. Morphology of zeolite (A), APTES-zeolite (B), and EFF-APTES-zeolite (C).

Weight loss of Zeolite, APTES-zeolite, and EFF-APTES-zeolite Using TGA

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TGA spectra of zeolites (zeolite, APTES-zeolite, EFF-APTES-zeolite) were carried out, showingweightlossatabout200℃. Figure3displaysthegradualweightlossofzeolite, APTES-zeolite, and EFF-APTES-zeolites. The weight loss of these zeolites are assigned to bound water or oxidant, or allocated to the degeneration of the samples' structure during the melting process. From Figures 3, it was found that the weight loss of EFF- APTES-zeolite was significantly higher than APTES-zeolites andzeolite.

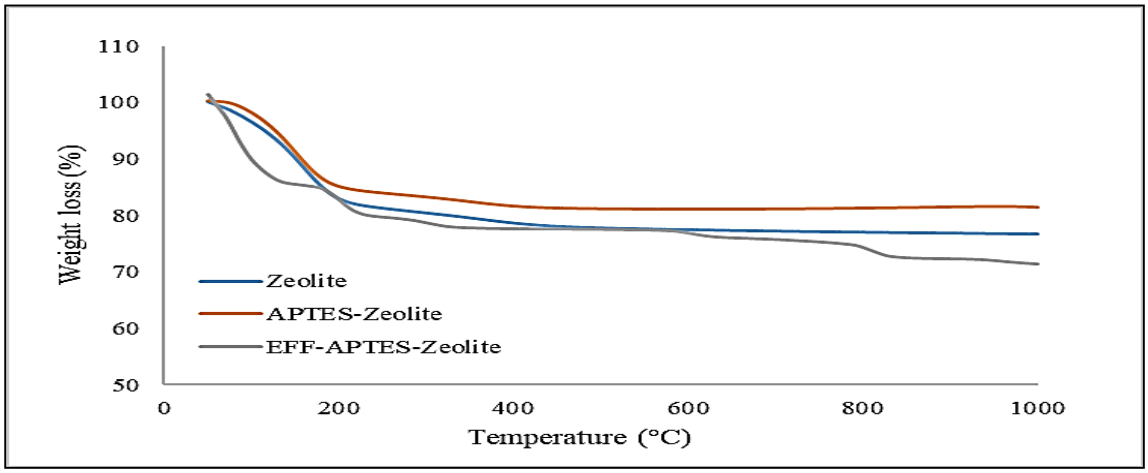

Figure 3. Weight loss of zeolite, APTES-zeolite, and EFF-APTES-zeolite at different temperatures

BET Surface Area of Zeolite, APTES-zeolite, andEFF-APTES-zeolite

In an adsorption study, the specific surface area of the zeolite, APTES-zeolite, and EFF-APTES-zeolite is the significant factor in showing molecules' physical adsorption on the zeolite surface. In the BET analysis, the shape of adsorption isotherm offers qualitative data on the adsorption procedure and the degree of the specific surface area accessible to theadsorbates.Inaparticularisotherm,theadsorbentissupposedtohavecertainporosity. Thespecificsurfaceareaofzeolite,APTES-zeolite,andEFF-APTES-zeolitewas3.5456, 5.1160, and 3.3835 m^2/g (Table 2). The surface is one of the most prominent attributes of zeolites in Cu^{2+} ions removal methods. Therefore, the zeolites having a greater surface area can absorb the higher amount of ions and effectively remove Cu^{2+} ions from aqueous water samples.

Table2.Surfaceareaandporevolumeofzeolite,APTES-zeolite,andEFF-APTES- zeolite.

Adsorbents	Surface Area (m^2/g)	Pore Volume (cc/g)
Zeolite	3.5456 m^2/g	0.32874 nm
APTES-zeolite	5.1160 m^2/g	0.10071 nm
EFF-APTES-zeolite	3.3835 m^2/g	0.38703 nm

As far as the BET surface area concerned, APTES-zeolite showed a larger surface area with 5.1160 m^2/g compared to zeolite and APTES-zeolite. BET result also showed that zeolite and EFF-APTES-zeolite had slightly higher mesoporous volume than APTES-zeolite.This is likely to be due to the position of the silane coupling agent in zeolite mesopores. BET result also showed that zeolite and EFF-APTES-zeolite had slightly higher mesoporous volume than APTES- zeolite. The technical reason based on the BET

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analysis zeolite surface can induce clogging and shrinking of the zeolite pores and openings, and effervescence helps prevent this blockage. EFF-APTES-zeolite has other advantages like faster adsorption rates, more effective and provides excess amino groups.

Effect of Different Parameters towards Cu^{2+} IonsRemoval

Effect of Initial Concentrations of Cu^{2+} ionsSolutions

The initial concentration of Cu^{2+} ions has a significant effect on the adsorption of Cu^{2+} ions on adsorbent's surface sites. Based on the current study's results, the removal percentage of Cu^{2+} ions decreased when the initial concentration of Cu^{2+} ions increased. ThereductioninpercentageremovalofCu^{2+}ionsduetotheinitialconcentrationofheavy metal is because of the non-availability of active sites on the adsorbent's surface. Figure4represents the percentage removal of Cu^{2+} ions and the initial concentration of heavy metal ions. At 50 and 100 ppm of initial concentrations of Cu^{2+} ions, the percentage of removal of Cu^{2+} ions obtained was (97.40) and (99.20), respectively, which means that this adsorbent is suitable only for 50 and 100 ppm of Cu^{2+} ions concentrations.

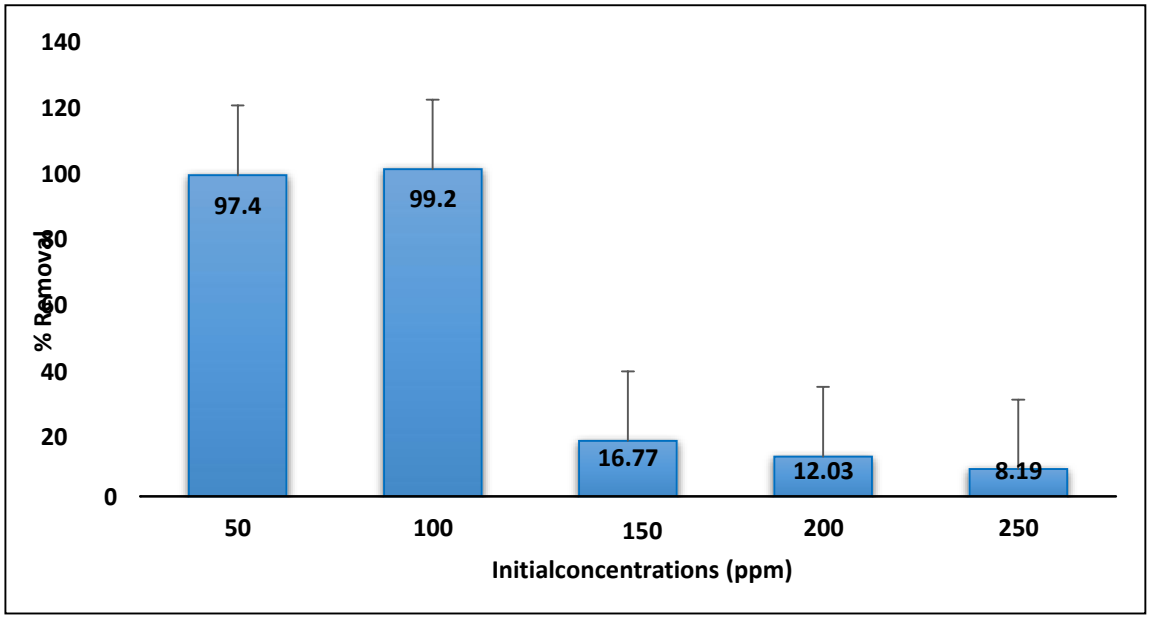

Figure 4. Effect of initial concentrations of Cu^{2+} ions (ppm)

Effect of Mass ofAdsorbent

The mass of EFF-APTES-zeolite significantly affects the adsorption of Cu^{2+} ions in aqueous solution. In general, it increased the mass of adsorbent results in the increase of active sites available in the adsorption procedure. The current study's results showed that the removal percentage of Cu^{2+} ions was increased since the dose of adsorbent increased. Figure 5 represents the percentage of removal of Cu^{2+} ions affected by the different adsorbent's masses. It demonstrates the removal percentage of Cu^{2+} ions reached up to optimum level (99.21) one the dosage of adsorbent was increased from 10 to 20 m. However, the further surge in adsorbent dosage (30-50 mg) gradually declined the removal percentage of Cu^{2+} ions, reaching its lowest (98.31%). Different dosages (10, 20, 30, 40 and 50 mg) of EFF-APTES-zeolite were used to identify the maximum adsorption. It was found that 20 mg of EFF-APTES-zeolite was the best adsorbent and depicted the highest

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removal percentage of Cu^{2+} ions. The concentration parameter was fixed at 100 ppm, and the contact of Cu^{2+} ions with EFF-APTES-zeolite was only 20 mg. The increase in dosage didn't affect the removal capacity of Cu^{2+} ions. The high adsorbent dosages of EFF-APTES-zeolite cannot cover the total solute (Cu^{2+} ions) at the available exchangeable sites, which will lead to low specific uptake. The decline in removal percentage of Cu^{2+} ions was due to lower surface area of adsorbent and deposition of metals ions on active sites of adsorbent's surfaces.

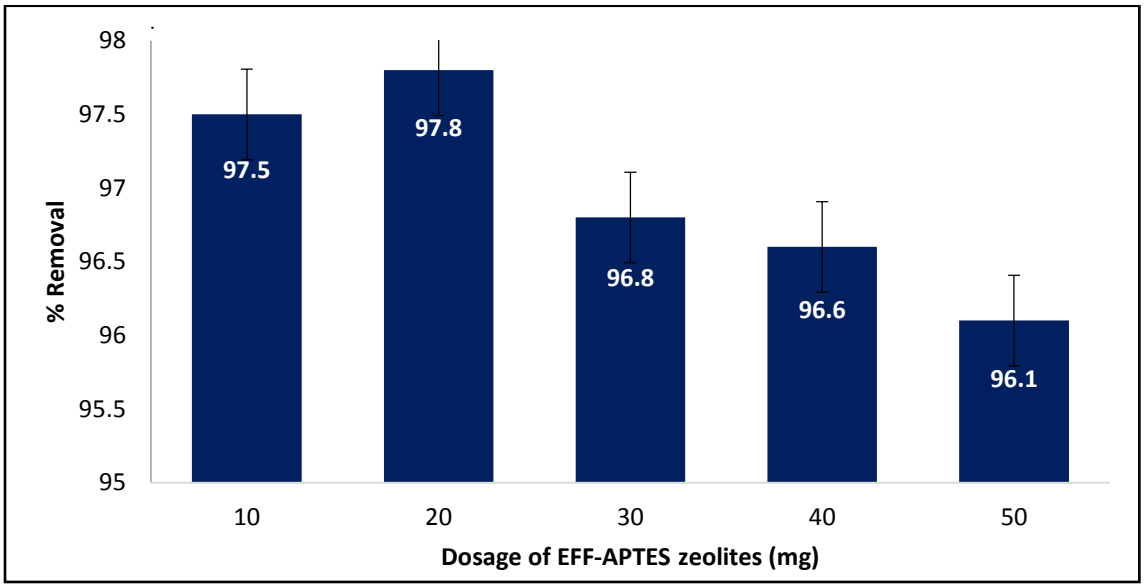

Figure 5. Effect of mass adsorbent on percentage removal of Cu^{2+} ions

Effect of pH

Optimization of pH lining was significant to determine the level of ionization and speciationoftheadsorbatesandsurfacevariationsoftheadsorbent.Figure 6 illustrated that pH significantly influences the adsorption ability of the Cu^{2+} ions by the tested adsorbent in a solution. The outcomes from the current study demonstrated that the adsorption of Cu^{2+} ions increased when the pH increased from 3 to 7. This surge in sorption is accredited to the rise in the negative sorption spots existing to bond with the Cu^{2+} ions. The highest removal percentage for Cu^{2+} ions was approximately 99.99% at pH 4. The free Cu^{2+} ions have usually been involved in the adsorption process when the pH was smaller than 4 for Cu^{2+} ions. At acidic pH, the removal percentage for Cu^{2+} ions were lesser than optimum pH due to the increase in H^{+} ions concentration on adsorbents' surface, which increase the competitionCu^{2+}ions withH^{+}ionstobindwiththehydroxylgrouponadsorbents'surface.[18] Once the pH is higher than 4, the Cu^{2+} ions activated to act as Cu(OH)2, due to the chances for Cu^{2+} ions to bind with adsorbents' surface decreased.

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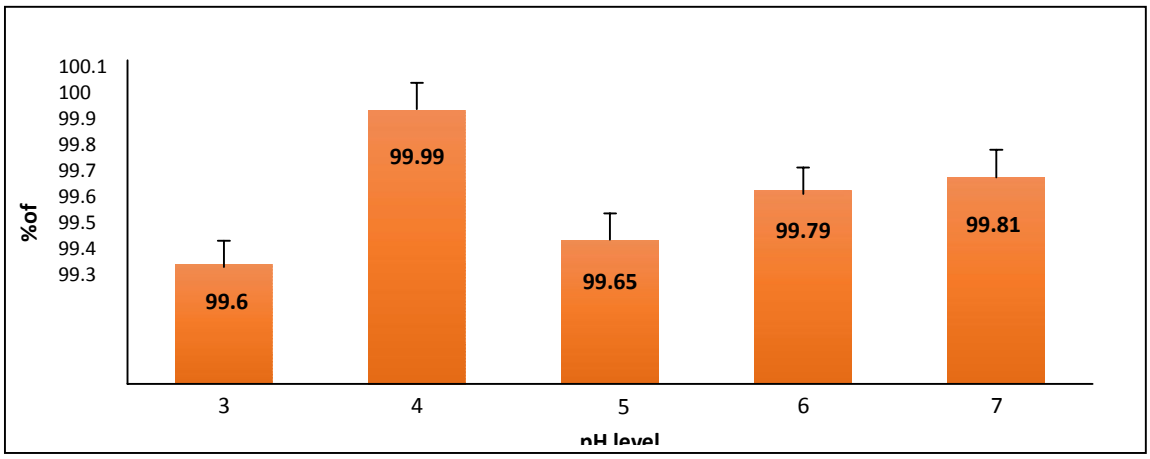

Figure 6. Percentage of Cu^{2+} removal ions on different pH

The rise in metaladsorptionwithhigherpHcouldbeexplainedbasedondeclininginpositivesurface charge and a decline in competition among proton and metal cations for the same functionalgroup,resultinginlowerelectrostaticrepulsionbetweenmetalionsandsurface oftheadsorbent.AccordingtoJain,solublehydroxycomplexes'development decreases the removal percentage at higher pH. Therefore, a pH of 4 Cu^{2+} ions has been applied throughout the study.[19]

Effect of Contact Time

The removal percentage of Cu^{2+} ions has been analyzed on different contact times, including 5, 15, 25, 35, and 45 min. It was to permit attraction and promptness of Cu^{2+}towards the active sites of the EFF-APTES-zeolite. In general, the percentage removal of adsorbentsincreasedassoonasthecontacttimeamidadsorbatesandactivesiteincreased untiltheequilibriumstateisreached.Generally,theremovalpercentageofCu^{2+}ionswas rapidlyincreasedinthefirst10minandreachedtheirhighestlevel(99.84%)owingtothe availabilityofactivespotsontheadsorbentuntiltheysaturated.After15min,theremoval percentageofCu^{2+}ionsabruptlydeclinedto99.79%andremainedconstantat25,35,and 45 min. This decrease could be due to the desorption of Cu^{2+} ions from the active sites of the adsorbent. Figure 7shows the removal percentage of Cu^{2+} ions along with various contacttimes.

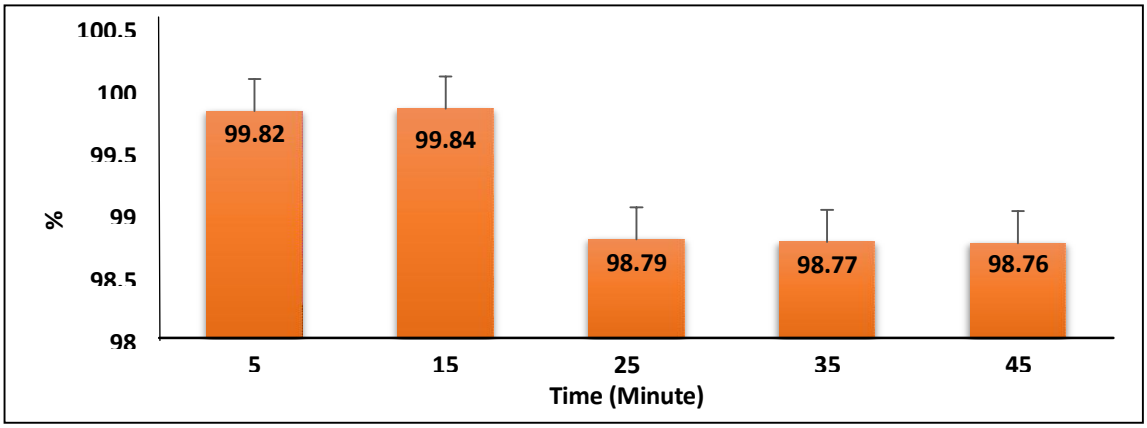

Figure 7. Effects of contact time on the removal percentage of Cu^{2+} ions

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Effect ofTemperature

The removal percentage of Cu^{2+} ions was analyzed at a different temperature, including 30, 40, 50, and 60℃. Generally, the removal percentage of Cu^{2+} ions rapidly increased and reached its highest level (99.69%) when the temperature has been raised from 30 to 40℃. However, a further increase in temperature gradually decreased the removal percentage by EFF-APTES-zeolite and dropped down at its lowest 98.73%level once the temperature rose to 60℃. This decline in removal percentage by EFF-APTES-zeolitecouldbeduetothedesorptionofCu^{2+}ionsfromtheactivesitesofadsorbentcaused by high temperature (Figure 8).

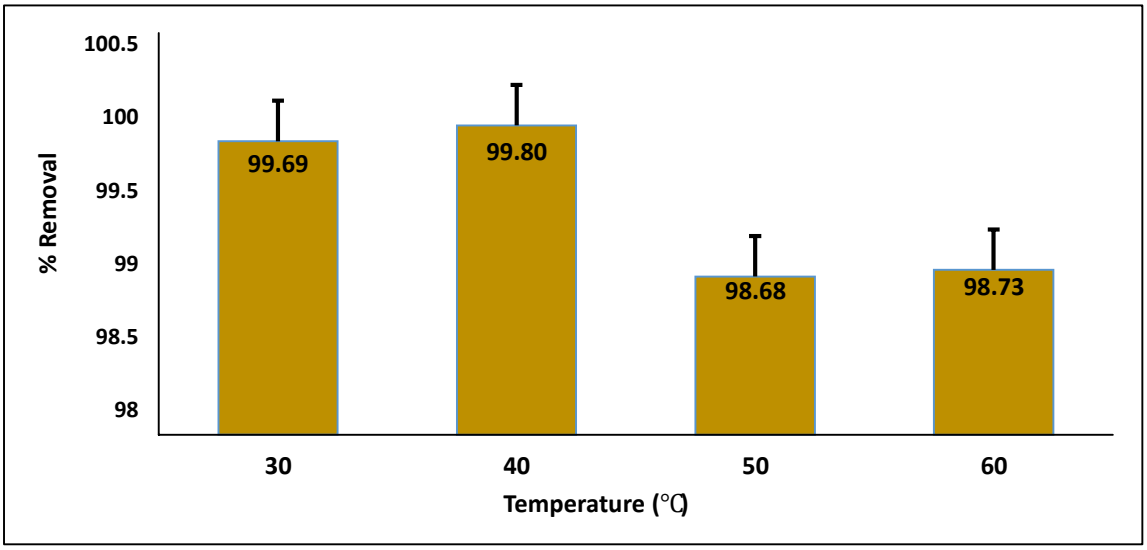

Figure 8. Effects of temperature on the removal percentage of Cu^{2+} ions.

Adsorption KineticStudy

Adsorption kinetic study is the most significant parameter of the adsorption study to realize the adsorbent's acceptable behavior and analyze the experimental results employing pseudo-first-order and pseudo-second-order kinetic models. The removal percentage of Cu^{2+} ions on EFF-APTES-zeolite at different contact times (5, 15, 25, 35, and45min)utilizing100-ppminitialconcentrationispresentedinFigure9and10.

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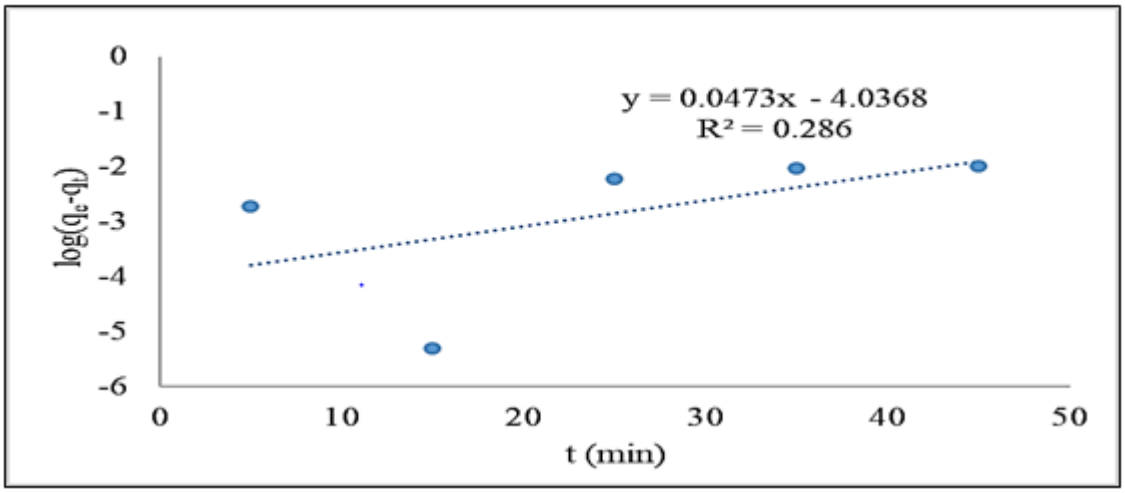
Figure 9. Pseudo-first-order of adsorption kinetics.



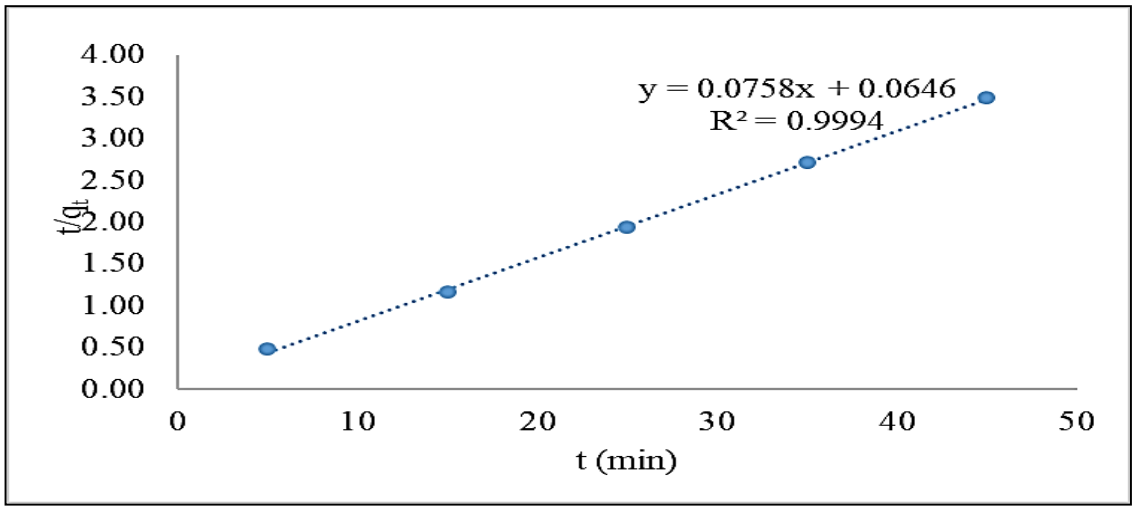


Figure 10. Pseudo-second-order of adsorption kinetics.

Figure 10, demonstrates that adsorption process of Cu^{2+} ions on EFF-APTES-zeolite swiftly happened within the initial 5 min that was owing to the higher accessibility of active sites on the adsorbent and instant attachment to the adsorbent's surface.[18, 20] It is for the reason that at first, all sorbent sites were empty. Afterward, the rise in adsorption was prolonged, owing to the decline of the emptyactive site on the adsorbent's surface.[21] The active sites have an affinity to saturate with the rise of contact time until the system achieved an equilibrium state after 15min. After which the removal percentage for Cu^{2+} ions declined as all the sorbent sites were occupied. Figures 9 and 10 represents the pseudo-first-order and pseudo-second-order adsorption isotherm towards Cu^{2+} ions utilizing EFF-APTES-zeolite.

In Figure 9, the plots were not linear, having a lousy correlation coefficient (R^2). The removal percentage of Cu^{2+} ions onto on EFF-APTES-zeolite was a pseudo-first-order since the correlation coefficient (R^2) was very low. In Figure 10, the linear regression coefficient for Cu^{2+} ions was 0.99, demonstrating that the adsorption capacity of Cu^{2+} ions on EFF-APTES-zeolite was suitable pseudo-second-order model. Based on the current study's findings, pseudo-second-order sorption mechanism was pre-dominant, and the overall degree of the Cu^{2+} ions sorption procedure was regulated by

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chemicalreactions,includingvalencyforcesthroughtheexchangeofelectronsamongsorbentsand sorbates.[21]Basedontheresults,itcanbeconcludedthatintheinitialphase,Cu^{2+}ions were immediately adsorbed on the surface of the adsorbent, dominating the initial kinetics of sorption,[22]givingthenon-linearregressioncoefficient(<0.6000).Inthesecondstage, Cu^{2+}ions gradually diffuse in the adsorbent's pores and are adsorbed on the internal sites.[23]

Adsorption IsothermStudy

The equilibrium data of adsorption is called adsorption isotherms. It demonstrates the distribution of adsorption molecules amongst the solid and the liquid phases once the sorption process achieves equilibrium. The isotherm data analysis is a significant factor in finding a suitable model employed for design drives.[21] Similarly, adsorption isotherm is significant in comparing the efficacy of adsorbents in diverse functional conditions. Moreover, it is essential in the optimization and designing of an adsorption method. The adsorption capacity of Cu^{2+} ions was plotted against the initial concentration, as presented in Figures 11 and 12.

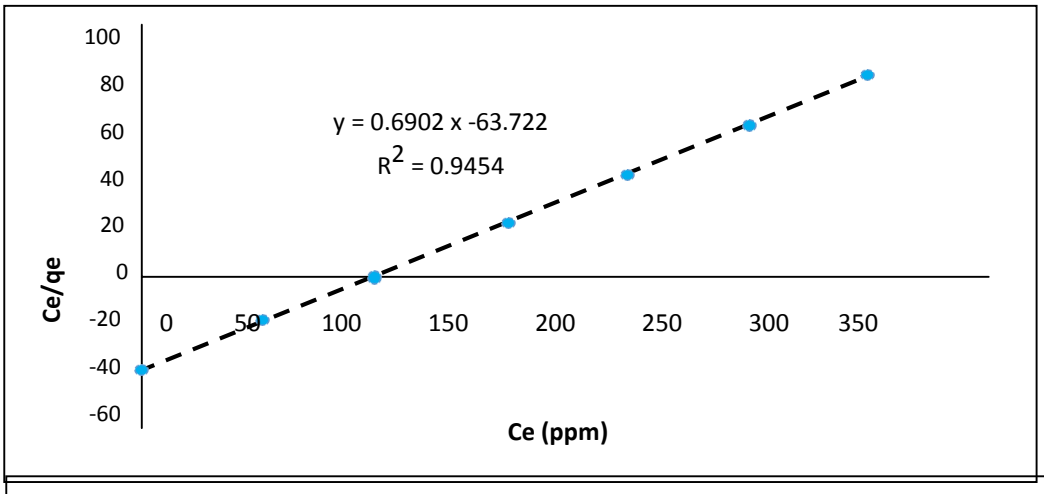

Figure 11. Langmuir Isotherm of adsorption.

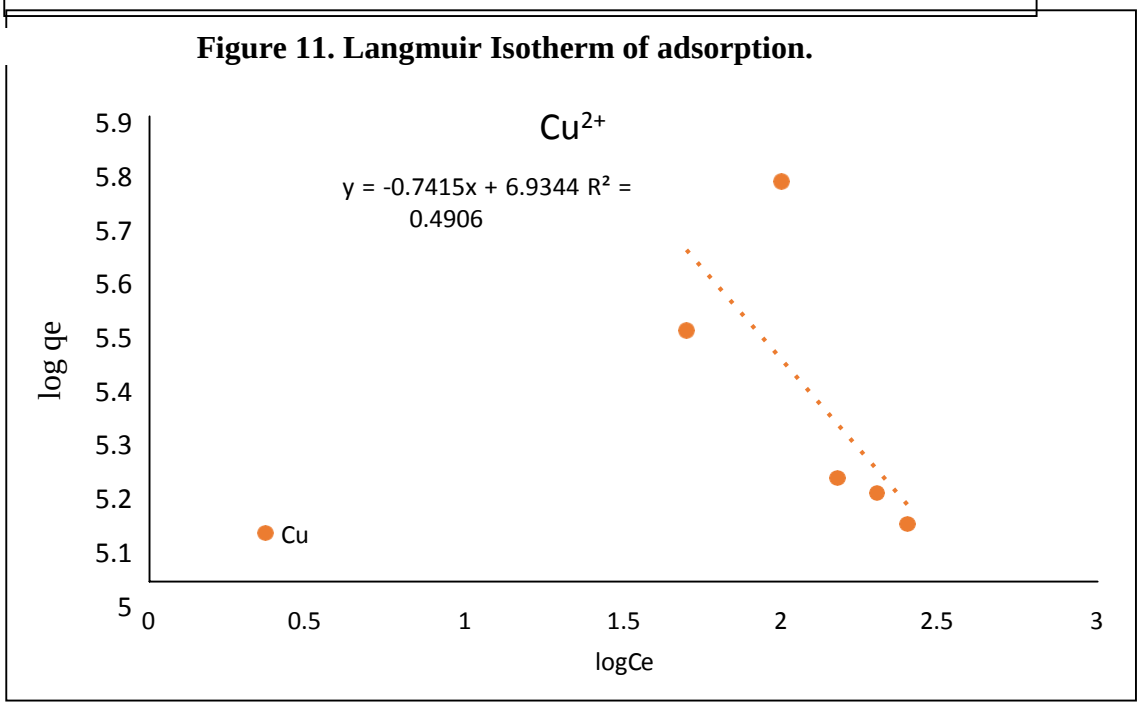

Figure 12. Freundlich Isotherm of adsorption

at equilibrium state has increased with the initial concentrations of Cu^{2+} ions (50, 100, 150, 200, 250 ppm). The experimental data were fitted in the Langmuir equations.TheLangmuiradsorptionisothermstowardsCu^{2+}ionsareshowninFigure 11. In the current work, the data were efficiently fitted into all adsorption isotherm models.Equatingthecorrelationcoefficients(R^2),ithasbeenobservedthattheLangmuir isotherm offers an efficient model for the adsorptionprocess.

Aqueous Water SampleStudy

The efficacy of EFF-APTES-zeolites to remove the Cu^{2+} ions was tested using aqueous water samples of two different lakes of the UPM area, Serdang, Malaysia.EFF- APTES-zeolitewasaddedwithoutanytreatment.Table3representstheefficiency of EFF-APTES-zeolites for the removal of Cu^{2+} ions. The values of removal percentage of Cu^{2+} ions from real water samples were less than one ppm, representing the lower concentrations of Cu^{2+} ions in these water samples and under the permissible limit authorized by World Health Organization.[24]

Table 4.3. The removal percentage of Cu^{2+} ions from environmental water samples (lake water)

Adsorbents	% of removal of Cu^{2+}	
EFF-APTES-zeolite	**Sample 1**	99.22
	Sample 2	99.39

CONCLUSION

In the current study, the EFF-APTES-zeolite was effectively prepared and used as adsorption towards Cu^{2+} ions in aqueous water samples. Moreover, the characterization of EFF-APTES-zeolite was conducted through FTIR, FESEM, TGA, BET analysis. The active sites of EFF-APTES-zeolite are comprised of amino (NH_2) groups where the Cu^{2+} ions interact. The removal percentage for Cu^{2+} ions using EFF-APTES-zeolite was evaluated under various factors, including initial concentration, the mass of adsorbent, pH, contact time, and temperature. Furthermore, the EFF-APTES-zeolite was tested for the removal of Cu^{2+} ions from aqueous water samples acquired from three lakes of the UPM area, Serdang, Malaysia. The formation of EFF-APTES-zeolite was confirmed by FTIR examination at the peaks of the broad band of hydrogen bonding of –OH groups detected at 1000 cm^{-1}. It also shows a peak of C=O at 500 cm^{-1} owing to the vibrational modes of C=O after casting. Furthermore, a C−H and −CO− stretching bands were also identified at 500 cm^{-1} and 512 cm^{-1}. The existence of the NH_2 group in APTES- Zeolite, EFF-zeolite at 3491 cm^{-1} directly relates to corresponding structure because of the addition of amino silane. The natural zeolite doesn't contain an amino group band. The stretching of the amino group at 3300- 3500 cm^{-1} is almost the same stretching pattern as the OH group. The presence of phosphate group in EFF-zeolite at 2500 cm^{-1} and the

absence of this strong band in APTES- zeolite and natural zeolite confirms the structure of EFF- zeolite. The adsorption results revealed that 100 ppm of Cu^{2+} ions was the optimum concentration for the removal of Cu^{2+} ions (99.02%) from aqueous water samples. Likewise, 20 mg was the optimum dosage of adsorbent, removing maximum ions concentration of Cu^{2+} from aqueous water samples. Moreover, the initial increase in pH significantly led to an increase of the removal percentage of Cu^{2+} ions. The results obtained from the current study presented that the optimum removal of Cu^{2+} ions through EFF-APTES-zeolite occurred at pH 4. Additionally, the findings showed that the optimal removal of Cu^{2+} ions has occurred at 30℃ with the contact time of 15 min. The removal percentage of Cu^{2+} ions by EFF-APTES-zeolite was dependent on the kinetic study and found fitted in the pseudo-second-order model. Regarding adsorption isotherm, the experimental data showed that Cu^{2+} ions followed the Langmuir model. Generally, EFF-APTES-zeolite was found to be influential in the removal of Cu^{2+} ions from aqueous water samples acquired from three different lakes of UPM regions, Malaysia.

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References

1. Siddique, A., Liess, M., Shahid, N., & Becker, J. M. (2020). Insecticides in agricultural streams exert pressure for adaptation but impair performance in Gammarus pulex at regulatory acceptable concentrations. *Science of The Total Environment*, 137750.
2. Fairbrother, A., Wenstel, R., Sappington, K., & Wood, W. (2007). Framework for metals risk assessment. *Ecotoxicology and environmental Safety*, *68*(2), 145-227.
3. Randall, G. W., & Goss, M. J. (2008). Nitrate losses to surface water through subsurface, tile drainage. In *Nitrogen in the Environment* (pp. 145-175). Academic Press.
4. Gupta, V. K., Ali, I., Saleh, T. A., Nayak, A., & Agarwal, S. (2012). Chemical treatment technologies for waste-water recycling—an overview. *Rsc Advances*, 2(16), 6380-6388.
5. Verma, R., & Dwivedi, P. (2013). Heavy metal water pollution-A case study. *Recent Research in Science and Technology*.
6. Chowdhury, S., Mazumder, M. J., Al-Attas, O., & Husain, T. (2016). Heavy metals in drinking water: occurrences, implications, and future needs in developing countries. *Science of the total Environment*, *569*, 476-488.
7. Singh, A., Sharma, R. K., Agrawal, M., & Marshall, F. M. (2010). Health risk assessment of heavy metals via dietary intake of foodstuffs from the wastewater irrigated site of a dry tropical area of India. *Food and chemical toxicology*, *48*(2), 611-619.
8. Barceloux, D. G. & Barceloux, D., (1999). Copper. *Journal of toxicology: clinical*

Toxicology, *37*(2), pp.217-230.

9. Mahmoud, M. E., Nabil, G. M., & Mahmoud, S. M. (2015). High performance nano-zirconium silicate adsorbent for efficient removal of copper (II), cadmium (II) and lead (II). *Journal of Environmental Chemical Engineering*, *3*(2), 1320-1328.
10. Gunatilake, S. K. (2015). Methods of removing heavy metals from industrial wastewater. *Methods*, *1*(1), 14.
11. Shaaran, S. N. A. (2009). Removal ofHeavy Metals From Effluents Using Ion-Exchange Resin.
12. Nik, O. G., Nohair, B., & Kaliaguine, S. (2011). Aminosilanes grafting on FAU/EMT zeolite: effect on CO2 adsorptive properties. *Microporous and Mesoporous Materials*, *143*(1), 221-229.
13. Garba, Z. N., Ugbaga, N. I., & Abdullahi, A. K. (2016). Evaluation of optimum adsorption conditions for Ni (II) and Cd (II) removal from aqueous solution by modified plantain peels (MPP). *Beni-Suef University Journal of Basic and Applied Sciences*, *5*(2), 170-179.
14. Ismail, A. I. M., El-Shafey, O. I., Amr, M. H. A., & El-Maghraby, M. S. (2014). Pumice characteristics and their utilization on the synthesis of mesoporous minerals and on the removal of heavy metals. *International scholarly research notices*, *2014*.
15. Acharya, J., Sahu, J. N., Sahoo, B. K., Mohanty, C. R., & Meikap, B. C. (2009). Removal of chromium (VI) from wastewater by activated carbon developed from Tamarind wood activated with zinc chloride. *Chemical Engineering Journal*, *150*(1), 25-39.
16. Gebru, K. A., & Das, C. (2017). Removal of Pb (II) and Cu (II) ions from wastewater using composite electrospun cellulose acetate/titanium oxide (TiO2) adsorbent. *Journal of Water Process Engineering*, *16*, 1-13.
17. Yakout, A. A., El-Sokkary, R. H., Shreadah, M. A., & Hamid, O. G. A. (2016). Removal of Cd (II) and Pb (II) from wastewater by using triethylenetetramine functionalized grafted cellulose acetate-manganese dioxide composite. *Carbohydrate Polymers*, *148*, 406-414.
18. Ji, F., Li, C., Tang, B., Xu, J., Lu, G., & Liu, P. (2012). Preparation of cellulose acetate/zeolite composite fiber and its adsorption behavior for heavy metal ions in aqueous solution. *Chemical Engineering Journal*, *209*, 325-333.
19. Jain, G. (2013). *Removal of copper and zinc from wastewater using chitosan* (Doctoral dissertation).
20. Ong, S. T., Lee, C. K., & Zainal, Z. (2007). Removal of basic and reactive dyes using ethylenediamine modified rice hull. *Bioresource technology*, *98*(15), 2792-2799.
21. Hameed, B. H., Ahmad, A. L., & Latiff, K. N. A. (2007). Adsorption of basic dye (methylene blue) onto activated carbon prepared from rattan sawdust. *Dyes and pigments*, *75*(1), 143-149.
22. Ncibi, M. C., Mahjoub, B., & Seffen, M. (2007). Kinetic and equilibrium studies of methylene blue biosorption by Posidonia oceanica (L.) fibres. *Journal of hazardous materials*, *139*(2), 280-285.

23. Hamdaoui, O., & Chiha, M. (2007). Removal of Methylene Blue from Aqueous Solutions by Wheat Bran. *Acta Chimica Slovenica*, *54*(2).
24. World Health Organization. (2017). *Patient safety: making health care safer* (No. WHO/HIS/SDS/2017.11). World Health Organization.