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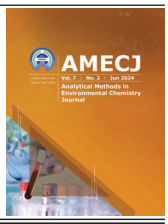

Dolomite utilization for removal of Zn^{2+} and Cu^{2+} ions from wastewater before determination by flame atomic absorption spectroscopy

Firas Fadhel Ali[a], Ahmed S. Al-Rawi[b], Abdulsalam M. Aljumialy[c], and Mohammed Oday Ezzat[*,a]

[a] *Department of Chemistry, Education College for Women, University of Anbar, Ramadi, Iraq*
[b] *Department of Chemistry, College of Science, University of Anbar, Ramadi, Iraq*
[c] *Department of Applied Chemistry, College of Applied Sciences, University of Fallujah, Fallujah, Iraq*

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ABSTRACT

This study aims to use dolomite to remove Zn^{2+} and Cu^{2+} from wastewater. The adsorption process of the Zn^{2+} and Cu^{2+} was performed using the batch method at various factors (such as the amount of adsorbent, contact time, particle size, pH media, temperature, and initial concentration) to investigate the optimum removal conditions. The flame atomic absorption spectroscopy (F-AAS) was used to determine Zn^{2+} and Cu^{2+} after removal steps. The LOD of Zn^{2+} and Cu^{2+} were 0.05 mg L^{-1} and 0.08 mg L^{-1}, respectively. Results showed that the adsorbent dolomite efficiently removed Zn^{2+} and Cu^{2+} with up to 98 % when 0.4 g of dolomite was used. The smaller dolomite particle size had higher removal efficiency for Zn^{2+} and Cu^{2+} ions. The results showed the removal of Zn^{2+} and Cu^{2+} was the maximum in the basic medium. Also, the removal of ions reached the maximum when dolomite had been in contact for 30 minutes with the wastewater. The experimental results of Langmuir and Freundlich adsorption isotherms show linearity where R^2 is more than (0.998 and 0.978) and (0.9915 and 0.9996) for Zn^{2+} and Cu^{2+}, respectively. The maximum monolayer capacities (q_{max}) were obtained at 91.74 mg g^{-1} for Cu^{2+} and 44.24 mg g^{-1} for Zn^{2+}.

1. Introduction

The decrease in the amount of rain around the world caused todecreasein the level of freshwater. On the other side, global freshwater demand is estimated to increase due to population growth and industrial development[1]. Therefore, it is very important to keep the water resources as clean as possible, whereby the contamination of resource water can lead to reducing accessible freshwater. The pollution of freshwater resources has become a serious problem that needs quick action before it is too late to handle[2–5]. Developing current and new industries including but not limited to batteries, paper mills, board mills, fertilizers, petrochemicals, inorganic chemicals, basic steel works, basic non-ferrous metal works, motor vehicles, steam generation power plants, plating and painting has resulted in the release a significant amount of heavy metal ions such as lead, cadmium, chromium, copper and zinc that end up in the environment, especially in the water resource[6–8]. The increasein pollutants discharged into the water resource affects the amount of usable water and the ecosystem because of their high toxicity[9]. These pollutants must be removed from wastewater before they are released into the surface water.

*Corresponding Author: Mohammed Oday Ezzat
Email: edw.mohamed_oday@uoanbar.edu.iq
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The researchers aim to find a way to reduce the release of pollutants into water resources[6,10]. Copper and zinc ions are considered toxic heavy metals. At the health-based guideline, copper and zinc concentrations in surface watersthat arebelow 2 mg L^{-1} and 3 mg L^{-1} respectively are deemed acceptable [9,11]. Thus, the concentration of heavy metals in wastewater should not exceed the maximum allowable concentration (MAC) before it is discharged to meet water quality guidelines. It is crucial to address the treatment of wastewater contaminated with heavy metals, which poses a significant challenge for industries[12]. Removal of heavy metal ions from wastewater can be accomplished by a variety of treatment methods including chemical methods such as precipitation, complexation, ion exchange, solvent extraction, and adsorption process by activated carbon and clay, and sieve process by membranes[1, 13, 14]. The use of an adsorption process to remove heavy metal ions from wastewater has recently achieved significant interest because it mainly depends on using environmentally friendly and economically effective materials as their adsorbents[3,15]. The heavy metal removal can be achieved by an adsorption process using minerals, which have essential properties that make them excellent adsorbents.The heightened capability to adsorb due to their high surface area, pores, and cavities are among these properties[16]. The minerals could also act as ion exchangers replacing the ions contained in their structure with the heavy metal ions in the wastewater[17,18]. These minerals can beeasily collected as waste or side products from numerous industries atzero value, and they have to be an effective adsorbent. Minerals like dolomite powder,which is regarded as waste from the residual of the build processes. Furthermore, it can be a viable choice to be used as an adsorbent for the removal of heavy metalsfrom wastewater[3,19].

This study aims to evaluate the potentialability of dolomite powder for removing of Zn^{2+} and $Cu^{2+}$from wastewater. Dolomite powder is naturally occurring rockproduced in large amounts as a byproduct withlow cost. So,the dolomite powder is used as an adsorbent for removing Zn^{2+} and Cu^{2+}ions in water samples before being determined by F-AAS.

2. Materials and Methods

2.1. Materials

Both Zn^{2+} and Cu^{2+}stock solutions were prepared by dissolving 3.8019 g of $Cu(NO_3)_2.3H_2O$(CAS N.: 10031-43-3, Sigma, Germany) and 2.0849 g $ZnCl_2$ (CAS N.: 7646-85-7, Sigma, Germany) in 1 L of deionized water to get 1000 mg L^{-1}as stock solutions. Hydrochloric acid (37%, CAS N.: 7647-01-0), Nitric acid (HNO_3, CAS N.: 7697-37-2), Ammonia-ammonium chloride buffer(CAS N,: 16052-06-5), sodium acetate -acetic acid buffer (pH 3.7-5.6, CAS N.:126-96-5), Na_2HPO_4-NaH_2PO_4 buffer (pH 5.8-8.0, CAS N.: 7558-79-4) purchased from Sigma, Germany.

2.2. Preparation of adsorbent

The dolomite was obtained from the residual of the building processes. The dolomite was firstly dried overnight, milled, and sieved to unify particles size of three sizes of 150, 250, and 300 μm[19].

2.3. Apparatus

Field emission scanning electron emission with Energy dispersive spectroscopy (FE-SEM with EDX) was utilized for screening of the morphology of dolomite and component analysis using HITACHI S4500. The X-ray diffraction (XRD) was achieved on a Bruker D8 Advance (Cu Kα radiation, λ = 1.5406 nm) to study the structure of dolomite. Thermal gravimetric analysis (TGA) was achieved using a Rheometric Scientific STA 1500 instrument to measure water contents and thermal stability. Flame atomic absorption spectroscopy (FAAS) (Phoenix 986 AAS, USA) was used to determine the remaining concentration of Zn^{2+} and Cu^{2+} in the solution after the adsorption process was conducted.

2.4. Adsorption Procedure

The adsorption experiment was accomplished usingthe batch method. 0.4 g of dolomite was mixed with 50 mL of Zn^{2+} and Cu^{2+}solutions in a 100 mL polyethylene tube. The samples were shaken under

controlled conditions for a specific time between 15-120 min. The adsorption process was achieved at pH between 2 - 10, temperatures between 293 - 323°K, and initial concentrations between 50-100 mg L^{-1}[17, 19]. By separating,the dolomitewas separated from the mixture via centrifugation.The last remainingconcentration of Zn^{2+} and Cu^{2+}in the solution after the adsorption process wasevaluated by flame atomic absorption spectroscopy (FAAS) by standard concentration between 0.1 and 1 mg L^{-1} for both ions Zn^{2+} and Cu^{2+}. The FAAS has a low detection limits (LOD) value, a limit of quantification (LOQ) value,and high selectivity, which make it the perfect apparatus for determining most heavy metal concentrations (Fig.1). The LOD of Zn^{2+} and Cu^{2+}were 0.05 mg L^{-1} and 0.08 mg L^{-1}, respectively. The LOQ of Zn^{2+} and Cu^{2+}were evaluated at 0.18mg L^{-1} and 0.25mg L^{-1}, respectively. The whole average relative standarddeviation (RSD) was 3.6% and 5.6% for Zn^{2+} and Cu^{2+}, respectively.

2.5. Adsorption Isotherms:

The relationship between the amount value of removed ions adsorbed and the amount value of dolomite at equilibrium conditionswas calculatedusing Equation 1which was published byVanderborght and Van Griekenm[20]. The Hanes–Woolf as Equation 2 was applied to express the Langmuir isotherms at equilibrium conditions[2, 17, 18]. The Freundlich adsorption modelwas used as another absorption model (Eq. 3). This model is useful to indicate that the adsorption energy value on a homogeneous surface is independent of surface coverage, according to the Equation 3[17].The Temkin model has been shown by the Equations 4 and 5 [21].

$$q_e = (C_o - C_e) * {}^{V}/_{m}$$

(Eq.1)

Where q_e=Quantity (mg g^{-1}) of ion adsorbed on the dolomite at equilibrium conditions, C_o=Initial concentration (mg L^{-1}) of the ion, C_e=Concentration (mg L^{-1}) at equilibrium conditions, m = Mass (g) of adsorbent and V=Volume of the solution

$${}^{C_e}/_{q_e} = {}^{1}/_{(K_L * q_m)} + ({}^{1}/_{q_m}) * C_e$$

(Eq.2)

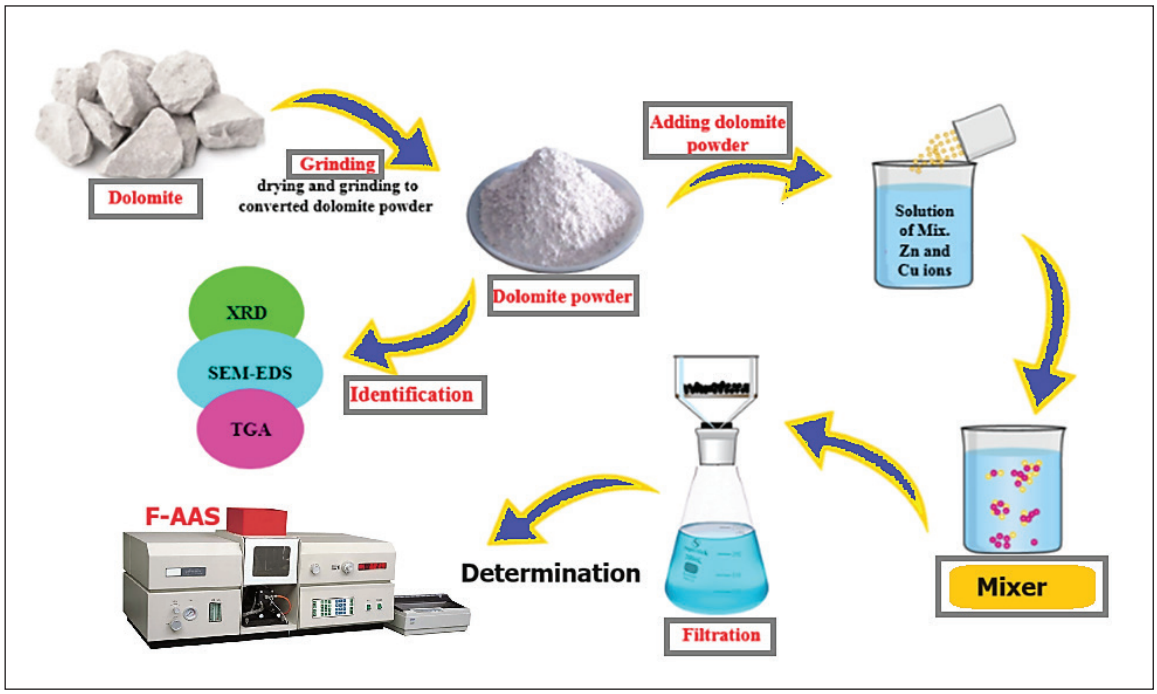

Fig. 1. The Zn^{2+} and Cu^{2+} removal/adsorption based on dolomite before determined by F-AAS

where q_{max} (mg g^{-1}) =The maximum amount value of ions adsorbed on the dolomite surface, leading to creating amonolayer of ions on the surface of dolomite, and K_L=The Langmuir constant corresponding to the adsorption energy value. The value of q_{max} was calculated from the slope and K_L was calculated from the crossing intercept of the plot of C_e/q_e against C_e.

$$q_e = K_f\, C_e^{1/n} \qquad \text{(Eq. 3)}$$

where K_f =Freundlich model constant (mg g^{-1}), n=Adsorption intensity, C_e=The remaining concentration (mg L^{-1}) at equilibrium, q_e = The quantity (mg g^{-1}) of ion adsorbed onto dolomite at equilibrium [17,18].

$$q_e = B\ In\ A_T + B\ In\ C_e \qquad \text{(Eq. 4)}$$

$$b_T = {}^{RT}/_{B} \qquad \text{(Eq. 5)}$$

where B=Constant related to heat of sorption ($Jmol^{-1}$), b_T = Temkin model constant, A_T =Temkin modelequilibrium binding constant (L g^{-1}), q_e = the quantity (mg g^{-1}) of ion adsorbed onto dolomite at equilibrium, R=Universal gas constant (8.314 $Jmol^{-1}K^{-1}$) and T= Temperature at 298°K.

3. Results and Discussion

3.1. Characterization of the synthesized materials

Scanning electron microscopy (SEM) was used to image the morphology of the dolomite. From the SEM images of dolomite shown in Figure 2, it was observed that the morphology of dolomite consists of irregularly shaped particles with rough surfaces[22]. The XRD patterns of dolomite powder are shown in Figure3. The results indicate that dolomite powder mainly consists of dolomite[23]. These results are consistent with the EDX spectrum shown in Table 1. EDX spectrum was used to study the components of dolomite. The results illustrated in Table 1 show that the dolomite is dominated by oxygen at ~ 41%, calcium at ~ 36%, and carbon at 22%[22].

The TGA (Fig. 4) shows weight loss at ~ 600°Csuggesting the release of CO_2 from the decomposition of dolomite ($CaCO_3$)[23].The reaction can be described by by Equation 6.

$MgCa(CO_3)_2 \grave{e} MgCaO_2 + CO_2$ (Eq.6)

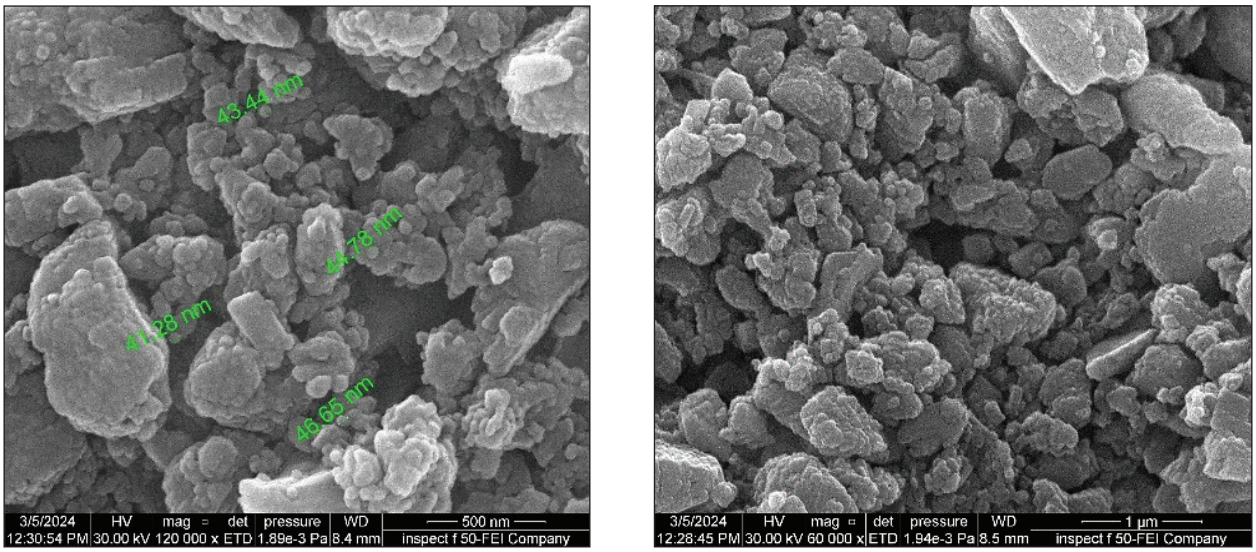

Fig. 2.SEM images of dolomite

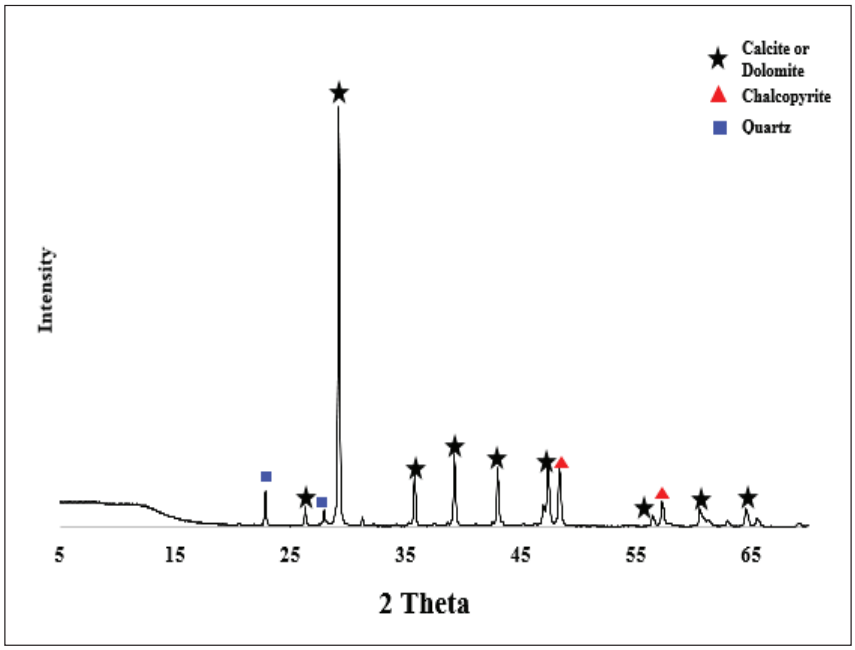

Fig.3.XRD of the dolomite

Table 1. The elemental analysis of dolomite

Element	Weight %
C	14.4
O	47.37
Mg	0.51
Al	0.25
Si	0.55
Ca	36.93
Total	100.00

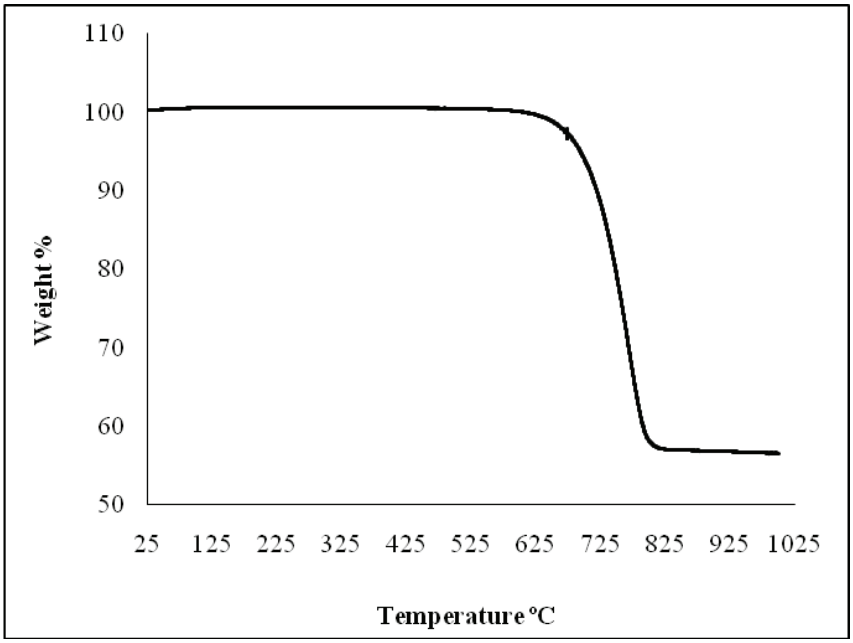

Fig.4.TGA of the dolomite

3.2. Adsorption study

3.2.1.Effect of dolomite amounts

A variety of dolomite amounts at 0.2, 0.4, 0.6, 0.8, and 1 g were used toremove of Zn^{2+} and Cu^{2+}as shown in Figure 5. The dolomite adsorption capacity for the removal of Zn^{2+} was around 82% when an amount of 0.2 g of dolomite was used. The adsorption capacity sharply increases up to 98% when the dolomiteamountisincreased to 0.4 g. On the other side, the adsorption capacity for the removal of Cu^{2+} was around 86% when 0.2 g of the dolomite was used. This adsorption capacity for the removal of Cu^{2+} was increased to 98% when the dolomite amount was increased to 0.4 g. The adsorption capacity for the removal of Zn^{2+} and Cu^{2+}showed no noticeable increase when the dolomite amount increased up to 1.0 g. According to these results, the 0.4 g of dolomite amount would be used to investigate other adsorption factors[24].

3.2.2.Contact time effect

The adsorption capacity for Zn^{2+} and $Cu^{2+}$was measured as an indicator for determining the optimum contact time for the removal of Zn^{2+} and $Cu^{2+}$by dolomite.The adsorption results obtained at 25°C for Zn^{2+} and Cu^{2+}have the same trend as shown in Figure 6. The results implicate that the adsorption on the dolomiteincreased rapidly when the time was increased from 15 min to 30 min after the adsorption became almost constant.The maximum removal of Zn^{2+} and Cu^{2+}, around 98.5%, was achieved after 30 min, and so, equilibrium was reached, where no noticeable change in the adsorption was observed. The contact time was kept to 120 min[24, 25].

3.2.3.Effect of pH

The pH of solution at which the adsorption process would take place is an important factor that affects the efficiency of adsorption. The pH can influence the solubility of the ions to be removed. It can also affect the charge of function group onto the surface of the adsorbent. This study investigated the adsorption at a range of pH between 2 and 10, time of 30 min, weight of adsorbent of 0.4 g, and size of particles of 150 µm. The removal percentage of Zn^{2+} and Cu^{2+}at the chosen range of pH is illustrated in Figure7.At a lower pH of 2, the removal percentage of the Zn^{2+} was 80% because metal ions were hindered by hydrogen ions that occupied active sites available on the adsorbent surface and competedwith the metal ions.

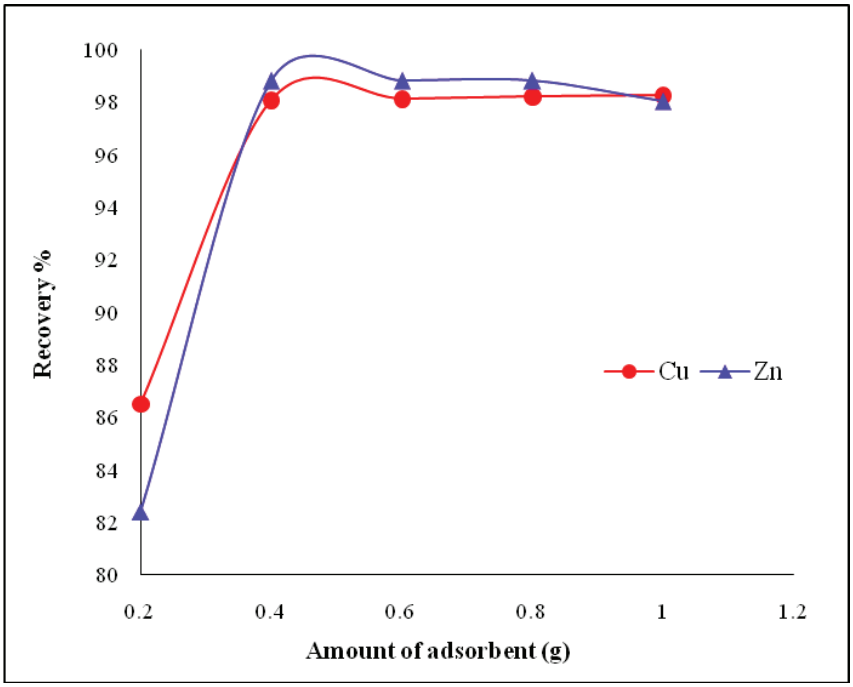

Fig. 5. The effect of dolomite amounts onZn^{2+} and Cu^{2+}removal

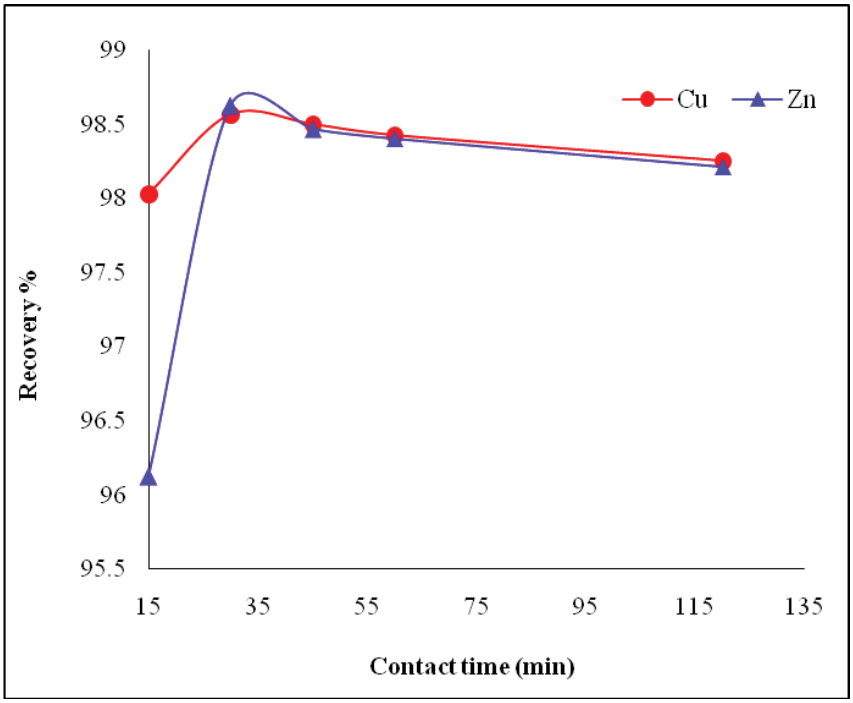

Fig. 6.The effect of time on the removal ofZn^{2+} and Cu^{2+}at 293K using dolomite as adsorbent

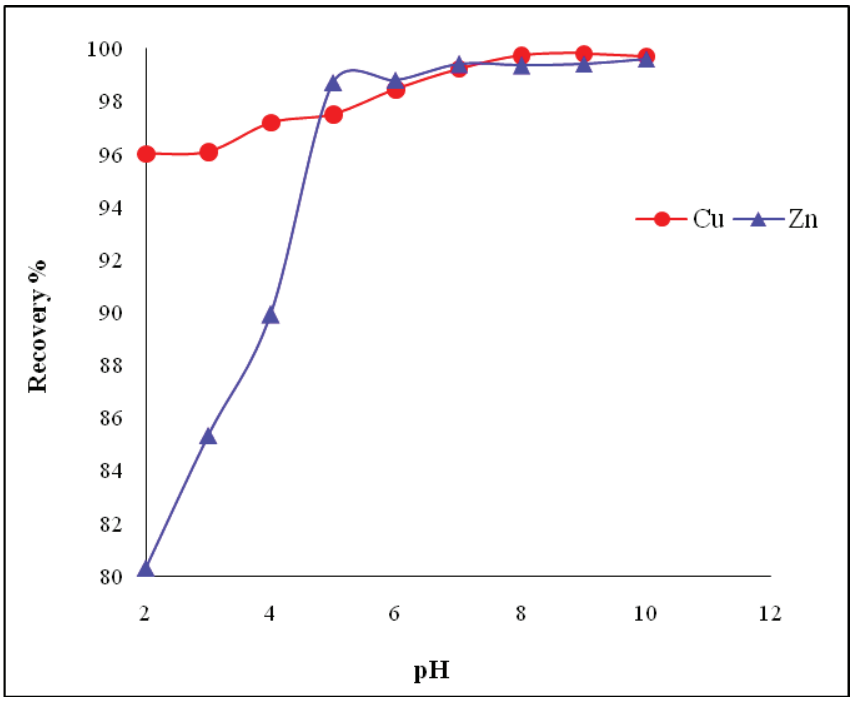

Fig. 7. The effect of pH on the removal ofZn^{2+} and Cu^{2+}using dolomite as adsorbent

As the pH increased, the removal percentage of the Zn^{2+} increased due to reducing the concentration of hydrogen ions in the solution and setting free the active site onto the adsorbent surface. The removal percentage reached 98.7% at a pH of 5, and no significant increase in the removal was observed at higher pH. The change of pH showed a slight effect on the removal of Cu^{2+} whereby the removal percentage also increased as the pH increased from 96% at a pH of 2 to 99.3% at a pH of 8[10, 24, 26].

3.2.4.Effect of dolomiteparticle size

The effect of dolomite particles size was studied, and thus three sizes of the dolomite were investigated 150, 250 and 300 µm., andthe results are illustrated in Figure 8. It can be noticed that the adsorption capacity of Zn^{2+} and Cu^{2+}did not change when the particle size increased from 150 to 250µm for both ions (Zn^{2+} and Cu^{2+}). On the other side, using dolomite at 300 µm showed a slight decrease in the adsorption capacity for Cu^{2+} owing to the reduction of the surface area of the dolomite. This result confirmed that decreasing the particle size leads to an increase in the surface area of the dolomite powder and simultaneously increases the removal capability of ions[10, 27].

3.2.5.Effect of adsorption temperature

The effect of solution temperature (293, 303, 313, and 323°K)on the adsorption process was studied and shown in Figure 9. Temperature was shownto have a noticeable effect on the adsorption capacity of the Zn^{2+} and Cu^{2+}. The adsorption capacity of dolomite for Zn^{2+} showeda slight decrease from 98.6% to 98.3% as the temperature increased from 293 to 323°K. On the other hand,the dolomite adsorption capacity for Cu^{2+} decreased from 98.4% to 97.3% when the temperature increased from 293 to 323^{0}K. These results confirmed that the adsorption is an exothermic process[28, 29].

3.2.6.Effect of initial concentration

The adsorption capacities ofZn^{2+} and Cu^{2+}onto the dolomite at various initial concentrations of the ions between 50–100 mg $L^{-1}$are shown in Figure10. It can be noticed that the adsorption capacity of Zn^{2+} and Cu^{2+}did not change and the adsorption capacity was almost the same for both ions. During the adsorption process, the initial concentration of targeted ions in the solution played a key role that limited the capacity of the adsorbent[30, 31]. Using the dolomite as an adsorbent for the removal of Zn^{2+} and Cu^{2+}showedthat the adsorption capacity waskept constant as high as 98.6% for Zn^{2+} and $Cu^{2+}$with a very slight decrease for the adsorption capacity of Zn^{2+} to 97.8% when the initial concentration increased from 50 to 100 mg L^{-1}.Increasing the initial concentration from 50 to 100 mg L^{-1}while the adsorption capacity was maintained as high as 98.8% confirms that the adsorbent did not reach the saturation point, and the initial concentration can be increased, where the adsorption capacity of $Cu^{2+}$was retained at 98.6% even though the concentration raised to 100 mg L^{-1}[30, 31].

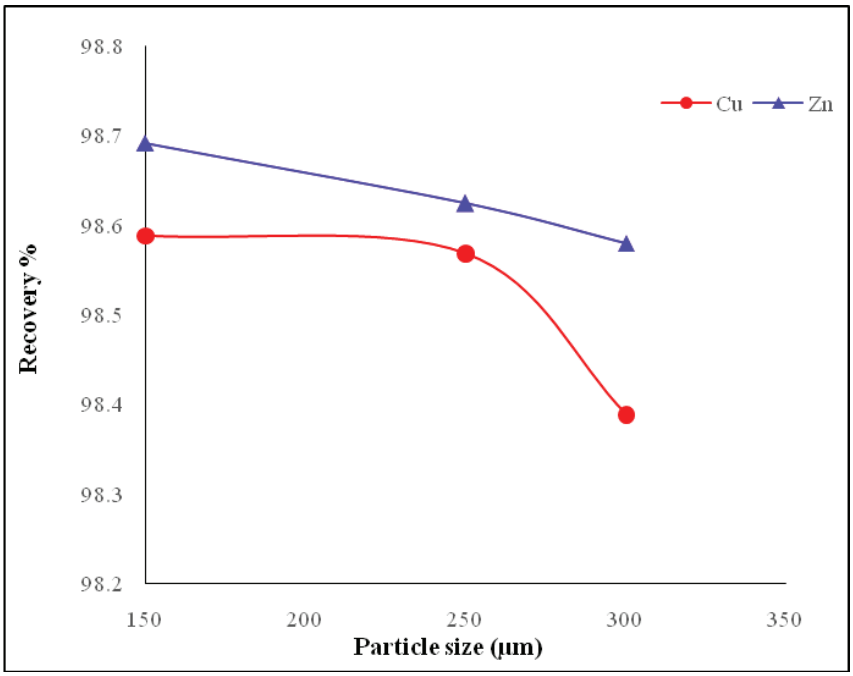

Fig. 8. The effect of dolomiteparticle size on the removal ofZn^{2+} and Cu^{2+}

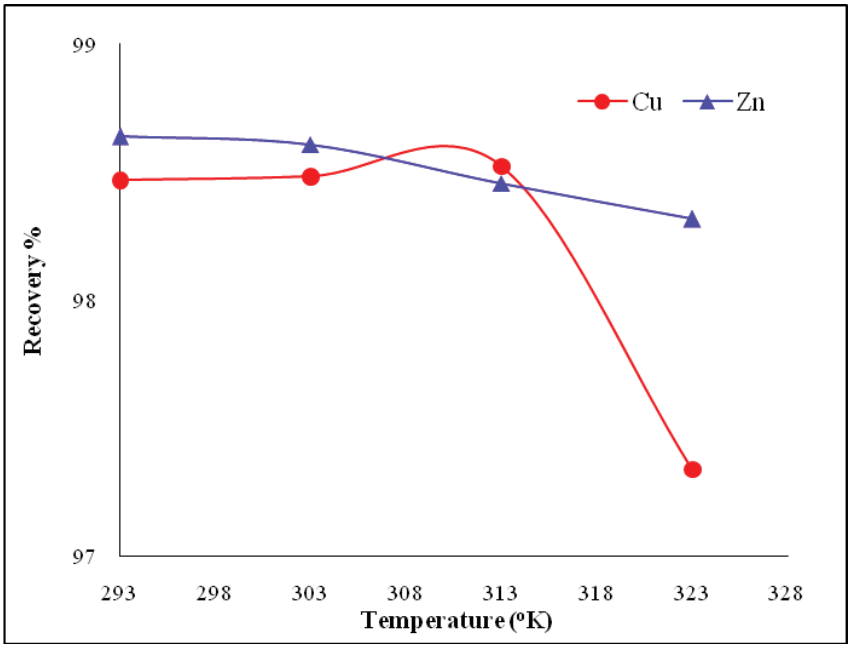

Fig. 9.The effect of temperature on the removal of Zn^{2+} and Cu^{2+}

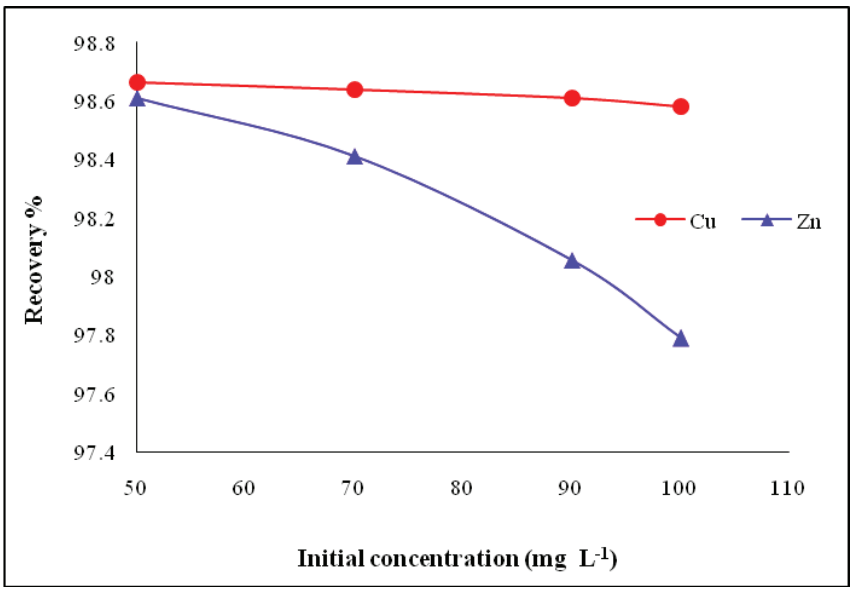

Fig. 10. The effect of initial concentration on the removal of Zn^{2+} and Cu^{2+}

3.2.7.Isotherm model

The adsorption experiments were conducted to determine the extent of corresponding with Langmuir, Freundlich, and Timken models at optimum conditions of (dolomite amount 0.4 g, time 30 min, initial Zn^{2+} and Cu^{2+}concentration 50, 70, 90, and 100 mg $L^{-1}$and pH 8). The association between the amounts of ions removed by the dolomite at equilibrium conditions was determined using the procedure illustrated in the experiment and materials section[17], [32–35]. According to the Langmuir isotherm models; the Hanes–Woolf equation has been used and the results are shown in Figure11. The correlation coefficient value summarized in Table 2 and obtained via this equation was up to 0.998 and 0.978 for Zn^{2+} and Cu^{2+}respectively.This suggests that the adsorption process is conformable with the Langmuir model and the Zn^{2+} and Cu^{2+}adsorbed onto

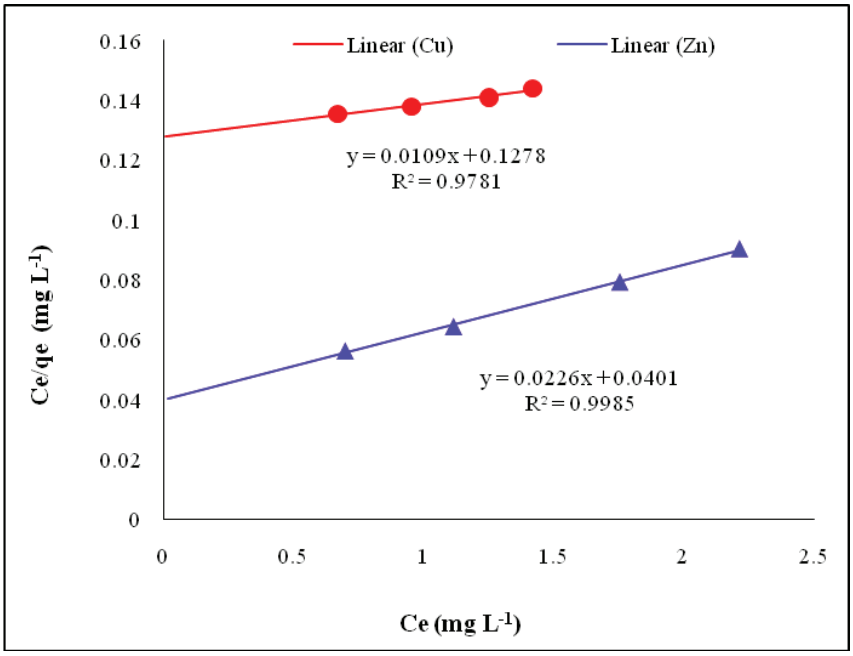

Fig. 11. Langmuirmodel at 293°K

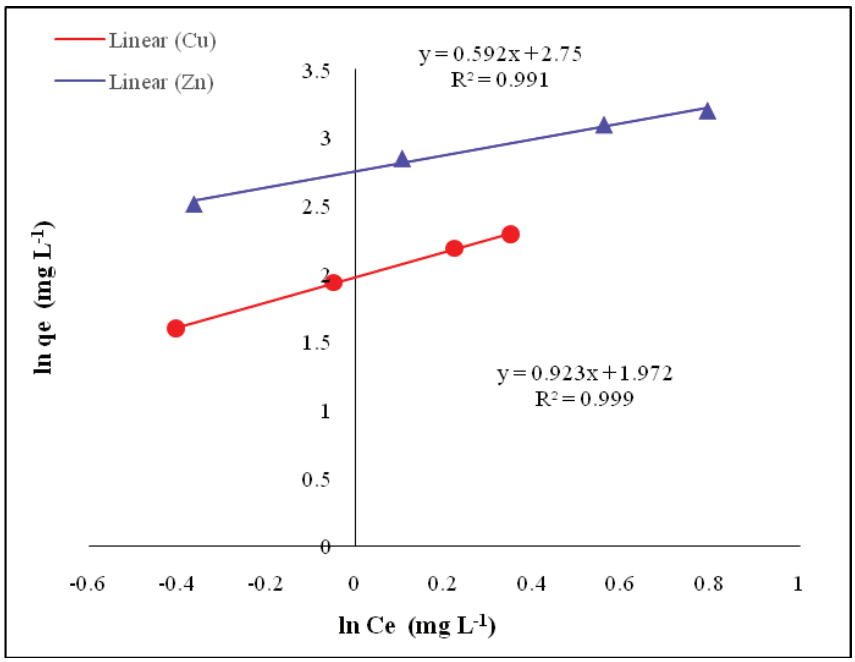

Fig.12. Freundlich model at 293°K

the dolomite surface initially formed a monolayer[32], [35]. The maximum monolayer capacities of Zn^{2+} and Cu^{2+}adsorbed onto the dolomite obtained by the Langmuir model are 44.24 and 91.74 (mg g^{-1}), respectively, as summarized in Table2.

The Freundlich isotherm model obtained using equation 3 is shown in Figure 12. The Freundlich isotherm showedgood linearity where the correlation coefficient (R^2) was 0.9915 and 0.9996 for Zn^{2+} and Cu^{2+},respectively,as summarized in Table 2. This confirms the multilayer adsorption of removed ions onto the dolomite surface and the obtained adsorption results agree with the Freundlich adsorption isotherm model[21,36–38]. The K_f is an estimated indicator for the adsorption capacity, while 1/n refers to the adsorption strength.

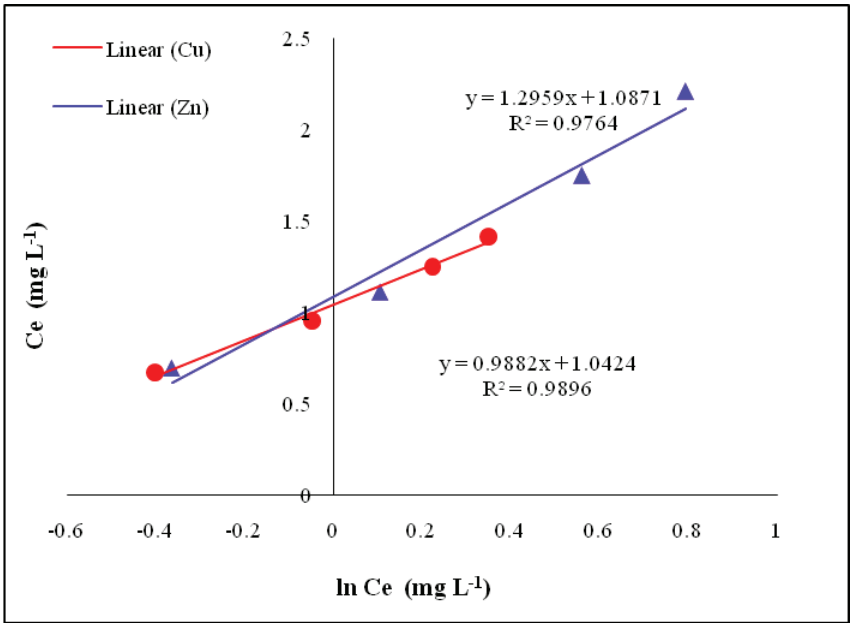

Fig. 13.Timken model at 293 K

Table 2. Adsorption models of Zn^{2+} and Cu^{2+} onto the dolomite

Ion	Model	Equation	Constant	Value
Cu	Langmuir	$C_e/q_e = 1/(K_L\, q_{max}) + (1/q_m)\, C_e$	R^2	0.997
			q_{max} (mg g^{-1})	91.743
			K_L (L mg^{-1})	0.085
	Freundlich	$q_e = K_f\, C_e^{1/n}$	R^2	0.999
			n	1.082
			1/n	0.923
			K_f (mg g^{-1})	-0.679
	Timken	$q_e = B \ln A_T + B \ln C_e$ $b_T = RT/B$	R^2	0.989
			B J mol^{-1}	0.988
			A_T (L g^{-1})	2.871
			b_T	2507.66
Zn	Langmuir	$C_e/q_e = 1/(K_L\, q_{max}) + (1/q_m)\, C_e$	R^2	0.999
			q_{max} (mg g^{-1})	44.247
			K_L (L mg^{-1})	0.563
	Freundlich	$q_e = K_f\, C_e^{1/n}$	R^2	0.991
			n	1.687
			1/n	0.592
			K_f (mg g^{-1})	-1.011
	Timken	$q_e = B \ln A_T + B \ln C_e$ $b_T = RT/B$	R^2	0.976
			B J mol^{-1}	1.295
			A_T (L g^{-1})	2.313
			b_T	1911.85

When 1/n is equal to 1, the separation between the two phases is independent of the concentration. If the value of 1/n is higher than 1, this indicates normal adsorption. When 1/n is lower than 1, this implies cooperative adsorption. According to the adsorption results summarized in Table 2, the value of 1/n of Zn^{2+} and Cu^{2+}=0.592 and 0.923 while n=1.687 and 1.082 respectively, indicating that the sorption of Zn^{2+} and Cu^{2+}onto dolomite is favorable[21, 36–38].

The R^2 values summarized in Table 2 were 0.976 and 0.989 for Zn^{2+} and Cu^{2+}, respectively. They wereobtained by fitting the adsorption experimental results to the Temkin model. Figure 13 shows that not all the plotted points of both ions were linear together. These findings suggest that the Langmuir and Freundlich models are highly convenient for predicting Zn^{2+} and Cu^{2+}adsorption onto the dolomite surface in comparison with the Timken model. From the Temkin plot, the following values were estimated for Zn^{2+} and Cu^{2+}: A_T= 2.313 Lg^{-1}, B=1.295 $Jmol^{-1}$, and A_T = 2.871 Lg^{-1}, B=0.988 $Jmol^{-1}$ respectively which represents the heat of adsorption suggesting a physisorption process[33, 35, 39,40].

4. Conclusion

In this paper, an investigation of the removal of Zn^{2+} and $Cu^{2+}$was carried out using dolomite as an adsorbent. This adsorption capacity was up to 98% when the amount of dolomite was 0.4 g. The amount of adsorption onto dolomite powder was slightly higher for Cu^{2+} compared to Zn^{2+} from wastewater, where the maximum monolayer capacities (q_{max}) was 91.74 mg g^{-1} for Cu^{2+} ion and 44.24 mg $g^{-1}$for Zn^{2+}. The value of 1/n and n for zinc and copper was obtained (0.592, 0.923) and (1.687, 1.082), respectively, indicating that the adsorption of zinc and copper onto dolomite is favorable. The experimental results agreed with the Langmuir, Freundlich, and Temkin model. The comparison between the three models shows that the Langmuir and Freundlich models have the highest correlation coefficient value of 0.998 compared with the Temkin model. It could be concluded that dolomite is an active adsorbent for the removal of Zn^{2+} and $Cu^{2+}$from wastewater.

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