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Efficient removal of Cu(II) and Zn(II) from aqueous solution and real acid mine drainage by natural vermiculite and kaolinite

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ABSTRACT

In this study, the removal of Cu(II) and Zn(II) by new natural native vermiculite and kaolinite from aqueous solution and real acid mine drainage (AMD) was investigated. The adsorbents were characterized using X-ray fluorescence, X-ray diffraction and Fourier-transform infrared spectroscopy analysis. The effect of pH, contact time, temperature, adsorbent dose, particle size, and initial metal concentration were determined in a batch experiment. Major chemical components of the vermiculite were CaO (43.31%) and SiO_2 (13.5%) and for kaolinite were SiO_2 (75.8%) and Al_2O_3 (14.7%). The most important functional group of vermiculite and kaolinite was O–H as an active site for binding positively charged cation. The removal efficiencies of Cu(II) and Zn(II) increased by increasing pH from 2 to 6 and increasing the temperature from 25°C to 35°C. The most removal efficiency by using vermiculite in contact time 45 min were 81% for Cu(II) and 74% for Zn(II) and for kaolinite were 67% and 76% for Cu(II) and Zn(II) in 30 and 45 min, respectively. The adsorption experiment data indicated that the Langmuir isotherm and the pseudo-second-order kinetic were more suitable for describing the adsorption process. Experiments on the real AMD sample showed that Cu(II) removal efficiency by vermiculite and kaolinite was 82% and 71% and for Zn(II) was 65% and 56%, respectively. Therefore, these natural native adsorbents are able to remove Cu(II) and Zn(II) from the AMD.

Keywords: Heavy metal removal; Acid mine drainage; Adsorption; Vermiculite; Kaolinite

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1. Introduction

Acid mine drainage (AMD) has been broadly accepted to be a major global environmental problem facing the mining industry, requiring expensive management and mitigation [1]. The exploitation of underground mines is conditional on drilling in metal-rich rocks. These metals are released into the environment and cause contamination of water and soil ecosystems that are hazardous to human health and other living organisms [2,3]. Heavy metals are a serious problem; since these metals are able to accumulate in ecological systems, and by increasing concentrations, they cause many adverse effects in these systems [4]. The transfer of heavy metals to the soil and water will increase the amount of

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hazardous materials in living tissues, including the human body [5,6]. Therefore, the concentration of these pollutants must be reduced to the permissible disposal level and, if they are economically valuable, they should be restored and reused [7,8]. The shape of the threat of heavy metals strongly depends on their mobility and bioavailability, and the difference is based on their geochemical forms. Water solubility and variable forms facilitate pollutant movement and make the contaminant easily accessible to living organisms [4]. Among these metals, extensive exposure to copper (Cu(II)) by humans causes mucosal inflammation, liver and kidney damage, muscle pain, hemolytic and heart failure [9]. Although copper is an essential element, its high levels can cause metabolic disorders. Chronic poisoning with copper can cause hemolytic anemia, nerve disorders and corneal opacity [10]. Zinc (Zn^{2+}) is a minor essential element for humans, which is not considered as a low toxicity, but its high exposure can cause stomach cramps and irritability, nausea, vomiting, anemia or even death [11].

There are several processes for appropriate removing of metal ions from aqueous solutions, including chemical treatment, flotation, biosorption, electrolytic recovery, membrane separation, activated carbon adsorption [12–14]. The adsorption of heavy metals from aqueous solutions has been the subject of many research studies in recent years [15–17]. Efforts have been made to develop and produce inexpensive materials for the removal and control of pollution by heavy metals from aqueous solutions, such as industrial and natural wastewater. The range of such materials is very wide and extensive, on the one hand, industrial and agricultural waste, and, on the other, various types of organic and inorganic materials [13]. Natural adsorbents, such as clay materials, coconut shells, chitin, and chitosan are attractive in terms of industrial applications due to their low cost, availability, and capacity to reduce the concentration of heavy metals to parts per billion [18]. Many studies have been carried out on the removal of heavy metals from aqueous solutions using mineral adsorbents, such as the removal of Zn^{2+} and Cd^{2+} from an aqueous solution using vermiculite adsorbent [19], the removal of Cu^{2+} by zeolite and vermiculite adsorbents [20], the removal of heavy metals from fluids using porous vermiculite adsorbent [21], the removal of Zn^{2+} from aqueous solution using kaolinite [22], and the removal of heavy metals from industrial wastewater using vermiculite [23].

This study investigated the efficiency of vermiculite and kaolinite as a natural, native (in Baft City, Kerman, Iran), and low-cost adsorbents for removing Cu(II) and Zn(II) from Sarcheshmeh acid copper mine drainage. Cu(II) and Zn(II) were selected due to their high concentration and relatively difficult treatment, respectively in acid copper mine drainage.

2. Material and methods

2.1. Adsorbents preparation and characterization

This study is an experimental and cross-sectional study carried out in Kerman University of Medical Sciences. Vermiculite and kaolinite are found in Baft, Kerman, Iran. Clay samples were crushed by a grinder and dried at laboratory temperature and exposed to airflow for two weeks. They were screened with 50 mesh sieve and particles of 0.5–0.8 mm and 2–6.8 mm selected for the experiments. Chemical compounds and geological structure of clays were determined by X-ray fluorescence (XRF) spectrometer (1800-Shimadzu, Japan) and X-ray diffraction (XRD) XMD-300 of Ynisantis Company from Germany. Fourier-transform infrared spectroscopy (FTIR) analysis (TENSOR 27, Bruker, Germany) was used to determine the functional groups on the adsorbent surface area.

2.2. Experiments set up

The chemicals used in this study included copper nitrate ($Cu(NO_3)_2$), zinc nitrate ($ZnSO_4$), nitric acid (HNO_3) and sodium hydroxide (NaOH) (Merck, Germany, with a purity of ≥99%). A special amount of copper and zinc nitrate salts and nitric acid were solved in deionized water (resistivity 18 MΩ cm). The concentration of standard solutions was selected 1,000 mg/L (ppm) as the stock solution. It is used for preparing other concentrations. pH was adjusted by 0.1 N HNO_3 or NaOH. Batch experiments were conducted in flasks with a volume of 300 cm^3, mixing speed of 150 rpm and a temperature of 25°C, 30°C and 35°C. The adsorption process was carried out using a magnetic stirrer at the speed of 150 rpm. Then, the samples were passed through a filter paper with a pore size of 0.45 μm. The concentration of Cu(II) and Zn(II) were determined using flame atomic absorption spectroscopy (Shimadzu-AA-670, Japan). The effect of each parameter, including pH (2–6), adsorbent dose (1–0.26 g/L), contact time (5–120 min), temperature (25°C, 30°C and 35°C), particle size (0.5–0.8 mm and 2–6.7 mm), and the initial metal concentration (20–100 mg/L) were determined while one variable parameter and the others were fixed. The adsorption capacity of Cu(II) and Zn(II) on the adsorbent were obtained according to Eq. (1):

$$q_e = \frac{\left(C_0 - C_e\right)}{w} V \tag{1}$$

where q_e is the adsorption capacity of the adsorbent for the metal solution (mg/g), C_0 is the initial concentration of the metal solution (mg/L), C_e is the equilibrium concentration in the metal solution (mg/L), W is the adsorbent weight (g), and V (L) is the volume of the metal solution.

Real solutions were picked up from Sarcheshmeh AMD at the end of summer and winter. Real samples were obtained by mixing all the gathered wastewater. The sampling method and experiments were carried out according to the Standard Methods for the Examination of Water and Wastewater [24].

2.3. Adsorption isotherms

Langmuir and Freundlich's isotherms were used to describe the adsorption capacity of adsorbents. Isotherm constants and correlation coefficient are related to the adsorbent capacity on removing metal ions. Two isotherm Eqs. (2) and (3), were used to determine the Freundlich and Langmuir models, respectively [25], in which q_e is the adsorption capacity of the adsorbent for the metal solution (mg/g) and C_e is the equilibrium concentration in the metal solution (mg/L).

$$\log q_e = \log K_F + \frac{1}{n} \log C_e \tag{2}$$

where K_F and n are Freundlich isotherm constant and K_F represents adsorption capacity and n is the adsorption energy.

$$\frac{C_e}{q_e} = \frac{1}{Q_0 b} + \frac{C_e}{Q_0} \tag{3}$$

where q_e is the amount of adsorbed heavy metal per unit clay mass (mg/g), Q_0 is the maximum adsorption capacity (mg/g), b is the equilibrium constant, and C_e is the equilibrium concentration of the solution (mg/L).

2.4. Adsorption kinetic

The kinetic equation of chemical reaction shows the important effect of reactive concentrations on the reaction speed. A substantial step for an understanding of the adsorption mechanism is adsorption kinetics. The integrity of the adsorption process is determined by adsorption kinetics. Two models widely used to analyze the solid–liquid adsorption are pseudo-first-order and pseudo-second-order kinetics. In order to evaluate the kinetics of Cu(II) and Zn(II) adsorption on vermiculite and kaolinite, the adsorption capacity of adsorbent (mg/g) was measured in optimal conditions; pH = 5, the initial heavy metal concentration of 50 mg/L, the adsorbent dosage of 24 g/L, the contact time of 0–95 min, the particle size of 0.5–0.8 mm, the temperature of 35°C, and mixing speed of 150 rpm. After filtration, the samples were transferred to flame atomic adsorption spectrometer due to measuring residual Cu(II) and Zn(II) in 3 repetitions. Adsorption kinetic was matched to pseudo-first-order and pseudo-second-order kinetic models. The adsorption data were evaluated according to the pseudo-first-order model by Eq. (4) [26].

$$\text{Ln}\left(q_e - q_t\right) = \text{Ln}\, q_e - k_1 t \tag{4}$$

where q_e and q_t are the sorption capacity at equilibrium and at time t, respectively (mg/g) and k_1 is the rate constant of pseudo-first-order adsorption. The adsorption data were also evaluated according to the pseudo-second-order reaction kinetic by Eq. (5):

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_t} \tag{5}$$

where k_2 is the second-order-reaction constant. The activation energy of the adsorption reaction can be found using first-order and second-order constants.

3. Results and discussion

3.1. Vermiculite and kaolinite adsorbents properties

The results of the XRF analysis for vermiculite and kaolinite are shown in Table 1. Major chemical components of vermiculite are CaO (43.31%) and SiO_2 (13.5%) and smaller percentages of sodium, potassium, barium, manganese, iron and magnesium oxides are also present. Moreover, major chemical components of kaolinite are SiO_2 (75.8%) and Al_2O_3 (14.7%) and smaller percentages of barium, calcium, sodium, potassium, manganese, iron, and magnesium oxides are also present. The results of the XRD pattern and XRD data analysis of vermiculite and kaolinite are shown in Fig. 1 and Table 2, respectively. The FTIR analysis of vermiculite and kaolinite are shown in Fig. 2. Also, the FTIR spectral data of vermiculite and kaolinite are shown in Table 3. The most important functional groups of vermiculite were O–H (3,689.18 cm^{-1}), C–O (1,080.94 cm^{-1}), C–Br (614.41 cm^{-1}), and =C–H & =H_2 (956.15 cm^{-1}). The most important adsorption bands of kaolinite were O–H (3,455.83–3,626.1 cm^{-1}), C–O (1,092.73 cm^{-1}), C–Br (532.94 cm^{-1}), C–I (469.5 cm^{-1}), S=O (1,031.23 cm^{-1}), and =C–H (788.35 cm^{-1}). Carbonyl, hydroxyl and carboxylic functional groups have an effective role in metal adsorption [27]. The absorption bands at 3,626.1 cm^{-1} in kaolinite represent the inner surface OH stretching vibration; while the absorption band at 3,455.83 cm^{-1} represents the outer surface OH stretching vibration. In vermiculite data analysis, the existence of an intense OH band at 3,689.18 cm^{-1} is the reason for the higher adsorption of Cu(II) and Zn(II). These OH groups function as an active site for the binding of positively charged cation [28].

Table 1
Results of XRF analysis for vermiculite and kaolinite

Chemical composition	Weight percent (wt.%)	
	Vermiculite	Kaolinite
SiO_2	13.51	75.8
Al_2O_3	3.7	14.7
Fe_2O_3	1.03	0.39
CaO	43.31	0.05
MgO	0.67	0.06
TiO_2	0.18	0.12
K_2O	0.72	1.8
BaO	0.26	0.28
Na_2O	0.07	0.47
P_2O_5	0.02	0.11
SO_3	0.15	0.93
Loss of ignition	35.88	4.93

3.2. Effects of initial pH

The effects of initial pH on the adsorption of Cu(II) and Zn(II) from synthetic samples using vermiculite and kaolinite adsorbents are shown in Fig. 3. The removal efficiency of Cu(II) and Zn(II) increased by increasing pH from 2 to 6 (Fig. 3). The removal efficiency of Cu(II) by vermiculite increased from 21% at pH = 2 to 94% at pH = 5. For Zn(II), the adsorption process by vermiculite, the removal efficiency was only 18% at pH = 2 and increased to 87% at pH = 5. When using kaolinite, the removal efficiency of Cu(II) was 17% at pH = 2 and 88% at pH = 6. For Zn(II)

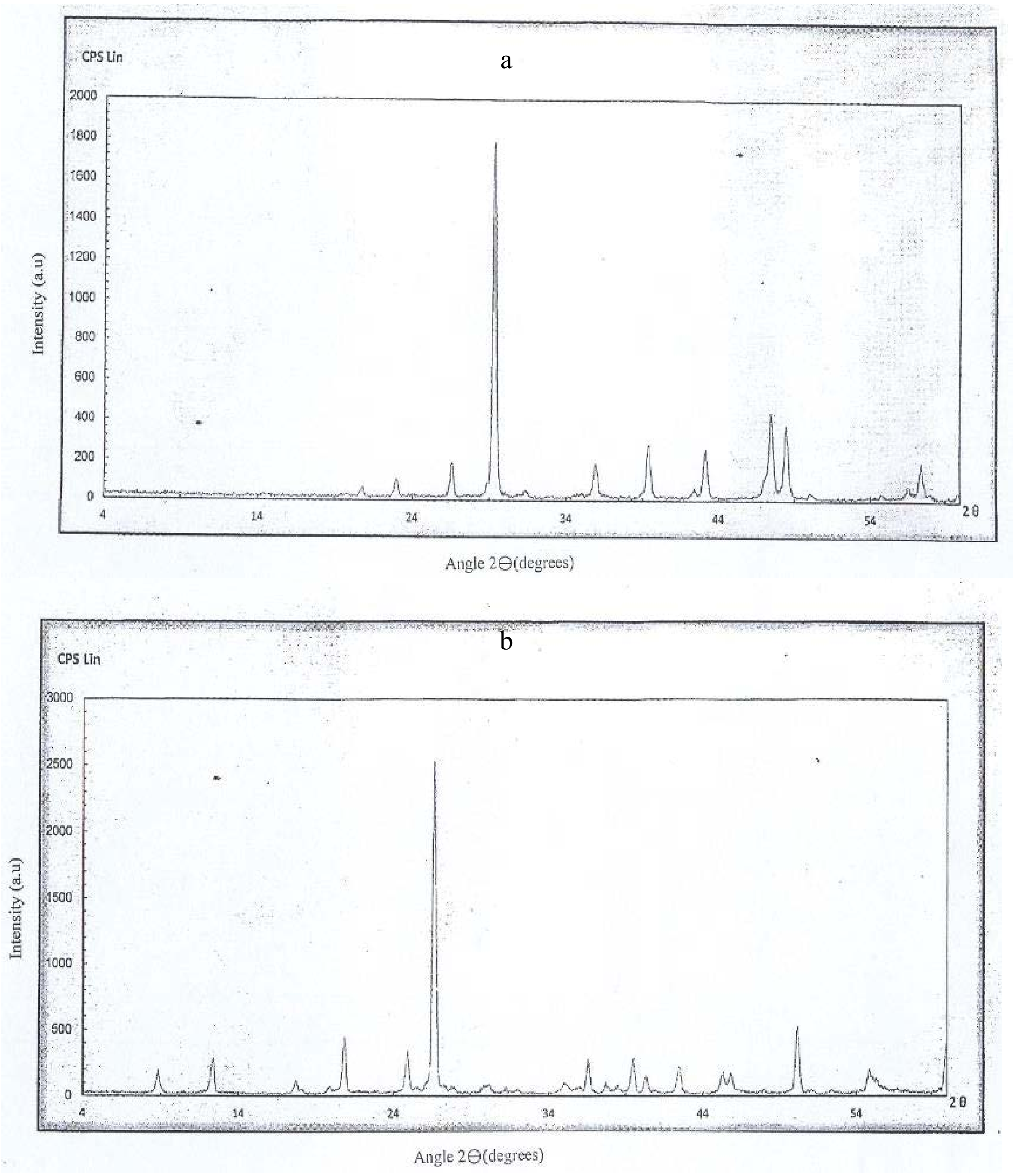

Fig. 1. XRD pattern of (a) vermiculite and (b) kaolinite.

Table 2
XRD data analysis of vermiculite and kaolinite

Phases	Vermiculite	Kaolinite
Major phase(s)	Calcite (05-0586), $CaCO_3$ Quartz (33-1161), SiO_2	Quartz (33-1161), SiO_2 Kaoline (29-1488), $Al_2Si_2O_5(OH)_4$ Muscovite-illite (26-0911), $KAl_2Si_3AIO_{10}(OH)_2$
Minor phase(s)	Muscovite-illite (26-0911), $KA(l)_2Si_3AIO_{10}(OH)_2$	Natroalunite (41-1467), $NaAl_3(SO_4)_2(OH)_6$
Trace phase(s)	Hematite (33-0664), Fe_2O_3	–

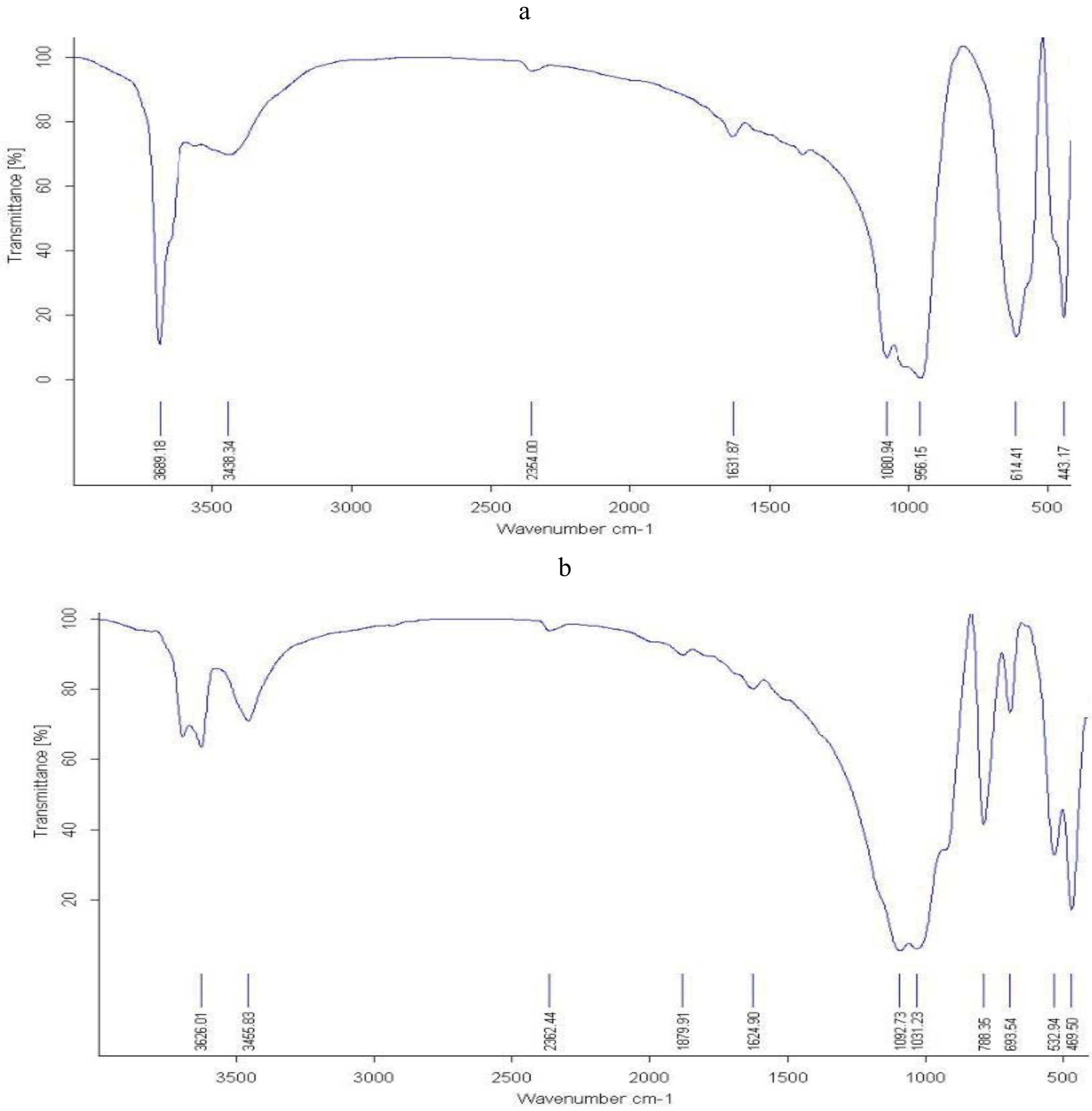

Fig. 2. FTIR spectra pattern of (a) vermiculite and (b) kaolinite.

Table 3
Results of FTIR spectral data of vermiculite and kaolinite

Structural group	Vermiculite (wavenumber cm^{-1})	Kaolinite (wavenumber cm^{-1})
O–H stretching alcohol-free	3,689.18	3,455.83–3,626.1
C–O stretching primary alcohol	1,080.94	–
C–O stretching secondary alcohol	–	1,092.73
C–Br stretching halo compound	614.41	–
C–I stretching alkyl halides	443.17	469.5
=C–H & =H_2	956.15	–
S=O stretching sulfoxide	–	1,031.23
C–H bending, 1-2-3 trisubstituted	–	788.35
C–Br stretching alkyl halides	–	532.94

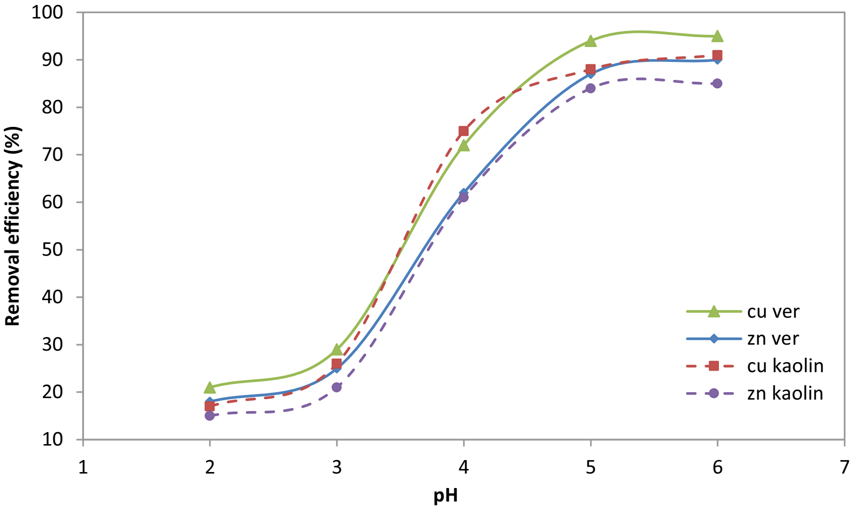

Fig. 3. Effects of pH on the adsorption of Cu(II) and Zn(II) using vermiculite and kaolinite (adsorbent concentration = 24 g/L; initial metal concentration = 50 mg/L; particle size = 0.5–0.8 mm; temperature = 35°C; contact time = 95 min; mixing speed = 150 rpm).

adsorption, the removal efficiency increased from 12% at pH = 2 and increased to 84% at pH = 6. By increasing pH up to 5, precipitation of metals was observed [29]. The pH of the solution has an important role in the removal of heavy metals and adsorption kinetics and equilibrium [30]. By increasing pH competition between protons and metal, cations decreased; whereas the surface positive charge reduced resulting in lower electrostatic disposal between the adsorbent surface and heavy metals [31]. In the present study, by increasing pH, the removal efficiency of Cu(II) and Zn(II) increased. Similar results have been reported in other studies. The study by Lasheen et al. [32] showed that in removing heavy metals from aqueous solution using a nanocomposite resin, increasing in pH leads to higher removal efficiency. In another study conducted on removing Cu(II) by chitosan, the researcher found out similar results by increasing pH [30]. The adsorption process of Cu(II) and Pb^{2+} on cadmium sulfide in another study also showed that by increasing pH, the removal efficiency increased [33]. Changing the functional groups at the adsorbent surface could be another reason for the removal efficiency reduction at lower pH. For example, at a high concentration of (H^+) ions, NH_3 and COO^- are converted to NH_4^+ and COOH with less adsorption capacity. Moreover, functional group conversion can create a charging network at the surface of the adsorbent particles, which in the next step; reduce access of Cu(II) and Zn(II) to the adsorbent surface by making an electric double layer. The FTIR spectra analysis (Fig. 2) showed the presence of 2 medium peaks of the hydroxyl group in kaolinite and a strong hydroxyl peak in vermiculite. It was due to the presence of hydroxyl group, negative charges on the vermiculite and kaolinite surface and oxygen atoms, an interaction occurred between the adsorbent surface and other components affecting the adsorption capacity. Changing pH can affect this interaction. The pH variation leads to the dissociation of the ion exchange process [30,34]. Given that the heavy metal removal from the solution is a combination of two mechanisms (adsorption and ion-exchange), it can be concluded that decreasing pH by breaking the ion exchange process leads to a decrease in the adsorption efficiency [35].

3.3. Effects of adsorbent dose

The effects of adsorbent concentration on the removal efficiency of Cu(II) and Zn(II) from synthetic samples using vermiculite and kaolinite adsorbents are shown in Fig. 4. The results showed that the removal efficiency of Cu(II) and Zn(II) was directly affected by adsorbent concentration. Increasing the adsorbent concentration resulted in higher removal efficiency. The maximum adsorption of Cu(II) and Zn(II) was in concentrations of 24 and 22 g/L for vermiculite and kaolinite, respectively. Increasing the adsorbent concentration also increased the removal efficiency of Cu(II) and Zn(II) from the solution which could be due to more access to cations to adsorption sites or increasing effective surfaces [36]. A high concentration of the adsorbent causes an increase in pH which is another reason for higher removal efficiency [37]. Doubling the adsorbent concentration from 10 to 20 g, increased the removal efficiency of Cu(II) and Zn(II) to 24.5% and 25.3%, respectively. The maximum removal efficiency of Cu(II) and Zn(II) by vermiculite was 94% and 85% when the adsorbent concentration was 24 g/L. In the case of kaolinite, the highest removal efficiency was obtained at 86% for Cu(II) and 82% for Zn(II) when the adsorbent concentration was 22 g/L. Similar results confirmed the result of this study [38].

3.4. Effects of contact time

The effects of contact time on removing Cu(II) and Zn(II) from synthetic samples using vermiculite and kaolinite adsorbents are shown in Fig. 5. The results showed that increasing the contact time from 5 to 20 min had a considerable effect on removal efficiency. The maximum removal efficiency of Cu(II) was reached within 95 min. Then, up to 110 min, the amount of adsorption persisted. Zn(II) showed different behavior. Equilibrium contact time for Zn(II) was

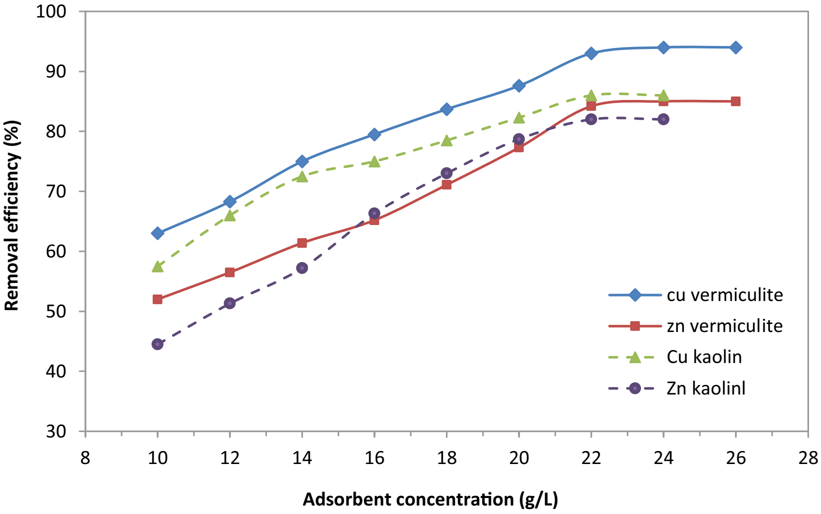

Fig. 4. Effects of adsorbent concentration on the removal efficiency of Cu(II) and Zn(II) using vermiculite and kaolinite (pH = 5; initial metal concentration = 50 mg/L; particle size = 0.5–0.8 mm; temperature = 35°C; contact time = 95 min; mixing speed = 150 rpm).

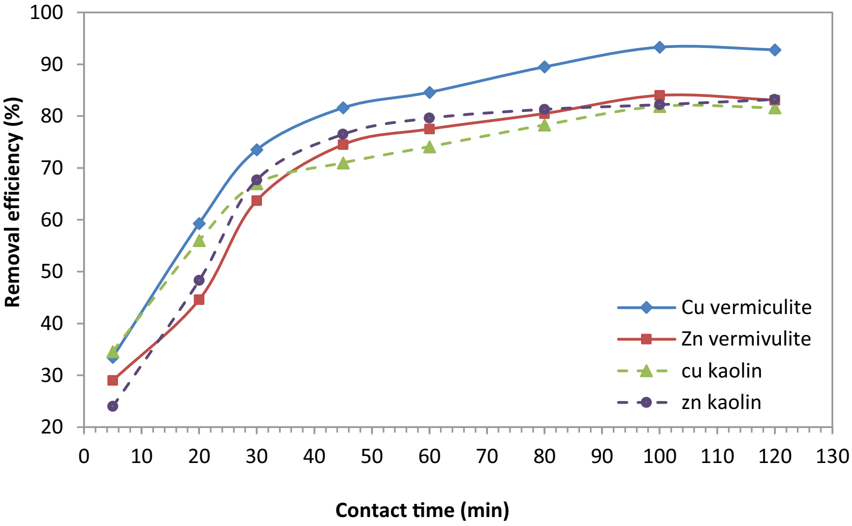

Fig. 5. Effects of contact time on the removal efficiency of Cu(II) and Zn(II) using vermiculite and kaolinite (pH = 5; initial metal concentration = 50 mg/L; particle size = 0.5–0.8 mm; temperature = 35°C; optimum adsorbent concentration; mixing speed = 150 rpm).

obtained within 95 and 80 min by vermiculite and kaolinite. The most removal efficiency by vermiculite was reached in the first 45 min which was 81% for Cu(II) and 74% for Zn(II). In the case of kaolinite, the removal efficiency was 67% and 76% for Cu(II) and Zn(II) in 30 and 45 min, respectively. After this time, the removal efficiency did not show a significant increase. The high adsorption in the early stages might be due to the initial concentration of the adsorbate in aqueous solution and the number of available binding sites on the adsorbent surface. After the mentioned time, decreasing the removal efficiency of Cu(II) and Zn(II) could be due to the limited mass transfer of the adsorbate particles from the bulk liquid to the external surface of adsorbent [39]. Other studies on heavy metals adsorption from aqueous solution have reported the same results [38,40].

3.5. Effect of temperature

The effects of temperature on the removal efficiency of Cu(II) and Zn(II) from synthetic samples by vermiculite and kaolinite adsorbents are shown in Fig. 6. The temperature has a significant effect on the removal efficiency of Cu(II) and Zn(II). By increasing the temperature from 25°C to 35°C, the removal efficiency of Cu(II) and Zn(II) increased using both adsorbents. Increasing temperature activates the metal ions and causes more adsorption at the coordinating sites of the mineral clays [41]. It has been proved that an increase in temperature leads to an increase in the diffusion rate of the adsorbate, owing to the decrease in the solution viscosity. In this study, increasing the temperature from 25°C to 35°C caused more removal efficiency for both adsorbents, the most effective of which was 16% enhancement

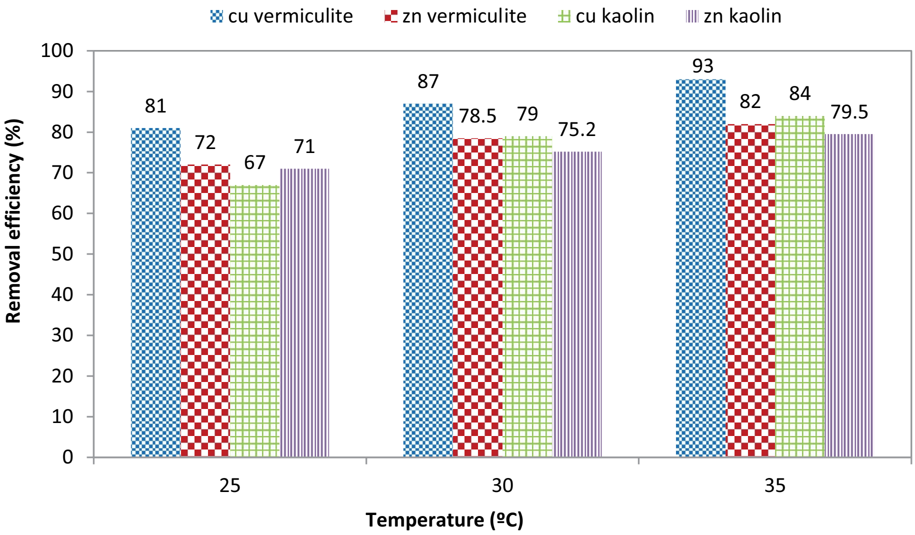

Fig. 6. Effects of temperature on the removal efficiency of Cu(II) and Zn(II) using vermiculite and kaolinite (pH = 5; initial metal concentration = 50 mg/L; particle size = 0.5–0.8 mm; optimum contact time; optimum adsorbent concentration; mixing speed = 150 rpm).

of Cu(II) by vermiculite. By rising temperature, Cu(II) and Zn(II) contacts to active sites increased and following that, the removal efficiency increased. The rapid movement of Cu(II) and Zn(II) could be because of less electrostatic interactions and reduction of ions due to solvation reduction [41]. It seems that higher temperature improves removal efficiency by either decreasing the thickness of the boundary layer surrounding the adsorbent and increasing the number of accessible sites [40]. The penetration capacity of Cu(II) and Zn(II) on the adsorbent is directly proportional to the solution viscosity. Increasing the temperature results in a higher diffusion rate of the adsorbate, a decrease in the viscosity of the solution, and an increase in the removal efficiency of Cu(II) and Zn(II) [30].

3.6. Effects of adsorbent particle size

The effects of an adsorbent particle on the removal efficiency of Cu(II) and Zn(II) from synthetic samples by vermiculite and kaolinite are shown in Fig. 7. Reduction in adsorbent particle size from 2–6.7 into 0.5–0.8 mm increased the removal efficiency of Cu(II) and Zn(II) approximately 11.5%–13% and 12.7%–14% by vermiculite and kaolinite, respectively. During the adsorption process,

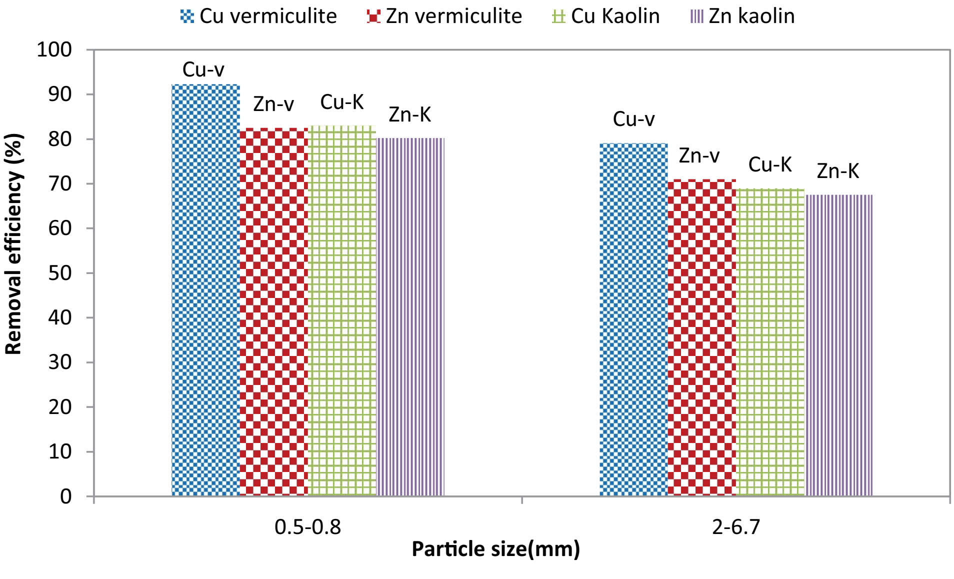

Fig. 7. Effects of vermiculite and kaolinite particle size on the removal efficiency of Cu(II) and Zn(II) (pH = 5; initial metal concentration = 50 mg/L; particle size = 0.5–0.8 mm; optimum contact time; temperature = 35°C; optimum adsorbent concentration; mixing speed = 150 rpm).

larger adsorbent surface area and more active sites are available for smaller particles at the constant mass [42]. Breaking big particles leads to open tiny cracks and channels on the particle surface of the adsorbent and results in more availability to a better diffusion of metal ions into the adsorbents [43]. Regarding adsorbent particle size of 2–6.7 mm, the diffusion resistance to mass transfer in higher particles and the most of internal surface of these particles may not be used for adsorption; therefore, the removal efficiency decreased. Given that all particles have a spherical shape, larger particles have more removal efficiency due to their higher external mass transfer than smaller particles [39]. Similar results for removing Cu(II) and Pb^{2+} by modified rice husk in Hongkong confirmed these results [44].

3.7. Effects of the initial concentration of metals

The effects of the initial concentration of metals on the adsorption of Cu(II) and Zn(II) from synthetic samples using vermiculite and kaolinite adsorbents are shown in Fig. 8. The results showed a reduction in the removal efficiency of Cu(II) and Zn(II) when the initial metal concentration increased; while the adsorption quantity on the basis of the adsorbent (mg/g) increased. This shows the application of adsorbents in the removal of Cu(II) and Zn(II) are acceptable for low initial concentration of solutions. At low initial concentration, a small ratio of ions number to accessible adsorption sites number makes the adsorption independent of the initial concentration. However, increasing the initial metal concentration increases the competition for adsorption sites [45]. When the initial concentration of metal ions was 20 mg/L, the removal efficiency rates by vermiculite for Cu(II) and Zn(II) were 97.2% and 88.5% and at the initial concentration of 100 mg/L were 28% and 24%, respectively. By using kaolinite, when the metal ion concentration was 20 mg/L, the removal efficiency of Cu(II) and Zn(II) was 92.5% and 87.4%. At the metal ion concentration of 100 mg/L, their removal efficiencies were 31% and 26%. Other studies reported similar results [46].

3.8. Determination of adsorption isotherms

The Freundlich and Langmuir isotherm of Cu(II) and Zn(II) using vermiculite and kaolinite are shown in Figs. 9 and 10, respectively. Correlation coefficients and other constants of Langmuir and Freundlich isotherms are shown in Table 4. The adsorption correlation coefficient (R^2) and isotherm constants show that the adsorption process of Cu(II) and Zn(II) by vermiculite and kaolinite are according to the Langmuir isotherm model and monolayer adsorption was carried out in the uniform surface. The correlation coefficient (R^2) for the Langmuir isotherm model is removing Cu(II) and Zn(II) were 0.997 and 0.993 for vermiculite and 0.996 and 0.994 for kaolinite, respectively. R^2 in the Freundlich model was obtained 0.79 and 0.813 for vermiculite and 0.806 and 0.829 while using kaolinite. While investigating the adsorption of Cu(II) and Zn(II) by mineral clays, adsorption equilibrium indicated that the Langmuir isotherm model represents a more considerable correlation compared to the Freundlich equation. The fitness of the Langmuir isotherm equation to describe the adsorption process was also validated by the separation factor value (R_L) in the range of $0 < R_L < 1$. Results of many research studies are consistent with this result (Desta [47]; Iskander et al. [48]; Lasheen et al. [32]; Omar and Al-Itawi [49]).

3.9. Kinetics of adsorption

Pseudo-first-order and pseudo-second-order reaction kinetics for copper and zinc adsorption using vermiculite and kaolinite are shown in Fig. 11. The adsorption constants of a first-order and second-order kinetic model

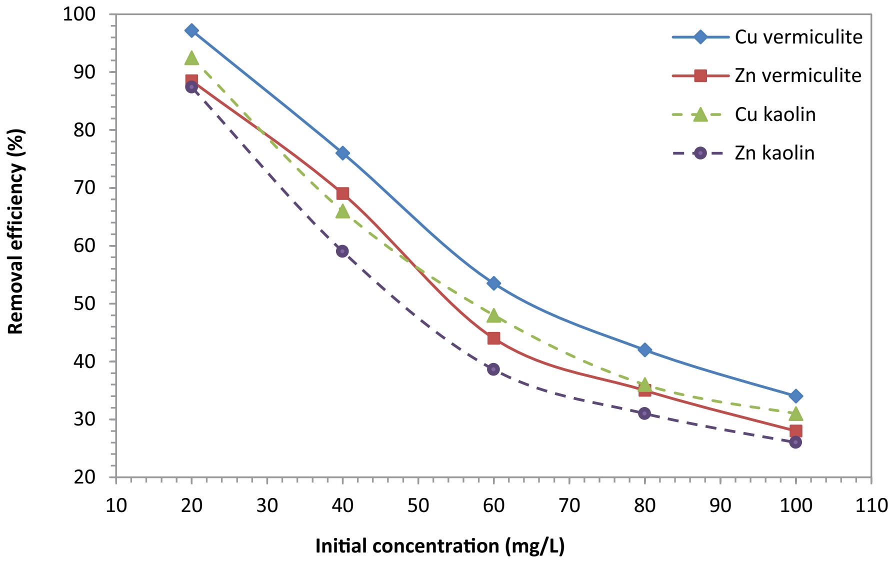

Fig. 8. Effects of initial concentration of metals on the removal efficiency of Cu(II) and Zn(II) using vermiculite and kaolinite (pH = 5; particle size = 0.5–0.8 mm; optimum contact time; temperature = 35°C; optimum adsorbent concentration; mixing speed = 150 rpm).

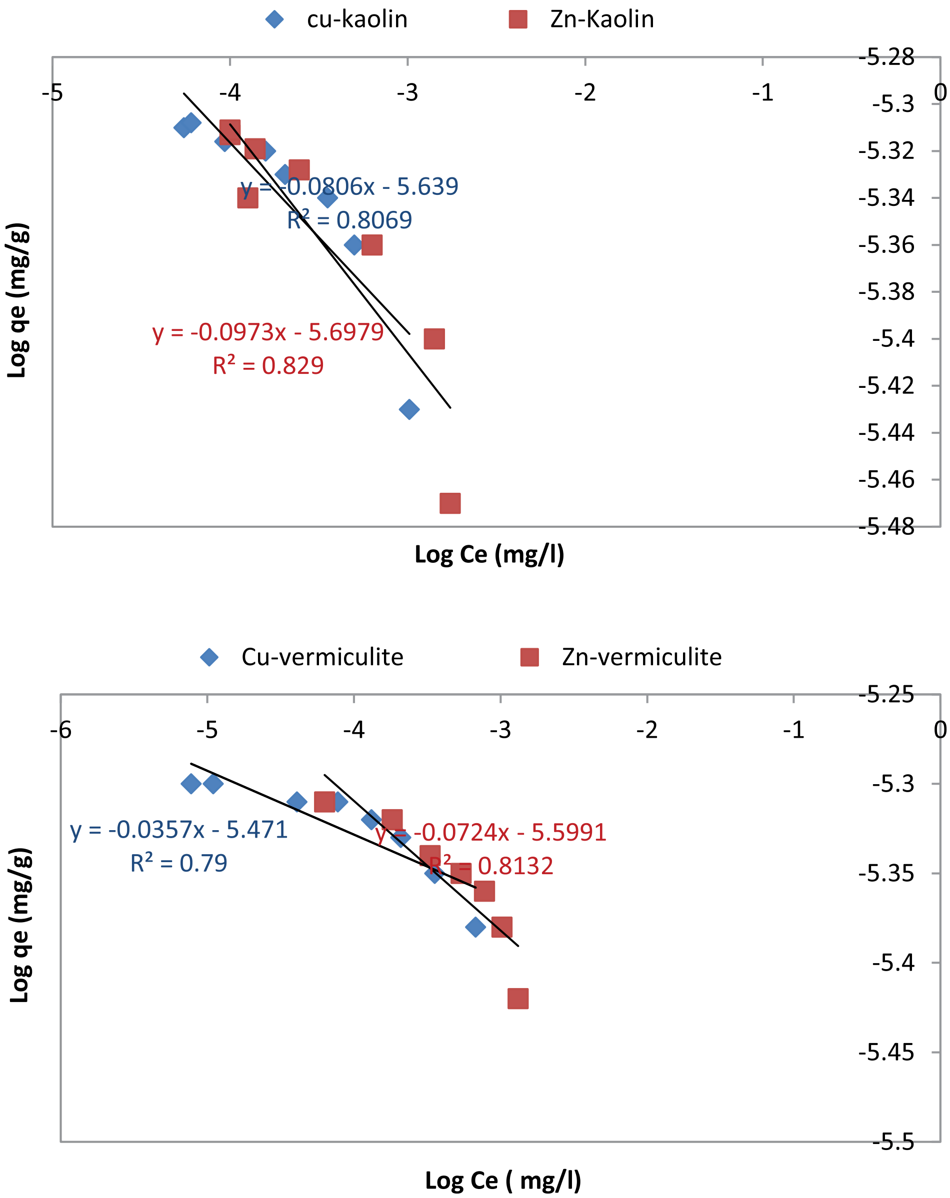

Fig. 9. Freundlich isotherm for adsorption of Cu(II) and Zn(II) on (a) kaolinite and (b) vermiculite.

for Cu(II) and Zn(II) by vermiculite and kaolinite are shown in Table 5. Kinetic models were used to analyze the experimental data regarding the adsorption mechanism and speed control steps [50]. The data of Table 5 and comparing correlation coefficients of 0.998 and 0.996 for Cu(II) and Zn(II) and proximity of $q_{e,\text{exp.}}$ and $q_{e,\text{cal.}}$ showed that in the initial concentration of 50 mg/L the pseudo-second-order kinetic model gave better results than pseudo-first-order kinetic. This result along with adsorption indicates that many other processes are taking places such as surface adsorption, diffusion into adsorbent particles, ion exchange, and precipitation [51,52]. Due to the higher concentration of Cu(II) in the real sample, the pseudo-second-order is more suitable for describing the adsorption process [44]. These results are in line with other studies [25,50,53].

3.10. Removal of Cu(II) and Zn(II) from real wastewater

The results of the chemical quality of AMD from Sarcheshmeh copper mine in Rafsanjan are shown in Table 6. According to Table 6, the highest AMD amount of Cu(II), Mg(II), Mn(II), Zn(II) and Si(II) in Sarcheshmeh copper mine were 133, 156, 58, 25 and 26 mg/L, respectively. The removal efficiencies of Cu(II) and Zn(II) in Sarcheshmeh AMD using vermiculite were 82% and 71% and by kaolinite were 65% and 56%, respectively. The priority of heavy metals adsorption from AMD with montmorillonite was Cd(II) = Zn(II) > Ni(II) and for mineral soils were Pb(II) > Cu(II) > Zn(II) > Cd(II). In this study, the experiments on the real sample showed that 82% of Cu(II) was removed using vermiculite and 71% by

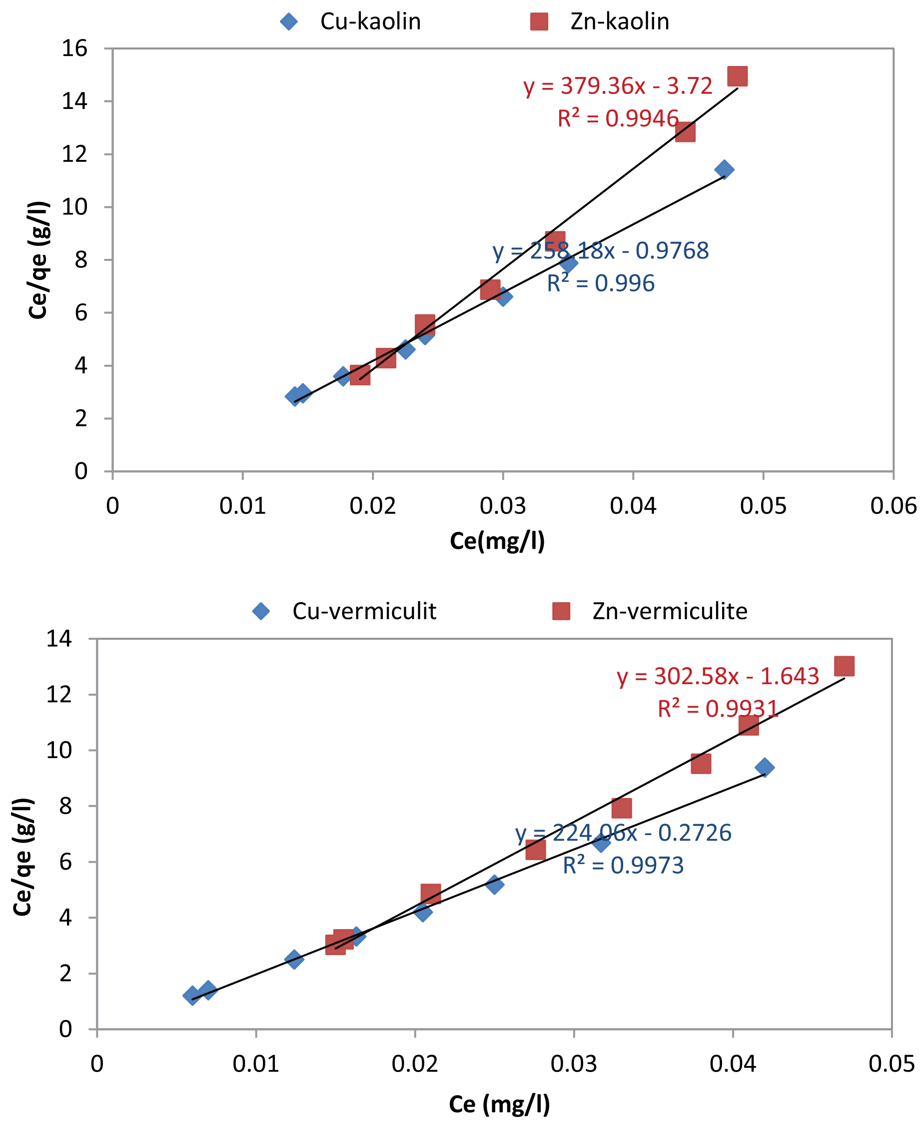

Fig. 10. Langmuir isotherm for adsorption of Cu(II) and Zn(II) on (a) kaolinite and (b) vermiculite.

Table 4
Parameters of the Langmuir and Freundlich adsorption isotherm models for the adsorption of Cu(II) and Zn(II) on vermiculite and kaolinite

Adsorbent		Langmuir				Freundlich		
		Q_0 (mg/g)	b (L/mg)	R_L	R^2	K_F (mg/g)	n	R^2
Vermiculite	Zn(II)	0.27	0.62	0.85	0.993	0.058	5.6	0.813
	Cu(II)	0.88	0.27	0.8	0.997	0.5	5.47	0.79
	Zn(II)	0.004	229.8	0.52	0.994	0.54	5.7	0.829
	Cu(II)	0.001	234.9	0.78	0.996	0.54	5.63	0.806

application of kaolinite. This study showed a lower efficiency for Zn(II) and the removal of 65% was achieved using vermiculite and 56% by application of kaolinite. Comparing the removal efficiency of Zn(II) in real and synthetic samples shows a decrease in the real sample (84% and 81.3% in synthetic and 65% and 56% in the real sample by using vermiculite and kaolinite, respectively). Less removal efficiency of Zn(II) in both real and synthetic

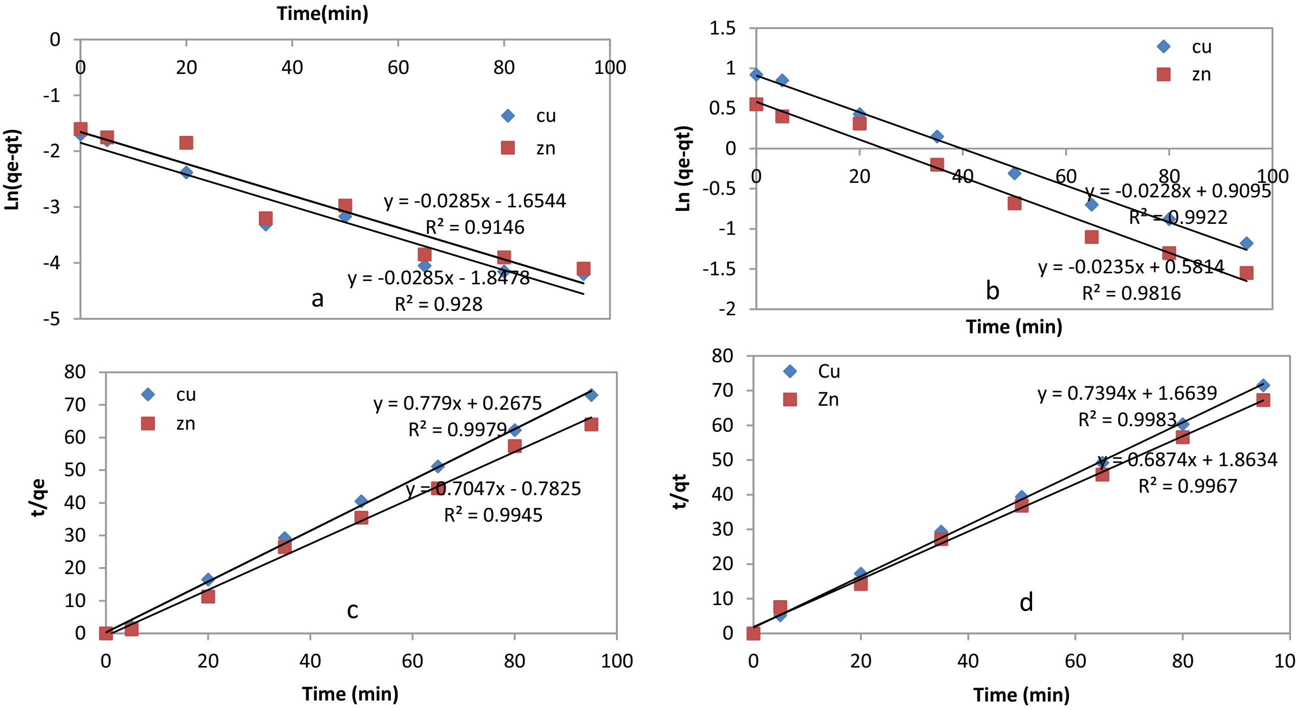

Fig. 11. Pseudo-first-order and pseudo-second-order kinetic model for adsorption of Cu(II) and Zn(II) on (a,c) vermiculite and (b,d) kaolinite.

Table 5
First-order and second-order adsorption rate constants for Cu(II) and Zn(II) removal efficiency with vermiculite and kaolinite

Adsorbent	Metal ion	$q_{e,\mathrm{exp.}}$	Pseudo-first-order parameters	Pseudo-second-order parameters
Vermiculite	Zn(II)	0.96	$k_1 = 0.0441$ g mg^{-1} min^{-1} $q_e = 0.097$ mg/g $R^2 = 0.914$	$k_2 = 1.73$ g mg^{-1} min^{-1} $q_e = 0.95$ mg/g $R^2 = 0.994$
	Cu(II)	0.92	$k_1 = 0.502$ g mg^{-1} min^{-1} $q_e = 0.068$ mg/g $R^2 = 0.928$	$k_2 = 2.78$ g mg^{-1} min^{-1} $q_e = 0.91$ mg/g $R^2 = 0.997$
Kaolinite	Zn(II)	0.915	$k_1 = 0.014$ g mg^{-1} min^{-1} $q_e = 0.125$ mg/g $R^2 = 0.981$	$k_2 = 1.92$ g mg^{-1} min^{-1} $q_e = 0.93$ mg/g $R^2 = 0.996$
	Cu(II)	0.936	$k_1 = 0.0135$ g mg^{-1} min^{-1} $q_e = 0.146$ mg/g $R^2 = 0.992$	$k_2 = 2.81$ g mg^{-1} min^{-1} $q_e = 0.92$ mg/g $R^2 = 0.998$

samples is due to the fewer chance of Zn(II) in competing with other existing metal ions. Zn(II) has a different removal efficiency in the single metal system (Zn(II)) and in the presence of other metals, such as the mine wastewater. Although Cu(II) and Zn(II) ions have an equivalent charge in their nature, the mode of their interaction with used adsorbents was different [54]. In this study, the concentration of positive metal ions, such as Mg^{+2}, Mn^{+2} and Si^{+2} in the AMD as the real sample was high. Therefore, due to the adsorption competition between these positive metal ions with Zn(II) and Cu(II), the smaller ion size with higher valence has greater adsorption [55], resulting in a decrease in the removal efficiency of Zn(II) and Cu(II) in the real samples. In this study Cu(II) (0.74 A) showed a stronger removal efficiency than Zn(II) (0.73 A). Ion exchange is a method to adsorb metal ions. Studies have shown that Cu(II) is twice eliminated rather than Zn(II) in this way [56]. In real samples, the combination of metal cations; Cu(II) and Zn(II) with organic and inorganic compounds occur; so the resulting compounds have a less positive charge. Positive charge or even some negative surface charge affects the adsorption process. Type and the amount of metal ions, adsorbent properties, the kind and amount of ligands, pH and solution compounds

Table 6
Chemical composition of AMD from the Sarcheshmeh copper mine in Rafsanjan

Parameter	Concentration range (mg/L)	Parameter	Concentration range (mg/L)	Parameter	Concentration range (mg/L)	Parameter	Concentration range (mg/L)
Na	12–31	Cu	62–133	Sb	0.01–0.08	PO_4^{-3}	0.9–1
K	1.6–5.3	Zn	11–25	Ni	0.7–3.6	NO_2	8–12
Mg	43–156	Pb	0.007–0.015	Se	0.001–0.15	NO_3	8–17
Ca	20–139	Mn	47–73	As	0.006–0.035	$NO_2 + NO_3$	16–27
Al	0.01–0.03	Mo	0.001–0.025	Si	21–26	SO_4	510–2,410
Fe	0.04–0.6	Co	0.2–0.65	Cr	0.01–0.06	$HCO_3^- + CO_3^{-2}$	7–9.5
Cd	0.02–0.15	Cl	11–22.5	pH	5.4		

are involved in the formation of this product. These compounds also affect the mobility and deposition of metals.

4. Conclusion

The removal of Cu(II) and Zn(II) from AMD was acceptable using vermiculite and kaolinite as new natural native adsorbents. The most important functional groups of vermiculite were O–H, C–O, C–Br and =C–H & =H_2 and for kaolinite were O–H, C–O, C–Br, C–I, S=O, and =C–H. The maximum removal efficiency of Cu(II) and Zn(II) by vermiculite was 94% and 85% when the adsorbent concentration was 24 g/L and for kaolinite, the highest removal efficiency was 86% for Cu(II) and 82% for Zn(II) when the adsorbent concentration was 22 g/L. Furthermore, when the initial metal concentration increased, the removal efficiency of Cu(II) and Zn(II) decreased. Adsorption isotherm constants showed that the adsorption process of Cu(II) and Zn(II) by vermiculite and kaolinite are according to the Langmuir isotherm model and the pseudo-second-order kinetic model gave better results. The adsorption efficiency reduction in the real sample was significant compared to the synthetic sample, and this reduction was higher for Zn(II) metal. Therefore, natural native vermiculite and kaolinite as accessible low-cost adsorbents had acceptable efficiency for removing Zn(II) and Cu(II).

References

[1] G.J. Qian, R.C. Schumann, J. Li, M.D. Short, R. Fan, Y.B. Li, N. Kawashima, Y. Zhou, R. St.C. Smart, A.R. Gerson, Strategies for reduced acid and metalliferous drainage by pyrite surface passivation, Minerals, 7 (2017) 1–15, https://doi.org/10.3390/min7030042.

[2] B. Vital, J. Bartacek, J.C. Ortega-Bravo, D. Jeison, Treatment of acid mine drainage by forward osmosis: heavy metal rejection and reverse flux of draw solution constituents, Chem. Eng. J., 332 (2018) 85–91.

[3] A. Esmaeili, M. Mobini, H. Eslami, Removal of heavy metals from acid mine drainage by native natural clay minerals, batch and continuous studies, Appl. Water Sci., 9 (2019) 1–6, https://doi.org/10.1007/s13201-019-0977-x.

[4] A. Khan, S. Khan, M.A. Khan, Z. Qamar, M. Waqas, The uptake and bioaccumulation of heavy metals by food plants, their effects on plants nutrients, and associated health risk: a review, Environ. Sci. Pollut. Res., 22 (2015) 13772–13799.

[5] H. Eslami, M.H. Ehrampoush, A. Esmaeili, A.A. Ebrahimi, M.T. Ghaneian, H. Falahzadeh, M.H. Salmani, Synthesis of mesoporous Fe-Mn bimetal oxide nanocomposite by aeration co-precipitation method: physicochemical, structural, and optical properties, Mater. Chem. Phys., 224 (2019) 65–72.

[6] B.S. Zohra, A. Habib, Assessment of heavy metal contamination levels and toxicity in sediments and fishes from the Mediterranean Sea (southern coast of Sfax, Tunisia), Environ. Sci. Pollut. Res., 23 (2016) 13954–13963.

[7] A. Akcil, S. Koldas, Acid mine drainage (AMD): causes, treatment and case studies, J. Cleaner Prod., 14 (2006) 1139–1145.

[8] H. Eslami, A. Shariatifar, E. Rafiee, M. Shiranian, F. Salehi, S.S. Hosseini, G. Eslami, R. Ghanbari, A.A. Ebrahimi, Decolorization and biodegradation of reactive Red 198 Azo dye by a new *Enterococcus faecalis–Klebsiella variicola* bacterial consortium isolated from textile wastewater sludge, World J. Microbiol. Biotechnol., 35 (2019) 1–10, https://doi.org/10.1007/s11274-019-2608-y.

[9] S.A. Ahmed, Batch and fixed-bed column techniques for removal of Cu(II) and Fe(III) using carbohydrate natural polymer modified complexing agents, Carbohydr. Polym., 83 (2011) 1470–1478.

[10] L. Reis, P.E. Pardo, A.S. Camargos, E. Oba, Mineral element and heavy metal poisoning in animals, J. Med. Med. Sci., 1 (2010) 560–579.

[11] I.A. Aguayo-Villarreal, A. Bonilla-Petriciolet, V. Hernández-Montoya, M.A. Montes-Morán, H.E. Reynel-Avila, Batch and column studies of Zn^{2+} removal from aqueous solution using chicken feathers as sorbents, Chem. Eng. J., 167 (2011) 67–76.

[12] F.L. Fu, Q. Wang, Removal of heavy metal ions from wastewaters: a review, J. Environ. Manage., 92 (2011) 407–418.

[13] M.A. Renu, K. Singh, Heavy metal removal from wastewater using various adsorbents: a review, J. Water Reuse Desal., 7 (2017) 387–419.

[14] D.H. Shahi, H. Eslami, M.H. Ehrampoosh, A. Ebrahimi, M.T. Ghaneian, S. Ayatollah, M.R. Mozayan, Comparing the efficiency of *Cyperus alternifolius* and *Phragmites australis* in municipal wastewater treatment by subsurface constructed wetland, Pak. J. Biol. Sci., 16 (2013) 379–384.

[15] A.E. Burakov, E.V. Galunin, I.V. Burakova, A.E. Kucherova, S. Agarwal, A.G. Tkachev, V.K. Gupta, Adsorption of heavy metals on conventional and nanostructured materials for wastewater treatment purposes: a review, Ecotoxicol. Environ. Saf., 148 (2018) 702–712.

[16] M.K. Uddin, A review on the adsorption of heavy metals by clay minerals, with special focus on the past decade, Chem. Eng. J., 308 (2017) 438–462.

[17] A. Esmaeili, H. Eslami, Adsorption of Pb(II) and Zn(II) ions from aqueous solutions by Red Earth, MethodsX, 7 (2020) 100804.

[18] W.-C. Tsai, S. Ibarra-Buscano, C.-C. Kan, C.M. Futalan, M.L.P. Dalida, M.-W. Wan, Removal of copper, nickel, lead, and zinc using chitosan-coated montmorillonite beads in single- and multi-metal system, Desal. Water Treat., 57 (2016) 9799–9812.

[19] X.F. Wu, F. Zhao, M.L. Chen, Y.L. Zhang, C. Zhao, H.L. Zhou, Factors affecting the adsorption of Zn^{2+} and Cd^{2+} ions from aqueous solution onto vermiculite, Adsorpt. Sci. Technol., 26 (2008) 145–155.

[20] M.A. Stylianou, V.J. Inglezakis, K.G. Moustakas, S.Ph. Malamis, M.D. Loizidou, Removal of Cu(II) in fixed bed and batch reactors using natural zeolite and exfoliated vermiculite as adsorbents, Desalination, 215 (2007) 133–142.

[21] T. Lee, Removal of heavy metals in storm water runoff using porous vermiculite expanded by microwave preparation, Water Air Soil Pollut., 223 (2012) 3399–3408.

[22] B. Meroufel, O. Benali, M. Benyahia, M.A. Zenasni, A. Merlin, B. George, Removal of Zn(II) from aqueous solution onto kaolin by batch design, J. Water Resour. Prot., 5 (2013) 669–680.

[23] P. Najafi, K. Asgari, N. Samadi, Heavy metal elimination from industrial wastewater using natural substrate on pitcher irrigation, Int. J. Recyl. Org. Waste Agric., 5 (2016) 333–337.

[24] E.W. Rice, R.B. Baird, A.D. Eaton, L.S. Clesceri, Standard Methods for the Examination of Water and Wastewater, American Public Health Association/American Water Works Association (APHA/AWWA/WPCR), Washington, 2012.

[25] S. Veli, B. Alyüz, Adsorption of copper and zinc from aqueous solutions by using natural clay, J. Hazard. Mater., 149 (2007) 226–233.

[26] A. Esmaeili, H. Eslami, Efficient removal of Pb(II) and Zn(II) ions from aqueous solutions by adsorption onto a native natural bentonite, MethodsX, 6 (2019) 1979–1985.

[27] E. Tajari, N.S. Langeroodi, M. Khalafi, Statistical modeling, optimization and kinetics of Mn^{2+} adsorption in aqueous solution using a biosorbent, Appl. Res. Chem., 11 (2016) 49–57.

[28] J. Yin, C.B. Deng, Z. Yu, X.F. Wang, G.P. Xu, Effective removal of lead ions from aqueous solution using nano illite/smectite clay: Isotherm, kinetic, and thermodynamic modeling of adsorption, Water, 10 (2018) 210.

[29] D. Mohan, K.P. Singh, V.K. Singh, Removal of hexavalent chromium from aqueous solution using low-cost activated carbons derived from agricultural waste materials and activated carbon fabric cloth, Ind. Eng. Chem. Res., 44 (2005) 1027–1042.

[30] J. Cao, H. Cao, Y.J. Zhu, S.S. Wang, D.W. Qian, G.D. Chen, M.B. Sun, W. Huang, Rapid and effective removal of Cu^{2+} from aqueous solution using novel chitosan and laponite-based nanocomposite as adsorbent, Polymers (Basel), 9 (2017) 5, doi: 10.3390/polym9010005.

[31] A.K. Meena, C. Rajagopal, Kiran, G.K. Mishra, Removal of heavy metal ions from aqueous solutions using chemically (Na_2S) treated granular activated carbon as an adsorbent, J. Sci. Ind. Res., 69 (2010) 449–453.

[32] M.R. Lasheen, I.Y. El-Sherif, S.T. El-Wakeel, D.Y. Sabry, M.F. El-Shahat, Heavy metals removal from aqueous solution using magnetite Dowex 50WX4 resin nanocomposite, J. Mater. Environ. Sci., 8 (2017) 503–511.

[33] S. Golkhah, H. Zavvar Mousavi, H. Shirkhanloo, A. Khaligh, Removal of Pb(II) and Cu(II) ions from aqueous solutions by cadmium sulfide nanoparticles, Int. J. Nanosci. Nanotechnol., 13 (2017) 105–117.

[34] S. Chen, M. Zhou, H.-F. Wang, T. Wang, X.-S. Wang, H.-B. Hou, B.-Y. Song, Adsorption of reactive brilliant red X-3B in aqueous solutions on clay–biochar composites from bagasse and natural attapulgite, Water, 10 (2018) 703, https://doi.org/10.3390/w10060703.

[35] Z. Mohamed, A. Abdelkarim, K. Ziat, S. Mohamed, Adsorption of Cu(II) onto natural clay: equilibrium and thermodynamic studies, Appl. Clay Sci., 7 (2016) 566–570.

[36] K.G. Bhattacharyya, S.S. Gupta, Influence of acid activation on adsorption of Ni(II) and Cu(II) on kaolinite and montmorillonite: kinetic and thermodynamic study, Chem. Eng. J., 136 (2008) 1–13.

[37] C.A. Ríos, C.D. Williams, C.L. Roberts, Removal of heavy metals from acid mine drainage (AMD) using coal fly ash, natural clinker and synthetic zeolites, J. Hazard. Mater., 156 (2008) 23–35.

[38] F.A. Dawodu, K.G. Akpomie, Simultaneous adsorption of Ni(II) and Mn(II) ions from aqueous solution unto a Nigerian kaolinite clay, J. Mater. Res. Technol., 3 (2014) 129–141.

[39] A.A. Okoya, A.B. Akinyele, I.E. Ofoezie, O.S. Amuda, O.S. Alayande, O.W. Makinde, Adsorption of heavy metal ions onto chitosan grafted cocoa husk char, Afr. J. Pure Appl. Chem., 8 (2014) 147–161.

[40] R. Mopoung, N. Kengkhetkit, Lead and cadmium removal efficiency from aqueous solution by NaOH treated pineapple waste, Int. J. Appl. Chem., 12 (2016) 23–35.

[41] N. Dizadji, M. Rashtchi, S. Dehpouri, N. Nouri, Experimental investigation of adsorption of copper from aqueous solution using vermiculite and clinoptilolite, Int. J. Environ. Res., 7 (2013) 887–894.

[42] S.K. Yadav, D.K. Singh, S. Sinha, Chemical carbonization of papaya seed originated charcoals for sorption of Pb(II) from aqueous solution, J. Environ. Chem. Eng., 2 (2014) 9–19.

[43] G. Karthikeyan, K. Anbalagan, N.M. Andal, Adsorption dynamics and equilibrium studies of Zn(II) onto chitosan, J. Chem. Sci., 116 (2004) 119–127.

[44] N. Barka, M. Abdennouri, M. El Makhfouk, S. Qourzal, Biosorption characteristics of cadmium and lead onto eco-friendly dried cactus (*Opuntia ficus indica*) cladodes, J. Environ. Chem. Eng., 1 (2013) 144–149.

[45] H.H. El-Maghrabi, S. Mikhail, Removal of heavy metals via adsorption using natural clay material, J. Environ. Earth Sci., 4 (2014) 38–46.

[46] M.R. Mahmoud, N.K. Lazaridis, K.A. Matis, Study of flotation conditions for cadmium(II) removal from aqueous solutions, Process Saf. Environ. Prot., 94 (2015) 203–211.

[47] M.B. Desta, Batch sorption experiments: Langmuir and Freundlich isotherm studies for the adsorption of textile metal ions onto teff straw (*Eragrostis tef*) agricultural waste, J. Thermodyn., 1 (2013) 1–6.

[48] A.L. Iskander, E.M. Khald, A.S. Sheta, Zinc and manganese sorption behavior by natural zeolite and bentonite, Ann. Agric. Sci., 56 (2011) 43–48.

[49] W. Omar, H. Al-Itawi, Removal of Pb^{+2} ions from aqueous solutions by adsorption on kaolinite clay, Am. J. Appl. Sci., 4 (2007) 502–507.

[50] H. Xiyili, S. Çetintaş, D. Bingöl, Removal of some heavy metals onto mechanically activated fly ash: modeling approach for optimization, isotherms, kinetics and thermodynamics, Process Saf. Environ. Prot., 109 (2017) 288–300.

[51] M.-Y. Chang, R.-S. Juang, Adsorption of tannic acid, humic acid, and dyes from water using the composite of chitosan and activated clay, J. Colloid Interface Sci., 278 (2004) 18–25.

[52] S.A.S. Mohammed, M. Naik, Utilization of red soils and amended soils as a liner material for attenuation of copper from aqueous solution: isotherm and kinetic studies, J. Environ. Sci. Technol., 4 (2011) 504–519.

[53] Z. Chen, W. Ma, M. Han, Biosorption of nickel and copper onto treated alga (*Undaria pinnatifida*): application of isotherm and kinetic models, J. Hazard. Mater., 155 (2008) 327–333.

[54] L.O.E. Agwaramgbo, R.F. Cardoso, T.S. Matos, Copper and zinc removal from contaminated water using coffee waste, J. Sci. Res. Rep., 12 (2016) 1–9.

[55] S.B. Chen, Y.B. Ma, L. Chen, K. Xian, Adsorption of aqueous Cd^{2+}, Pb^{2+}, Cu^{2+} ions by nano-hydroxyapatite: single- and multi-metal competitive adsorption study, Geochem. J., 44 (2010) 233–239.

[56] J. Perić, M. Trgo, N.V. Medvidović, Removal of zinc, copper and lead by natural zeolite—a comparison of adsorption isotherms, Water Res., 38 (2004) 1893–1899.