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Removal of iron and copper from aqueous solutions using Jordanian kaolin and zeolitic tuff

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ABSTRACT

The goal of this paper is to investigate the removal of iron and copper from aqueous solutions using adsorption. Zeolitic tuff and kaolin were used as adsorbents and were collected from different areas in Jordan. Batch adsorption experiments using synthetic Fe^{3+} and Cu^{2+} solutions were employed to study the effects of adsorbent dose, initial concentration, particle size, pH, and temperature on metal uptake. Zeolitic tuff had higher Fe^{3+} and Cu^{2+} adsorption capacities (20.70 and 20.83 mg/g, respectively) compared with kaolin (14.68 and 9.81 mg/g, respectively). The optimum pH values for Fe^{3+} and Cu^{2+} removal on kaolin were found to be 4 and 6, respectively. For the initial metal concentration of 100 ppm, 100% of Fe^{3+} and 62% of Cu^{2+} were adsorbed. As the temperature increased from 25 to 55°C, the adsorption capacity of Fe^{3+} on kaolin increased, thereby indicating the endothermic nature of the process. At the highest investigated temperature of 55°C, the Fe^{3+} removal using kaolin was 95.5%. The kinetic data obtained for Cu^{2+} removal confirmed the pseudo-second-order model. Fe^{3+} removal using zeolitic tuff was not affected by the particle size, while Cu^{2+} removal increased as the particle size decreased. This study suggests that zeolitic tuff and kaolin can be used as low-cost adsorbents for Fe^{3+} and Cu^{2+} removal with high efficiency. Kaolin was modified by pillaring with Al_{13} polyoxycation and acid activation. The mineralogy of the kaolin, analyzed using X-ray diffraction, confirmed that its structure was not changed significantly due to Al-pillared activation. Both pillaring and acid activation decreased the adsorption capacity.

Keywords: Adsorption; Copper; Iron; Jordan; Kaolin; Kinetics; Zeolitic tuff

1. Introduction

Heavy metals in the environment are detrimental to a variety of living species including humans due to their hazardous and toxic nature, their accumulation in living tissues, and consequent biomagnifications in the food chain [1,2]. The contamination of aqueous systems by toxic heavy metals has been recognized as a worldwide environmental problem [3].

Iron and copper are heavy metals that are concerning for the environment. Although iron is an essential element in human nutrition, its presence at high levels in aqueous streams renders water unusable. Iron ions dissolve from rocks and soils into ground water at

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low levels, but it can be present at high levels either through contamination from waste effluent of industrial processes (e.g. pipeline corrosion, engine parts, metal finishing, and galvanized pipe manufacturing) or from certain geological formations [4]. According to the US Environmental Protection Agency (US EPA), the maximum contaminant level (MCL) of iron in drinking water is 0.3 mg/l [5].

Increased industrial activities (e.g. copper mining and smelting, brass manufacture, petroleum refineries, and electroplating) have led to the discharge of wastewater containing excessive copper into the environment, which has caused serious contamination of aqueous systems. The MCL of copper is 1.3 mg/l [5]. It has been demonstrated that drinking water with a copper concentration above the MCL for long periods can cause many diseases, such as liver and kidney damage, stomach ailments, and intestinal distress [6].

Several methods have been used for the removal of iron and copper from aqueous systems (e.g. ion exchange, precipitation, ultra filtration, reverse osmosis, and adsorption). Among these methods, adsorption is one of the most efficient and cost-effective methods, especially at low heavy metals concentrations [7]. Activated carbon has undoubtedly been one of the most popular and widely used adsorbents in wastewater treatment applications throughout the world. In recent years, research into the production of alternative adsorbents to replace the costly activated carbon has intensified [8,9].

Natural materials, such as chitosan, zeolites, clay, and several waste products from industrial operations (e.g. fly ash, coal, and oxides), are classified as low-cost adsorbents [10,11]. Among clays, kaolin is one of the most common and abundant minerals in nature. It is considered as low-cost natural adsorbent and has been widely used for the removal of a variety of heavy metals [12–16]. In addition to clays, natural zeolites have gained significant interest in the field of heavy metals removal due to their valuable adsorption properties, such as ion exchange capability [10,17–19]. Therefore, the goal of this paper is to investigate iron and copper removal from aqueous solutions by batch adsorption using Jordanian natural kaolin and zeolitic tuff.

2. Materials and methods

2.1. Adsorbents

In this study, zeolitic tuff and kaolin were used as adsorbents, they were collected and supplied by Jordan Natural Resources Authority (JNRA). Zeolitic tuff was collected from Al-Azraq city in east Jordan, whereas kaolin was collected from the Batn El-Goul area in south Jordan.

Kaolin is a white, soft, plastic clay mainly composed of the fine-grained platy mineral kaolinite, and occurs as extremely small hexagonal-shaped crystals with micron and submicron sizes [16]. Kaolin deposits in Jordan are exposed in four main locations in south Jordan, namely, Batn El-Ghoul (Jabal al Harad), Al-Mudawwara, Jabal Umm Sahm, and Dubaydib. All areas have been exploited to a small extent. Mudawwara kaolin has not yet been exploited. Kaolin deposits in Batn El-Ghoul are mainly composed of kaolinite and quartz minerals and small amounts of mica, feldspar, gypsum, and pyrite. According to the JNRA, the kaolin reserves in Batn El-Goul contain an estimated 2,200 Mt. Kaolin from Batn El-Goul contains major oxides, such as Al_2O_3 (14.01–25.37%), SiO_2 (47.79–68.32%), and Fe_2O_3 (4.05–8.37%) [20].

Zeolites are hydrated framework aluminosilicates of the alkali and alkaline earth elements and consist of infinitely three-dimensional frameworks of AlO_4 and SiO_4 tetrahedra, called the primary building units, which are linked to each other via oxygen atoms. They have a net negative charge due to the isomorphic replacement of Si^{4+} by Al^{3+}, and this negative charge is balanced by the extra-framework cations (Na^+, K^+, Ca^{2+}, and Mg^{2+}) [21,22]. Zeolites are abundant in Jordan in three locations: the northeastern, central, and southern areas of Jordan. Zeolitic tuffs are located at Jabal Aritayn (30 km NE of Azraq), Tlol Al-shahba (20 km E of Al safawi), Tell-Rmah (35 km NE of Al Mafraq), and other small deposits in the South Jordan (Tell Burma, Tell Juhaira, and Wadi El-Hisa) and in Central Jordan (Makawer, Al-Zara, Wadi Heidan, and Wadi Al-Walah). According to JNRA, the estimated zeolitic tuff reserves in various areas in Jordan are as follows: Tell Rmah 46 Mt, Al-Aritain 170 Mt, Tlol Al-Shahba 9.2 Mt, North East Areas 472 Mt, and other areas 1,340 Mt [23]. The pH values of Jordanian kaolin are in the range 6–8 [20], and those of zeolitic tuff are in the range 7.54–10.05 [24].

The zeolitic tuff was milled using a ball mill and then sieved. Kaolin was crushed using a Dodge Jaw crusher and then milled using a ball mill. Both milled samples were used as raw materials (without any modification). The particle sizes of both adsorbents used in all experiments were in the range of 106–125 μm, except for the study of particle size effect in which the range was between 75 and 300 μm.

Kaolin samples were collected from two different sites. The qualities of the samples were different; therefore, they were called kaolin1 and kaolin2. In an attempt to improve the quality and characteristics of kaolin as an adsorbent, both aluminum pillaring and acid activation were applied. Aluminum-pillared kaolin was prepared as reported by Yan et al. [3] where 200 ml of 0.2 M NaOH was added to 100 ml of 0.2 M $AlCl_3 \cdot 6H_2O$. The prepared solutions were subsequently aged for two days at room temperature prior to examination. This pillared kaolin was designated Al-kaolin. Acid activation was carried out by adding 50 g of kaolin to 250 ml of sulfuric acid (1 M) for 24 h. The resulting suspension was then filtered, repeatedly washed with distilled water to remove any unspent acid, and dried in an oven for 3 h at 105˚C. The acid treated sample is referred to as acid-kaolin. Table 1 shows the six samples used (three raw samples and three modified samples). X-ray diffraction (XRD) analysis was conducted using a computer controlled Hiltonbrooks generator with a Philips X'Pert Pro PW 3040/60 diffractometer and an automatic divergence slit and Cu anode producing X-rays with a wavelength of 1.54056 Å [25].

2.2. Batch adsorption experiments

All chemicals were of analytical grade (from Sigma Aldrich) and were used without further purification. Fe^{3+} and Cu^{2+} solutions at different concentrations (20, 50, 70, 100, and 200 ppm) were prepared by dissolving $FeCl_3$ and $CuSO_4 \cdot 5H_2O$ in distilled water, respectively. The synthetic Fe^{3+} and Cu^{2+} solutions had pH values of 2.5 ± 0.2 and 5.5 ± 0.2, respectively.

Batch adsorption experiments were carried out by allowing an accurately weighed amount of zeolitic tuff or kaolin (0.5 ± 0.0005 g) to reach equilibrium with 50 ml of aqueous heavy metal ions solutions of known concentrations in 100-ml amber bottles. The bottles were capped with screw caps fitted with parafilm and shaken at 250 rpm using a rotary shaker. At the end of equilibration period, the contents of the bottles were centrifuged at 2,000 rpm for 6 min. Then, the filtrate and supernatant were subsequently analyzed for residual heavy metal concentration using atomic absorption spectrometry (AAS NOVA 300 Analytik Jena AG).

Table 1
A summary of the used samples

Symbol	Sample
Z	Zeolitic tuff
K1	Kaolin 1
K2	Kaolin 2
K3	Aluminum-pillared kaolin 1
K4	Aluminum-pillared kaolin 2
K5	Acid-kaolin 2

To obtain the optimum conditions for the removal of iron and copper from aqueous solutions, the effects of initial concentration, adsorbent dose, contact time, pH, temperature, and particle size on metal removal and uptake were studied. Details on the methods used in studying these effects are provided in the following subsections.

2.2.1. Effect of initial concentration

The initial Fe^{3+} and Cu^{2+} concentrations were 20, 50, 70, 100, and 200 ppm. The effect of heavy metal initial concentration on its uptake was conducted at room temperature for 24 h.

2.2.2. Effect of adsorbent dose

To obtain the optimum dose of each adsorbent, different adsorbent masses (from 0.1 to 1 g) were examined. The adsorbents concentrations were 2, 6, 10, 14, 18, and 20 mg/ml. The adsorption experiments for both Fe^{3+} and Cu^{2+} were investigated with an initial concentration of 100 ppm. The solutions were shaken using a rotary shaker for 30 min at room temperature.

2.2.3. Effect of contact time

The selected time intervals were varied from 10 min to 24 h (10 and 30 min; 1, 2, 4, 6, and 24 h). Adsorption experiments were carried out using different initial Fe^{3+} and Cu^{2+} concentrations at room temperature.

2.2.4. Effect of pH

The solutions pH were adjusted to 1, 2, and 4 for Fe^{3+} and to 2, 4, and 6 for Cu^{2+}. The pH values of the solutions were adjusted using 0.1 M HCl and 0.1 M NaOH and were measured using an Inolab pH 720 pH meter. The pH effect was investigated at room temperature and a contact time of 24 h for Fe^{3+} and Cu^{2+} with initial concentrations of 50 and 100 ppm.

2.2.5. Effects of temperature

The effects of temperature on Fe^{3+} and Cu^{2+} removal using kaolin1 and zeolitic tuff were investigated at four temperatures (25, 35, 45, and 55˚C) for 24 h. Temperatures were adjusted using a temperature-controlled water bath shaker.

2.2.6. Particle size effects

The size fractions of zeolitic tuff were 75–106, 125–180, and 250–300 μm. For kaolin1, the particles size fractions used were <75, 75–106, and 125–180 µm. The tests were investigated using Fe^{3+} and Cu^{2+} initial concentrations of 50 and 100 ppm at room temperature for 24 h.

2.3. Adsorption isotherms

When analyzing adsorption processes, it is important to study the adsorption equilibrium relationship. This is usually done by fitting experimental data to an isotherm model. In this work, Langmuir and Freundlich isotherms were used to obtain the adsorption results.

According to Freundlich [26], the linear form of the Freundlich isotherm model is:

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

where q_e is the adsorbent phase concentration after equilibration (mg/g), C_e is the metal ion concentration in the liquid phase at equilibrium (mg/l), and K_F and n are the Freundlich constants related to adsorption capacity $[(mg/g)\,(L/mg)^n]$ and adsorption intensity, respectively, of the adsorbent.

The heavy metal ion uptakes were calculated from the mass balance, i.e. the amount of solute adsorbed onto the solid according to Kannan and Veemaraj [27] as:

$$q_e = \frac{(C_0 - C)V}{m} \tag{2}$$

where C_0 is the initial metal ion concentration in the liquid phase (mg/l), C is the heavy metal concentration after adsorption has occurred (mg/l), V is the total volume of the metal ion solution (L), and m is the mass of adsorbent (g).

The linear form of the Langmuir isotherm model is [28]:

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

where q_m is the maximum metal ions uptake per unit mass of adsorbent (mg/g), which is related to adsorption capacity, and b is the Langmuir constant (L/mol), which is exponentially proportional to the heat of adsorption and related to the adsorption intensity.

The percentage of heavy metal removal was calculated as [28]:

$$\text{Removal } \% = \frac{(C_0 - C)}{C_0} \tag{4}$$

2.4. Kinetic modeling (the pseudo-second-order equation)

The study of sorption kinetics in water treatment is significant because it provides valuable insights into the reaction pathways and into the mechanisms of the sorption reactions. Kinetics describe the solute uptake rate which in turn controls the residence time of sorbate uptake at the solid–solution interface [29]. The pseudo-second-order rate equation according to Ho and McKay [29] is:

$$\frac{t}{q_t} = \frac{1}{k_2 q_{e2}^2} + \frac{t}{q_{e2}} \tag{5}$$

where q_t is the amount of adsorbate adsorbed (mg/g) at time t (h), q_{e2} is the equilibrium adsorption capacity or uptake (mg/g), and k_2 is the pseudo-second-order rate constant of adsorption (g/(mg h)).

3. Results and discussion

3.1. Chemical composition and XRD of adsorbents

The chemical compositions of the raw and modified adsorbents, made according to the DIN22022 test that was conducted using ICP-OES, are listed in Table 2. SiO_2 was the most chemically stable component and accounted for the highest concentration (42.8–76.9%) followed by Al_2O_3 (10.1–14.1%) and Fe_2O_3 (3.46–13.3%). The highly water reactive components (i.e. Mg, Ca, Na, and K)were present in trace amounts. On acid activation, the activated kaolin sample showed a slight decrease in alumina percentage and an increase in the silica percentage, which indicated a small preferential dissolution of aluminum. The Si/Al ratio increased from 6.88 for kaolin2 to 7.614 for acid-kaolin2. An increase in alumina and silica percentage was noticed after Al activation. The Si/Al ratio decreased from 5.616 to 4.645 for kaolin1 and Al-kaolin1, respectively, and from 6.88 to 6.256 for kaolin2 and Al-kaolin2, respectively.

The mineralogies of the kaolin1 and Al-kaolin1 samples were analyzed using XRD, as shown in Fig. 1. In this figure, the peaks marked *K*, *Q*, *M*, and *F* are related to kaolinite, quartz, mica, and feldspar, respectively. The XRD analysis indicated a low percentage of kaolinite clay in the kaolin samples. In addition, both samples were similar, indicating that the kaolin1 structure was not changed significantly due to Al-pillared activation.

3.2. Effect of adsorbent dose

The effects of the kaolin, Al-activated kaolin, and acid-activated kaolin concentrations on Cu^{2+} removal

Table 2
Chemical analysis of the raw and modified adsorbents

Oxide (%)	Zeolitic tuff	Kaolin1	Kaolin2	Al-K1[a]	Al-K2[b]	Acid-K2[c]
Al_2O_3	13.2	11.20	10.90	14.10	12.10	10.10
CaO	8.89	0.556	0.278	0.325	0.220	0.132
Fe_2O_3	13.30	5.11	4.28	5.52	4.36	3.46
K_2O	1.82	3.20	3.59	3.25	3.95	3.63
MgO	11.10	0.983	1.30	1.22	1.34	0.95
Na_2O	3.20	0.727	0.774	0.593	0.870	0.774
P_2O_5	0.578	0.166	0.112	0.239	0.115	0.049
SO_3	0.083	0.128	0.059	0.101	0.076	0.053
SiO_2	42.80	62.90	75.00	65.50	75.70	76.90
TiO_2	2.97	0.824	0.463	0.880	0.462	0.495

[a] Aluminium-pillared kaolin1.

[b] Aluminium-pillared kaolin1.

[c] Acid activated kaolin 2.

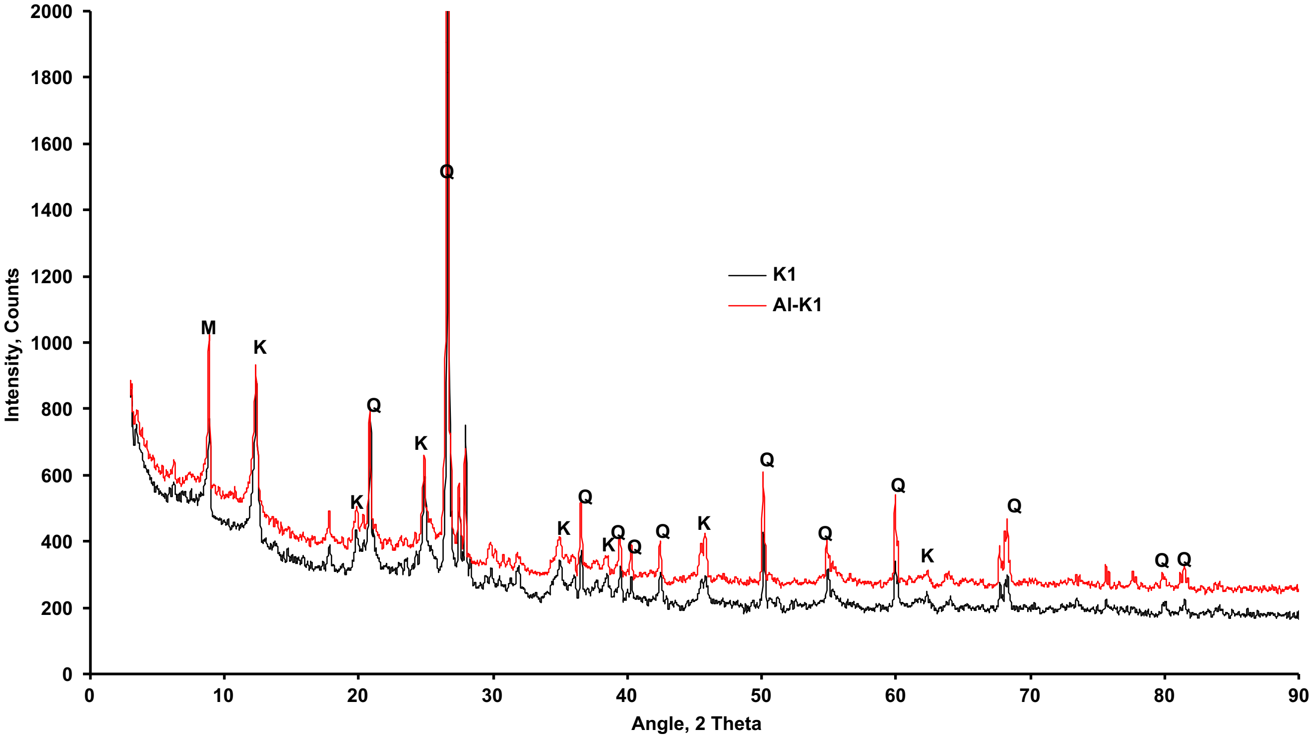

Fig. 1. XRD patterns of Kaolin1 and Al-Kaolin1 samples.

from aqueous solutions are shown in Fig. 2. Kaolin1 was the best adsorbent among all of the investigated kaolin samples. As the kaolin1 concentration increased from 0 to 20 mg/ml, the Cu^{2+} concentration decreased from 100 to 33.5 ppm with a removal efficiency of 66.5%. However, when kaolin2 was used as adsorbent, a Cu^{2+} removal of only 34.7% was achieved at an adsorbent concentration of 20 mg/ml. This result can be explained by the fact that kaolin1 had the lowest Si/Al ratio compared with the other kaolin samples. Impurities exist in the crystal structure of kaolin1, especially mica, which may contribute to the improved Cu^{2+} removal. Mica is a mineral from the illite clay mineral group, which has a cation exchange capacity ranging from 10 to 40 meq/100 g [30].

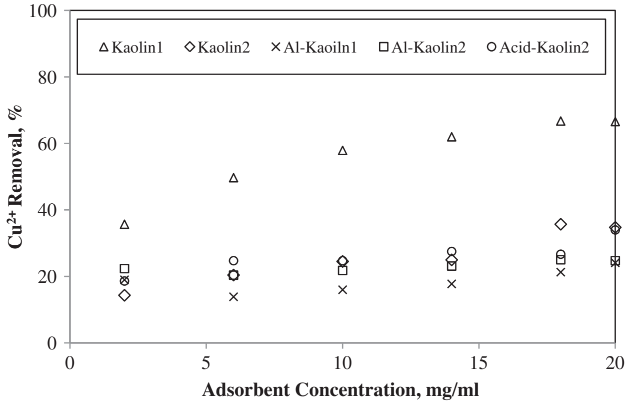

Fig. 2. Effect of kaolin (1 and 2), Al-activated kaolin (1 and 2), and acid-activated kaolin2 concentration on the removal of Cu^{2+}, contact time = 30 min.

Al activation did not enhance the removal of copper in both kaolin samples, and the efficiency of Cu^{2+} removal was lower than that using the raw kaolin samples, especially in the case of kaolin1. At an adsorbent concentration of 20 mg/ml, the Cu^{2+} removals were 24.1 and 24.7% using Al-kaolin1 and Al-kaolin2, respectively. Additionally, acid-treated kaolin2 did not enhance Cu^{2+} removal, even though Cu^{2+} removal was slightly higher than Al-kaolin2. The results indicated that Al pillaring and acid activation decreased the cation exchange capacity, which were in agreement with Dekany et al. [31] who found that Al pillaring is not effective at increasing kaolin's cation capacity or enhancing its adsorbent characteristics. The acid activation results were also in good agreement with Suraj et al. [15] who observed a decrease in the cation exchange capacity for the raw kaolinite due to acid treatment. The acid strength plays an important role. Panda et al. [32] found that as the acid strength increases to 3–5 M and higher, the effect of acid activation is clearer.

Zeolitic tuff and kaolin1 were used to study the effect of adsorbent concentration on Fe^{3+} and Cu^{2+} removal at an initial metal concentration of 100 ppm. The results were exhibited in Fig. 3. When the effects of the two adsorbents were compared, Cu^{2+} removal using zeolitic tuff was faster and higher. At an adsorbent concentration of 20 mg/ml, the Cu^{2+} removal efficiency was 91.7% using zeolitic tuff and only 66.5% using kaolin1. In the case of Fe^{3+} removal, when the adsorbent concentration was lower than 10 mg/ml, the removal using kaolin1 was higher than that using zeolitic tuff. As the adsorbent concentration was equal to or greater than 10 mg/ml, the Fe^{3+} removal using zeolitic tuff was higher than that using kaolin1. The results showed that Fe^{3+} and Cu^{2+} removal increased as the adsorbent concentration increased, which were in agreement with Yousef et al. [33] who found that the increase in the adsorbent amount enhances the removal efficiency because it provides a greater surface area (or more adsorption sites).

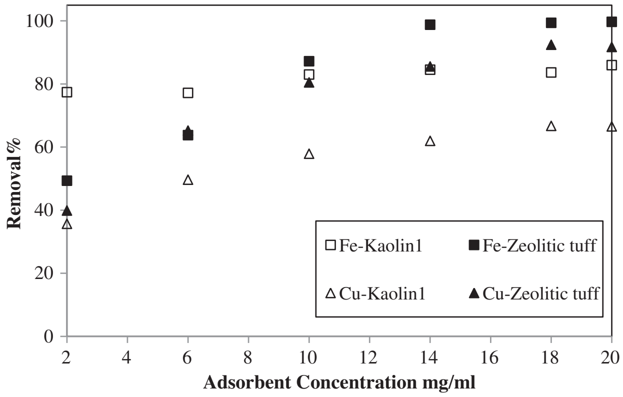

Fig. 3. Effect of adsorbent concentration on the removal of Fe^{3+} and Cu^{2+}, contact time = 30 min.

3.3. Adsorption kinetics

Zeolitic tuff and kaolin1 with heavy metal concentrations of 10 mg/ml were used to study Fe^{3+} and Cu^{2+} removal kinetics and the variables that affect their removal. The influence of contact time on Fe^{3+} and Cu^{2+} uptake at room temperature using zeolitic tuff and kaolin1 is shown in Figs. 4 and 5. It was found that the adsorbate (i.e. Fe^{3+} or Cu^{2+}) concentration decreased as the contact time between the adsorbent (i.e. zeolitic tuff or kaolin1) and adsorbate increased until the equilibrium concentrations were reached. Fe^{3+} uptake was very fast; the system was at equilibrium by the first measurement of the initial adsorbate concentration.

Cu^{2+} kinetic uptake plots (Fig. 5) indicated that two or more adsorption steps might occur. The first step was fast and characterized by the rapid attachment of Cu^{2+} to the surface of the adsorbent. The second step was slower due to repulsive forces, especially at 100 and 200 ppm. The third step was the equilibrium stage. When using zeolitic tuff at low initial Cu^{2+} concentrations of 20 and 50 ppm, 10 min was required to reach the equilibrium state, while at 100 ppm, the equilibrium time was 6 h. When using kaolin1 as an adsorbent with initial Cu^{2+} concentrations of 20, 50, and 100 ppm, the equilibrium times were 10 min, 2 h, and 6 h, respectively. To ensure equilibrium during the study of initial metal

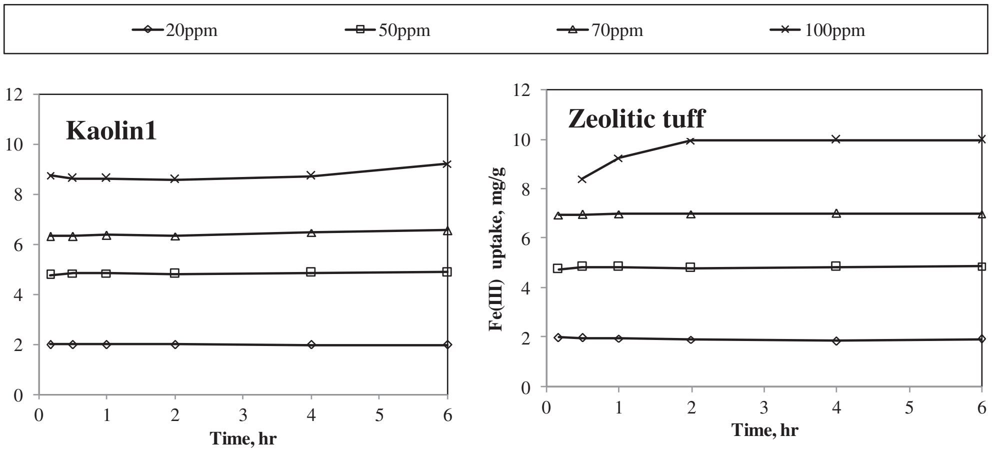

Fig. 4. Kinetics of Fe^{3+} uptake by kaolin1 and zeolitic tuff at various initial Fe^{3+} concentrations.

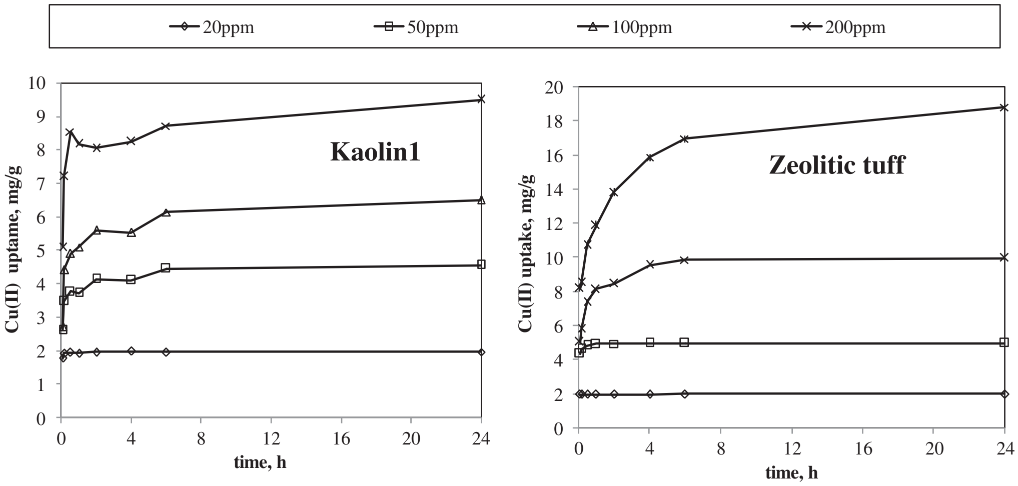

Fig. 5. Kinetics of Cu^{2+} uptake by kaolin1 and zeolitic tuff at various initial Cu^{2+} concentrations.

concentration, pH, particle size, and temperature effects, the experiments were conducted for 24 h.

Different models (Eqs. (1)–(5)) have been used to test the kinetics of the adsorbents (Fe^{3+} and Cu^{2+}) interactions. The kinetics results were used to determine if particle diffusion was the rate limiting step for adsorption. Weber and Morris [34] reported that if particle diffusion is involved in the sorption process, then a plot of adsorbate uptake vs. the square root of time would result in a linear relationship and that particle diffusion would be the rate controlling step if this line passes through the origin. In this paper, it was found that Fe^{3+} and Cu^{2+} uptake results for both adsorbents were represented by such a linear relationship, but they do not pass through the origin. This indicates that particle diffusion was involved in the adsorption process, but it was not the only rate-limiting mechanism, which indicated that some other mechanisms were involved [35,36].

Linear plots of t/q_t vs. t were obtained with high correlation coefficients (i.e. 0.99–1) for Cu^{2+} removal using both adsorbents. The linear plots for Cu^{2+} adsorption are shown in Fig. 6. The parameters k_2 and q_{e2} were calculated from slopes and intercepts of the linear plots and were listed in Table 3. A comparison of $q_{e2,exp}$ (experimental) values showed a good agreement with those obtained from the slopes of the second-order plots. The pseudo-second-order model was based on the assumption that the rate limiting step might be chemical adsorption or chemisorption involving valency forces through sharing or exchange of electrons between adsorbent and adsorbate [29,37]. The particle diffusion was involved in the adsorption process and the chemical reaction was the rate controlling mechanism during Cu^{2+} adsorption on Jordanian zeolitic tuff and kaolin1.

3.4. Effects of initial concentration

The influences of the initial Fe^{3+} and Cu^{2+} concentrations (from 20 to 200 ppm) on their adsorptions were investigated using kaolin1 and zeolitic tuff at room temperature. The results are shown in Fig. 7. The uptake increased with increasing initial Fe^{3+} and Cu^{2+} concentration for both adsorbents. Increasing the initial heavy metal concentration increases the mass transfer driving force and, therefore, the rate at which Fe^{3+} and Cu^{2+} molecules pass from the bulk solution to the particle surface. It was found that the uptake was almost constant at the initial concentrations of 20 and 50 ppm using both adsorbents for Fe^{3+} and Cu^{2+} adsorption. Using both adsorbents, a rapid and steep increase in Fe^{3+} uptake was noticed in the initial concentration range of 100–200 ppm. Using zeolitic tuff, a rapid and steep increase in Cu^{2+} uptake was also noticed, while the steepness was lower in the case of kaolin1.

By comparing the remaining Fe^{3+} and Cu^{2+} concentrations after 24 h of adsorption with the maximum allowable values (MCL), it was found that zeolitic tuff can be used to remove Fe^{3+} and Cu^{2+} to concentrations lower than the MCL values when the initial concentrations were lower than 70 and 100 ppm, respectively. When using kaolin1, the Fe^{3+} and Cu^{2+} concentrations were lower than the MCL when the initial adsorbate concentrations were equal to and lower than 20 ppm.

3.5. Adsorption isotherms

Langmuir and Freundlich isotherms were applied to the Fe^{3+} and Cu^{2+} adsorption results at room temperature. The Cu^{2+} adsorption isotherms using kaolin1 and zeolitic tuff are shown in Fig. 8. Freundlich and Langmuir constants for Fe^{3+} and Cu^{2+} adsorption were calculated and listed in Table 4. For the Freundlich isotherm, the values of K_F and $1/n$ were obtained from the intercept and slope, respectively, of the linear plot of experimental data of $\ln q_e$ vs. $\ln C_e$. The linear form of the Langmuir was obtained by plotting C_e vs. C_e/q_e. The result was a straight line with a slope of $1/(q_m)$ and an intercept of $1/(q_m b)$. This linear form gives extra weight to higher values of C_e and was useful because quite often this was more reliable due to poor analytical sensitivity at low adsorbate concentrations q_e (or high $1/q_e$).

For Cu^{2+} removal using kaolin1, both adsorption isotherms were applicable with high correlation coefficients. Using zeolitic tuff, the correlation coefficient values indicated that the obtained results with Langmuir isotherms were better than those obtained with Freundlich isotherms. It was found that the Fe^{3+} adsorption results using zeolitic tuff were well described by both linearized Freundlich and Langmuir isotherms, even though the Langmuir isotherm was better. It is clear from Table 4 that zeolitic tuff had higher Fe^{3+} and Cu^{2+} removals than kaolin1. The maximum adsorption capacities using zeolitic tuff were 20.70 and 20.83 mg/g for Fe^{3+} and Cu^{2+}, respectively. Meanwhile, the maximum adsorption capacity using kaolin1 was 9.81 mg/g for Cu^{2+}.

3.6. Effect of pH

To ensure that precipitation did not occur, the adsorption of Fe^{3+} and Cu^{2+} was studied over pH ranges of 1–4 and 1–6, respectively. The adsorption process was carried out at room temperature until equilibrium was reached. It was noticed that the Fe^{3+} and Cu^{2+} uptakes for both investigated initial heavy metals concentrations using kaolin1 increased when

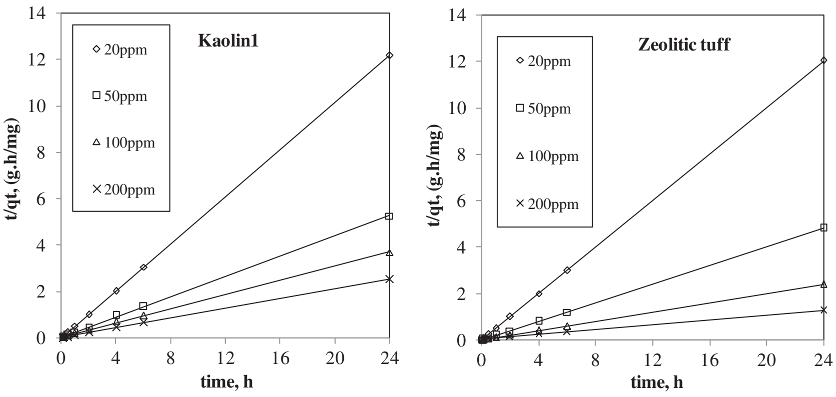

Fig. 6. Test of the pseudo-second-order equation for the adsorption of Cu^{2+} using kaolin1 and zeolitic tuff.

Table 3
Pseudo-second-order parameters for Cu^{2+} adsorption by kaolin1 and zeolitic tuff

	Kaolin1				Zeolitic tuff			
C_0[a] (ppm)	$q_{e2,exp}$[b] (mg/g)	k_2 (g/mg min)	q_{e2} (mg/g)	R^2	$q_{e2,exp}$ (mg/g)	k_2 (g/mg min)	q_{e2} (mg/g)	R^2
20	1.9725	58.3742	1.9732	1	2.000	39.0938	1.9992	1
50	4.5576	1.2115	4.5829	0.9997	4.9869	14.3716	4.9850	1
70	5.8407	0.1457	6.1199	0.9993	6.9950	1.9420	7.0028	1
100	6.5024	0.5245	6.5531	0.9993	9.9848	0.5533	10.020	1

[a] Initial Cu^{+2} concentration.

[b] Experimental value of Cu^{2+} uptake.

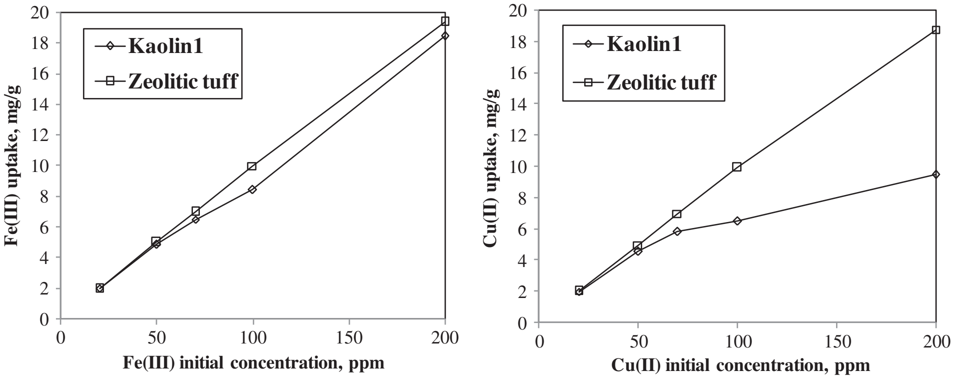

Fig. 7. Effect of Fe^{3+} and Cu^{2+} initial concentration on uptake using kaolin1 and zeolitic tuff.

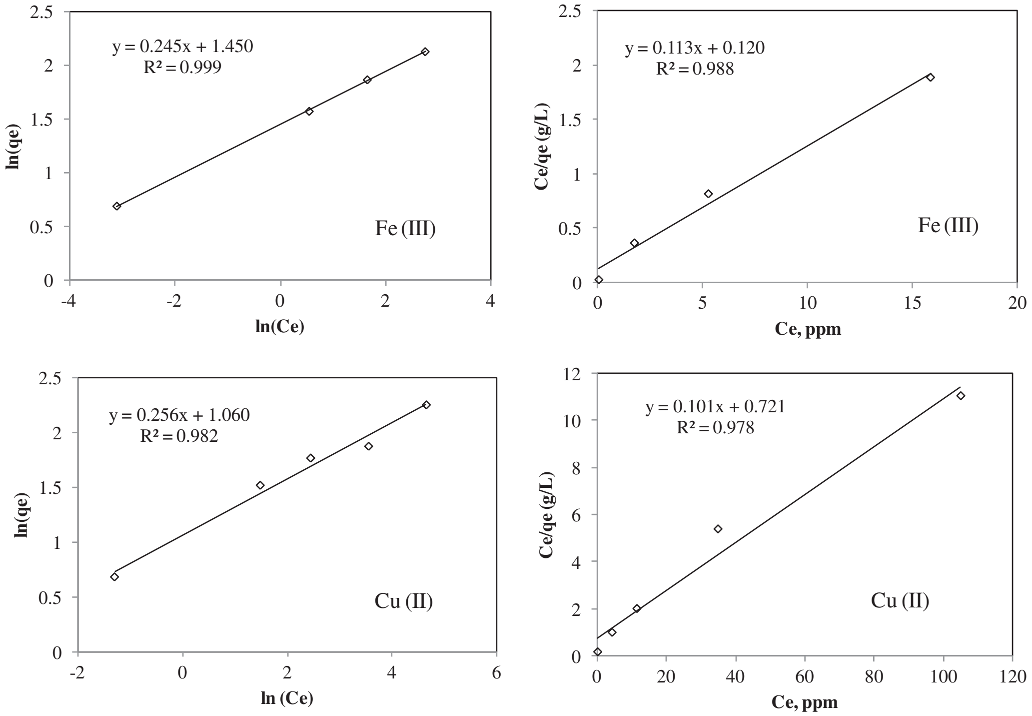

Fig. 8. Freundlich and Langmuir adsorption isotherm for Cu^{2+} using kaolin1 and zeolitic tuff at room temperature.

Table 4
Langmuir and Freundlich adsorption isotherms constants for Fe^{3+} and Cu^{2+} adsorption by zeolitic tuff and kaolin1 at room temperature

	Langmuir			Freundlich		
	q_m (mg/g)	b (l/g)	R^2	$1/n$	K_F ((mg/g) (mg/l)^n)	R^2
Cu-kaolin1	9.8135	0.1412	0.9781	0.2563	2.8875	0.9827
Cu-zeolitic tuff	20.830	1.8462	0.9990	0.4566	9.6707	0.8367
Fe-zeolitic tuff	20.7039	2.257	0.9983	0.3167	11.1173	0.8493

the pH value increased, as shown in Fig. 9. This behavior can be referenced to the number of available H_3O^+ ions, which was high at low pH in the adsorption medium, and therefore, Fe^{3+} and Cu^{2+} ions have to compete with them for the adsorption sites on the adsorbent surface resulting in a lower uptake of metal ions [38]. With the increase in pH, the concentration of H_3O^+ ions decreased and some of the sites become available resulting in a higher uptake of Fe^{3+} and Cu^{2+} ions [13,39]. The optimum pH value was 4. Fe^{3+} uptake (10 mg/g) was considerably higher than Cu^{2+} uptake (5.33 mg/g) for the initial metal concentration of 100 ppm. Moreover, the Fe^{3+} concentration after adsorption was lower than the MCL when using both adsorbents, which indicated that, by increasing the pH value of iron aqueous solutions to 4, the maximum allowable concentration limit was met using kaolin1 as the adsorbent when starting with initial iron concentrations of 100 ppm or lower.

3.7. Effect of temperature

The effect of temperature on Fe^{3+} removal using kaolin1 was investigated at 25, 35, 45, and 55˚C. Freundlich and Langmuir isotherms at the studied temperatures are shown in Fig. 10. The Freundlich and Langmuir adsorption isotherm parameters were calculated and listed in Table 5. The Langmuir and Freundlich constants (q_{max} and K_F), which were related to the adsorption capacity, increased with increasing temperature. At the highest investigated temperature of 55˚C, the obtained value for q_{max} was 19.96 mg/g. Hence, under the investigated conditions, the process of Fe^{3+} adsorption on kaolin1 was endothermic.

3.8. Effect of particle size

Batch adsorption experiments were carried out using different zeolitic tuff particle sizes (75–106 μm, 125–180 μm, and 250–300 μm). The initial solutions concentrations were 50 and 100 ppm. The results for Fe^{3+} and Cu^{2+} removal are shown in Fig. 11. The removal of Fe^{3+} using zeolitic tuff was not affected by the particle size because the percentage removal was almost 100% for all particle sizes, while for Cu^{2+}, it was noticed that the percent of Cu^{2+} removal after 24 h increased as the particle size decreased for both investigated initial concentrations. For example, at an initial solution concentration of 100 ppm and using the smallest studied particle size (75–106 μm), the Cu^{2+} removal percentage was 97.6%, while when using the largest studied particle size (i.e. 250–300 μm), only 65.6% of Cu^{2+} was removed. Similar results were reported by Ali and El-Bishtawi [40].

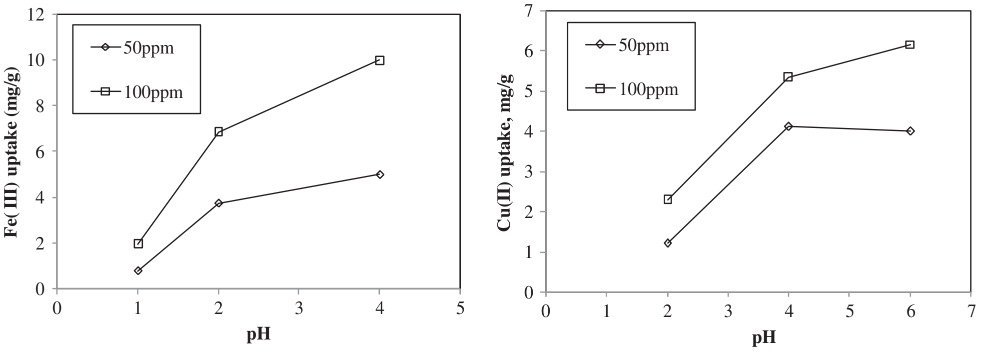

Fig. 9. Effect of pH on Fe^{3+} and Cu^{2+} uptake using kaolin1 at room temperature.

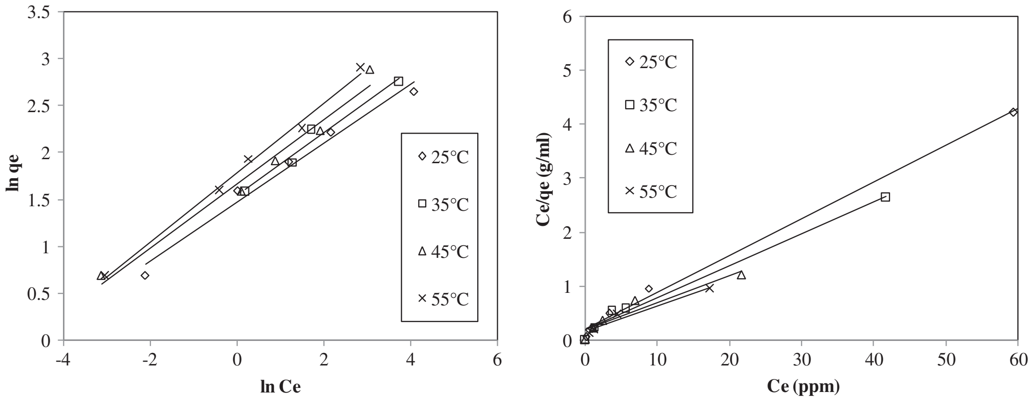

Fig. 10. Freundlich and Langmuir adsorption isotherm for Fe^{3+} uptake using kaolin1 at different temperatures (25, 35, 45, and 55 °C).

Table 5
Langmuir and Freundlich adsorption isotherm parameters for Fe^{3+} adsorption by kaolin1 at different temperatures

	Langmuir			Freundlich		
	q_m (mg/g)	b (l/g)	R^2	$1/n$	K_F ((mg/g) (mg/l)^n)	R^2
25 °C	14.6843	0.3407	0.9951	0.3145	4.3422	0.9795
35 °C	16.8919	0.3191	0.9861	0.3355	4.6730	0.9689
45 °C	19.7630	0.2697	0.9129	0.3405	5.2836	0.9765
55 °C	19.9601	0.4387	0.9505	0.3687	5.9954	0.9939

3.9. Fe^{3+} and Cu^{2+} removal vs. different conditions

A comparison was made between the Fe^{3+} and Cu^{2+} removal percentages using zeolitic tuff and kaolin1, as shown in Fig. 12. The adsorption experiments were conducted at room temperature and 55 °C with initial heavy metal concentrations of 100 ppm and contact times of 24 h. Zeolitic tuff was better than kaolin1 as an adsorbent for both Fe^{3+} and Cu^{2+} removal, indicating that the ion exchange capacity of zeolitic tuff was higher than that of kaolin1. Additionally, it is important to note that the kaolin1 adsorption capacity for Fe^{3+} removal was much better than that for Cu^{2+} removal, which could be due to the difference in the ionic radius of Fe^{3+} (63×10^{-12} m) and Cu^{2+} (87×10^{-12} m), i.e. the diffusion of Fe^{3+} ions is faster than that of Cu^{2+} ions. In addition, an enhancement in Fe^{3+} removal using kaolin1 was achieved as the

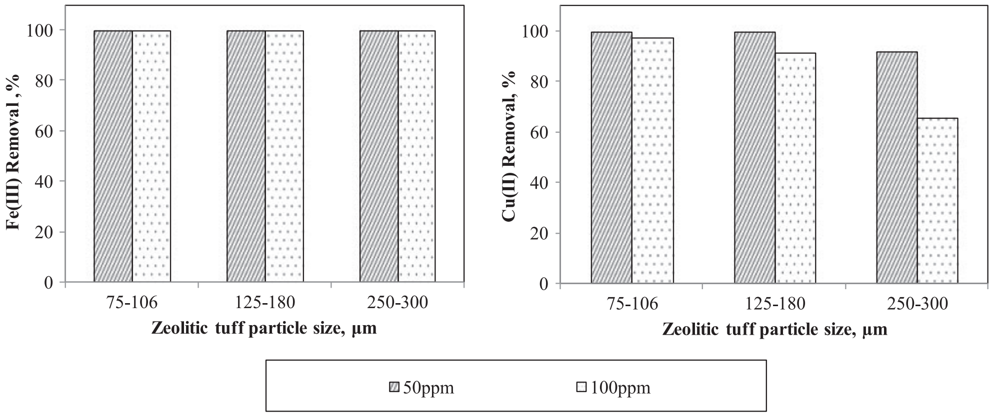

Fig. 11. Effect of particle size on Fe^{3+} and Cu^{2+} removal using zeolitic tuff at room temperature.

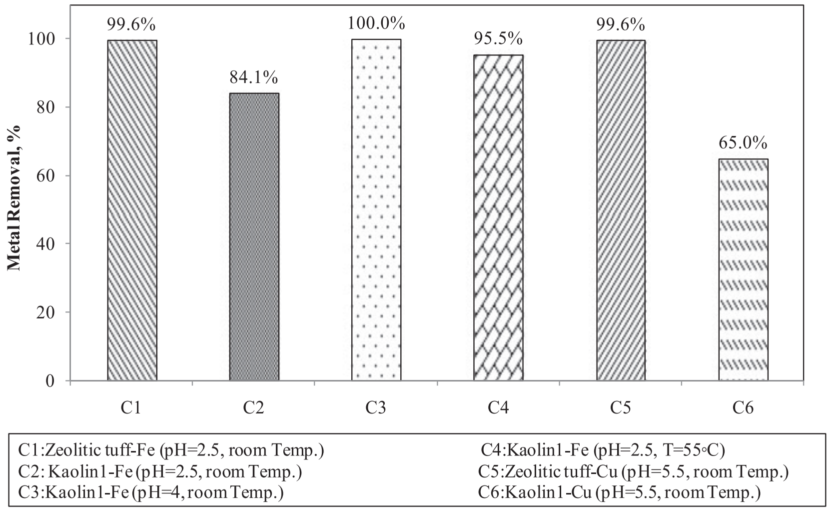

Fig. 12. Comparison between Fe^{3+} and Cu^{2+} removal percentage using zeolitic tuff (Z) and Kaolin1 (K) at different conditions, initial heavy metal concentration = 100 ppm.

temperature and pH (until pH 4) increased. The effect of the pH increase on Fe^{3+} removal was considerably higher than the temperature increase. The Fe^{3+} removal increased from 84% to almost 100% when the pH of the solution was adjusted to 4, while only 95.5% removal was achieved when the temperature was increased to 55°C.

4. Conclusions

Fe^{3+} and Cu^{2+} removals using adsorption onto Jordanian zeolitic tuff and kaolin (two different qualities 1 and 2) were successfully investigated. The Jordanian zeolitic tuff and kaolin1 are good, low-cost, and highly efficient adsorbents that can be used as alternatives to activated carbon, especially at low initial heavy metal concentrations. Kaolin1 was the best of the investigated kaolin samples for Cu^{2+} removal. Modifications of kaolin by pillaring and acid activation did not enhance Cu^{2+} removal. Zeolitic tuff had higher Fe^{3+} and Cu^{2+} adsorption capacities (20.70 and 20.83 mg/g, respectively) than kaolin1 (14.68 and 9.81 mg/g, respectively). Among the examined parameters (i.e. initial concentration, adsorbent dose, contact time, pH, temperature, and particle size), temperature and pH were the most important parameters that affect the Fe^{3+} and Cu^{2+} removals from aqueous solutions. The removal of the adsorbates (Fe^{3+} and Cu^{2+}) increased as the adsorbent concentrations increased. At constant adsorbent concentrations, the heavy metal uptake increased as the initial concentration of Fe^{3+} and Cu^{2+} increased from 20 to 200 ppm. The batch adsorption technique for Fe^{3+} removal from aqueous solutions could be used efficiently at pH ≤ 4. As the pH of the iron synthetic solution (100 ppm, pH 2.5) increased to 4, Fe^{3+} removal using kaolin1 was enhanced by 16%, while as the temperature increased to 55°C, an enhancement of only 11.5%was achieved. By increasing the pH value of the iron aqueous solutions to 4, the maximum allowable concentration limit could be met using kaolin1 as the adsorbent when starting with initial iron concentrations of 100 ppm and lower. The kinetics of Cu^{2+} adsorption onto zeolitic tuff and kaolin1 were observed, and a pseudo-second-order model was confirmed. This result indicated that chemical reaction may be the rate controlling mechanism. Additionally, particle diffusion was involved in the adsorption process. Fe^{3+} and Cu^{2+} adsorption results were well described by the linearized Langmuir and Freundlich isotherms. The increase in the Langmuir and Freundlich constants q_m and K_F with increasing temperature from 25 to 55°C during adsorption of Fe^{3+} using kaolin1 suggested an endothermic process.

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References

[1] H.K. An, B.Y. Park, D.S. Kim, Crab shell for the removal of heavy metals from aqueous solution, Water Res. 35(15) (2001) 3551–3556.

[2] F. Güzel, H. Yakut, G. Topal, Determination of kinetic and equilibrium parameters of the batch adsorption of Mn(II), Co(II), Ni(II) and Cu(II) from aqueous solution by black carrot (*Daucus carota* L.) residues, J. Hazard. Mater. 153(3) (2008) 1275–1287.

[3] L. Yan, X. Shan, B. Wen, G. Owens, Adsorption of cadmium onto Al13-pillared acid-activated montmorillonite, J. Hazard. Mater. 156(1–3) (2008) 499–508.

[4] J.D. Zuane, Handbook of Drinking Water Quality, Van Nostrand Reinhold, New York, NY, 1990.

[5] 40CFR141 and 40CFR142, National Primary Drinking Water Regulations and Implementation, US EPA Report No: 816-F-09-004, May 2009.

[6] ATSDR: Draft toxicological profile for copper [Internet], 2004 [cited 2015. Available from: <http://www.atsdr.cdc.gov>.

[7] H.H. Tran, F.A. Roddick, J.A. O'Donnell, Comparison of chromatography and desiccant silica gels for the adsorption of metal ions—I. Adsorption and kinetics, Water Res. 33(13) (1999) 2992–3000.

[8] Z. Elouear, J. Bouzid, N. Boujelben, M. Feki, F. Jamoussi, A. Montiel, Heavy metal removal from aqueous solutions by activated phosphate rock, J. Hazard. Mater. 156(1–3) (2008) 412–420.

[9] S.H. Lin, R.S. Juang, Adsorption of phenol and its derivatives from water using synthetic resins and low-cost natural adsorbents: A review, J. Environ. Manage. 90(3) (2009) 1336–1349.

[10] S. Babel, T.A. Kurniawan, Low-cost adsorbents for heavy metals uptake from contaminated water: A review, J. Hazard. Mater. 97 (2003) 219–243.

[11] T.A. Kurniawan, G. Chan, W.H. Lo, S. Babel, Comparisons of low-cost adsorbents for treating wastewaters laden with heavy metals, Sci. Total Environ. 366(2-3) (2006) 409–426.

[12] K.G. Bhattacharyya, S.S. Gupta, Adsorption of a few heavy metals on natural and modified kaolinite and montmorillonite: A review, Adv. Colloid Interface Sci. 140(2) (2008) 114–131.

[13] K.G. Bhattacharyya, S.S. Gupta, Removal of Cu(II) by natural and acid-activated clays: An insight of adsorption isotherm, kinetic and thermodynamics, Desalination 272 (2011) 66–75.

[14] C. Ma, R.A. Eggleton, Cation exchange capacity of kaolinite, J. Clays Clay Min. 47 (1999) 174–180.

[15] G. Suraj, C.S.P. Iyer, M. Lalithambika, Adsorption of cadmium and copper by modified kaolinites, Appl. Clay Sci. 13(4) (1998) 293–306.

[16] S. Wang, Z. Nan, Y. Li, Z. Zhao, The chemical bonding of copper ions on kaolin from Suzhou, China, Desalination 249(3) (2009) 991–995.

[17] K.S. Hui, C.Y.H. Chao, S.C. Kot, Removal of mixed heavy metal ions in wastewater by zeolite 4A and residual products from recycled coal fly ash, J. Hazard. Mater. 127(1–3) (2005) 89–101.

[18] M. Vaca Mier, R.L. Callejas, R. Gehr, B.E. Jiménez Cisneros, P.J.J. Alvarez, Heavy metal removal with mexican clinoptilolite, Water Res. 35(2) (2001) 373–378.

[19] R. Petrus, J. Warcho, Heavy metal removal by clinoptilolite. An equilibrium study in multi-component systems, Water Res. 39(5) (2005) 819–830.

[20] S.M. Yasin, A. Ghannam. Kaolin, Jordan Natural Resources Authority, Amman,Jordan, 2006.

[21] S.T. Bosso, J. Enzweiler, Evaluation of heavy metal removal from aqueous solution onto scolecite, Water Res. 36(19) (2002) 4795–4800.

[22] R.S. Bowman, G.M. Haggerty, R.G. Huddleston, D. Neel, M. Flynn, Sorption of nonpolar organics, inorganic cations, and inorganic anions by surfactant-modified zeolites, in: D.A. Sabatini, R.C. Knox, J.H. Harwell, Surfactant-enhanced Remediation of Subsurface Contamination, in: ACS Symposium Series 594, American Chemical Society, Washington, DC, 1995, pp. 54–64.

[23] M.K. Nawasreh, S.M. Yasin, N.A. Zurquiah, Zeolitic Tuff, Jordan Natural Resources Authority, Amman, Jordan, 2006.

[24] M.M. Hussein, K.M. Khader, S.M. Musleh, Characterization of raw zeolite and surfactant-modified zeolite and their use in removal of selected organic pollutants from water, Int. J. Chem. Sci 12(3) (2014) 815–844.

[25] M. Al-Harahsheh, R. Shawabkeh, A. Al-Harahsheh, K. Tarawneh, M.M. Batiha, Surface modification and characterization of Jordanian kaolinite: Application for lead removal from aqueous solutions, Appl. Surf. Sci. 255(18) (2009) 8098–8103.

[26] H. Freundlich, Über die Adsorption in Lösungen (Adsorption in solutions), Z. Phys. Chem. 57 (1906) 385–470.

[27] N. Kannan, T. Veemaraj, Removal of lead(II) ions by adsorption onto bamboo Dust and commercial activated carbons—A comparative study, E-J. Chem. 6(1) (2009) 247–256.

[28] M.A. Al-Anber, Removal of high-level Fe^{3+} from aqueous solution using natural inorganic materials: Bentonite (NB) and quartz (NQ), Desalination 250(3) (2010) 885–891.

[29] Y.S. Ho, G. McKay, Pseudo-second order model for sorption processes, Process Biochem. 34(5) (1999) 451–465.

[30] G.N. Eby, Desalination, first ed., Brooks/Cole-Thomson Learning, USA, 2004, p. 216.

[31] I. Dékány, L. Turi, A. Fonseca, J.B. Nagy, The structure of acid treated sepiolites: small-angle X-ray scattering and multi MAS-NMR investigations, Appl. Clay Sci. 14(1–3) (1999) 141–160.

[32] A.K. Panda, B.G. Mishra, D.K. Mishra, R.K. Singh, Effect of sulphuric acid treatment on the physico-chemical characteristics of kaolin clay, Colloids Surf., A 363(1–3) (2010) 98–104.

[33] R.I. Yousef, M.F. Tutunji, G.A.W. Derwish, S.M. Musleh, Chemical and structural properties of Jordanian zeolitic tuffs and their admixtures with urea and thiourea: Potential scavengers for phenolics in aqueous medium, J. Colloid Interface Sci. 216(2) (1999) 348–359.

[34] W.J. Weber, J.C. Morris, Kinetics of adsorption on carbon from solution, J. Sanit. Eng. Div. 89 (1963) 31–59.

[35] F.A. Banat, B. Al-Bashir, S. Al-Asheh, O. Hayajneh, Adsorption of phenol by bentonite, Environ. Pollut. 107(3) (2000) 391–398.

[36] V.J.P. Poots, G. McKay, J.J. Healy, The removal of acid dye from effluent using natural adsorbents—I peat, Water Res. 10(12) (1976) 1061–1066.

[37] R.S. Juang, S.H. Lin, K.H. Tsao, Mechanism of sorption of phenols from aqueous solutions onto surfactant-modified montmorillonite, J. Colloid Interface Sci. 254(2) (2002) 234–241.

[38] A. Aklil, M. Mouflih, S. Sebti, Removal of heavy metal ions from water by using calcined phosphate as a new adsorbent, J. Hazard. Mater. 112(3) (2004) 183–190.

[39] M.Q. Jiang, X.Y. Jin, X.Q. Lu, Z.I. Chen, Adsorption of Pb(II), Cd(II), Ni(II) and Cu(II) onto natural kaolinite clay, Desalination 252 (2010) 33–39.

[40] A.A. Ali, R. El-Bishtawi, Removal of lead and nickel ions using zeolite tuff, J. Chem. Technol. Biotechnol. 69(1) (1997) 27–34.