Removal of copper(II) from aqueous solution by Jordanian pottery materials

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Abstract

The aim of this work was to assess the possibility of removing some heavy metals from water by a low-cost adsorbent, like Jordanian raw pottery. Five types of raw and modified pottery materials have been investigated. The effects of initial metal concentration, agitation time, pH and temperature on the removal of Cu(II) were studied. A pseudo-first order was used to test the adsorption kinetics. In order to investigate the sorption isotherm, two equilibrium models, the Freundlich and Langmuir isotherms, were analyzed. The effect of solution pH on the adsorption onto pottery was studied in the pH range 1–5. The adsorption was exothermic at ambient temperature and the computation of the parameters, ΔH, ΔS and ΔG, indicated the interactions to be thermodynamically favorable.
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1. Introduction

Heavy metals such as chromium(III), cadmium(II), zinc(II) and copper(II), etc., in wastewater are hazardous to the environments [1]. The removal of heavy metal ions from industrial wastewaters using different adsorbents is currently of great interest and is becoming more important with the increasing of industrial activities [2–4]. Many methods have been proposed for heavy metal removal. Chemical precipitation, membrane filtration, electrolytic method, chemical coagulation, ion exchange and adsorption are some of the most commonly used processes; each has its merits and limitations in application. Adsorption is one of the more popular methods for the purification process; low cost purificant-adsorbent systems are preferred. For this reason, industrial wastes and metallurgical by-products are used; also natural substances like zeolites particularly clays [5–15]. In Jordan, large deposits of clay minerals were explored in different locations. The possibility of the use of Jordanian pottery as a sorbent material for metal ions removal has been a focus of our research. A survey of the literature has shown that only very small attempt has been made to use a pottery to remove

heavy metals. Jordanian pottery was chosen due to its low cost, its granular structure, insolubility in water, chemical stability and local availability. In this work, the potential of Jordanian pottery to be used in the removal of Cu(II) from aqueous solutions was investigated. The isotherm models (i.e. Langmuir and Freundlich) and adsorption kinetics models (e.g. pseudo-first order and pseudo-second order) were used for simulating the adsorption system in the batch experiments under controlled conditions, such as pH, ionic strength, temperature and initial Cu(II) concentration. Thermodynamic data have been calculated in some cases to interpret the results.

2. Materials and methods

2.1. Sorbents and sorbates

A pottery used in this study was supplied by a factory near Zarqa (40 km Eastern Amman). Zeolite name is phillipsite and has the chemical formula $KCa(Si_5Al_3)O_{16}\cdot6H_2O$. Analytical grade reagents were used in all the experiments.

2.2. Sample preparation

Samples from alumina, zeolite, and titanium oxide were subjected to some treatments. These samples were dried in an oven

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Table 1
Labeling of pottery samples

Sample	Composition
I	100% pottery
II	90% pottery + 10% Al_2O_3
III	90% pottery + 10% zeolite
IV	90% pottery + 10% TiO_2
V	70% pottery + 30% (Al_2O_3 + TiO_2 + zeolite)

at 100 °C for a period of 24 h and crushed to a size lower than 63-μm and stored in closed amber glass bottles. The resulting samples were mixed in different quantities with a pottery as shown in Table 1.

Samples I–V were dried at room temperature for 10 days, dried in an electrical oven at 900 °C for 1 h, then the samples were kept inside the oven for 24 h. The pottery samples were crushed and ground in a ball mill.

In order to eliminate soluble components, pottery samples were treated as follows: a mixture of 100 g dried pottery samples and 2.0 L HNO_3 (0.10 M) was shaken for 24 h and pH was recorded. This step was repeated until a constant pH was achieved. Pottery samples were filtered, successively washed with doubly distilled water and dried at 150 °C for 24 h.

The chemical compositions of the raw and modified pottery were estimated by XRF (Philips Magix PW 2424). The results of XRF are listed in Table 2.

Mineralogical composition was determined by the analysis of X-ray diffractograms (Philips, PW 3040/60 X'PertPRO Console). X-ray diffractograms were recorded using Cu Kα radiator and RTMS detector X'celerator.

The stock solution of copper(II) (1000 mg L^{-1}) was prepared from analytical-grade nitrate salt in distilled water separately. The initial metal ion concentration ranged from 20 to 500 mg L^{-1}. For pH adjustments, HNO_3 and NaOH solutions were used.

2.3. Adsorption tests

Sorption experiments for Cu(II) ion on different potteries were carried out in batches as follows: 100.0 mL Cu(II) solution with different initial concentrations (50–500 ppm) was added to conical flask already containing 1.0 g of raw or modified pottery (particle size ≤ 250 μm). The mixture was mechanically shacked with a temperature-controlled water bath at various pH values (2–6). The mixtures were shaken at predetermined temperature at the rate of 120 cycles min^{-1} at the end of contact periods, final pH of suspensions (pH$_f$) were measured and

the mixtures were centrifuged at 3500 rpm for 10 min, Cu(II) concentrations of supernatants were diluted and determined using flame atomic absorption spectrometry (Unicam 929). The amount of Cu(II) adsorbed per unit mass of the adsorbent (q_e in mg g^{-1}) was computed using the following equation:

$$q_e = \frac{C_i - C_e}{m} V \tag{1}$$

where C_i and C_e are the initial and equilibrium concentrations (mg L^{-1}), m the mass of pottery (g), and V is the volume of the solution (L).

The percent adsorption (%) is calculated using the equation

$$\% \text{ adsorption} = \frac{C_i - C_e}{C_e} \times 100 \tag{2}$$

2.4. Experiments for studying adsorption kinetics

For adsorption kinetics a different set of experiments was carried out in which 100 mL of 500 ppm Cu(II) solution was adsorbed on 1.0 g of raw or modified clay's pottery with a particle size of 250 μm or less over a time period of 0–300 min following the procedure outlined in Section 2.3.

3. Results and discussion

3.1. Sorption kinetics

Preliminary experiments were carried out to determine the time of equilibrium for sorption. The kinetics of the interactions were studied by determining the amount adsorbed at different agitation times for various amounts of the adsorbent at constant Cu(II) concentration. The order of adsorbate–adsorbent interactions has been described by using various kinetic models. Traditionally, the pseudo-first order model derived by Lagergren [16] has found wide application. On the other hand, several authors [17–19] have shown that second-order kinetics can also very well describe these interactions in certain specific cases. When adsorption is preceded by diffusion through a boundary, the kinetics in most cases follow the pseudo-first order rate equation of Lagergren:

$$\frac{dq_t}{dt} = k_{ads}(q_e - q_t) \tag{3}$$

where q_e and q_t (mg g^{-1}) are the amounts of Cu(II) adsorbed at equilibrium and at any time t (min), and k_{ads} (min^{-1}) is the first-order adsorption rate constant. The integrated rate law, after

Table 2
Chemical compositions (wt.%) of raw and modified pottery

Clay's type	SiO_2	Al_2O_3	TiO_2	K_2O	MgO	CaO	Fe_2O_3	Others
I	60.41	13.87	1.851	2.35	1.31	10.84	8.67	0.70
II	50.03	25.88	1.72	1.83	1.08	11.57	7.24	0.65
III	69.24	7.92	2.75	2.27	2.27	4.83	9.69	1.03
IV	41.79	10.63	26.96	1.56	1.03	9.91	7.52	0.60
V	36.94	19.98	25.42	1.52	1.60	6.07	7.71	0.76

Table 3
Adsorption kinetic parameters by Lagergren equation

Clay's type	k_{ads} (min^{-1})/r^2			q_e (mg g^{-1})		
	25 °C	35 °C	45 °C	25 °C	35 °C	45 °C
I	0.0013/0.891	0.0026/0.910	0.0032/0.884	7.928	7.291	5.488
II	0.0025/0.925	0.0021/0.919	0.0041/0.983	7.273	11.423	15.475
III	0.0011/0.979	0.0030/0.989	0.0031/0.926	7.314	12.911	16.369
IV	0.0025/0.951	0.0025/0.945	0.0036/0.974	3.639	5.815	6.422
V	0.0028/0.948	0.0049/0.928	0.0047/0.916	6.548	10.194	15.718

applying the initial condition of $q_t = 0$ at $t = 0$; is

$$\ln(q_e - q_t) = \ln q_e - k_{ads}t \qquad (4)$$

The linear plot of $\ln(q_e - q_t)$ versus t at three different temperatures (25, 35 and 45 °C) shows the applicability of the Lagergren equation as shown in Fig. 1 (Table 3).

3.2. Adsorption isotherm

The sorption isotherm represents the relationship between the amount adsorbed by a unit weight of solid sorbent and the amount of solute remaining in the solution at equilibrium. Both Langmuir and Freundlich isotherm models have been shown to be suitable for describing short-term and monocomponent adsorption of metal ions by different materials [10,20–24]. So, in order to investigate the sorption capacity of pottery, these equilibrium models were fitted to the experimental data. Applicability of the isotherm equations was compared by using the correlation coefficients, R^2.

3.2.1. Langmuir model

The Langmuir equation is the most widely used two-parameter equation, commonly expressed as

$$\frac{C_e}{q_e} = \frac{1}{Q_o b} + \frac{C_e}{Q_o} \qquad (5)$$

where C_e is the equilibrium concentration of Cu^{2+} remaining in the solution (mg dm^{-3}). q_e is the amount of adsorbate adsorbed per mass unit of adsorbent at equilibrium (mg g^{-1}). Q_o and b are Langmuir constants. Langmuir equation can be used to calculate the maximum adsorption Q_o (mg g^{-1}) and the energy parameter

of adsorption b (dm^3 mg^{-1}). From a plot of C_e/q_e versus C_e, b and Q_o can be determined from its slope and intercept.

The linear plots of C_e/q_e versus C_e for different adsorbents (Fig. 2) suggests the applicability of the Langmuir adsorption isotherm and indicates the formation of monolayer coverage of the sorbate at the outer surface of the sorbent. The straight line plot shows the applicability of the model for adsorbents studied. Langmuir monolayer adsorption capacity (Q_o) for samples I–V were in the order III < I < V < IV < II.

The last trend indicates that the addition of TiO$_2$ or Al$_2$O$_3$ to the raw pottery will increase the adsorption capacity, while the addition of zeolite will reduce its capacity toward heavy metal that studied.

The adsorption equilibrium parameter, b, shows a decreasing trend of 0.0866 to 0.794 L mol^{-1} with the following tend II < V < I < IV < III.

Langmuir constants and correlation coefficients are given in Table 4.

3.2.2. Freundlich model

The Freundlich isotherm is an empirical equation and shown to be satisfactory for low concentrations. Freundlich isotherm model has the following linear form:

$$\log q_e = \log k_F + (1/n) \log C_e \qquad (6)$$

where C_e and q_e have the same meaning; k_F and $1/n$ are constants that are considered to be relatively indicators of adsorption capacity (or related to the bonding energy) and adsorption intensity, respectively. A value for $1/n$ below one indicates a

Fig. 1. Lagergren plot for adsorption of Cu^{2+} on clay's pottery at 25, 35, 45 °C (powder amount: 1.0 g/100.0 mL).
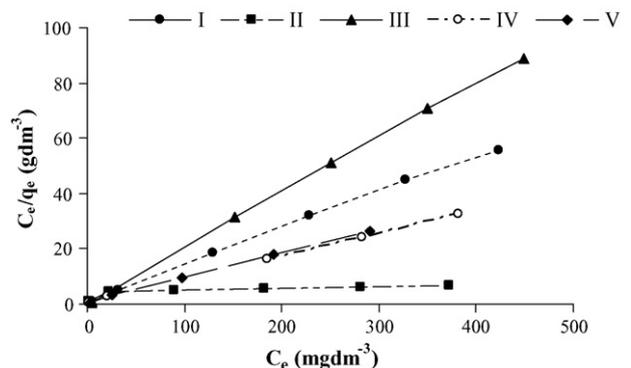
Fig. 2. Linearized form of Langmuir isotherm for the adsorption of Cu^{2+} onto raw and modified clay's pottery at 30 °C (Cu(II) concentrations of 50, 100, 200, 300, 400, 500 ppm, agitation time: 300 min).

Table 4
Isotherm constants and correlation coefficients

Clay's pottery	Langmuir isotherm			Freundlich isotherm		
	Q_o 6 (mg g^{-1})	b (L mol^{-1})	r^2	k_F	$1/n$	r^2
I	7.5529	0.1434	0.9985	4.1816	0.1017	0.8659
II	12.837	0.0866	0.9970	4.680	0.1736	0.9872
III	5.005	0.7938	0.9995	4.361	0.0222	0.9691
IV	11.9904	0.1445	0.9997	4.354	0.177	0.9814
V	11.236	0.1232	0.9993	4.007	0.1951	0.9691

Langmuir-type isotherm because it becomes more and more difficult to adsorb additional adsorbate molecules at higher adsorbent at constant [25]. A plot of $\log q_e$ versus $\log C_e$ (Fig. 3) enables the empirical constants k_F and $1/n$ to be determined from the slope and intercept of the linear regression.

The numerical value of $1/n < 1$ indicates that adsorption capacity is only slightly suppressed at lower equilibrium concentrations. Saturated pottery materials with adsorbed Cu(II) ion was no evident by this isotherm; thus infinite coverage is predicted mathematically; indicating multilayer adsorption on the surface [26].

Four isotherm constants, Q_o, b, k_F and $1/n$ shown in Table 4 can be evaluated from the linear plots represented by Eqs. (5) and (6), respectively.

Table 4 also presents the results of the Langmuir and Freundlich models, indicating the satisfactory good correlation between the Langmuir model and the experimental data. Obviously, it can be seen that the Langmuir model yields a somewhat better fit than the Freundlich model as shown in Fig. 4.

3.3. Effect of pH

The removal of metal ions from aqueous solution by adsorption is dependent on the pH of the solution. Experiments with solution pH as a variable were also conducted to determine the optimum pH range for maximum Cu adsorption by raw and modified pottery. Graphical representation of the adsorption data for Cu ions on raw and modified pottery over the studied pH range is shown in Fig. 5. In the present work, adsorption could not be carried out beyond pH 5.0 due to precipitation of Cu(OH)$_2$

Fig. 4. Adsorption isotherm of Cu^{2+} onto clay's pottery at 30 °C (Cu(II) concentrations of 50, 100, 200, 300, 400, 500 ppm, agitation time: 300 min).

and therefore, the experiments were done in the pH range 1.0–5.0.

The results reveal that adsorption increases with the increase in pH from 1 to 5 and the maximum adsorption is at pH 5, but we chose pH 4 to avoid hydrolysis of Cu(II) [26].

3.4. Effect of temperature

The thermodynamic parameters such as Gibbs energy (ΔG), enthalpy (ΔH) and entropy changes (ΔS) for the adsorption process can be determined using following equations [27,28]:

$$\ln b = \ln b' - \frac{\Delta H}{RT} \tag{7}$$

$$\ln b = -\frac{\Delta G}{RT} \tag{8}$$

Fig. 3. Linearized form of Freundlich isotherm for the adsorption of Cu^{2+} onto modified clay's pottery at 30 °C (Cu(II) concentrations of 50, 100, 200, 300, 400, 500 ppm, agitation time: 300 min).
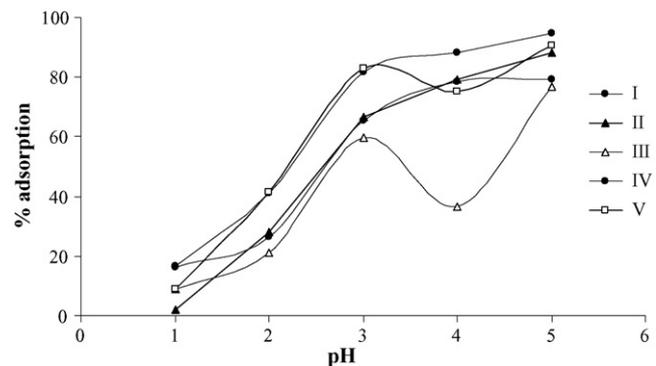
Fig. 5. Effect of pH on adsorption of Cu(II) on pottery at 25 °C (Cu(II): 100 ppm, adsorbent: 1.0 g, agitation time: 300 min).

Table 5
Thermodynamic parameters for the uptake of Cu(II) over pottery

Adsorbent	ΔG (kJ mol^{-1})			ΔH (kJ mol^{-1})	ΔS (J K^{-1} mol^{-1})
	30 °C	40 °C	50 °C		
I	4.865	6.288	9.336	−85.219	−298.1
IV	5.277	6.804	8.854	−65.613	−234.3
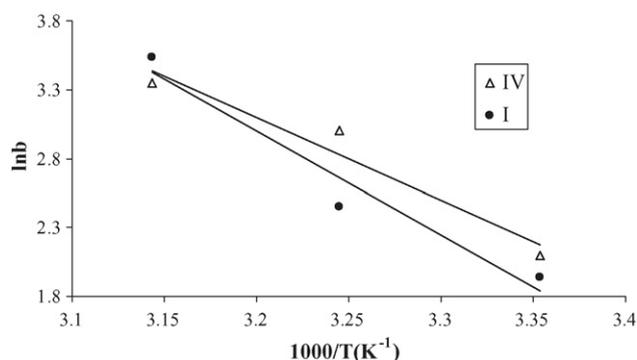
Fig. 6. Variation of ln b vs. $1/T$ (agitation time: 300 min, powder amount: 1.0 g/100.0 mL).

$$\Delta S = \frac{1}{T}(\Delta H - \Delta G) \qquad (9)$$

where b is the equilibrium constant at different temperatures obtained from the slopes of adsorption isotherms at different concentrations.

The enthalpy change (ΔH) is determined graphically by plotting ln b versus $1/T$ (Fig. 6) which gives a straight line and the values of ΔG and ΔS computed numerically are presented in Table 5.

Gibbs energy values (ΔG) are very small and positive, and increases with increase of temperature. This indicated that better adsorption is obtained at higher temperature. Adsorption of Cu(II) on pottery decreased when the interaction temperature was increased from 30 to 45 °C (Fig. 6). The process was thus exothermic in nature with heats of adsorptions −85.219 and −65.613 kJ mol^{-1}, for pottery I and IV, respectively. The process was accompanied by a decrease in entropy (ΔS values 298 and 234 J K^{-1} mol^{-1} for pottery I and IV, respectively). Which could be attributed to the higher degree of ordering of the small number of the Cu(II) molecules on the solid phase compared to their ordering in the aqueous phase.

4. Conclusions

Results indicate that pottery shows the following adsorption affinity order for Cu(II): II > IV > V > I > III.

The equilibrium adsorption isotherm of copper onto natural and modified Jordanian pottery is well described by Langmuir and Freundlich model, but Langmuir model fits the experimental data better than Freundlich model. Thermodynamic calculations show that the copper sorption process by pottery was exothermic in nature with the copper removal capacity decreasing with increasing temperature. The enthalpy change for the adsorption process ΔH has a large values (−85 and −65 kJ mol^{-1}) indicate very strong chemical forces between the adsorbed Cu(II) molecules and the pottery surface.

Therefore, pottery may be used to remove trace amounts of Cu(II) from aqueous solution.

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