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Adsorption of copper (II) ions on montmorillonite and sepiolite clays: equilibrium and kinetic studies

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ABSTRACT

The removal of Cu(II) with montmorillonite and sepiolite clays in aqueous solutions has been studied. The optimum conditions for adsorption using a batch method were evaluated by changing various parameters such as contact time, adsorbent amount, initial pH of the solution and initial metal concentration. The equilibrium adsorption data were analyzed by Langmuir, Freundlich and Temkin adsorption isotherm models. By comparing the Akaike's Information Criterion (AIC) and the sum of error squared (SSE) of these models in the three kinetic systems. The Freundlich isotherm best describe the adsorption of Cu(II) on montmorillonite and sepiolite. The adsorption kinetic data were modeled using the Lagergren-first order, pseudo-second order, and Elovich. Adsorption data of the Cu(II) were fitted well by the Elovich model. The results indicate that montmorillonite and sepiolite are good adsorbents for Cu(II) in aqueous solutions.

Keywords: Copper; Montmorillonite; Sepiolite; Adsorption; Isotherm; Kinetics

1. Introduction

The release of heavy metals such as Ni(II), Cu(II), Zn(II), Pb(II), and Co(II) into the environment in aqueous waste streams is a potential threat to water and soil quality as well as to plant, animal, and human health. Unlike organic pollutants, heavy metal ions are not biodegradable and tend to accumulate in living organisms, leading to several types of disseases and disturbances [1,2]. Copper ions represent a hazardous pollutant in wastewater and are released by metallurgical, plating, printing circuits and mining activities. This element is one of the principal heavy metals responsible for degrading the environment. High concentrations of copper have been observed to have a detrimental effect on fish and other marine creatures because they cause extensive damage to the gills, liver, kidneys, and nervous system [3,4]. The heavy metal level in drinking water, wastewater, and water used for agriculture must be reduced to at least the lowest permissible concentrations. The EPA requires that copper in drinking water not exceed 1.3 mg l^{-1} [4–9].

Numerous techniques and treatment technologies have been developed to remove heavy metals from wastewaters, including chemical precipitation, ion exchange, membrane separation, chemical coagulation, solvent extraction, complexation/sequestration, cementation, electrochemical operation, coagulation-flocculation, biological treatment, and adsorption [10–14]. One of the major methods for the removal of pollutants from aqueous effluent is adsorption by using porous solid adsorbents. Adsorption has demonstrated its efficiency,

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easy handling, availability of different adsorbents, and economic feasibility as a wastewater treatment process compared to the other purification and separation methods, and has gained importance in industrial applications [15–17]. Many natural and synthetic materials are used for this method. Recently, several low-cost and nonconventional natural materials, industrial by-products, and agricultural wastes have gained importance [15,18]. Studies so far have focused on adsorbents such as alumina, magnetite, silica, goothite, bentonite, activated carbon, clay, perlite, zeolite, sawdust, banana and orange peels, rice husks, fly ash, red mud, tea industry waste, bagasse fly ash, phosphogypsum, sepiolite, kaolinite, and others [5,6,19–24].

Clays are hydrous aluminosilicates broadly defined as those minerals that make up the colloid fraction of soils, sediments, rocks and water [25,26]. Clays are widely used in polymer nano-composites, adsorbents for heavy metal ions, catalysts, photochemical reaction field ceramics, paper filling and coating, sensors and biosensors, because of their high specific surface area, chemical and mechanical stabilities, and various surface and structural properties [27,28]. Clay's structure is layered with interlayer spaces, and the layers may be electrically neutral or charged. The high specific surface area, chemical and mechanical stability, variety of structural and surface properties and higher values of cation exchange capacities make clays excellent group adsorbents for removing various metals and organic compounds. The smectite group is a family of nonmetallic clays primarily composed of hydrated sodium calcium aluminum silicate, a group of monoclinic clay-like minerals with the general formula of $(Ca,Na,H)(Al,Mg,Fe,Zn)_2(Si, Al)_4O_{10}(OH)_2.nH_2O$. Naturally occurring clays are used as sorbents for the removal of various metals and organic compounds due to their high specific surface areas. Montmorillonite (MMT) is a member of the general mineral group of the clays. Chemically, it is hydrated sodium calcium aluminium magnesium silicate hydroxide $[(Na, Ca)_{0.33}(Al,Mg)_2(Si_4O_{10})(OH)_2.nH_2O]$. Owing to the crystal chemical features of MMT, heavy metal retention by the mineral can occur by adsorption and/or cation exchange reaction. The ability of MMT to adsorb heavy metal ions from water is significant for the removal of toxic pollutants from the environment [12,26,29]. Sepiolite $[(Si_{12}O_{30}Mg_8(OH)_4(H_2O)_48H_2O)]$ is a natural, fibrous clay mineral with fine microporous channels with dimensions of 0.37 × 1.06 nm running parallel to the length of the fibers. This mineral is widely used to remove undesired components from household and industrial wastewaters and in various industrial manufacturing processes, such as removing some organic matters from wastewater, heavy metals, ammonium and phosphate, color and other undesirable components, dyes, phenol, and lignin. Studies conducted recently showed that sepiolite can retain a significant amount of Cu(II), Zn(II), Cd(II), Co(II) and Pb(II) ions from aqueous solutions [30,31]. Most of the world's sepiolite reserves are in Turkey. Thus it is important characterize this clay mineral and evaluate how important physicochemical properties are altered during chemical and thermal treatment [30,32–34].

The object of this study is to investigate the efficiency of two clays from Turkey in removing copper ions from aqueous solutions. The effects of contact time, adsorbent dosage, pH and metal ion concentration on the adsorption process were examined. Experimental data have been analyzed by adsorption isotherms and kinetics parameters.

2. Materials and methods

2.1. Materials

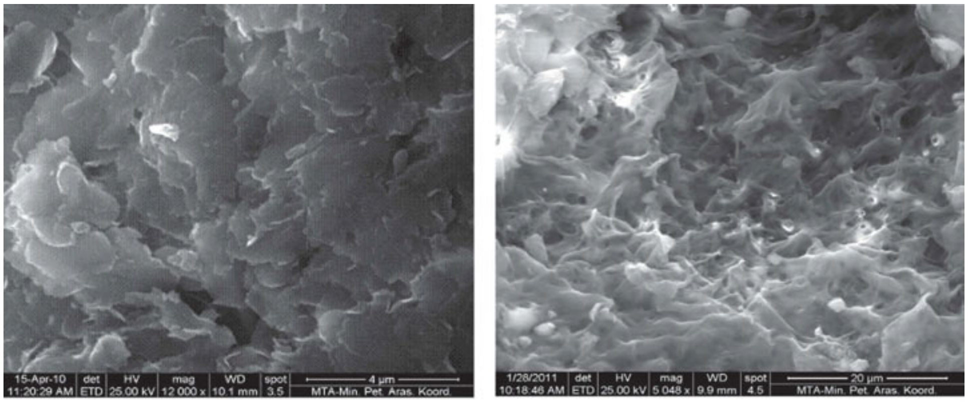
The adsorbents used for the Cu(II) uptake were local two raw minerals: montmorillonite (Samsun) and sepiolite (Eskişehir). They were crushed into small pieces from rock forms and then powdered in a mortar. Prior to batch adsorption experiments, the adsorbents were washed with distilled water in order to remove the surface dust, and dried at 103°C. The chemical compositions of these materials are given Table 1. In BET measurements, 82.35 and 73.92 $m^2 g^{-1}$ values were obtained for sepiolite and montmorillonite, respectively. SEM analyses (scanning electron microscopy) of sepiolite and montmorillonite are given in Fig. 1.

2.2. Method

The Cu(II) solutions used in experiments were prepared by dissolving $CuCl_2.6H_2O$ in distilled water. The pH of the solutions was adjusted with HNO_3 (Merck) or NaOH (Merck) solutions by using a WTW 330 pH-meter with a combined pH electrode. An ATI-UNICAM 929

Table 1
Chemical composition of montmorillonite and sepiolite samples (wt.%)

Major components	Montmorillonite	Sepiolite
SiO_2	57.80	53.47
Al_2O_3	1.70	0.19
Fe_2O_3	7.90	0.16
CaO	1.50	0.71
MgO	2.40	23.55
K_2O	1.60	–
Na_2O	0.50	–
TiO_2	0.80	–
others	25.6	21.49



a) montmorillonite b) sepiolite

Fig. 1. SEM microphotograph of montmorillonite and sepiolite crystals with drusy texture.

model Atomic Absorption Spectrophotometer (AAS) was used for dentifying Cu(II) ions.

The effects of contact time in the range of 5–480 min were studied using a constant concentration of copper violet solution at 25°C. Adsorption experiments were performed by shaking 0.125–4.0 g of montmorillonite and sepiolite samples in a 100 ml of aqueous solutions of Cu(II). The effect of pH on the copper adsorption was investigated using 50 mg l^{-1} Cu(II) containing solution over the pH range of 3.0–9.0. The pH of copper solutions was adjusted by appropriate using HNO_3 or NaOH. Batch mode adsorption isotherm and kinetic studies were carried out at 25°C. Adsorption isotherms were performed for initial Cu(II) concentrations of 12.5, 25, 50, 100, 200, and 400 mg l^{-1}. After the adsorption period, the mixtures were filtered with a 0.45 *m*m filter and acidified with HNO_3 to decrease the pH to below two before the AAS measurement was taken.

To obtain the adsorption capacity, the amount of copper adsorbed on the montmorillonite and sepiolite (mg g^{-1}) was calculated using the following expression:

$$q_e = \frac{(C_o - C_e)V}{m} \tag{1}$$

where C_o and C_e are the initial and equilibrium concentrations of copper in the solution, respectively (mg l^{-1}), V is the volume of solution (l), and m is the weight of the adsorbent (g).

3. Results and discussion

3.1. Effect of contact time

Time dependent experiments for metal ions removal were investigated to understand adsorption behavior of montmorillonite and sepiolite with Cu(II). Fig. 2 shows the plot of the copper ion sorbed q_e (mg g^{-1}) as a function of the time. The contact time ranges between 5 and 480 min. The results showed that the adsorption of Cu(II) increases rapidly with time (in the first 30 min) and reaches saturation in about 120–240 min.

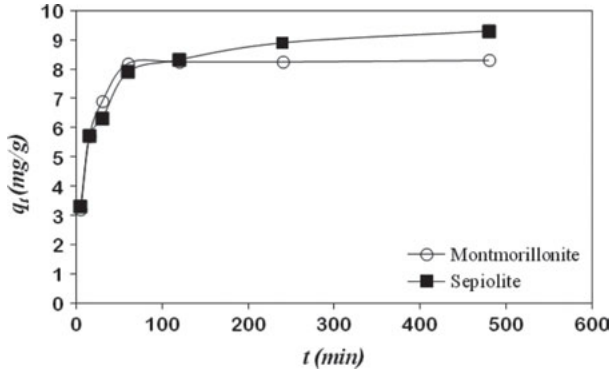


Fig. 2. Effect of contact time on the adsorption capacity (Co: 50 mg l^{-1}, adsorbent amount: 5 g l^{-1}).

3.2. Effect of adsorbent dosage

Fig. 3 presents the effect of the amount of montmorillonite and sepiolite dosages on the copper removal. As it can be seen from Fig. 3 the adsorption capacity of Cu(II) decreased with the increase adsorbent dosage. The adsorption capacities for 1.25 g l^{-1} of montmorillonite and sepiolite were found to be 8.96 and 9.44 mg g^{-1}, respectively but as the montmorillonite and sepiolite amounts were increased to 20 g l^{-1}, adsorption capacities were found to be 2.42 and 2.48 mg g^{-1}, respectively. From Fig. 3, the decrease the adsorbed amount with the increase in adsorbent dosage may result from the electrostatic interactions, interference between binding sites, and reduced mixing at higher adsorbent densities. Also, the reason for decrease in the sorption capacity was due to the increasing interface area when the suspension was diluted [34–36].

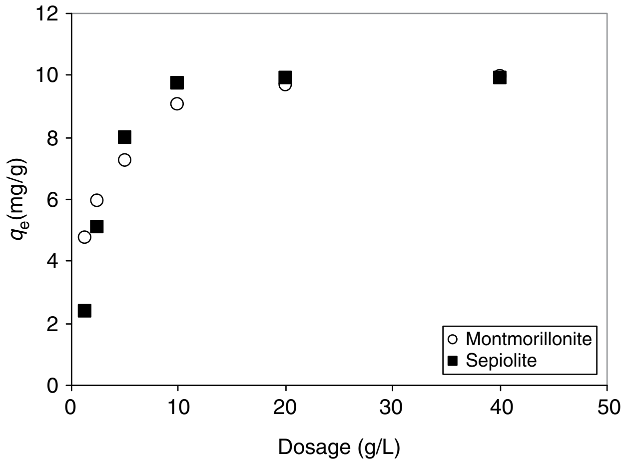


Fig. 3. Effect of adsorbent dosage on the adsorption capacity (Co: 50 mg l^{-1}, contact time: 4 h).

3.3. Effect of pH

It is well known that the pH of the aqueous solution is an important controlling parameter in the adsorption and ion exchange processes, and metal removal typically increases with increasing pH values. The removal efficiency of metal ions generally increased with increasing pH to a pH of around 7–8, and then increased only slowly thereafter, with further pH increases resulting in precipitation [4,5,37–39]. The effect of hydrogen ion concentration on removal of Cu(II) ions from solutions was studied at pH levels ranging from 3 to 9; Cu(II) precipitates at pH levels higher than 7. The effect of pH on Cu(II) adsorption by natural clays is given in Fig. 4, which shows that adsorption capacity of both materials increased the initial pH of the solution from 3 to 5 and reached a maximum in the pH range of 7–9.

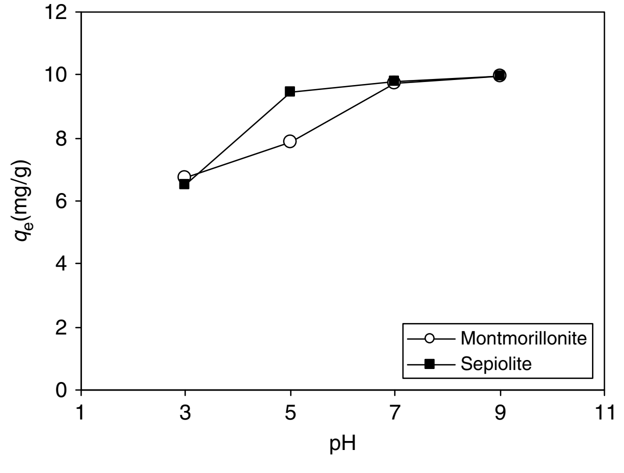


Fig. 4. Effect of pH on the adsorption capacity (Co: 50 mg l^{-1}, contact time: 4 h).

The selectivity of metal ion by clays is influenced by the character of the metal complex that predominates at a particular solution pH. The adsorption capacity generally increased when the initial pH of the solution was increased. As the pH is lowered, the hydrogen ions compete with the metal ions for the sorption sites in the sorbent and may hinder the binding of positively charged metal ions. Similar adsorption mechanisms have been reported by various authors [5,12,40].

As the pH increased to 6.0 some Cu(II) may attach to OH^- mainly because Cu(II) can be best precipitated as hydroxides at pH 6., leading to a lower removal rate (Zhang et al., 2009). We also suggested that the separation should be carried out at acidic conditions. This removal involved the testing of the of the adsorption of the monomeric and dimeric hydrolytic complexes of the Cu(II) along with the uncomplexed copper (II) cation. For example, the complex reactions of copper ion [Cu(II)] are listed as follows [41]:

([S] sepiolite, [M] montmorillonite)

$$\text{[S] [M]-OH} + Cu^{2+} \leftrightarrow \text{[S] [M]-}O^- Cu^{2+} + H^+$$

$$\text{[S] [M]-}O^- + Cu^{2+} \leftrightarrow \text{[S] [M]-}O^- Cu^{2+}$$

$$2(\text{[S] [M] –OH}) + Cu^{2+} \leftrightarrow (\text{[S] [M] –}O^-)_2\, Cu^{2+} + 2H^+$$

$$2(\text{[S] [M] –}O^-) + Cu^{2+} \leftrightarrow (\text{[S] [M] –}O^-)_2\, Cu^{2+}$$

3.4. Effect of initial metal concentration

The results are presented in Fig. 5, which shows that the amount adsorbed of Cu(II) increased with increasing metal ion concentration. The higher the initial metal ion concentration, the larger the metal ion sorbed per unit weight of adsorbent at equilibrium. The adsorption capacities for 25 mg l^{-1} of montmorillonite and sepiolite were found to be 4.14 and 4.52 mg g^{-1}, respectively but as the initial metal ion concentration were increased to

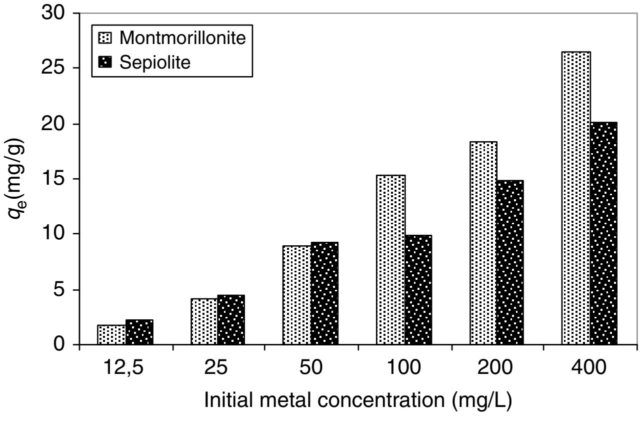


Fig. 5. Effect of initial metal concentration on the adsorption capacity (Dosage: 5 g l^{-1}, contact time: 2 h).

100 mg l^{-1}, adsorption capacities were found to be 15.28 and 9.92 mg g^{-1}, respectively. The adsorption capacities for 400 mg l^{-1} of montmorillonite and sepiolite samples were found to be 26.5 and 20.1 mg g^{-1}, respectively. It can be explained by the saturation of the sorption sites on the adsorbent as the concentration of the metal increased. Also, there are number of exchangeable sites in clay structure at low Cu(II)/montmorillonite and sepiolite ratios. As Cu(II)/montmorillonite and sepiolite ratio increases, exchangeable sites are saturated, resulting in a decrease in the adsorption efficiency.

3.5. Adsorption isotherm

The equilibrium adsorption isotherms are among the most important data to understanding the mechanism of the adsorption systems. Adsorption isotherms give an idea about the adsorption capacity of an adsorbent for the removal of some compounds. The sorption data have been subjected to different sorption isotherms [34,42]. In this research, to determine the mechanism of copper adsorption on montmorillonite and sepiolite, the experimental data were applied to the Langmuir, Freundlich, and Temkin isotherm equations.

The data conform to the linear form of Langmuir model [Eq. (2)] expressed below:

$$\frac{C_e}{q_e} = \frac{1}{q_m K_L} + \frac{C_e}{q_m} \tag{2}$$

where, q_e is the amount adsorbed per unit weight of adsorbent (mg g^{-1}), C_e is the equilibrium concentration of adsorbate in solution after adsorption (mg l^{-1}), and q_m and K_L are the Langmuir constants related to the saturated monolayer sorption capacity and the sorption equilibrium constant, respectively. Linear plots of C_e/q_e vs. C_e were employed to determine the value of q_m and K_L (Fig. 6a). The data for the sorption of metal ion by the clays has been processed in accordance with a linear form of the Langmuir isotherm equation. The linear model, which describes the accumulation of solute by the sorbent was shown to be directly proportional to the solution concentration [11]. The essential characteristics of Langmuir isotherm can be expressed in terms of a dimensionless constant separation factor, R_L, which is defined as:

$$R_L = \frac{1}{(1 + K_L C_o)} \tag{3}$$

where C_o is the initial concentration and K_L is the Langmuir isotherm constant. The feasibility criteria of the process can be judged as unfavorable ($R_L > 1$), irreversible ($R_L = 0$), favorable ($0 < R_L < 1$) or linear ($R_L = 1$) patterns. The R_L values varied within a range of, 0.662–0.057 and 0.537–0.034 for montmorillonite and sepiolite, respectively, for the initial Cu(II) concentration values of 12.5–400 mg l^{-1}. They are in the range of 0–1, which indicates favorable adsorption.

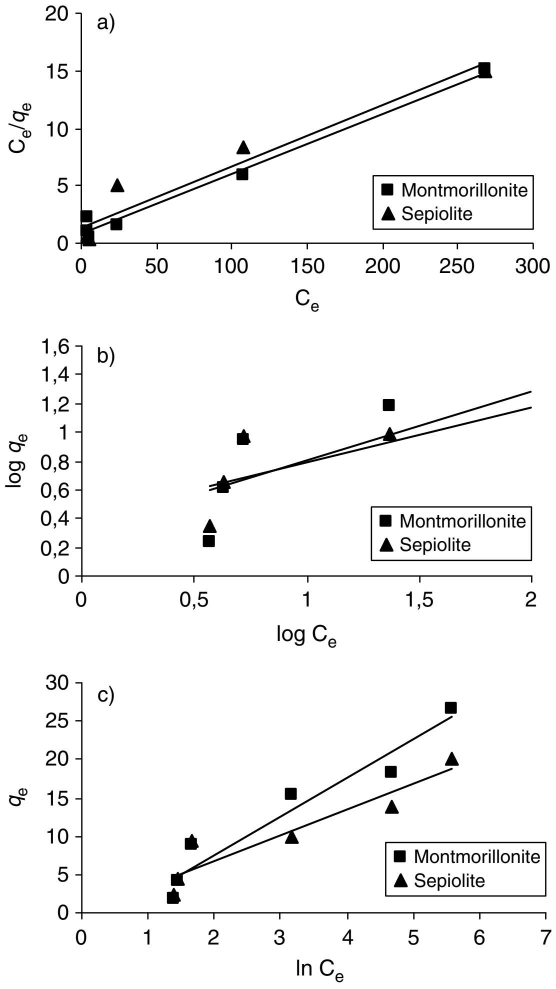


Fig. 6 (a) The Linearized Langmuir isotherm of Cu(II) uptake by montmorillonite and sepiolite. (b) The Linearized Freundlich isotherm of Cu(II) uptake by montmorillonite and sepiolite. (c) The Linerized Temkin isotherm of Cu(II) uptake by montmorillonite and sepiolite.

The Freundlich equation assumes a heterogeneous surface with a non-uniform distribution of heat of adsorption. Freundlich isotherm in logarithmic form is given as Eq. (4):

$$\log q_e = \log K_F + \frac{1}{n} \log C_e \tag{4}$$

where q_e is the amount of metal ions adsorbed per gram of adsorbent at equilibrium (mg g^{-1}), C_e is the equilibrium concentration in mg l^{-1}, and K_F and n were the empirical Freundlich constants indicative of adsorption capacity and adsorption intensity, respectively. It has been established that for favorable adsorption, $n > 1$; for unfavorable adsorption, $0 < n < 1$; and for linear adsorption, $n = 1$.

Table 2.
The parameters for Langmuir, Freundlich and Temkin isotherms

Isotherms	Montmorillonite	Sepiolite
Langmuir constants		
q_m (mg g^{-1})	18.69	19.01
K_L(l mg^{-1})	0.041	0.069
R^2	0.9850	0.9311
SSE	5.03	2.49
AIC	6.94	2.72
Freundlich constants		
K_F (mg g^{-1})	2.34	2.61
$1/n$(g l^{-1})	0.485	0.378
R^2	0.7448	0.8328
SSE	5.40	2.25
AIC	7.37	2.11
Temkin constants		
A (l g^{-1})	1.62	1.01
B (j mol^{-1})	4.987	3.335
R^2	0.9326	0.8759
SSE	4.23	6.47
AIC	5.91	8.45

The value of n determined from the Freundlich isotherm was $n > 1$ as shown in Table 2, indicating that the adsorption of Cu(II) ions on montmorillonite and sepiolite is favorable [11,43,44]. Fig. 6b exhibits the Freundlich isotherm of Cu(II) adsorption on montmorillonite and sepiolite.

Temkin isotherm assumes that a decrease in the heat of adsorption is linear and the adsorption is characterized by a uniform distribution of binding energies. Temkin isotherm model is given in Eq. (5):

$$q_e = B \ln A + B \ln C_e \quad (5)$$

where $B=(RT)/b$, q_e (mg g^{-1}) and C_e (mg l^{-1}) are the amounts of adsorbed Cu(II) per unit weight of adsorbent and unadsorbed Cu(II) concentration in solution at equilibrium, respectively. Also, T, the absolute temperature in K and R is the universal gas constant, 8.314 J (mol K)$^{-1}$. The constant B is related to the heat of adsorption [2,45]. Fig. 6c exhibits the Temkin isotherm of Cu(II) adsorption on montmorillonite and sepiolite.

Comparison of adsorption capacity (q_m) for the adsorption of Cu(II) by different adsorbents are presented in Table 3.

3.5.1. Comparison of adsorption isotherms

It is customary in batch adsorption studies to fit the equilibrium uptake data to several isotherms, then to use R^2 to compare the goodness of fit and select the best isotherm model. With the best isotherm supposedly idendified, conclusions are usually presented regarding the homogeneity of the adsorbent surface and the mechanism of adsorption. Akaike's information criterion (AIC) is a well established statistical method that can be used to compare models. It is based on information theory and maximum likelihood theory, and as such, it determines which model is more likely to be correct and quantifies how much more likely. For a small sample size, AIC is calculated for each model from the equation:

$$\mathrm{AIC} = N \ln\left(\frac{\mathrm{SSE}}{N}\right) + 2N_\mathrm{p} + \frac{2N_\mathrm{p}\left(N_\mathrm{p}+1\right)}{N - N_\mathrm{p} - 1}$$

where N is the number of data points, N_p is the number of parameters in the model and SSE is sum of the error squares.

The adsorption isotherms models having two parameters can be transformed into linear forms to obtain adjustable parameters just by graphical means or by linear regression analysis. But, the models having more than two adjustable parameters are not fitted to experimental data by linear regression or graphical means. In this case it is necessary to apply nonlinear least squares analysis. For that reasons, a minimization procedure has been adopted to solve isotherms and kinetic equations by minimizing the sum of error squared (SSE) between the predicted values and the experimental data using the solver add-in function of the Microsoft Excel. The term SSE generally refers to a "sum of squared errors."

Table 3
Comparison of adsorption capacity (q_m) for the adsorption of Cu(II) by different adsorbents

Adsorbents	q_m (mg g^{-1})	Reference
Clinoptilolite	18.52	[46]
Kaolinite	4.30	[26]
Montmorillonite	7.62	[14]
Red mud	19.72	[47]
Sewage sludge	3.28	[41]
Lignite	6.35	[48]
Phosphate rock	10.80	[15]
Hazelnut shell	6.60	[18]
Perlite	1.01	[49]
Vermiculite	8.57	[50]
Fly ash	1.39	[51]
Activated carbon	38.0	[51]
Walnut shell	6.74	[11]
Montmorillonite	18.69	Present study
Sepiolite	19.01	Present study

The errors are the difference between the observed value and the value predicted by the model:

$$\mathrm{SSE} = \sqrt{\sum \left(q_{\mathrm{exp}} - q_{\mathrm{cal}}\right)^2 / N}$$

where the subscripts "exp" and "cal" are the experimental and calculated values of q, espectively and N is the number of measurements.

The results of nonlinear regression are presented in Table 2. This study concluded, on the basis of R^2 comparison to montmorillonite and sepiolite, that the Langmuir isotherm is a better fit. However, AIC would be a more sound method to compare the goodness of fit to Langmuir, Freundlich and Temkin isotherm. Accordingly, AIC values to montmorillonite and sepiolite were calculated for Langmuir (6.94 and 2.72), Freundlich (7.37 and 2.11) and Temkin (5.91 and 8.45) isotherms, respectively. Having a smaller AIC value to montmorillonite and sepiolite suggests that Temkin and Freundlich isotherms are more likely to be a better fit, respectively.

The parameters of each isotherm equation can be determined by minimizing the SSE. The best-fit model should have the least SSE value; therefore, this model can be obtained bycomparing the SSE of each model. The SSE values are compared in Table 2. By comparing the SSE of different models in the three isotherm systems, it seems that Freundlich isotherm was the best fit although the SSE for the Freundlich and the Langmuir are very similar.

3.6. Adsorption kinetics

Several kinetics models are used to examine the controlling mechanism on the adsorption process such as chemical reaction, mass transfer, and diffusion control. The parameter values obtained from the application of kinetic models were used to predict the variation of adsorbed Cu(II) ion with time using montmorillonite and sepiolite. The rate constant of each metal ion removal from the solution was determined using pseudo-first-order, pseudo-second-order, and Elovich rate models, applying those models given in literature [52–55].

The Lagergren-first-order model is one of the most widely used procedures for the adsorption of a solute from aqueous solution. The Lagergren-first order equation is written as:

$$\ln(q_{\mathrm{e}} - q_{\mathrm{t}}) = \ln q_{\mathrm{e}} - k_1 t \tag{7}$$

where q_e and q_t were the amounts of copper adsorbed (mg g^{-1}) at equilibrium and at time t, respectively and k_1 is first order rate constant for adsorption (l min^{-1}). The rate constant, k_1, were calculated from the plots of ln (q_e–q_t) versus t for copper adsorption (Fig. 7a). The pseudo-first order rate constants k_1 and correlation coefficients are presented in Table 4. The correlation coefficients for the Lagergren-first-order model are between 0.8006 and 0.9618. Therefore, that this adsorption system is not a the Lagergren-first-order model.

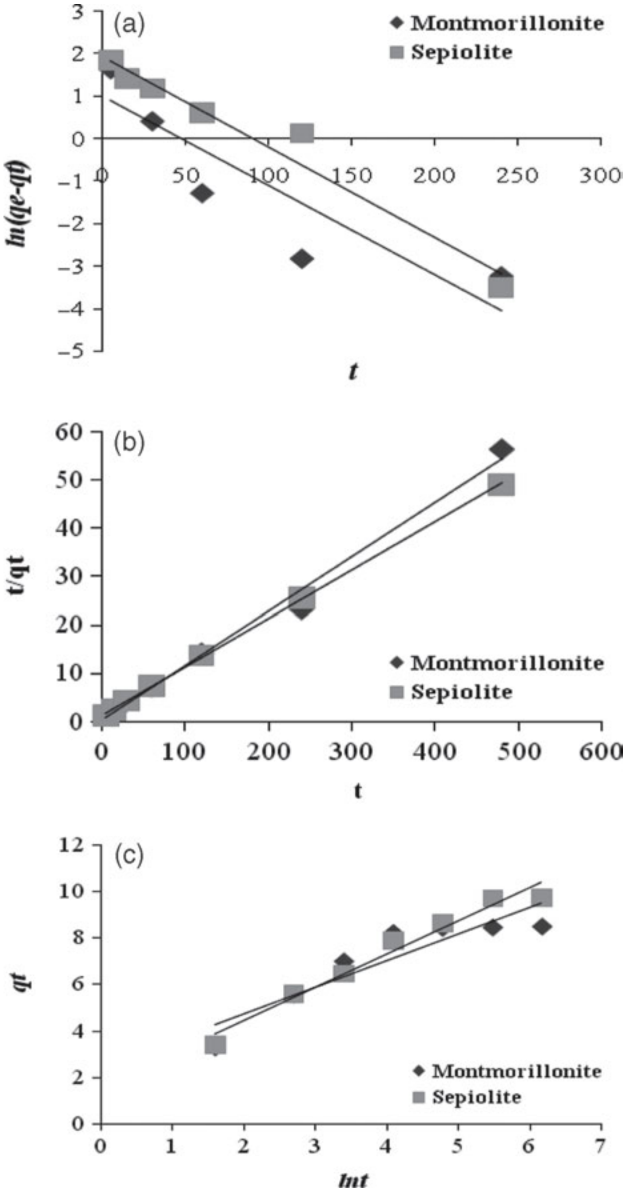


Fig. 7 (a) Linerized Lagergren first-order kinetics plots for Cu(II) adsorption (Co: 50 mg l^{-1}, 150 rpm, 293 K). (b) Linerized second-order kinetics plots for Cu(II) adsorption (Co: 50 mg l^{-1}, 150 rpm, 293 K). (c) Linerized Elovich kinetics plots for Cu(II) adsorption (Co: 50 mg l^{-1}, 150 rpm, 293 K).

Pseudo second-order kinetics may be expressed as the following equation [10,45,55–57]:

$$\frac{t}{q_{\mathrm{t}}} = \frac{1}{k_2 q_{\mathrm{e}}^2} + \frac{t}{q_{\mathrm{e}}} \tag{8}$$

where q_e and q_t are the amounts of the heavy metal (mg g^{-1}) adsorbed at equilibrium (mg g^{-1}), and k_2 [g (mg min)$^{-1}$] is

Table 4
The kinetics constants for the removal of Cu(II) by montmorillonite and sepiolite

Isotherms	Montmorillonite	Sepiolite
Lagergren-first-order		
q_e (mg g^{-1})	2.77	7.05
k_1 (I min^{-1})	0.021	0.021
R^2	0.8006	0.9618
SSE	6.62	6.99
AIC	8.57	8.91
Pseudo-second-order		
q_e (mg g^{-1})	8.86	9.97
k_2 [g (mg min)$^{-1}$]	0.034	0.007
R^2	0.9906	0.9996
SSE	1.27	0.87
AIC	–1.36	–3.62
Elovich		
a [(mg (g min)$^{-1}$]	8.56	2.94
β [g (mg)$^{-1}$]	1.14	1.43
R^2	0.8329	0.9683
SSE	0.85	0.89
AIC	–3.88	–3.42

the rate constant of the second-order kinetic equations. The pseudo-second order kinetic for Cu(II) removal using montmorillonite and sepiolite is presented Fig. 7b. The second-order kinetic rate constants k_2 and correlation coefficients are presented in Table 4. The correlation coefficients for the Pseudo second-order kinetics model are between 0.9906 and 0.9996.

The Elovich equation has general application to chemisorption kinetics. This equation has been applied satisfactorily to some chemisorption data and has been found to cover a large range of slow adsorption. The Elovich equation is often valid for systems in which the adsorbing surface is heterogeneous. The rate parameter for the Elovich equation is determined as [58–60]:

$$q_t = \beta \ln(\alpha) + \beta \ln t \tag{3}$$

where α (mgg^{-1}min^{-1}) and β (gmg^{-1}) are the equilibrium rate constants for Elovich model. The equation constants can be obtained from the slope and intercept of a straight-line plot of q_t against *ln t.* The values of constants can be obtained from the slope and intercept of the plots (Fig. 7c). The values of kinetic constants are presented in Table 4. The correlation coefficients for the Elovich model are between 0.8329 and 0.9683.

3.6.1. Comparison of adsorption kinetics

The rate constants and other parameters of the three different batch kinetic equations were obtained by minimizing SSE and AIC by using the Excel program by iteration. The results of nonlinear regression are presented in Table 4. These results clearly showed that the Pseudo second-order kinetics model provided the data better than Lagergren-first-order and Elovich kinetic models. However, AIC would be a more sound method to compare the goodness of fit to Lagergren-first-order, Pseudo second-order and Elovich kinetic models. Accordingly, AIC values to montmorillonite and sepiolite were calculated for Lagergren-first-order (8.57 and 8.91), Pseudo second-order (–1.36 and –3.62) and Elovich (–3.88 and –3.42) kinetics, respectively. Having a smaller AIC value to montmorillonite and sepiolite suggests that Pseudo second-order and Elovich kinetic models are more likely to be a better fit, respectively.

The SSE values are compared in Table 4. By comparing the SSE of these models in the three kinetic systems, it seems that Elovich kinetic model was the best fit although the SSE for the Pseudo second-order is very similar.

4. Conclusions

The aim of this study was to investigate the potential use of montmorillonite and sepiolite as a sorbent for Cu(II) was studied. The adsorption process is a function of the contact time, adsorbent amount, pH and metal ion concentration. As the montmorillonite and sepiolite amounts increased, the removal efficiencies increased. The removal efficiency of montmorillonite and sepiolite clays is strongly affected by the pH of the solution. The effect of pH of the solution could significantly improve the adsorption rate and adsorption capacity of Cu(II) ions. The maximum adsorption capacities of montmorillonite and sepiolite clays were found to be 18.69 and 19.01 mg g^{-1}, respectively. AIC is a well established statistical method that can be used to compare models. Of the two-parameter isotherm models, freundlich isotherm best describe the adsorption of Cu(II) on montmorillonite and sepiolite. The adsorption kinetic data were modeled using the Lagergren-first order, pseudo-second order and Elovich. By comparing the SSE of these models in the three kinetic systems, it seems that Elovich kinetic model was the best fit.

These result showed that montmorillonite and sepiolite clays have a special importance in terms of using a locally available, environmentally friendly material, in environmental and health protection applications, namely, water and wastewater treatment units.

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