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The adsorption of Cu(II) ions on bentonite—a kinetic study

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Abstract

The kinetics of sorption of Cu^{2+} on a Saudi clay mineral (bentonite) was investigated at $20 \pm 0.5\,^{\circ}C$ using different weights of the clay (0.5, 1.0, 1.5, and 2 g). Each weight represents a certain sample size. The order of the process appeared to be 1 with respect to the Cu^{2+}, and $1\frac{1}{2}$ with respect to the clay surface area. The rate was found to depend on internal diffusion.,which produced a decrease in the specific rate of sorption as a function of time. Sorption characteristics were described using two site Langmuir isotherms. The desorption experiments proved that Cu^{2+} ions are chemisorbed on the bentonite surface. The maximum adsorption obtained was 909 mg Cu^{2+}/g clay. This value is of great significance, as it is much higher than any reported one.
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Keywords: Bentonite; Sorption; Kinetics; Desorption; Cu^{2+} ions

1. Introduction

With the rapid increase in global industrial activities, heavy metal pollution has become serious. Among various treatment technologies, montmorillonite is commonly used, due to its relatively high surface area, cation exchange capacity, harmlessness to the environment, and ease of operation [1–3]. The adsorption properties of this clay mineral have intrigued soil scientists for over a century. Most investigators [4–6] have been interested in the total exchange capacity and equilibrium exchange relationships, but few [7–10] have studied the rate of cation exchange on clay minerals. One reason for this was the general finding [11] that cation exchange in clays occurs relatively rapidly, within 1 to 3 min. The reaction kinetics can suggest mechanistic details of the adsorption process; they are also of fundamental importance for a complete understanding of interfacial phenomena at the solid liquid interface. The main objective of this research is to determine the sorption process of Cu^{2+}

ions under different experimental conditions on a Saudi clay mineral. This allows us to predict and control the Cu^{2+} behavior on this clay surface. For this purpose, besides the equilibrium adsorption experiments that had been made, the kinetic behavior also seems to be of great interest. This interest arises from the fact that for each specific metal, the rate constant of sorption is directly related to the nature of the substrate, i.e., the surface properties of the clay.

This research was undertaken to determine a suitable expression that describes the adsorption of Cu^{2+} on this clay surface in order to delineate a predictive model regarding the kinetics of heavy metal adsorption by the clay.

Bentonite is the clay mineral that was chosen for this study. It is a soft, plastic, and porous rock. It was proved by previous X-ray analysis on this clay [15] that the dominant component is montmorillonite. The remaining components are quartz, feldspar, illite, and organic substances (10.3% all). It was found [12–17] that the untreated clay had a higher affinity for Cu^{2+} than the treated one. Therefore, the bentonite samples in this study were used in their natural state without any treatment, i.e., without saturation with any cation. This increases the adsorbent capacity, which finds many applications.

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2. Experimental work

2.1. Materials

The clay samples used in this study were collected from the Geda area, located in the southwestern region of Saudi Arabia. The untreated clay was used in its natural state. Solutions of $Cu(NO_3)_2$ and $CaCl_2$ were prepared using Analar reagents and deionized water.

2.2. Kinetic procedure

The rate of copper sorption was determined as described by Eiseman et al. [16]. Kinetic runs were started by the addition of a weighted air-dried clay sample in a 100-ml $Cu(NO_3)_2$ solution. Two milliliters of 5 M $NaNO_3$ was added to operate at constant ionic strength. Kinetic runs were carried out at constant temperature ($20 \pm 0.5\,°C$). These experiments were performed using four different weights of the clay: 0.5, 1.0, 1.5, and 2 g. Each weight represents a certain sample size value, i.e., a fixed surface area of the clay. For each sample size, three kinetic experiments were carried out, using three different initial concentrations of $Cu(NO_3)_2$: 60, 80, and 100 ppm.

Changes in metal ion concentration in the solution as a function of time were followed using a WTW pM $\times$ 3000/ion microprocessor-controlled high-performance pH ion meter. The instrument was previously calibrated in terms of concentration using a set of Cu^{2+} standard solutions.

In this method, the dried clay sample was added very rapidly to the stirring Cu^{2+} solution and allowed to stand at the required temperature. As Cu^{2+} displaced the exchangeable cations from the clay sample, the activity of the Cu^{2+} ions in the suspension decreased, causing a change in the emf of the Cu^{2+} ion-specific electrode. A continuous record of Cu^{2+} ion activity versus time was obtained at different time intervals using a strip chart.

2.3. Sorption experiments

Sorption was carried out by mixing 2.00 g of air-dried bentonite with 100 ml of $Cu(NO_3)_2$ solution. After a shaking period of 24 h at $20 \pm 0.5\,°C$, suspensions were centrifuged and supernatants were analyzed for Cu^{2+} potentiometrically. The amount of Cu^{2+} sorbed was calculated from the initial and final concentrations of metal ions in solution.

2.4. Desorption experiment

Desorption was carried out using samples with the highest Cu^{2+} equilibrium concentration in the sorption experiments. The supernatant removed for analysis of sorption was replaced by the same volume of deionized water. A vortex mixer was used to disperse the clay pellets, and the suspensions were mechanically shaken for 24 h at $20 \pm 0.5\,°C$. The supernatant was separated and analyzed for Cu^{2+}. The same experiment was repeated by replacing the supernatant liquid with the same volume of 100 ppm $CaCl_2$ solution to test the exchange of Cu^{2+} by Ca^{2+}.

3. Results and discussion

Kinetics of Cu^{2+} sorption on the studied clay was followed by the differential method. In this method the instantaneous rates of reaction were determined by calculating the slopes of tangents of concentration versus time curves.

Fig. 1 shows the changes of concentration of Cu^{2+} as a function of time under different experimental conditions. As can be seen from this figure, the sorption processes was relatively fast in the first few minutes and then became slow after reaching 80% of the total sorption. Similar trends were found for Cu^{2+} adsorption by Italian soil by Arinnghieri [17], who suggested from a qualitative point of view that the whole process consisted of two distinct steps: an initial fast adsorption, followed by a much slower adsorption. Arinnghieri ascribed the fast step to a rapid diffusion of ions from the solution to external clay surfaces, and the slow step to the diffusion of ions into pores of inner soil surfaces. Under our experimental conditions of continuous stirring, it is unlikely that the external diffusion could regulate the adsorption process.

For a complex solid–liquid reaction, such as this reaction, diffusion, adsorption, and chemical reaction may take place. The rate equation can be represented by

$$-dc/dt = k[A/V]^{\alpha} C^{\beta}, \tag{1}$$

$$R = k[A/V]^{\alpha} C^{\beta}, \tag{2}$$

where R is the reaction rate, A is the area of bentonite (m^2), V is the solution volume (m^3), and α and β are the orders of the reaction with respect to clay surface area and copper ion concentration (C), respectively. If, therefore, for a certain sample size, the velocity is measured at various Cu^{2+} concentrations in parts per million, a double logarithmic plot of the rate against the concentration will give a straight line. The slope of this relation represents the order of reaction with respect to Cu^{2+} (β), while the intercept is $\ln k_{obs}$, where $k_{obs} = k(A/V)^{\alpha}$. Fig. 2 represents this relation for the 80 ppm Cu^{2+} initial concentration at different clay sample size values (0.5, 1, 1.5, and 2 g bentonite). It was found that the slopes were almost constant in all cases and the average value was about 1, representing the order with respect to Cu^{2+}. The rate constants k_{obs} were calculated from the intercepts of the linear least mean square analysis of this relation at 80 ppm Cu^{2+} for different clay sample sizes. The obtained values are listed in Table 1, which shows that k_{obs} increased with increasing sample size of bentonite. This is in accordance with the increased amount of Cu^{2+} ions sorbed on the surface as the surface area of clay increased.
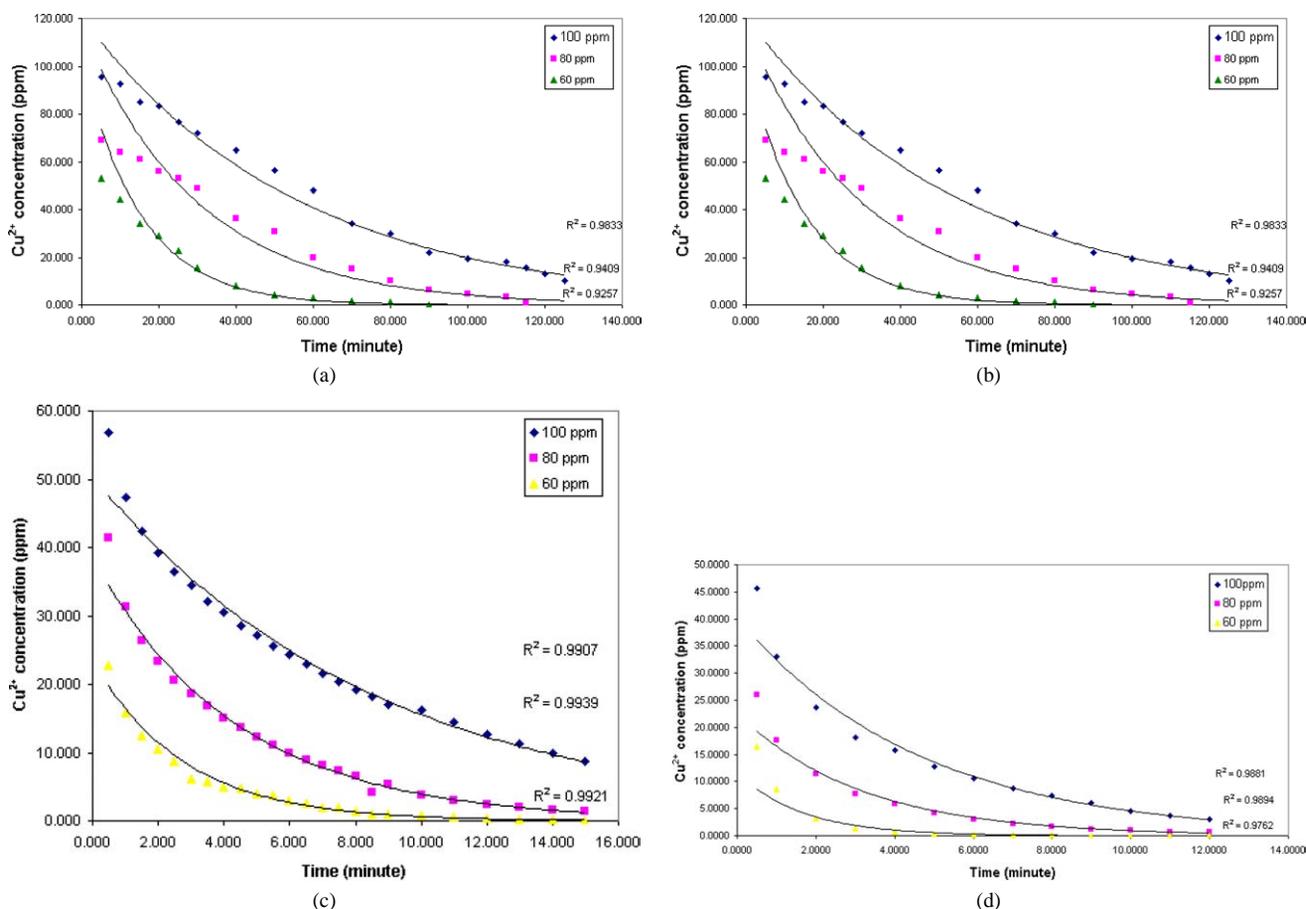
Fig. 1. Relation between time and different Cu^{2+} concentrations at (a) 0.5, (b) 1.0, (c) 1.5, and (d) 2.0 g of clay.

In Fig. 3, $\ln(k_{obs})$ is linearly correlated to ln(bentonite sample size). The slope of the straight line is 1.5, representing the order of the reaction with respect to the clay surface area (α). By applying the first-order kinetic rate law to the sorption of Cu^{2+} (Fig. 4), a curved relationship was produced instead of linear graphs expected. It was supposed that curves in the last figure represent a process whose rate for a certain sample size value and at constant temperature depends on two factors: first, the concentration of the reactive species, Cu^{2+}; second, the internal diffusion, which produced a decrease of specific rate as a function of time. Two distinct reactions existed for Cu^{2+} sorption on bentonite. The first reaction resulted from a rapid exchange of Cu^{2+} with the cations on the external planar surfaces and the interlattice edges, followed by a second, slow reaction, in which Cu^{2+} diffuses into the inter-layer. An indication of these two reactions was found in comparing Cu^{2+} sorption initial rates having different clay sample sizes for 80 ppm Cu^{2+} concentration. When the clay sample size increased from 0.5 to 2.0 g, the initial rates increased from 0.02 to 0.8 (ppm min^{-1}), respectively. However, at the end of the Cu^{2+} sorption process, the rates of the slow diffusion reaction remained the same (nearly equal 0.01 ppm min^{-1}). The external planar and the edge surface together made up about

4% of the total surface area of the clay [18], which represents the dominant copper adsorption sites described by Ding and Frost [19]. Hence, surface sites to which the first fast reaction was attributed did not greatly exceed the Cu^{2+} ions added. Therefore an increase in sample size increased the surface area, and the Cu^{2+} sorbed initially also increased (fast reaction). In contrast to the surface sites, the interlayer sites, which constituted >90% of the exchange sites, greatly exceeded the quantity of Cu^{2+} added. Accordingly, the rates representing the diffusion of Cu^{2+} into interlayers did not change. Similar conclusions were drawn about the kinetics of phosphate adsorption on $CaCO_3$ and Ca–kaolinite (kaolinite saturated by calcium ions) by Kuo and Lotse [20], who suggested that diffusion was an important factor in governing the rate of adsorption. Also, Sawhney [21], in studying the adsorption of cesium by different clays, concluded that the movement of Cs through the interlayer of clays was a slow diffusion process. This finding was also confirmed in the present work by plotting the percentage of uptake of Cu^{2+} against the square root of time. A linear correlation was obtained (Fig. 5), indicating that an intraparticle diffusion process is rate-limiting [22]. The determination of the rate constants by utilizing the first-order kinetic law was not therefore possible.
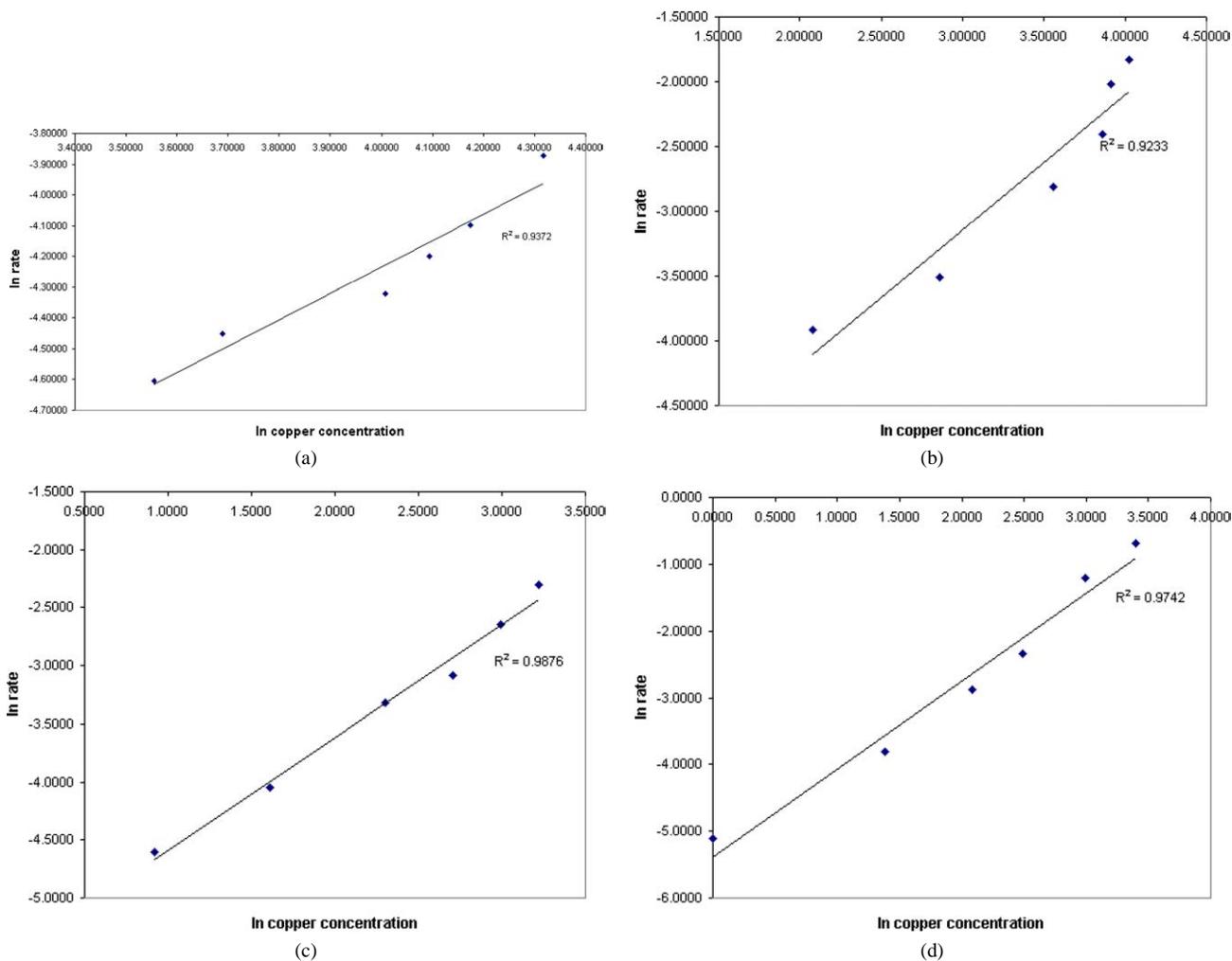
Fig. 2. Relation between ln Cu^{2+} concentration and ln rate at (a) 0.5, (b) 1.0, (c) 1.5, and (d) 2.0 g of clay.

Table 1
Rate constant (k_{obs}) of Cu^{2+} adsorption at different bentonite sample sizes

Bentonite sample size (g)	Rate constant, k_{obs} (min^{-1})
0.5	4.67×10^{-4}
1.0	1.84×10^{-3}
1.5	3.84×10^{-3}
2.0	4.69×10^{-3}

3.1. Sorption studies

The sorption process was investigated by means of the Langmuir isotherm (Fig. 6). Copper sorption data conform to the Langmuir equation in the form

$$C/(x/m) = 1/ab + C/b, \tag{3}$$

where C is the equilibrium concentration of the metal in solution (ppm), (x/m) is the amount of metal sorbed by unit weight of bentonite, b is the maximum sorbed amount (mg/g), and a is the affinity constant, which represents the affinity of the surface for the adsorbent. Values of b and a for Cu^{2+} sorption were 909 mg Cu^{2+}/g bentonite and 0.167,

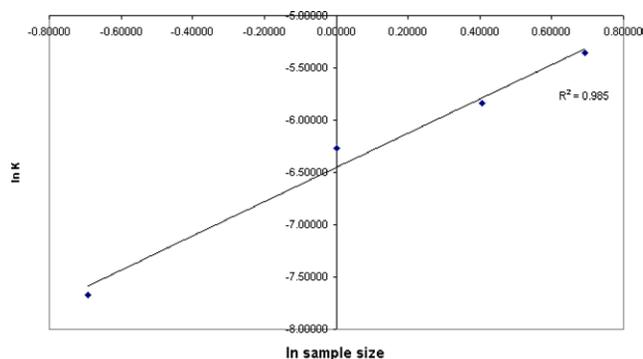Fig. 3. Relation between ln K and ln clay content.

respectively, and the regression coefficient was 0.997. The maximum adsorbed amount is much greater than those reported by Matthes et al. (0.635 mg Cu^{2+}/g clay) [23] and Laired and co-workers (63.5 mg Cu^{2+}/g clay) [13] for Cu^{2+} adsorption on bentonite. This finding is of great environmental concern and adds many applications for this clay in industry, mining purification, processing, and waste disposal [24].
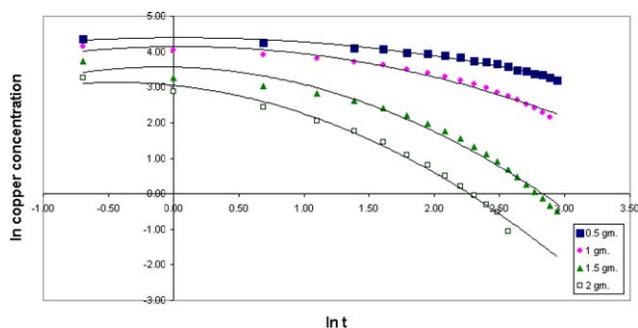
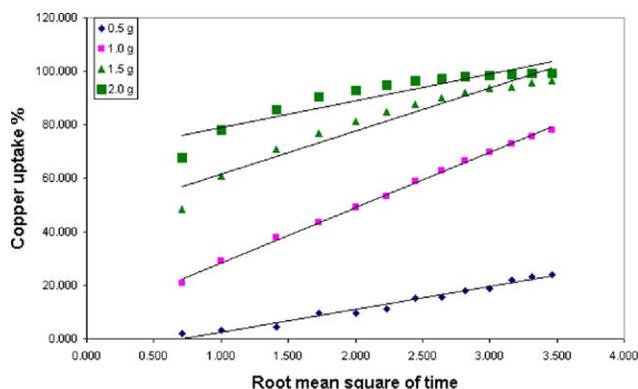Fig. 4. Relation between ln Cu^{2+} concentration and $\ln t$ at different clay contents.

Fig. 5. Relation between root mean square of time versus percentage of Cu^{2+} in 80-ppm solution at different clay contents.

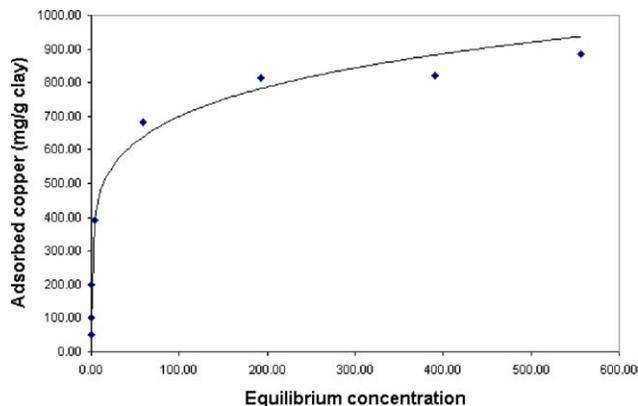Fig. 6. Langmuir isotherm for Cu^{2+} sorption using 2-g clay sample.

According to Fig. 6, the sorption of Cu^{2+} can be described by a high-affinity Langmuir isotherm. Heavy metals can be sorbed by clay minerals via complexation on surface hydroxyl groups at the edges and via cation exchange at the negatively charged surface of the crystallites. The capacity of montmorillonite for surface complexation is considerably smaller than for electrostatic interactions. Moreover, because of the organic matter associated with the surfaces of the untreated clay samples, other different types of interactions among different soil components are likely to participate. The Cu^{2+} ion may directly be bonded to two or more organic functional groups, for example carboxyl or

Table 2
Percentage of Cu^{2+} exchanged by Ca^{2+} after shaking for 24 h

Clay sample size (g)	Exchange % of Cu^{2+}
0.5	0.38
1.0	0.5
1.5	0.8
2.0	1.2

phenol [24,25]. But despite what was reported [11] about untreated clay having high affinity for Cu^{2+} due to the reactivity of the organic matter on its surface, it is not the case in this study. The adsorption of Cu^{2+} by the clay used herein may be attributed approximately, solely, to the montmorillonite component ($\sim$90% of the clay [15]) as discussed above. Such findings, together with the high value of the Langmuir bonding term (a), suggest that most Cu^{2+} ions are strongly sorbed by layer silicate clays.

3.2. Desorption study

The Cu^{2+} ions were not detected for all samples of different clay contents when the desorption experiments were carried out using deionized water. In the second case when the supernatant was replaced by a 100-ppm $CaCl_2$ solution, very small amounts of Cu^{2+} were detected in the solutions, as can be seen in Table 2. This result indicates that the desorption process is limited. This would be expected due to the difficulty in desorbing Cu^{2+} from partially collapsed interlayer positions of bentonite clay minerals. Once Cu^{2+} is adsorbed into this peripheral space, the Columbic attractions between the Cu^{2+} ions and the silicate layers would be greater than the hydration forces between the individual Cu^{2+} ions. Thus, a partial layer collapse would occur [26–28]. This behavior was observed for similar systems [28,29], where the rate of Cu^{2+} exchange by potassium was very slow. The poor desorption of Cu^{2+} by Ca^{2+} is in good agreement with adsorption parameter values obtained, indicating that Cu^{2+} was chemisorbed on the bentonite surface.

4. Conclusions

Cu^{2+} sorption on a Saudi clay mineral followed first-order kinetics with respect to Cu^{2+}, while it was found to be $1\frac{1}{2}$-order with respect to clay surface area. The linear correlation between the percentage of Cu^{2+} uptake and the square root of time indicated that intraparticle diffusion is rate-determining. The sorption of Cu^{2+} on the clay surface can be described by the high-affinity Langmuir isotherm. The poor desorption of the copper ion indicated that Cu^{2+} ions are strongly sorbed mainly by layered silicate surface. The affinity of the clay surface to Cu^{2+} ions is much higher than other reported values, which adds many applications.

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