

## Research Article

# Adsorptive Applications of Montmorillonite Clay for the Removal of Ag(I) and Cu(II) from Aqueous Medium

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Received 13 February 2019; Accepted 17 May 2019; Published 23 June 2019

Academic Editor: Yuangen Yang

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The present work aims to investigate the ability of Saudi clay containing montmorillonite to remove Ag(I) and Cu(II) ions from aqueous solutions for waste water purification. The effect of pH, adsorbent mass, metal concentration, and contact time on the removal process has been investigated. The batch method was applied, using solution metal concentrations ranging from 40 to 2000 mg/L. Adsorption percentage and distribution coefficients ( $K_d$ ) were determined as a function of metal concentration. pH 6 was found to be optimal for the adsorption. Adsorption reached equilibrium in 5 min for both Ag(I) and Cu(II) ions. The study on adsorption's kinetic characteristics showed the adsorption process of these metal ions was of pseudo-second-order. Furthermore, the adsorption rate of Ag(I) was higher than that of Cu(II), and their adsorption appeared to follow the Langmuir isotherm. From the equilibrium studies, it was observed that the selectivity of Ag(I) was higher than that of Cu(II). The results showed that Saudi clay has the potential to be a suitable adsorbent for Ag(I) and Cu(II) removal from aqueous solutions compared with other adsorbents.

## 1. Introduction

Industrial waste discharge can cause serious water and soil pollution [1, 2]. Metals, such as copper (Cu), chromium (Cr), silver (Ag), cadmium (Cd), mercury (Hg), nickel (Ni), lead (Pb), and zinc (Zn), are considered to be hazardous to the environment, when they are present in insufficient distribution and abundance [3–11]. Ag is a useful raw material in many industries. Significant quantities of silver are present in the effluents discharged from such industries, and the removal of this toxic element from wastewaters is an important concern for protection of living organisms [12]. Copper electroplating and industrial cooling water systems are one of the main sources of copper-containing waste streams in industries [13, 14]. Copper concentrations range between 20 and 2200 mg/L, and US EPA suggested 1.3 mg/L as the copper maximum

contaminant level. Copper can exist in the form of Cu(0), Cu(I), and Cu(II), but in the aqueous solution, the main species of concern is Cu(II) [15]. Organic and inorganic matters in the aqueous solution are easily bonded to Cu(II) depending on the pH of the solution. Aquatic life is seriously affected by these Cu(II) species. Natural water sources are also affected to a level of becoming unsuitable for public use [3, 13, 14, 16].

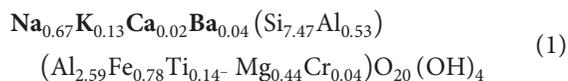
For over the years, a number of technologies have been developed to remove heavy metal ions from aqueous solutions [17–20]. These methods include electrochemical methods, membrane filtration, chemical precipitation, ion exchange, and adsorption [21–24]. The adsorption treatment has attracted much consideration in the past decades due to its cost-effectiveness, high efficiency, environmental compatibility, and ease of operation [25–30]. Clay acts as a natural scavenger of pollutants in nature by which it plays

an important role in the environment. It takes up cations and anions through either ion exchange or adsorption or both. Clays invariably contain exchangeable cations and anions held to the surface and hence are strong candidates as adsorbents for the removal of heavy metals from waste waters [31, 32]. Clays actually are excellent adsorbent materials due to their large specific surface area, chemical and mechanical stability, layered structure, high cation-exchange capacity, etc. [32]. The removal of heavy metals using different types of clays is reported in some earlier studies [32–36]. In the north of Jeddah, Saudi Arabia, a clay containing montmorillonite has been selected as the candidate of backfill material for heavy metal adsorption. In this present work, we studied the adsorption of Cu(II) and Ag(I) onto this clay for four objectives: (1) the effect of contact time, (2) the influence of pH, (3) the effect of clay's mass, and (4) the adsorption properties and mechanisms of Cu(II) and Ag(I) ions.

## 2. Experimental

**2.1. Materials.** Silver nitrate ( $\text{AgNO}_3$ ) and copper nitrate ( $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ ) were used as sources of ions. 0.1 N HCl and 0.1 N NaOH were used to carry out pH adjustments. Ultrapure water was used to prepare all Ag(I) and Cu(II) solutions. The clay from Khulays region, north of Jeddah, Saudi Arabia, was collected and grinded in the laboratory and used without any chemical treatment.

**2.2. Characterization of the Clay Sample.** The clay sample was characterized by X-ray diffraction (XRD) in an earlier study [37]. The main components are montmorillonite (35.22%), mica (22.8%), kaolinite (13.33%), quartz (8.57%), feldspars (6.66%), and ilmenite (5.71%). The remaining components are dolomite (3.81%) and gypsum (3.89%). The X-ray fluorescence (XRF) data of the sample lead to the following structural formula of montmorillonite:



The ions in bold font represent the exchangeable ions. The first bracket is for silica tetrahedral, and the second is for aluminum or ferric octahedral.

**2.3. Adsorption Experiment.** The adsorption process was carried out in a batch reactor. Standard metal solutions ranging from 40 to 2000 mg/L were prepared by diluting the stock solutions. 0.5 g of the clay sample was mixed with 50 mL of the metal solution. The mixture was shaken at 162 rpm stirring rate and 298 K for 1 h followed by centrifugation. Afterward, the metal concentration of the remaining in the supernatant was analyzed by using a PerkinElmer Optima optical emission spectrometer (5300 DV ICP). The adsorption percent and distribution coefficients ( $K_d$ ) [38, 39] were calculated using the following equations:

$$\% \text{ adsorption} = \frac{C_i - C_e}{C_e} \times 100, \quad (2)$$

$$K_d = \frac{C_i - C_e}{C_e} \times \left(\frac{V}{m}\right),$$

where  $C_i$  is the initial concentration of metal ions (mg/L),  $C_e$  is the concentration of metal ions at equilibrium (mg/L),  $V$  is the initial volume of metal ions in the solution (mL), and  $m$  is the dry weight of biomass used (g). The adsorbed amount ( $q_e$ ) by the clay sample during the series of batch adsorptions was determined using the following equation:

$$q_e = \left(\frac{C_i - C_e}{m}\right) \times V. \quad (3)$$

**2.4. Kinetic Studies.** The kinetic runs were carried out using a 200 mg/L solution of silver and copper. 50 mL of each solution was added in a flask with 0.5 g of the clay sample. Flasks were kept in a shaker at a speed of 162 rpm and 298 K. The kinetic experimental data were observed, when each flask was removed from the shaker at various contact times (5–300 min), the solution was filtered, and aqueous-phase cations were analyzed by optical emission spectroscopy. All runs were carried out twice.

The adsorption capacity is normally controlled by pH of the system, which also has effects on surface properties of the adsorbent and ionic forms of metal ions in the solution. The influence of pH in the range of 2–8 was studied keeping all other parameters constant (metal ion concentration = 500 mg/L; stirring speed = 162 rpm; contact time = 1 h; clay mass = 0.5 g; temperature = 25°C). Dilute concentrations of NaOH and HCl solutions were used to adjust the pH of the metal solution after the addition of the clay.

The adsorption percent (%) of metal ions on the raw clay sample was studied for different clay masses (0.1–5 g/50 mL metal ion solutions) for a metal ion concentration of 500 mg/L with 162 rpm stirring speed at 25°C for one hour.

## 3. Results and Discussion

**3.1. Characterization of the Clay Sample.** The BET (Brunauer, Emmett, and Teller) equation was applied to calculate the specific surface area of the clay sample. The resulted surface area observed was  $S_{\text{NB}} = 69 \text{ m}^2/\text{g}^{-1}$ . Particle size analysis of the clay sample was also carried out using Zetasizer (Nano S ZEN 1600, Malvern). The particle size distribution for 74.7% of the clay sample was 1445 nm, 18.9% was 344 nm, and 6.3% was 5387 nm. Microstructure image of the clay sample is shown in Figure 1. It was obtained by SEM (Philips XL30S-FEG). The sample was gold-coated before SEM analysis. Irregular porous surface shown by the image indicates a relatively high surface area. The BET surface area results support these observations.

**3.2. Kinetics of Adsorption.** To determine the time required for adsorption to reach equilibrium, the contact time between the adsorbent and the adsorbate was varied from 5 to

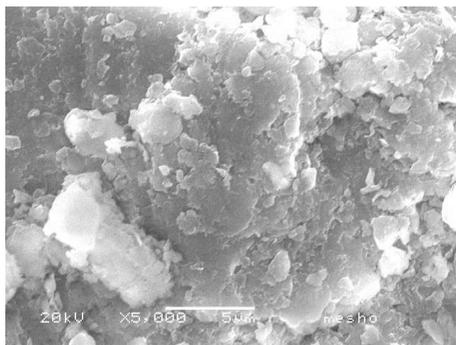


FIGURE 1: SEM image of the clay sample.

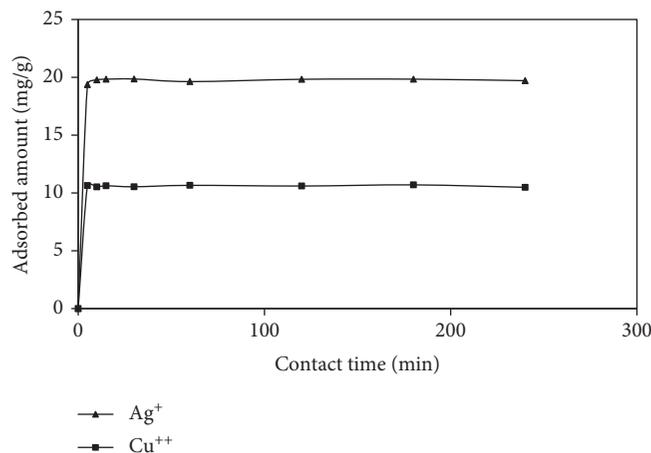
300 min, the initial concentration of Cu(II) and Ag(I) was fixed at 200 mg/L, and the clay in dispersion concentration was at 10 g/L. The adsorbed amount of Cu(II) and Ag(I) per gram of clay was evaluated using the method of residues (equation (4)). Figure 2 shows the plot of these quantities vs. contact time. The slopes reflect the initial adsorption rates of Ag(I) and Cu(II) were very fast and then plateau values were reached within 15 min. The adsorption rate of the clay seemed to be very satisfactory. Minimum energy consumption and short adsorption time make Saudi clay an efficient adsorbent for Cu(II) and Ag(I). A contact time of 1 h was chosen for further experiments. The pseudo-second-order equation and pseudo-first-order Lagergren models were applied for Cu(II) and Ag(I) kinetics. Lagergren's pseudo-first-order model is generally expressed as

$$\ln(q_e - q_t) = \ln q_e - k_1 t, \quad (4)$$

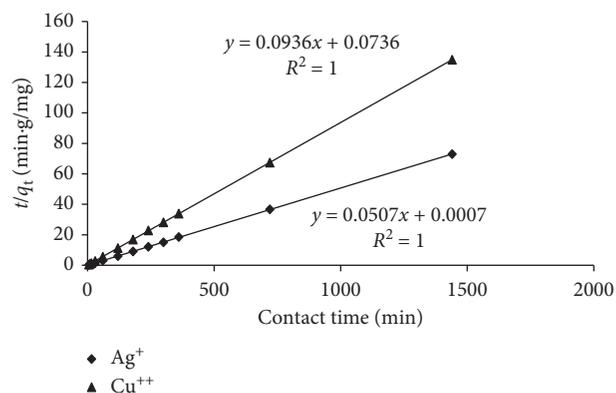
where  $q_t$  and  $q_e$  (mg/g) are the adsorption capacity at time  $t$  and equilibrium, respectively, and  $k_1$  is the Lagergren rate constant of pseudo-first-order adsorption ( $\text{min}^{-1}$ ). Plotting  $\log(q_e - q_t)$  vs.  $t$  should give a linear relationship with slope  $q_e$  and with intercept  $k_1$ . The pseudo-second-order model is expressed as

$$\frac{t}{q_t} = \frac{1}{k_2} q_e^2 + \frac{t}{q_e}, \quad (5)$$

where  $k_2$  is the pseudo-second-order adsorption rate constant (g/mg·min). The rates of adsorptions of Ag(I) and Cu(II) onto the clay surface were evaluated for these models. From the linear plots of  $t/q_t$  vs.  $t$ ,  $k_2$  and  $q_e$  can be determined from the slope and intercept [40]. The plots of  $\ln(q_e - q_t)$  vs.  $t$  for the Lagergren first-order model (not shown here) do not fit with the model. Table 1 shows the calculated results of the first-order rate equation with low correlation coefficients values, showing bad quality of linearization. Furthermore, the  $q_e$  value acquired by this method is contrasted with the experimental value, which means that adsorption of Ag(I) and Cu(II) onto clay is not a pseudo-first-order process. Figure 3 represents the linearized form of pseudo-second-order model in which the values of correlation coefficients were all extremely high ( $R^2 = 1$ ) compared to those of the pseudo-first-order model (Table 1). Besides, the calculated  $q_e$  values agreed very well with experimental data, which suggests that the pseudo-second-order model is more likely to predict kinetic behavior of adsorption of Ag(I) and Cu(II)

FIGURE 2: Effect of contact time on  $\text{Ag}^+$  and  $\text{Cu}^{++}$  adsorption onto Saudi clay, at metal concentration = 200 mg/L, temperature = 25°C, and clay mass = 10 g/L.TABLE 1: Adsorption rate constants of  $\text{Ag}^+$  and  $\text{Cu}^{++}$  adsorption onto clay derived from the pseudo-first-order and pseudo-second-order kinetic models.

	Pseudo-first-order			Pseudo-second-order		
	$q_e$ (mg/g)	$k_1$ ( $\text{min}^{-1}$ )	$R^2$	$q_e$ (mg/g)	$k_2$ (g/mg·min)	$R^2$
$\text{Ag}^+$	0.377	0.914	0.197	19.70	3.67	1
$\text{Cu}^{++}$	0.200	1.600	0.002	10.68	0.119	1

FIGURE 3: Pseudo-second-order adsorption kinetics of  $\text{Ag}^+$  and  $\text{Cu}^{++}$  on the clay surface.

with chemical sorption being the rate-controlling step [40]. Comparing the adsorption rate constants of Ag(I) and Cu(II), it was found that Ag(I) was adsorbed by the clay sample faster than the adsorption of Cu(II).

3.3. *Effects of Clay Mass.* Adsorbent mass is an important parameter that determines the capacity of an adsorbent for a given initial concentration of the adsorbate. The clay mass effect was studied on Ag(I) and Cu(II) ion removal from

aqueous solutions by changing the amount of clay from 0.1 to 5 g/50 mL while keeping other parameters constant (pH = 6; metal concentration = 500 mg/L; temperature = 298 K; contact time = 1 hour). The effect of clay mass on adsorption of Ag(I) and Cu(II) is shown in Figure 4. The percent adsorption of Ag(I) and Cu(II) increased from 14.2 to 82.6% and from 0.02 to 80%, respectively, for clay mass of 0.1 and 5.0 g. As dosage increased, adsorbent capacity increased due to availability of more binding sites.

**3.4. Effects of pH.** The solution's pH plays an important role in determining the rate of surface reactions. The variation in adsorption capacity in a pH range is largely due to influence of pH on adsorption characteristics of the clay surface. Figure 5 shows the effect of pH on the adsorbed amount of Ag(I) and Cu(II) onto the clay surface. For Cu(II), the adsorbed amount increased from 33.3 to 49.87 mg as the pH increased from 2 to 8, but for Ag(I), it was weakly influenced by the pH. The increase in Cu(II) removal as the pH increased can be explained by surface sites and by decreased positive charge, which results in a lower repulsion on the basis of decreased competition between protons and positively charged copper ions at the adsorbing metal ion [41]. This indicated that adsorption capacity of the adsorbent is clearly pH dependent.

**3.5. Adsorption Isotherm.** The adsorption of Ag(I) and Cu(II) onto the clay sample as a function of their concentrations was studied at 298 K. The metal concentrations were varied from 40 to 2000 mg/L while keeping all other parameters constant. Figure 6 shows the adsorption of Ag(I) and Cu(II) as a function of metal ion concentration at 298 K. The percentage of adsorption decreases with increasing metal concentration in aqueous solutions. This may be because at lower concentrations almost all ions were adsorbed very quickly, but further increases in initial metal ion concentrations led to saturation of the clay surface. Figure 7 illustrates the distribution coefficient ( $K_d$ ) as a function of metal ion concentrations. Decreasing metal ion concentrations led to increasing  $K_d$  values. A high  $K_d$  value represents a high clay affinity with the metal and indicates a low mobility, while a low  $K_d$  value indicates a high mobility through the clay surface. These results indicate increasing metal concentrations in the aqueous solution causing energetically less favorable sites to become involved. The heavy metal uptake is attributed to dissimilar mechanisms of ion-exchange processes and to the adsorption process. During the ion-exchange process, metal ions had to move through pores of clay mass. The maximal exchange levels attained were 92.13% for Ag(I) and 92% for Cu(II).

The equilibrium data for Ag(I) and Cu(II) over concentrations ranging from 40 to 2000 mg/L have been correlated with the well-known Langmuir isotherm model, which is represented mathematically as follows:

$$\frac{C_e}{q_e} = \frac{1}{K_L q_m} + \frac{C_e}{q_m} \quad (6)$$

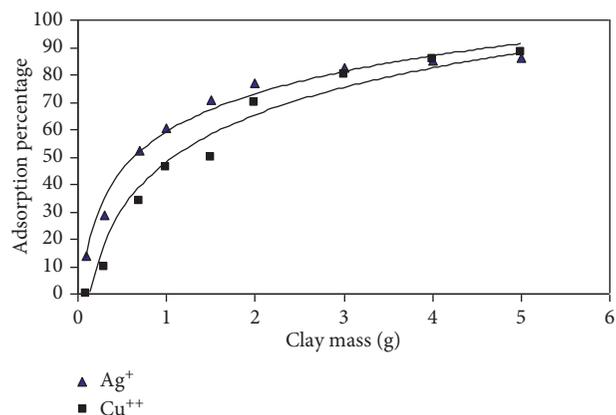


FIGURE 4: Effect of clay mass on the adsorption percentage.

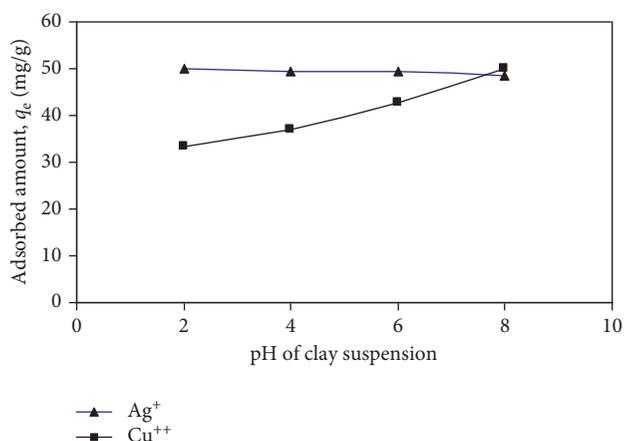


FIGURE 5: Effect of pH on Ag<sup>+</sup> and Cu<sup>++</sup> removal by Saudi clay at initial metal concentration concentration = 500 mg/L and clay mass = 10 g/L.

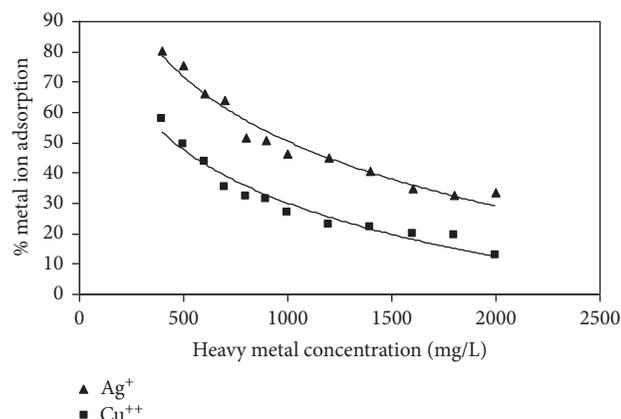


FIGURE 6: Adsorption of Ag<sup>+</sup> and Cu<sup>++</sup> by the Saudi clay sample as a function of initial concentration.

where  $q_e$  and  $K_L$  are Langmuir constants. They are related to maximum sorption capacity and sorption energy, respectively.  $K_L$  represents enthalpy of sorption and should

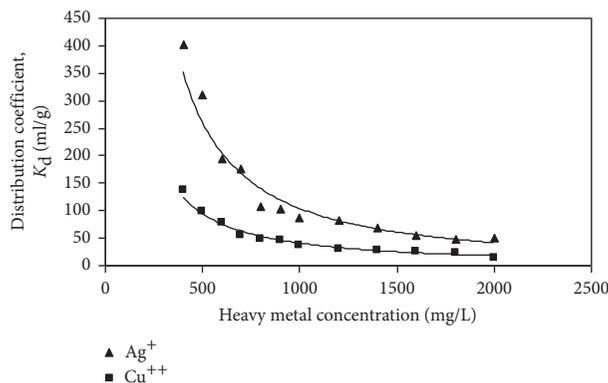


FIGURE 7: Distribution coefficient of  $\text{Ag}^+$  and  $\text{Cu}^{++}$  on Saudi clay as a function of initial concentration.

vary with temperature, and maximum sorption capacity ( $q_m$ ) represents monolayer coverage of the sorbent with the sorbate.

The Freundlich adsorption isotherms were also applied to removal of  $\text{Ag}(\text{I})$  and  $\text{Cu}(\text{II})$  on the clay sample:

$$\log q_e = \log K_F + \frac{1}{n} \log C_e, \quad (7)$$

where  $K_F$  and  $n$  are Freundlich constants that are related to adsorption capacity and adsorption intensity, respectively.

Figure 8 displays linear plots of  $C_e/q_e$  vs.  $C_e$  at 298 K. The values of  $q_m$  and  $K_L$  were determined for the Langmuir isotherm from experimental data by linear regression. For the Freundlich isotherm, values of  $K_F$  and  $n$  were obtained similarly (Table 2). The correlation coefficients  $R^2$  indicate that the Langmuir isotherm fitted adsorption data of  $\text{Ag}(\text{I})$  and  $\text{Cu}(\text{II})$  on the clay surface better than the Freundlich isotherm. It appears that the adsorbed amount ( $q_e$ ) of  $\text{Ag}(\text{I})$  and  $\text{Cu}(\text{II})$  was 63.29 and 32.36 mg/g, respectively. The ionic radii of the metal ions can explain this result. Indeed, it is reported that the amount of uptake of cations from the solution was related to the ionic radii [41–43]. When the ionic radius increases (or the hydrated radius decreases), the removal of metal from the solution increases. For example,  $\text{Ag}$  (ionic radius = 1.26 Å; hydrated radius = 2.12 Å) shows a higher adsorbed amount, while copper (ionic radius = 72 pm; hydrated radius = 295 pm) shows low adsorbed amount. The elements with lower ionic radius will compete faster for exchange sites on the clay surface than those with higher ionic radius. The higher charge of an ion means lower ionic radius, and hence, the charge of an ion can influence its ability to adsorb on the adsorbent surface [44]. The ionic radii of  $\text{Ag}(\text{I})$  and  $\text{Cu}(\text{II})$  are 1.26 and 0.71 Å, respectively [45]. Therefore, it will be expected that  $\text{Cu}(\text{II})$  must be adsorbed more than  $\text{Ag}(\text{I})$ , but in this work, the contrary took place. The adsorbed amount of  $\text{Ag}(\text{I})$  and  $\text{Cu}(\text{II})$  was 63.29 and 32.36 mg/g, respectively. The relative selectivity of metal cations can be explained according to the Lewis hard-soft acid-base (HSAB) principle. Hard Lewis acids prefer to react or complex with hard Lewis bases, and in the same manner, soft acids prefer soft bases [44]. The term “hard” indicates high electronegativity, low polarizability, and small radius, and the term “soft” implies the opposite. Hard Lewis

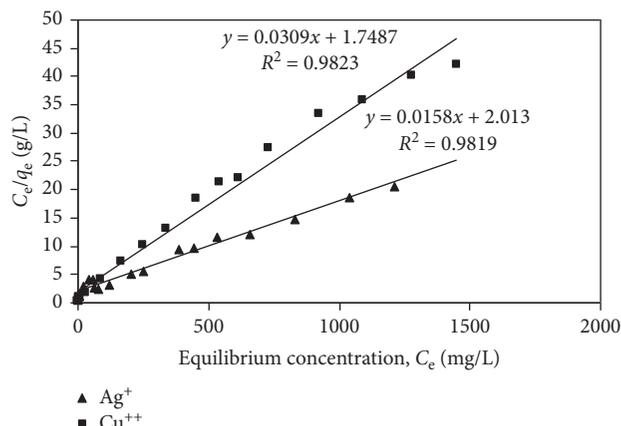


FIGURE 8: Linearized Langmuir isotherm models for  $\text{Ag}^+$  and  $\text{Cu}^{++}$  adsorption by the Saudi clay at 298 K (clay mass 10 g/L and shaking time 2 h).

TABLE 2: Langmuir and Freundlich parameters obtained from the plots of  $\text{Ag}^+$  and  $\text{Cu}^{++}$  adsorption onto Saudi clay at 298 K.

Metals	Langmuir			Freundlich		
	$q_m$ (mg/g)	$K_L$	$R^2$	$K_F$	$n$	$R^2$
$\text{Ag}^+$	63.29	0.0078	0.98	2.39	2.1	0.93
$\text{Cu}^{++}$	32.36	0.0176	0.98	5.44	4.46	0.32

TABLE 3: Comparison of adsorption capacity of Saudi clay with other adsorbents reported in previous works.

Adsorbent	Maximum adsorbed amount (mg/g)		References
	$\text{Ag}^+$	$\text{Cu}^{++}$	
Zeolite	33.2	—	[12]
Activated carbon	—	25	[46]
Peat	10.8	6.2	[10]
Spent activated carbon	—	13	[33]
Red mud	—	5.3	[34]
Expanded perlite	0	8.62	[45]
Natural zeolite	—	8.69	[31]
Clay	—	12.84	[11]
Shells of wheat	—	17.42	[8]
Bulgarian clay	—	3.11	[25]
Expanded perlite	0.8	0.18	[4]
Saudi clay	63.2	32.36	This work

acids include  $\text{Li}(\text{I})$ ,  $\text{Na}(\text{I})$ ,  $\text{Mg}(\text{II})$ ,  $\text{Ca}(\text{II})$ , and  $\text{Sr}(\text{II})$ , while soft Lewis acids include  $\text{Ag}(\text{I})$ ,  $\text{As}(\text{I})$ ,  $\text{Hg}(\text{II})$ , and  $\text{Pd}(\text{II})$ . Borderline metals include  $\text{Fe}(\text{I})$ ,  $\text{Co}(\text{I})$ ,  $\text{Ni}(\text{II})$ , and  $\text{Cu}(\text{II})$ . Water is considered a very hard base, whilst clay minerals behave as soft bases; thus, in our study, clay showed a preference to  $\text{Ag}(\text{I})$ , relative to  $\text{Cu}(\text{II})$ .

3.6. Comparison of  $\text{Ag}(\text{I})$  and  $\text{Cu}(\text{II})$  Adsorption with Different Adsorbents. In Table 3, the maximum adsorption capacity of Saudi clay for  $\text{Ag}(\text{I})$  and  $\text{Cu}(\text{II})$  has been compared to other

adsorbents. The adsorption values obtained for the Ag(I) and Cu(II) ions onto Saudi clay in this study were found to be comparable and higher than those of many corresponding adsorbents reported in previous works (Table 3). Economically, the adsorbent and its treatment cost are an important issue and must be considered when selecting an adsorbent. In this work, Saudi clay was used without any chemical treatment; therefore, it could especially be considered a potential adsorbent for Ag(I) and Cu(II) removal from aqueous solutions comparing with other adsorbents.

#### 4. Conclusions

This study clearly suggests that Saudi clay could be considered an active adsorbent for treatment of wastewater containing Ag(I) and Cu(II) ions. The adsorption process is dependent on numerous factors such as solution pH, initial metal concentration, contact time, and adsorbent mass. The isotherm study indicates that adsorption data interrelated well with the Langmuir isotherm model. The kinetic data followed the pseudo-second-order kinetic model better than the pseudo-first-order kinetic model. The adsorption capacity of Saudi clay for Ag(I) and Cu(II) removal from aqueous solutions was very higher than that of other adsorbents.

#### Data Availability

The data used to support the findings of this study are available from the corresponding author upon request.

#### Conflicts of Interest

The authors declare that there are no conflicts of interest regarding the publication of this article.

#### Acknowledgments

This project was supported by Deanship of Scientific Research, College of Science Research Centre, King Saud University.

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