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Adsorption of Cu(II) onto natural clay: Equilibrium and thermodynamic studies

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Abstract

In this study,abundant and low coast natural clay is tested for its ability to retain copper cations.The experiments have been carried out batch wise and the influence of physico-chemical key parameters such as the solution pH, the temperature,etc.The obtained experimental results have been fitted according to the two known adsorption models of Langmuir and Freundlich.The adsorption depending on the temperature shows that the amount adsorbed by the clay increases with the increase of temperature, the thermodynamic parameters shows that the retention process was spontaneous, endothermic and involves two mechanisms: adsorption and ion exchange.

Keywords: Clay, Copper adsorption, Isotherms, Thermodynamic.

Introduction

The presenceof heavy metals in water cause serious health problems to living species[1]. And the removal of these heavy metals from water and wastewater is important in terms of public health and environment[2][3].

The contaminants enter the water environments through various ways. It can enter directly from direct discharge of industrial effluents, wastewater treatment facilities,refineries, etc[4][5].

Clay and clay minerals have been widely used as the adsorbents for the removalof heavy metals from aqueous solution. The advantages of using clay minerals as the alternative adsorbents for the removal of heavy metals are: high ion sorption/exchange capacity, low permeability, swelling ability, chemical and mechanical stability, and large specific surface area[5,6].

Precipitation, ion-exchange, ultrafiltration, membrane separation and adsorption are the usual methods for the removal of heavy metals from aqueous solutions[8].

Due to its simplicity and easy operational conditions, the adsorption is used in this study to report the retention of copper ions from aqueous solutions by raw clay[9].

2. Materials and methods:

2.2 Adsorbent

The raw clay was collected from the north of morocco, in sites located at a small village at 29km from Alhoceima called Bniabdellah.The sample was washed by distilled water, grounded and sieved to 63µm and dried at 100°C for 24 hours.

The experiments of copper retention were performed batch wise. The following operating procedure was followed:

Solutions of copper ions of different concentrations (200, 250, 300, 350 mg.l^{-1}) were prepared from a stock solution of $CuSO_4$. The pH was adjusted with 0.1 NaOH or H_2SO_4.

A 200 mg of clay were added in a 50 ml of copper solution and shaken during 2h at different temperatures. The dispersions were filtered and the copper concentration was determined by UV-Visible spectrophotometry (Jasco V 630) at a wavelength of 805 nm.

2.2. Adsorption isotherm models

Langmuir (Eq.1) and Freundlich (Eq.2)isotherm models were used in this study to establish the relationship between the amounts of adsorbed metal (Eq.3) onto clay and its equilibrium concentration in aqueous system[10][11].

Eq.1: $\frac{C_e}{q_e} = \frac{C_e}{q_m} + \frac{1}{K_l q_m}$

Eq.2: $\log q_e = \log K_f + n \log C_e$

Eq.3: $q_e = \frac{(C_0 - C_e) \cdot V}{m}$

3. Results and discussion:

3.1 Characterization of clay sample

The analysis per X-ray diffraction shows the existence of: muscovite, dolomite, silica and calcite (Fig. 1).

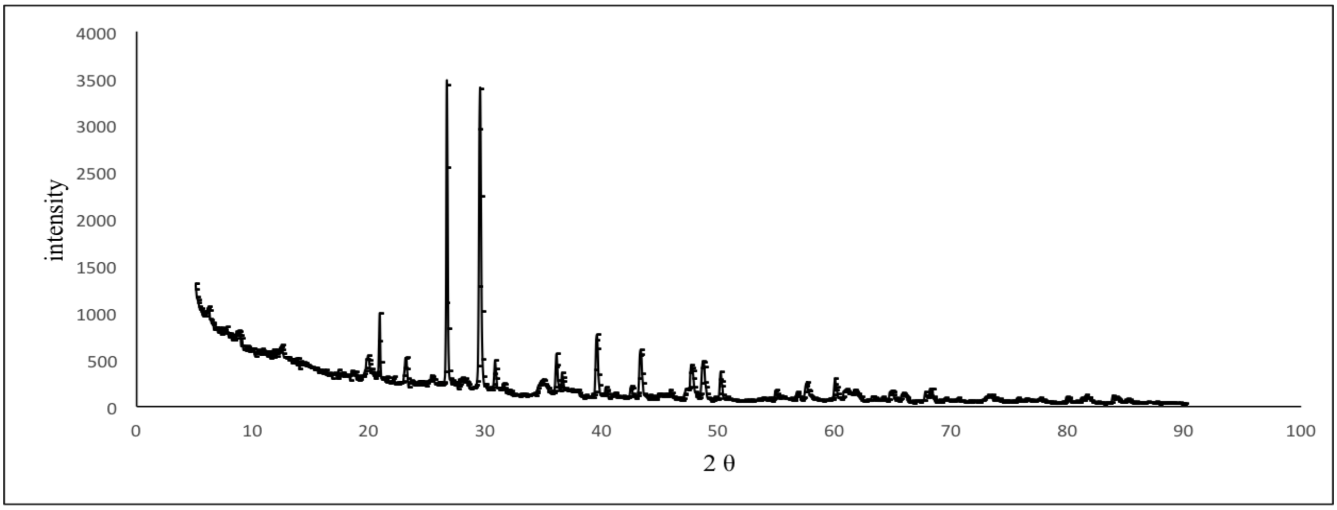


Fig. 1:XRD pattern for natural clay

The adsorbent was also characterized using an FT-IR spectrophotometer at room temperature, and it shows the stretching vibrations of the surface hydroxyl groups (Si-Si-OH or Al-Al-OH) near at 3608 $cm^{-1}$and 3626cm^{-1}[12]. The other vibration at 1735 cm^{-1} was attributed to the bending of adsorbed water[13]. The stretching bands near 1417, 872, 711 cm^{-1} were assigned to calcite[14](Fig .2).

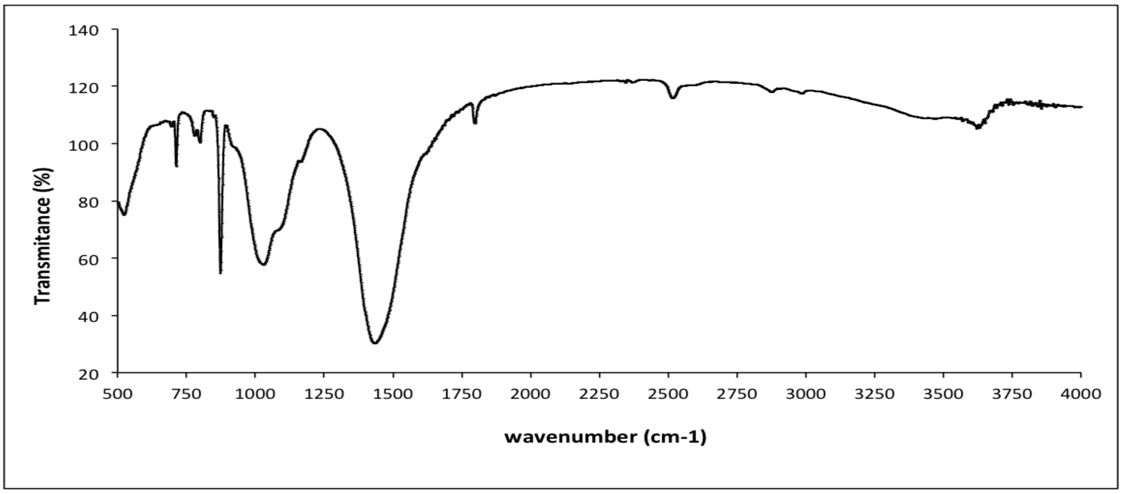
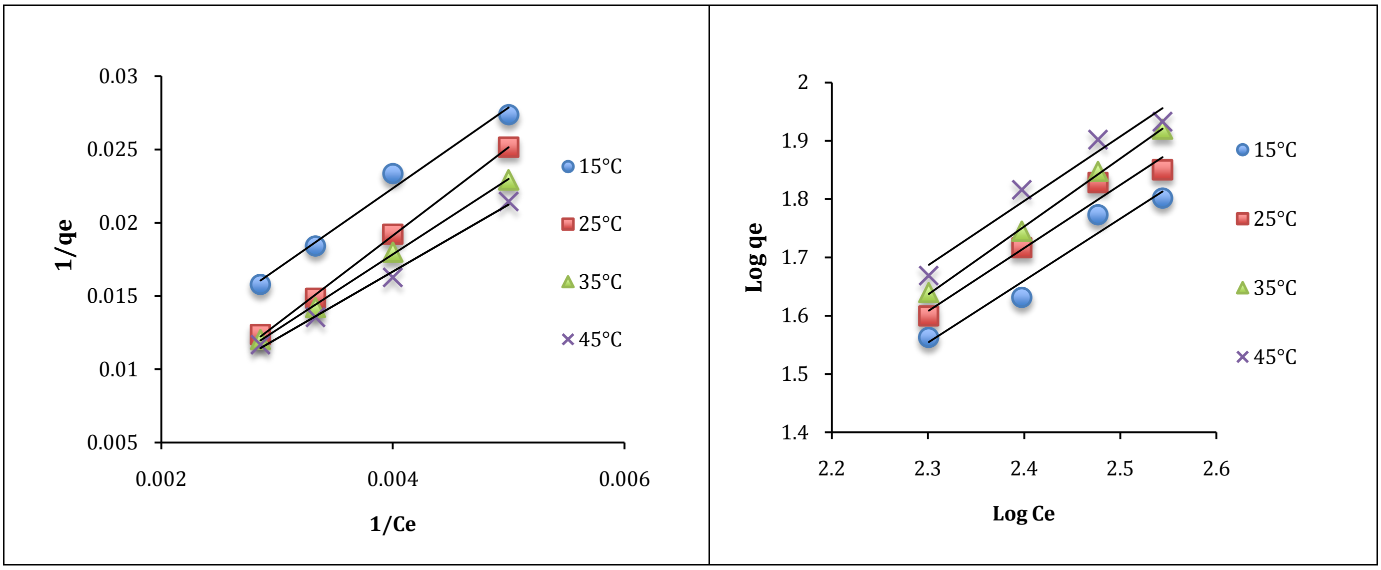


Fig. 2:FTIR spectra of raw clay

3.2 Adsorption isotherms

Linear Langmuir and Freundlich equations are presented in (Fig.3).
The coefficient of correlation ($R^2 \approx 1$) indicated that Langmuir isotherm fitted the experimental data better than Freundlich isotherm[15][16].



a) Langmuir linear equation. b) Freundlich linear equation.

Fig.3: Langmuir and Freundlich linear equations.

3.3. Effect of pH solution

The removal of heavy metals by adsorption is reported in the literature as dependent on pH [17,18]. To verify and assess this effect, we varied the pH of copper solutions from 3 to 6 at room temperature; the results are presented in (Fig. 3).

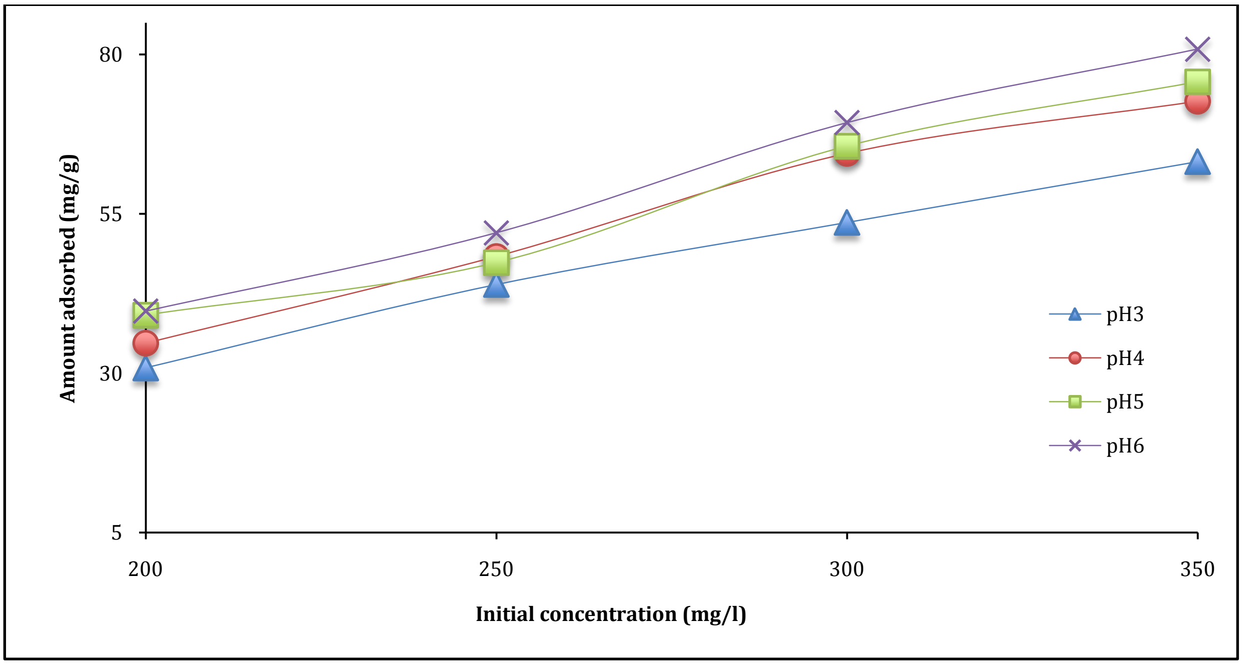


Fig.4: Effect of initial pH on Cu(II) adsorption at 25°C.

We can observe that the retention increases with pH solution due to the increase of surface negative charge. Moreover the increase in pH favors often precipitation, and then copper could probably be eliminated through precipitation as well[17].

3.4 Effect of temperature

In order to determine the effect of temperature on the adsorption of copper ions on clay, experiments were run with four different values 15, 25, 35 and 45°C.

From the curves of fig.4, we can notice that the amount of adsorbed ions increase with temperature which indicates that the adsorption process is endothermic.

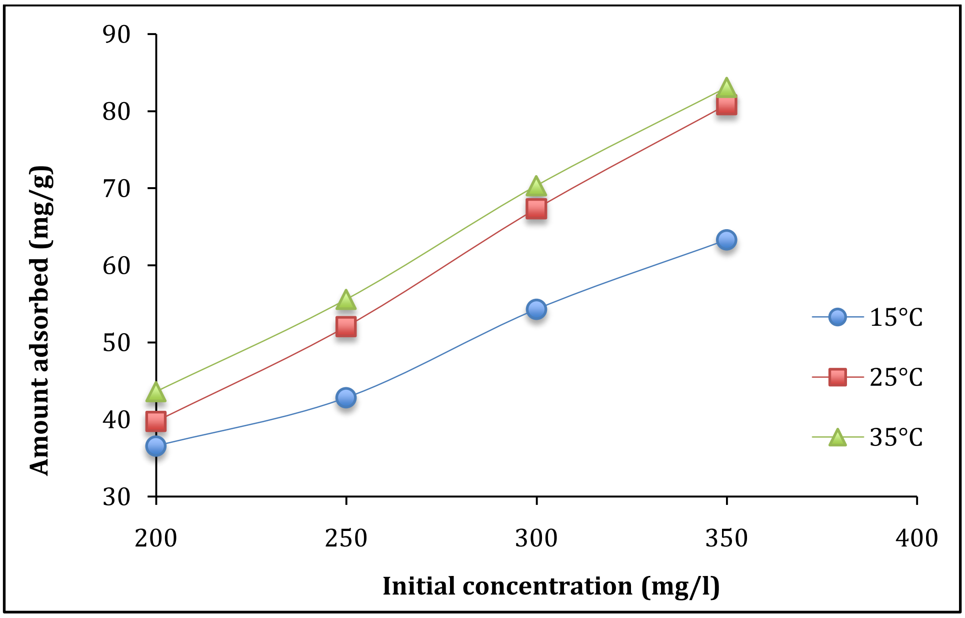


Fig. 5: Effect of temperature on Cu(II) adsorption at pH 6.

The thermodynamic parameters are listed in Tab 1. The positive ΔH° value confirms the endothermic process, and the negative value of ΔG° indicate that sorption was spontaneous in nature[10]. Also those values imply that the retention process of copper by the clay is a combination of two mechanisms: ions exchange and adsorption[17].

Table 1: thermodynamic parameters

T (K)	**ΔH°**	**ΔS°**	**ΔG°**
288	68908.9262	248.979358	-6274.846989
298			-30117.12327
308			-48384.78226
318			-120607.0056

Conclusion

This experimental study of copper adsorption by raw clay shows that this material has an important removal capacity. The study considered the effect of different physical and chemical parameters on copper adsorption by this adsorbent.

The retention of copper ions by clay fitted to the Langmuir isotherm, the adsorption capacity increases with temperature and pH.
The positive ΔH° value for the removal quatity of copper indicated an endothermic process. Also the negative ΔG° value confirmed the feasibility of sorption process and itsspontaneous nature.

Symbols :

K_f: Freundlich constant (mg/g) $(L/g)^{1/n}$
1/n: Freundlich exponent
K_L: Langmuir isotherm constant (L/mg)
q_m: monolayer sorption capacity (mg/g)
q_e: Equilibrium solid-liquid copperconcentration (mg/g)
C_0, C_e: Initial and equilibrium liquidphase copper concentrationsrespectively (mg/g)
ΔG°: Apparent Gibbs free energy (J/mole)
ΔH°: Apparent enthalpy of adsorption (J/mole)
ΔS° : Apparent entropy of adsorption (J/mole K).

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