

Original Research Paper

Removal of Copper from Aqueous Solution using Tunisian Clay

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Abstract: Natural adsorbents such as clay was used to replace expensive imported synthetic adsorbents. In this study, Scanning Electron Microscopy (SEM), Infrared spectroscopy and X-ray diffraction techniques were used to characterize the used sorbent (clays C). Batch experiments were performed to evaluate the effects of contact time, solution pH and temperature on copper removal onto used sorbent from aqueous solution. Equilibrium data were analyzed using Langmuir and Freundlich isotherm models to calculate isotherm constants. Kinetic studies showed that an equilibrium time of 1 h was required for the adsorption of Cu(II) onto Tunisian clay. Equilibrium adsorption is affected by the initial pH of the solution. The maximum adsorption capacity was obtained at pH 5. Adsorption tests in synthetic wastewater revealed that the adsorption data of this material for copper ions were better fit to the Langmuir isotherm based on correlation coefficients. The influence of temperature on the adsorption process was also evaluated. Results indicated that adsorption of Cu(II) on the sorbents is endothermic. The thermodynamic parameters (ΔG° , ΔH° and ΔS°) for Cu(II) sorption were also determined from the temperature dependence. Results of this study suggest that used Tunisian clay may be a promising adsorbents for environmental remediation.

Keywords: Copper, Adsorption, Clay, Isotherms

Introduction

The potential sources of copper in industrial waste streams include metal cleaning and plating baths, pulp, paper and paperboard mills, wood pulp production, fertilizer industry, etc. (Dean *et al.*, 1972). Excessive intake of copper results in its accumulation in the liver. The chronic copper poisoning is related to hemochromatosis when present in large amounts (Camp, 1964). It is also toxic to fish life even when its content is in low amounts in natural waters (Camp, 1964).

Removal of heavy metals from contaminated aquatic systems is deemed important for the protection of environmental health. Therefore, it is urgent to remove those toxic heavy metals from wastewater. Although heavy metal removal from aqueous solutions can be achieved by conventional methods, including chemical precipitation, oxidation/reduction, electrochemical treatment, evaporative recovery, filtration, ion exchange and membrane technologies, they may be ineffective or cost-expensive, especially when the metal ion

concentrations in solution are in the range of 1-100 mg L⁻¹ (Dhakal *et al.*, 2005; Liang *et al.*, 2009). Recently, adsorption technology has become one of the alternative treatments in either laboratory or industrial scale (Kumar and Bandyopadhyay, 2006; Singh *et al.*, 2006). Therefore, adsorption is the most frequently applied technique owing to its advantages, such as variety of adsorbent materials and high efficiency at a relatively lower cost (Mohan and Pittman, 2006). Although activated carbon is one of the most popular adsorbents for removal of metal ions (Schindler *et al.*, 1996; Mohan and Pittman, 2006; Zhang *et al.*, 2007), current investigations tend towards achieving high removal efficiencies with much cheaper materials which are mostly cheap and abundant matter. The development of new and more effective adsorbents, like clay, has become essential, but at the same time it should be of low cost.

Mineral clay can absorb heavy metals via two different mechanisms: (1) Cation exchange at the planar sites, resulting from the interactions between metal ions

and negative permanent charge (outer-sphere complexes) and (2) innersphere complexes formation through SiO₂ and AlO₃ groups at the clay particle edges (Babel and Kurniawan, 2003). Both mechanisms are pH dependent but the latter is particularly influenced by pH because in acidic conditions (pH <4) most silanol and aluminol groups on edges are protonated. For this reason, it is necessary to improve the knowledge of the effect of pH on the sorption capacity of mineral clay in solid-solution system.

The aim of this work is to study the removal of Cu(II) from aqueous solution by adsorption on Tunisian clay (C) after physicochemical characterization of the used sorbent.

Materials and Methods

Sorbent and Adsorbate

The raw clay used in this study was collected from Cap Bon region In the North East of Tunisia. Clay sample was collected from Jbel Abderrahmen.

Aqueous solutions containing copper ions (Cu II) at various concentrations were prepared from copper salts (CuSO₄·5H₂O). All chemicals used for the treatment of the different sorbents and for adsorption tests were of analytical quality. The various solutions are prepared in distilled water.

Mineral Identification of Adsorbents

The mineralogical analysis of the raw sample was carried out by X-ray diffraction (Phillips X'Pert diffractometer) on the oriented aggregates; normal (N), was treated with ethylene glycol (T) and heated at

500°C for 2 h (H). The XRD spectrum of oriented aggregates is presented in Fig. 1. The chemical composition was determined by ICP-AES. Loss On Ignition (LOI) was considered as the weight percent difference between sample heated at 100 and 1,000°C. An IR transmittance spectrum of the mineral clay sample was obtained in the 4,000-500 cm⁻¹ range using a SHIMATZU IR 470 spectrometer.

The used clay specific surface area (m²/g) was determined by the single-point BET adsorption procedure. Standard report of clay and distilled water (with stirring) is dosed by methylene blue, until saturation of clay particles. The end of the test is determined by the persistence of a clear blue halo, indicating the saturation of the clay.

The X-ray diffraction analysis indicated that the raw clay is mainly composed of Kaolinite (51%), Illite (45%) and 4% Smectites (Table 1).

The chemical analysis showed that the clay sample was characterized by a rate of 50.59% SiO₂ (Table 2) the alumina is 17,24%. This verifies the presence of an aluminosilicate material in the studied samples. The percentage of iron oxide is relatively high (9.97%) This is typical clays Tunisian (Benzina and Bellagi, 1990).

The loss at high fire is due to the presence of a slightly higher rate of smectite in which are intercalated water molecules, with the presence of MgO and CaO.

The BET surface area of clay sample was found to be 180.2 m²/g.

The infrared absorption spectrum (Fig. 2) of clay showed the presence of peaks characteristic of the silica present in the sample. The results confirm those found in the chemical composition of the support.

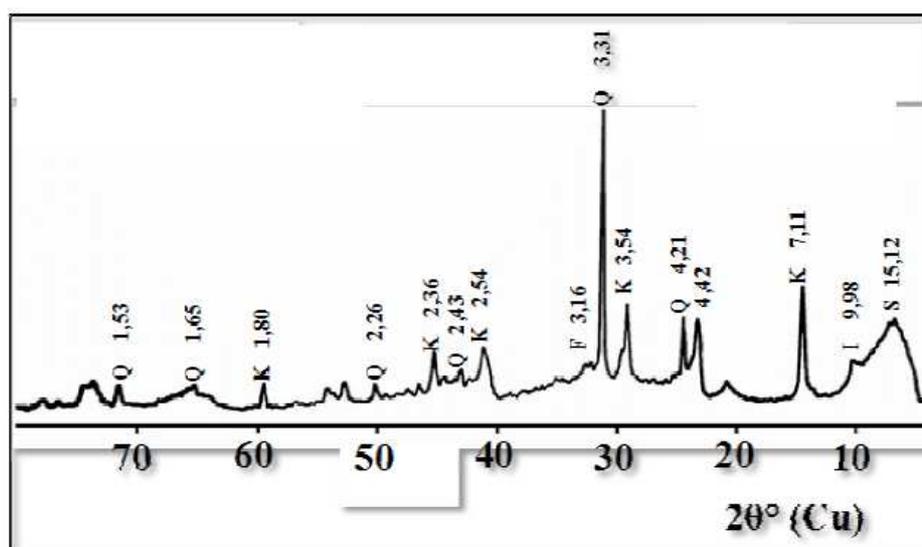


Fig. 1. XRD spectrum of oriented aggregates of clay sample

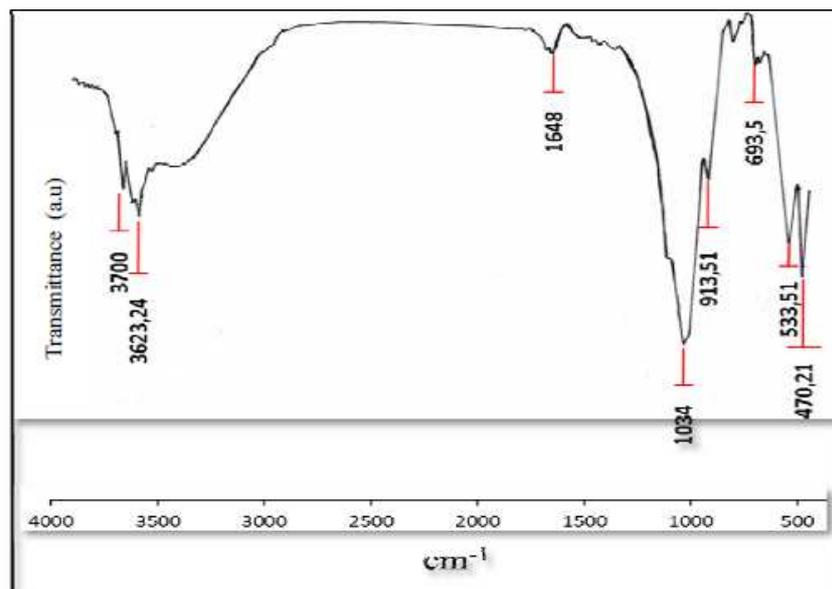


Fig. 2. FT-IR spectra of clay

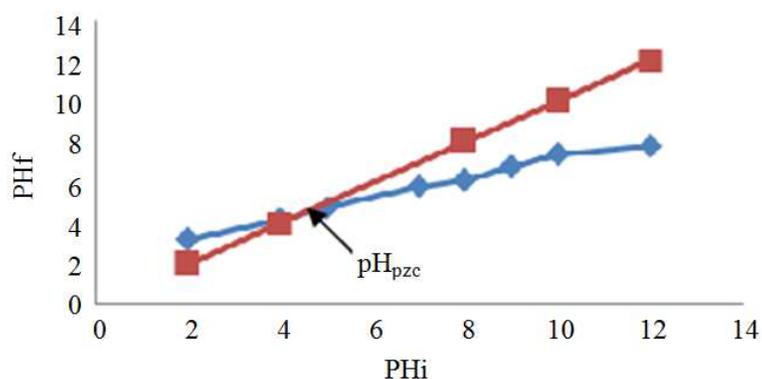


Fig. 3. Point of zero charge of used clay

Table 1. Mineralogical composition of clay

Mineral	Illite (I)	Kaolinite (K)	Smectite (S)	Phyllosilicate (PH)	Calcite (C)	Quartz (Q)	Feldspath (F)
Ab	45	51	4	76	3	19	2

Table 2. Chemical composition of clay

Samples	Composition (%)														
	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	Na ₂ O	K ₂ O	MnO	Cr ₂ O ₃	P ₂ O ₅	TiO ₂	PF	Pb ₂ O ₃	ZnO	Ni ₂ O ₃
Clay	22,38	1,53	-	0,46	3,96	1,7	10,01	-	-	-	-	-	0,017	0,045	0,029

The powder morphology of sorbents was obtained using a Philips XL 30 Scanning Electron Microscope (SEM). Elemental spectra were obtained using energy dispersive X-ray spectroscopy during SEM observations.

The image obtained is shown in Fig. 3 note the presence of micropores. The crude clay is a porous material whose porosity depends on the geometry, size

and distribution of pores. We can see in this figure the clay structure layers of this mineral.

The pH of zero point of charge (pH_{zpc}) was determined by adding a known amount of adsorbent (0.1 g) to a series of bottles that contained 50 mL of deionised water. Before adding the adsorbent, the pH of the solutions was adjusted to be in the range of 1.0-

9.0 by the addition of either 0.1 M HNO₃ or 0.1 M NaOH. These bottles were then rotated for 1 h in a shaker and pH values were measured at the end of the test. The pH of the suspensions is represented as a function of the initial pH of the solutions. The curve obtained theoretically cross the bisector of axes at the point of zero charge.

According to Fig. 4, it is found that the p*H*_{ZPC} is equal to 5.6 for the adsorbent considered.

For p*H*_i values acid increased final pH is faster than for a p*H*_i alkaline. The variation in the p*H*_f is due to the interaction of the support with the solution aqueuse. En acid medium equilibrium occurs from the left to the right, thereby producing the rapid increase p*H*_f (Mohan and Pittman, 2006). The value of p*H*_{ZPC} is dependent on several factors including: The crystalline form, Originally, the conditions of preparation, the presence of impurities ... for this reason it varies of a given type of clay to another.

A pH meter (models pH 540 GLP) equipped with a combined glass electrode SENTIX 41 was used to

measure the pH of the solutions. A preliminary calibration is systematically carried out using suitable buffer solutions. The concentrations of copper ions were measured by an atomic absorption spectrometer (HITACHI Z-6100) by electrothermal atomization mode.

Effect of Various Operating Parameters on Copper (II) Removal

Effect of Adsorbent Amount

The influence of the amount of clay adsorbent (0.1-2 g/200 mL) on Cu(II) removal at constant values of initial metal concentration, contact time (60 min) and temperature (25°C) is shown in Fig. 5. The results showed that the removal of copper increased rapidly to 80%, until a sorbent dose of 1.5 g/200 mL and moderately beyond this value. This was an expected result since as the sorbent dose increased, the number of adsorbent sites increased; therefore, these amounts attached more ions to their surfaces (Abollino *et al.*, 2002).

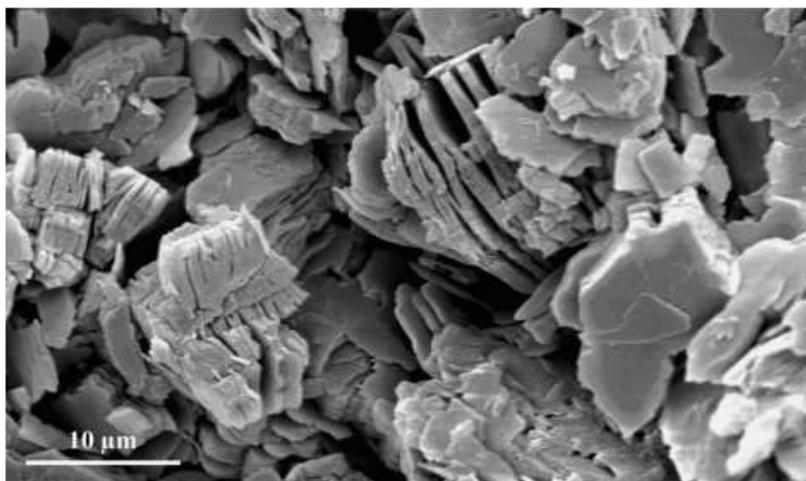


Fig. 4. SEM micrograph of used clay

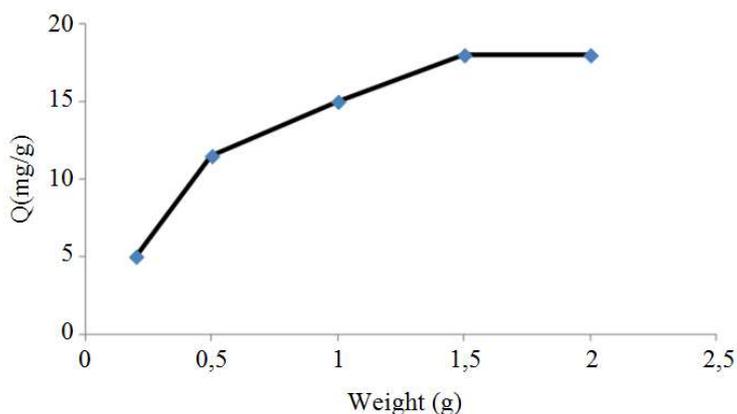


Fig. 5. Effect of adsorbent amount on Cu(II) adsorption

Effect of pH

The influence of pH on the removal of Cu(II) ions by clay sample was investigated. In the present work, copper adsorption was studied in the pH range of 2-6 with a constant clay amount of 1.5 g/200 mL of effluent and a shaking time of 60 min.

The results presented in Fig. 6 reveal that the adsorption of copper increases from 91 to 95.7% with an increase in solution pH from 2 to 6 and then decreases rapidly at $\text{pH} \geq 6$. The effect of pH can be explained in terms of pzc (point of zero charge) of the adsorbent MOM R equal to 5.6 (Shukla *et al.*, 2005). Above 5.6, adsorbent surface is a negatively charged clay; therefore, adsorption percentage progressively increases from 2 to 6 pH by electrostatic attraction.

Below pzc adsorption decreases due to electrostatic repulsion between the positively charged surfaces of adsorbent and cationic metal Cu.

Effect of Shaking Time

The time-dependent behavior of copper adsorption was studied by varying the contact time between the adsorbate and adsorbent in the range 1-120 min. The clay sample dose was 1.5 g/200 mL and the solution pH was fixed at 5.6. The data showed that the adsorption was very fast (Fig. 7). According to the experimental results of several authors (Gupta and Bhattacharyya, 2006; Das and Jana, 2005) on the retention of heavy metals on clay minerals, the adsorption process is fast at the beginning of the reaction due to the adsorption of copper on the surface sites of clay, then it becomes slow due to the diffusion of heavy metals from the surface sites to the interlayer of the solid. Therefore, a 60 min shaking time was found to be appropriate for maximum adsorption and was used in all subsequent measurements.

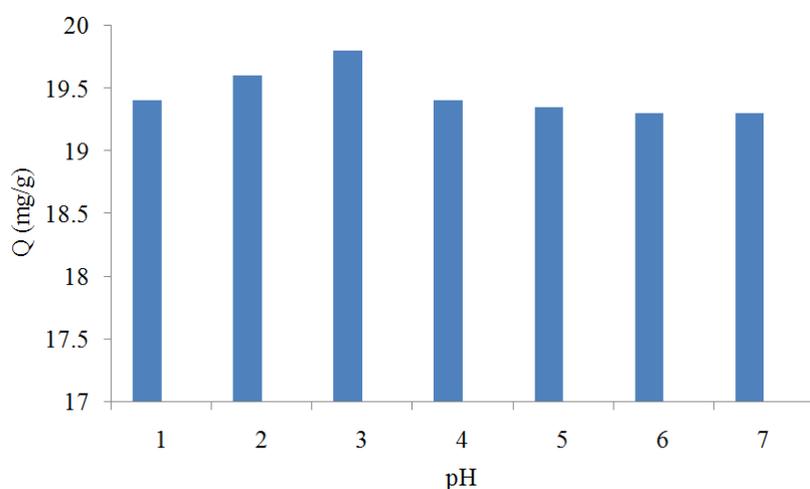


Fig. 6. Effect of pH on Cu(II) adsorption

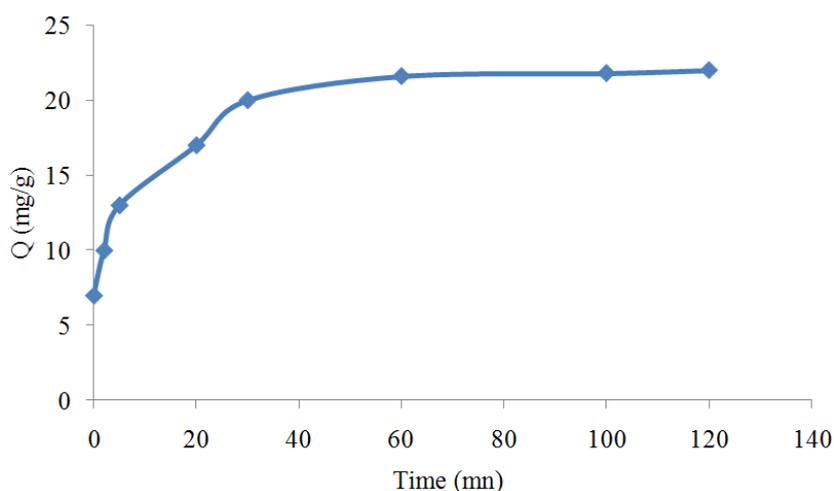


Fig. 7. Effect of shaking time on Cu(II) adsorption

Adsorption Isotherm

Copper ions adsorption isotherms obtained for mineral clay adsorbents are shown in Fig. 8. These isotherms represent the adsorption behavior of Cu(II) ions on the clay adsorbents as a function of increasing aqueous copper concentration, for a contact time of 60 min.

The Freundlich isotherm model used for copper adsorption (Fig. 9) is the earliest known relationship describing the adsorption equilibrium.

This fairly satisfactory empirical model can be used for non-ideal adsorption and is expressed by the following Equation 1:

$$Q = K_F C_e^{1/n} \quad (1)$$

where, K_F and n are constants related to the adsorption capacity and affinity, respectively. The equation is conveniently used in the linear form by taking the logarithm of both sides (Equation 2):

$$\log(Q) = \log K_F + 1/n \log C_e \quad (2)$$

Table 4 indicates that there is a slight deviation from linearity using the Freundlich isotherm model for

describing C(II) adsorption (R^2 equal to 0.89). Freundlich parameters (K_F and n) indicate whether the nature of adsorption is either favorable or unfavorable (Frimmel and Huber, 1996). The intercept is an indicator of adsorption capacity and the slope is an indicator of adsorption intensity. In the adsorption systems, values obtained of $1 < n < 10$ imply favorable adsorption. The K_F values, reported in Table 3b, can be used to indicate the relative adsorption capacity of the system (Mohan and Singh, 2002).

The results of copper ions adsorption onto clay (Fig. 10) were also analyzed using the Langmuir model to evaluate parameters associated to the adsorption behavior. The linear form of Langmuir equation at a given temperature is represented by Equation 3:

$$\frac{C_e}{Q} = \frac{1}{Q_0 b} + \frac{C_e}{Q_0} \quad (3)$$

where, C_e is the aqueous phase equilibrium concentration (mg/L), q_e the amount of metal ions adsorbed onto 1 g of the considered adsorbent, b the adsorption constant (L/mg) related to the energy of adsorption and Q is the maximum adsorption capacity (mg/g).

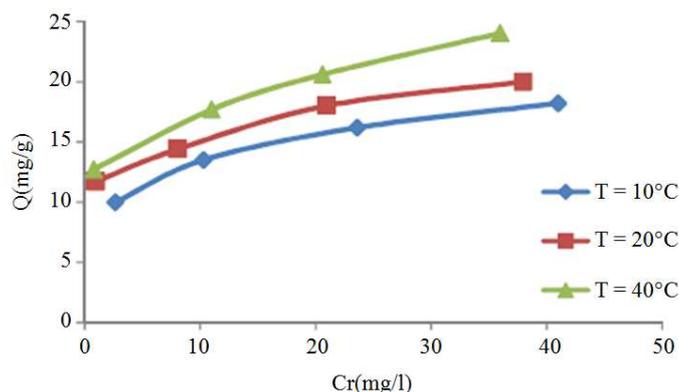


Fig. 8. Equilibrium isotherms for Cu(II) ions removal by clay (1.5 g adsorbent/200 mL effluent, T = 10, 25 and 40°C, pH 5)

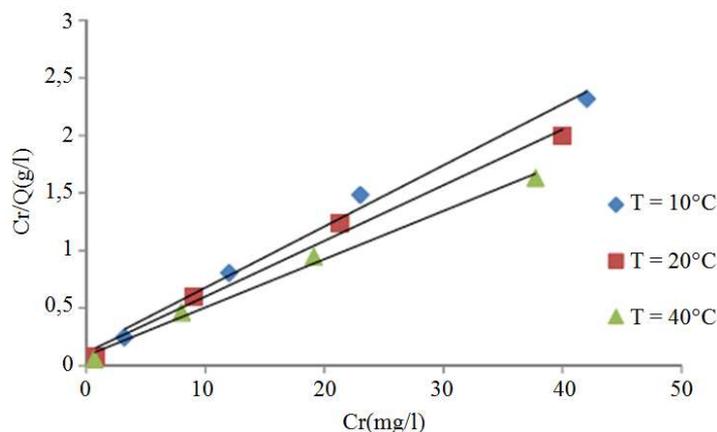


Fig. 9. Freundlich isotherms for the adsorption of Cu(II) at T = 10, 25 and 40°C on clay

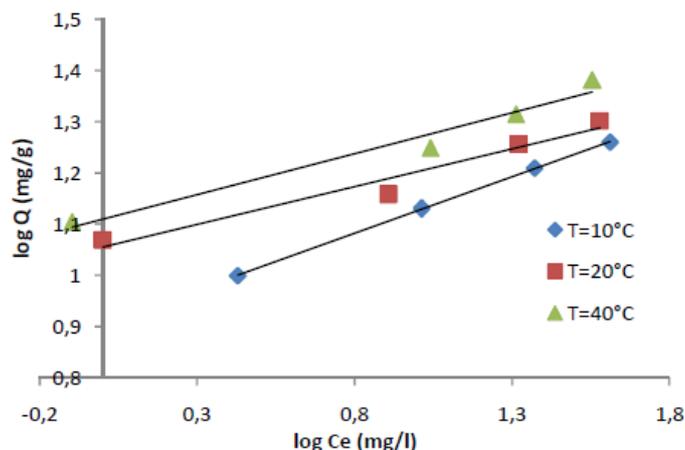


Fig. 10. Langmuir isotherms for the adsorption of Cu(II) at T = 10, 25 and 40°C on clay

Table 3. Freundlich and Langmuir constants for Cu(II) adsorption on clay

Temperature (°C)	Q ₀ (mg/g)	b (l/mg)	R ²
10	19.60	0.286	0.994
20	22.22	0.310	0.983
40	25.02	0.353	0.978
	K _f	1/n	R ²
10	8.83	0.191	0.911
20	11.01	0.158	0.891
40	13.93	0.128	0.883

Table 4. Thermodynamic parameters for the adsorption of Cu (II) at various temperatures on clay

Temperature (°C)	ΔH° (KJ/ mol)	ΔG° (KJ/mol)	ΔS° (KJ/K.mol)
10	5.18	-22.95	0.099
20	5.18	-23.94	0.099
40	5.18	-25.92	0.099

Table 3a indicates that the Langmuir equation gives a fairly good application for copper adsorption with a regression coefficient, R² equal to 0.98. The maximum adsorption capacity at 298°K for the metals can be estimated at 22.22 mg/g. This capacity is high compared to other adsorbents (iron oxide coated sand Q₀ is equal to 5.93 mg/g (Boujelben, 2011); and phosphate rock, Q₀ is equal to 11.77 mg/g (Elouear, 2011)). Thus, notes the effectiveness of the used sorbent.

Adsorption Thermodynamic Parameters

In order to explain the effect of temperature on the adsorption thermodynamic parameters, standard Gibbs free energy (ΔG°), standard enthalpy (ΔH°) and standard entropy (ΔS°) were determined. The adsorption process of metal ions can be summarized by the following reversible process which represents a heterogeneous equilibrium. The equation (Equation 4) given below was used to determine the Gibbs free energy of adsorption (ΔG°) (Altin *et al.*, 1999; Mohan and Singh, 2002):

$$\Delta G^\circ = -RT \ln b \quad (4)$$

where, *R* is the gas constant 8.314 10⁻³ kJ/(mol K), *T* is absolute temperature, *K* and *b* are equilibrium constants at temperature *T*, respectively. The other useful relationships are the change in standard enthalpy, ΔH° and standard entropy, ΔS° and they are given by Equation 5:

$$\log b = \frac{\Delta S^\circ}{2.303R} - \frac{\Delta H^\circ}{2.303RT} \quad (5)$$

When ln *b* is plotted against 1/*T*, a straight line with slope ΔH°/*R* and intercept ΔS°/*R* is obtained. The values of ΔH° and ΔS° were obtained from the slope and intercept of the Van't Hoff plots of ln *b* Vs. 1/*T*.

The thermodynamic parameters for the adsorption process are given in Table 4. The Gibbs free energy indicates the degree of spontaneity of the adsorption process and the higher negative value reflects a more energetically favorable adsorption.

However, Positive values of ΔH suggest the endothermic nature of the Cu(II) adsorption on clay adsorbent. The positive values of ΔS reflect the affinity of clay for Cu (II) and show the increasing randomness at the solid/liquid interface during the sorption of metal ions on clay.

Conclusion

The above results can provide a process for developing a low-cost technology based on adsorption by natural materials for metal ions removal from wastewater. The wide range of experiments performed showed essentially that:

- The mineralogical and chemical analyzes showed that the types of natural material used were illite kaolinite
- The adsorption of copper depended on the solution pH. Maximum retention occurred at around; pH 5, shaking time 60 min, adsorbent amount 1.5 g/200 mL and temperature 40°C
- For the adsorption isotherms of copper ions, both Langmuir and Freundlich equations were fitted to experimental data satisfactorily
- These results led to classify the Tunisian illite kaolinite of the Cap bon region as a new lowcost adsorbent of some well-known adsorbents for wastewater cleanup

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Author's Contributions

Nesrine Boujelben: Participated in all experiments, coordinated the data-analysis and contributed to the writing of the manuscript.

Sana Ghrab: Participated in all experiments and coordinated the data-analysis.

Farah Bouhamed: Designed the research plan and organized the study.

Zouheir Elouear and Jalel Bouzid: Coordinated the mouse work.

Ethics

This article is original and contains unpublished material. The corresponding author confirms that all of other authors have read and approved the manuscript and no ethical issues involved.

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