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Natural Algerian Marl as a Potentiel Low-Cost Adsorbent for the Removal of Copper Ions: Isotherm, Kinetic and Thermodynamic Studies

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ABSTRACT

The present work aimed to study the removal of copper ions using marl found in large deposits in R'ghiss mountain located in Oum-El-Bouaghi region (Algeria). The marl has been characterized by XRF, XRD and BET. The operational parameters such as adsorbent mass, agitation rate, and pH were studied. To better explain the experimental results, the adsorption isotherms and kinetics were modeled using the method of non-linear regression. The results showed that the adsorption of copper onto natural untreated marl obeyed the Langmuir model, maximum monolayer adsorptioncapacity (qm) of 130.70mg/g and the kinetic data followed a pseudo first order. Thermodynamic parameters such standard Gibbs free energy (ΔG°), standard enthalpy (ΔH°) and standard entropy (ΔS°), were also calculated. The value and the sign of the standard enthalpy of adsorption showed that the adsorption process was endothermic and followed a physisorption mechanism. These results suggested that marl (Oum El Bouaghi) could be used as an efficient adsorbent for removal of copper (11) ions from wastewaters.

Keywords: Cu(II) Ions, Modeling, Natural Adsorbent, Removal, Validity of the Adsorption.

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1. INTRODUCTION

Heavy metals discharges have posed serious problems to the environment, because they are hazardous and not biodegradable. In addition, they can interfere with the food chain, and concentrate in living organisms. Hence, they can exceed the allowable levels in some largely consumed foods, such as fish. The bioaccumulation of these metals have explained their very high risk (Singh et al. 2011; Fu & Wang 2011).

There are several purification methods such as: precipitation, filtration, coagulation, flotation, complexation, solvent, extraction, membrane separation, electrochemical technique, biological process, and ion exchange (Meunier et al. 2006; Rafatullah et al. 2011). Adsorption technique is simple, low cost and flexible, consequently it is the most preferred for removal of toxic metals. The search for new porous materials in the field of the treatment of effluents containing heavy metals has remained a subject of relevance. In most cases, these materials have been issued from natural resources. Given the high cost of the transformation processed by these raw materials into porous materials, several current studies have been directed towards the use of natural porous materials, often without any prior treatment and conditioning. Marls are sedimentary rocks with a composition between that of clay stone and carbonate formed by the erosion of other rocks

(Millot 1970; Sokouti & Razagi 2015). Only few studies have been reported in literature about adsorption of toxic metals ions onto marl such as adsorption of cesium (Cornell 1992), nickel (Cornell and Aksoyoglu,1992) and chromium (Jabari et al. 2009).

The objective of this work was studying the adsorption of cupric ions in aqueous solutions on natural marl from Oum El Bouaghi used as a new low cost adsorbent. Copper in the form of Cu^{2+} ions has been generally recognized as toxic to aquatic organisms and vascular plants. For humans, the maximum concentration permitted according to world health organization (WHO) is 2 mg/L (WHO 2008). The effect of various operating parameters, such as marl mass, stirring speed and pH were considered. Adsorption isotherms and kinetics were modelled using non-linear regression method, also, thermodynamic study was investigated.

2. MATERIALS AND METHODS

Adsorbent

In this study, the researchers chose a very abundant and unexploited black marl, located in R'ghiss mountain situated in Oum-El-Bouaghi region (Algeria) whose geographic coordinates are 35°54'11.83'' north latitude and 7°07'24.45'' east longitude. The collected marl was washed with distilled water, and then exposed to open air for a week until dryness. Its apparent density, determined at 293 K by the flask method, was estimated at 2.51 and its natural pH was 8. The basic solution was due to the presence of basic salts such as carbonates.

Solution of adsorbate

The Cu²⁺ solutions were prepared by dissolving appropriate amount of copper sulphate pentahydrate crystals (CuSO₄.5H₂O, molar mass=249.68g.mol⁻¹, purity: 99%, Riedel-de Haën) in distilled water using an analytical balance (Kern model). The pH was adjusted by adding HCl solution (Merck product). The determination of Cu²⁺ in aqueous solution has been carried out by molecular absorption spectrophotometry at 810 nm (Spectronic 70 Spectrophotometer).

Characterization

The chemical composition of marl was determined by X-ray fluorescence spectrometry (Sequential Panalytical Pro-Magix). The mineralogical composition was investigated by X-ray diffraction using a Panalytical X-Pert Pro MPD diffractometer with Cu K α radiation (45 kV, 40 mA), wavelength λ =1.5406 Å, X'Celerator detector, 0°-100°scan range, 0.017° step size and 62.0270 s as counting time. The specific surface area, pore volume, pore width were measured by BET (ASAP 2020 MICROMIRITICS).

Procedure

The dry marl was finely ground in an agate mortar, and sieved until full passage through 180µm sieve (Retsch model), then, kept for further use. The adsorption of Cu2+ ions onto marl was performed under static conditions in a stirred reactor immersed in a 25 ml thermostatically controlled and agitated water bath (Heizung model). The effects of different parameters like the adsorbent mass, stirring speed and pH of the adsorption solution were determined. The Jenway pH meter was used for pH measurements. The sample was then centrifuged for 5 minutes at 3500 rpm (Hettich Universal) and immediately the supernatant was analyzed bv spectrophotometry. The amount of Cu²⁺ adsorbed at time t per unit mass of marl was determined by eqn. (1):

$$q_t = (C_0 - C_t) \frac{v}{m} \tag{1}$$

where q_t is the amount of Cu²⁺ adsorbed at time t (mg. g⁻¹), C_{θ} and C_t are the initial and residual concentration of Cu²⁺ (mg. L⁻¹), V is the volume of solution volume (L) and *m* is the mass of marl (g).

Adsorptions isotherms

The purpose of the study of adsorption isotherms was to model the experimental results, that is to say, determine the equation of the mathematical function which best described the experimental curve. Many models were reported in the literature. In this work, the researchers applied a model called mono-solute two adjustable parameters, described independently by Langmuir (1918), Freundlich (1906) and Tempkin & yzhev (1940). Adsorption isotherm constants were used to evaluate the adsorptive properties of a material, and determine if the adsorption is favorable or not.

Langmuir isotherm

The model is based on the following assumptions (Langmuir 1918)

- formation of a monolayer of adsorbate on the outer surface of the adsorbent;
- the adsorbent has a limited adsorption capacity, denoted q_m;

- all the adsorption sites are identical and they can react only one solute molecule;
- there are no interactions between the adsorbed molecules.

Langmuir isotherm can be written as follows:

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

where q_e is the amount of adsorbed Cu²⁺ per unit marl mass at equilibrium (mg. g⁻¹), q_m is the maximum adsorption capacity (mg. g⁻¹), C_e is the residual concentration at equilibrium (mg. L⁻¹), and K_L is the equilibrium constant of Langmuir isotherm (L.mg⁻¹).

Freundlich isotherm

The Freundlich isotherm is an empirical model used to describe the adsorption characteristics over a heterogeneous surface (Freundlich 1906). It is often expressed by the following empirical equation

$$q_e = K_F C_e^{1/n} \tag{3}$$

where K_F is the Freundlich isotherm constant (mg⁽¹⁻ⁿ⁾. Lⁿ. g⁻¹) and *n* is the adsorption intensity (Without units)

Tempkin isotherm

Tempkin model assumes that during the adsorption, the adsorption heat due to interactions with the adsorbate decreases linearly with the recovery rate of the surface of the adsorbent (Tempkin & yzhev 1940). The model can be described by eqn. (4):

$$q_e = \frac{RT}{b_T} ln K_T + \frac{RT}{b_T} ln C_e \tag{4}$$

where K_T is the Tempkin isotherm constant (L.mg⁻¹), b_T is the Tempkin isotherm constant, T is the absolute temperature (K) and R is the universal gas constant (8.314 J.mol⁻¹. K⁻¹).

Validity of adsorption Mathematical models

The parameters of the preceding isotherms can be estimated by non-linear regression. In order to evaluate the validity of the adsorption mathematical models with experimental

results, a number of error functions have been available in the literature. In this work, the researchers chose four types of error function (equations (5), (6), (7) and (8)) among the most widely used in such studies (Foo & Hameed 2010; Vasanth Kumara et al. 2008).

Average relative error (ARE)

$$4RE = \frac{100}{N} \sum_{i=1}^{N} \left| \frac{q_{e,cal} - q_{e,exp}}{q_{e,exp}} \right|_{i}$$
(5)

- The Sum of Squared Errors (SSE)
 - $SSE = \sum_{i=1}^{N} (q_{e,cal} q_{e,exp})_i^2$ (6)
- Chi-square test (χ²)

$$\chi^{2} = \sum_{i=1}^{N} \left[\frac{(q_{e,exp} - q_{e,cal})^{2}}{q_{e,cal}} \right]_{i}$$
(7)

Coefficient of determination(R²)

$$R^{2} = 1 - \left[\frac{\sum_{i=1}^{N} (q_{e,cal} - q_{e,exp})_{i}^{2}}{\sum_{i=1}^{N} (q_{e,cal} - \bar{q}_{e,exp})_{i}^{2}} \right]$$
(8)

where $q_{e, cal}$ and $q_{e, exp}$ are the calculated and experimental amount of adsorbed Cu²⁺ per unit marl mass at the equilibrium (mg. g⁻¹) and *N* is the number of experimental data points. The values of ARE, SSE, χ^2 are low, and R² tends to unity. The chosen model described the experimental results of adsorption well, and seemed to be relevant.

Determination of thermodynamic parameters

The constant of the Langmuir isotherm K_L depended on the temperature, and consequently it can be used for estimating the thermodynamic parameters of the adsorption process, such as the standard free enthalpy ΔG° , the standard enthalpy ΔH° and the standard entropy ΔS° from the following equations (Cottet et al., 2014):

$$\Delta G^{\circ} = -RT \ln K_L \tag{9}$$

$$\Delta G^{\circ} = \Delta H^{\circ} - T \Delta S^{\circ} \tag{10}$$

$$\ln K_L = \frac{\Delta S^{\circ}}{R} - \frac{\Delta H^{\circ}}{RT}$$
(11)

measuring the enthalpy of adsorption ΔH° differentiated between chemisorption and physisorption.

Kinetic study

Understanding the kinetic mechanisms of the operations based on the phenomena of the adsorption presented a considerable practical interest for the optimal implementation of an adsorbent, and the knowledge of the factors that must be optimized to manufacture or improve an adsorbent leading to the fastest possible kinetic. The adsorption process occured via a series of steps that determined the overall speed of the process. Several models have been developed to examine the mechanism of the adsorption process of a liquid on a solid surface; of these models, the researchers retained two kinetic models which have been the most discussed in the literature. As for the adsorption isotherms, the results could be modelled either by linear regression, or by nonlinear regression.

Pseudo-first -order kinetic model

The pseudo first order model was described by Lagergren (1898). This model was valid, in general, in the first minutes of the adsorption phenomena (linearity results in this region of the curve):

$$\frac{dq_t}{dt} = k_1(q_e - q_t) \tag{12}$$

Integrating equation (12) with the boundary conditions, t=0 to t and from 0 to q_t led to a non-linear form as shown in eqn. (13):

$$q_t = q_e \big(1 - exp(-k_1 t) \big) \tag{13}$$

Pseudo-second –order kinetic model

This model described by Ho & Mckay (1999) has been the most used model, it is valid for a wide range of time and requires a chemisorption mechanism. The expression of the pseudo second order model has been written as eqn. (14):

$$\frac{dq_t}{dt} = k_2 (q_e - q_t)^2 \tag{14}$$

The integration of equation (14) led to the non-linear form:

$$q_t = \frac{k_2 q_e^2 t}{1 + k_2 q_e t}$$
(15)

where *t* is the contact time (min), k_1 is the rate constant of pseudo-first-order adsorption kinetic (min⁻¹) and k_2 is the rate constant of pseudo-second-order adsorption kinetic (g.mg⁻¹.min⁻¹).

So, the advantage of using the non-linear form lies directly in the fact that the researchers don't need to know the equilibrium capacity q_e from experience, since it can be determined from the model. This made it possible to determine k_2 and the initial rate of adsorption:

$$V_i = k_2 \, (q_e)^2 \tag{16}$$

3. RESULTS AND DISCUSSION

Characterization

The results of X-ray fluorescence analysis are summarized in Table 1.

Compound	Amount [%]		
SiO ₂	46.63		
Al_2O_3	17.78		
Fe ₂ O ₃	07.05		
CaO	09.30		
MgO	01.84		
SO ₃	00.02		
K ₂ O	03.22		
Na ₂ O	00.64		
P ₂ O ₅	00.19		
TiO ₂	00.74		
LOI*	12.59		

Table 1. Chemical composition of marl (%)

*Loss on ignition

The mass ratio silica/alumina was 2.62, this high value indicated the presence of free silica (quartz) and other clay minerals (Koffi 2006). The X-ray diffractogram of the marl is shown in Figure 1 and the results in Table 2.



Figure 1. X-ray diffractogram of the marl

3				
Minerals present	Mineralogical composition [%]			
Quartz	15			
Calcite	17			
Albite	05			
Illite	23			
Kaolinite	13			
Montmorillonite	20			
Ferruginous minerals+ other	07			

Table 2. Mineralogical composition of marl

The analysis of the results of Tables 1 and 2 showed that:

- The calcium and iron contents in marl were important;
- The total alkali content was relatively low;
- The clay fraction consisted of essentially illite, montmorillonite, kaolinite with low amount of albite.

The values of the specific surface area, pore volume and pore width were 14.6026 $m^2/g,\ 0.023489\ cm^3/g$ and 64.3428 Å; respectively.

Study of the adsorption

Effect of adsorbent mass

The influence of the mass of the marl was studied in the range of 400-1000 mg. The obtained results are illustrated by the curves of Figure 2. From these results it seemed clear, with an increase in the adsorbent amount, the uptake capacity of marl for Cu2+ ion was found to decrease. The amount of adsorbed Cu2+ decreased from 104.45 mg/g to 42.82 mg/g, as the adsorbent amount was increased from 400 to 1000mg for a contact time of 210 min. This phenomenon can be explained by the formation of stable aggregates between the cations in solution and the clay particles. These aggregates altered the behaviour of the marl in aqueous solution. Indeed, clays contained in marl, had a negative electrostatic charge, and cations in solution had a positive one. If we consider that the surface area where concentrated electrostatic charges were the adsorption sites, attracting cations by these surfaces resulted in the formation of aggregates of cationic bridges and therefore the decrease of the adsorption sites in the marl.



Figure 2. The effect of the adsorbent mass (Cu²⁺ concentration: 2000 mg/L, temperature: 293 K, pH: 8, agitation rate: 475rpm)

Effect of agitation rate

The stirring conditions were of great importance because they could influence the distribution of the adsorbate in the solution, and consequently their diffusion and the formation of a film around the adsorbent. The agitation provided good homogenization of the suspension so as to achieve equilibrium state. The stirrer speed was varied between 200 to 475 rpm. The results were recorded on the curves of Figure 3. In the case studied, the stirring speed had very little influence on the process of adsorption. It showed that, whatever the stirring speed in the studied speed range, the distribution of components of the adsorbent-adsorbate system was homogeneous.



Figure 3. The effect of agitation rate (Cu²⁺concentration: 2000mg/L, adsorbent mass: 400 mg, pH: 8, temperature: 293 K)

Effect of PH

The pH has been an important factor in studies of adsorption, because it can influence both the adsorbent and adsorbate structure and the adsorption mechanism. The pH studied ranged from 1 to 8. The results of these measurements have been recorded on the curves of Figure 4.

When $1 < pH \le 3$ adsorption increased because there was a competition between hydronium ions and Cu(II)ions .When pH

 \geq 3, there was no change in the amount adsorbed at equilibrium for different amounts of pH because the concentration of hydronium ions decreased.



Figure 4. The Effect of pH (Cu²⁺concentration: 2000mg/L, adsorbent mass: 400 mg, temperature: 293 K, agitation rate: 475rpm)

Depending on the pH of the solution, the copper element in solution formed more different hydroxo species (Table 3) (Das & Jana 2006; Weng et al. 2007; Yen 2007).

Table 3. Stability constants for Cu(II) hydrolysis reactions

Reaction	logβi*
$Cu^{2+} + OH^- \leftrightarrow Cu \ (OH)^+$	6.5
$Cu^{2+} + 30H^- \leftrightarrow Cu (OH)_3^-$	14.7
$Cu^{2+} + 40H^- \leftrightarrow Cu \ (OH)_4^{2-}$	16.4
$2Cu^{2+} + 20H^- \leftrightarrow Cu_2 (0H)_2^{2+}$	17.6
$Cu^{2+} + 20H^- \leftrightarrow Cu \ (OH)_{2(s)}$	logK _{sp} =19.4

*stability constants

where K_{sp} is the metal hydroxide solubility product (molesⁿ/Lⁿ).

The total concentration of aqueous dissolved species of copper in the presence of the precipitate of copper hydroxide was designated by s (s is expressed taking into account the five existing ions in solution).

$$s = [Cu^{2+}] + [CuOH^+] + [Cu(OH)_3^-] + [Cu(OH)_4^{2-}]$$

$$+2[Cu_2(OH)_2^{2+}] \tag{17}$$

$$s = \frac{K_{sp}}{k_w^2} [H^+]^2 + \frac{K_{sp}\beta_1}{k_w} [H^+] + \frac{K_{sp}\beta_2 k_w}{[H^+]} + \frac{K_{sp}\beta_3 k_w^2}{[H^+]^2} + \frac{2K_{sp}^2\beta_4 [H^+]^2}{k_w^3}$$
(18)

where Kw is ionic product for water

 $x_i = [i] / s$, i=1-5.

[i] shows the contribution of the ion i in the expression of s. The variation of x_i as a function of pH has been shown in the

curves of Figure 5 at pH=6 Cu₂(OH)₂²⁺ was being disappeared. The predominant forms of copper at pH=8 were Cu²⁺ (x_{Cu2^+} =0.2343) and CuOH⁺ (x_{CuOH^+} =0.7582). Both forms were adsorbed on the surface of the clays contained in the marl. This surface contained active sites such as Si–O⁻ and Al–O⁻, at pH>9 the appearance of negative ions such as Cu(OH)₃-, Cu(OH)₄²⁻ and adsorption was not favored due to the electrostatic repulsion between the negatively charged sites and cupric ions.



Figure 5. Distribution of Cu(II) species as a function of pH

Adsorption isotherms

The adsorption isotherms were obtained at three different temperatures of 293 K, 298 K

and 303K with a volume of 25 ml of a solution containing Cu²⁺ ions with different initial concentrations (1600 to 4000 mg/l), stirring for 475rpm, 400 mg of marl and pH=8. The parameters of models (Langmuir, Freundlich and Tempkin) are summarized in Table 4.

 Table 4. Parameters of the Langmuir, Freundlich, and Tempkin isotherms for the Cu(II) onto marl

		()			
Isotherm	Demonster	T(K)			
model	Parameter	293	298	303	
	K _L (L.mg ⁻¹)	0.00523	0.00629	0.00757	
	qm	130.70	129.11	129.41	
Langmuir	SSE	109.16	239.17	254.89	
20118	χ^2	1.15	2.35	2.58	
	ARE	3.78	5.47	5.14	
	R ²	0.990	0.978	0.977	
	K _F	29.29	34.66	38.32	
	1/n	0.187	0.165	0.154	
	N	5.35	6.06	6.49	
Freundlich	SSE	180.78	325.34	306.99	
	χ^2	1.93	3.31	3.13	
	ARE	4.70	6.12	6.26	
	R ²	0.843	0.721	0.734	
	K _T (L.mol ⁻¹).10 ⁴	1.41	2.90	4.97	
	b _T (J.g.mol ⁻²).10 ⁶	7.81	8.84	9.53	
Tomplein	SSE	158.46	304.60	293.27	
тепркп	χ ²	1.69	3.08	2.99	
	ARE	4.35	5.94	6.04	
	R ²	0.862	0.739	0.746	

The researchers noted that the Langmuir constant K_L increased with increasing temperature. As the value of K_L measured the intensity of adsorption, so it can be deduced that the affinity

between Cu2+ and marl increased with the increase in temperature, and also it was indicated that the adsorption mechanism was endothermic (Dong et al. 2017). The value of the constant Freundlich n determined whether the adsorption of Cu2+ on the marl was favourable or not. As this value was greater than 1, the adsorption was favourable. The adsorption model Tempkin explained the nature of the interactions of marl-Cu²⁺while giving information about the energy of the adsorption process. If the Tempkin constant (b_T) is positive, then the marl-Cu²⁺ interactions are of an attractive nature and in the opposite case, they are repulsive. For the studied cases, these constants were all positive, and increased with temperature; Thus, the marl-Cu²⁺ interactions were attractive in nature. This deduction has been confirmed by the Langmuir and Freundlich isotherm models. For the choice of the isotherm that best explains the experimental results, the researchers considered the statistical calculations from the error functions. The comparison of these values showed that the Langmuir isotherm gave the best fit of the experimental data compared to the models of Freundlich and Tempkin. So, Langmuir isotherm appeared the most satisfactory and best suitable for modeling the adsorption of Cu²⁺ ions on the marl.

Table 5 gives a comparison of the adsorption capacity of marl with the other adsorbents. By comparison, it has been found that marl (Oum El Bouaghi) was considered very effective because it showed a high removal capacity of Cu (II) ions.

 Table 5. Comparison of the adsorption capacity of local marl

 with the other adsorbents

Adsorbents	q _m (mg/g)	References
Cankırı bentonite	44.84	Veli & Aly¨uz (2007)
Shekarbani	45.45	Baghernejad et al. (2015)
Sepidan	50	Baghernejad et al. (2015)
Natural bentonite	30.99	Budsaereechai et al. (2012)
Natural clay from Constantine (Aïn Smara)	140.15	Bellir et al. (2005)
Raw green clay (RGC)	17.98	Eloussaief et al. (2009)
Marl (Oum El Bouaghi)	130.70	This work

Determination of thermodynamic parameters

The lnK_L the plotted against 1/T gives a straight line with slope, $-\Delta H^{\circ}/R$ and intercept $\Delta S^{\circ}/R$. The results of the calculations are summarized in Table 6.

Table 6. Thermodynamic parameters of the adsorption of
Cu(II) calculated from the constant K_L of the Langmuir
instheme

	Isoulei III					
	Parameters	тк	ΔG°	ΔS°	ΔH°	R2
		1(11)	(Kj.mol ^{.1})	(J.K ¹ .mol ¹)	(Kj.mol ^{.1})	n
		293	-14.14			
	Values	298	-14.84	141.41	27.29	0.9999
		303	-15.56			

The value of the standard enthalpy of adsorption - ΔH° (<40 kJ/mol) showed that it is a physisorption (Wang et al. 2017), and that the adsorption process was endothermic. Negative values of ΔG° demonstrated that the adsorption in this case was spontaneous, and the spontaneity increased with temperature. The decrease in ΔG° with temperature implied more efficient adsorption at higher temperatures. The positive value of ΔS° showed that the adsorption was carried out with

increasing disorder in the solid-solution interface (Gusain et al. 2014; Baker, 2009).

Kinetic study

In this study, three different temperatures of 293K, 298K and 303K were considered. Kinetic parameters are exhibited in Table 7.

Kinetic model	Parameter	Temperature		
		293 K	298 K	303 K
Pseudo-first order	k1	0.01506	0.02333	0.0281
	q _{e,exp}	104.45	104.45	104.45
	q _{e,cal}	107.31	105.46	105.39
	R ²	0.9935	0.9983	0.9978
	k ₂	1.038E-4	2.001E-4	2.744E-4
Pseudo-second order	q _{e,exp}	104.45	104.45	104.45
	q _{e,cal}	138.99	128.40	124.14
	Vi	2.005	3.299	4.229
	R ²	0.9981	0.9944	0.9936

Table 7. Kinetic parameters for adsorption of Cu(II) onto marl

It was noticed that the coefficients of determination for the two models were very close to unity. The calculation results showed that the adsorption kinetics of Cu(II) on the marl in aqueous solution was a pseudo first order kinetics, partial order 1 relative to the concentration of free sites, and a partial order 0 relative to the solute in solution. That is to say, an irreversible kinetic model was based solely on the amount of copper attached to the surface of the marl.

4. CONCLUSION

In this work, removal copper ions using marl of Oum El Bouaghi as a novel low-cost adsorbent was found to be very effective. Spectroscopic analysis showed that the study was calciferous marl clay. The application of three isotherm monosolute equilibrium models with two-parameters (Langmuir, Frendlich and Tempkin) confirmed that the adsorption of Cu2+ obeyed the Langmuir model. The kinetic study of the adsorption of Cu2+ was described by the pseudo first order model. Thermodynamic calculations indicated that the standard adsorption enthalpy ΔH° had a positive value less than 40 kJ.mol⁻¹, which was indeed an endothermic physical adsorption of Cu²⁺ onto marl. Negative values of ΔG° proved that the adsorption was spontaneous, and the spontaneity increased with temperature. The positive value of ΔS° suggested that the adsorption occured with increasing disorder in the solid-solution interface.

REFERENCES

- Baghernejad M, Javaheri F, Moosavi AA (2015) Adsorption isotherms of copper and zinc in clay minerals of calcareous soils and their effects on X-ray diffraction. Arch. Agron. Soil Sci 61: 1061–1077.
- Baker H (2009) Characterization for the interaction of Nickel(II) and Copper(II) from aqueous solutions with natural silicate minerals. Desalination 244: 48–58.
- Bellir K, Bencheikh-Lehocine M, Meniai AH, Gherbi N (2005) Study of the retention of heavy metals by natural material used as liners in landfills. Desalination 185: 111–119.

- Budsaereechai S, Kamwialisak K, Ngernyen Y (2012) Adsorption of lead, cadmium and copper on natural and acid activated bentonite clay. Asia Pac J Sci. Technol 17: 800–810.
- 5. Cornell RM (1992) Adsorption behaviour of cesium on marl. Clay Miner 27: 363-371.
- Cornell RM, Aksoyoglu S (1992) Sorption of nickel on marl. J. Radioanal. Nucl. Chem., Letters164: 389-396.
- Cottet L, Almeida CAP, Naidek N, Viante MF, Lopes MC et al. (2014) Adsorption Characteristics of montmorillonite clay modified with iron oxide with respect to methylene blue in aqueous media. Appl. Clay Sci 95: 25–31.
- Das N, Jana RK (2006) Adsorption of some bivalent heavy metal ions from aqueous solutions by manganese nodule leached residues. J. Colloid Interface. Sci 293:253–262.
- Dong L, Wen C, Junxia Y, Yigang D (2017) Polyamine chitosan adsorbent for the enhanced adsorption of anionic dyes from water. J. Dispersion Sci.Technol 38: 1832-1841.
- Eloussaief M, Jarraya I, Benzina M (2009) Adsorption of copper ions on two clays from Tunisia: pH and Temperature effects. Appl. Clay Sci.46: 409–413.
- Foo KY, Hameed BH (2010) Insights into the modeling of adsorption isotherm systems. Chem. Eng. J 156: 2– 10.
- Freundlich H (1906) Over the adsorption in solution. J. Phys. Chem 57: 385-470.
- Fu F, Wang Q (2011) Removal of heavy metal ions from wastewaters: A review. J. Environ. Manage 92: 407–418.
- Gusain D, Srivastava V, Sharma YC (2014) Kinetic and thermodynamic studies on the removal of Cu(II) ions from aqueous solutions by adsorption on modified sand. J. Ind. Eng. Chem 20: 841–847.
- HO YS, McKAY G (1999) Pseudo-second order model for sorption processes. Process Biochem 34: 451-465.
- 16. Jabari M, Aqra F, Shahin S, Khatib A (2009) The treatment of chromium tanning wastewater using natural marl. Chem. Spec. Bioavail 21: 185-191.
- 17. Koffi LK. (2006) Interactions entre des matériaux argileux et un milieu basique riche en calcium. Ph.D. Thesis, University of Limoges, France.

- Lagergren S (1898) About the theory of so-called adsorption of soluble substance. Kungliga Svenska Vetenskapsakademiens Handlingar 24: 1-39.
- Langmuir I (1918) The adsorption of gases on plane surfaces of glass, mica and platinum. J. Am. Chem. Soc 40: 1361–1403.
- Meunier N, Drogui P, Montane C, Hausler R, Mercier G et al. (2006) Comparison between electrocoagulation and chemical precipitation for metals removal from acidic soil leachate. J. Hazard.Mater 137: 581–590.
- 21. Millot G (1970) Geology of clays. Springer -Verlag, New York.
- Rafatullah M, Sulaiman O, Hashim R, Amini MHM (2011) Adsorption of copper (II) ions onto surfactantmodified oil palm leaf powder. J. Dispersion Sci.Technol 32: 1641-1648.
- Singh R, Gautam N, Mishra A, Gupta R (2011) Heavy metals and living systems: An overview. Indian.J. Pharmacol 43: 246–253.
- 24. Sokouti R, Razagi S (2015) Erodibility and loss of marly drived soils. Eurasian J. Soil Sci 4: 279-286.
- 25. Tempkin MJ, yzhev VP (1940) Kinetics of ammonia synthesis on promoted iron catalysts. Acta Physicochimica URSS 12: 217–222.
- Vasanth Kumara K, Porkodi K, Rocha F (2008) Isotherms and thermodynamics by linear and nonlinear regression analysis for the sorption of methylene blue onto activated carbon: Comparison of various error functions. J. Hazard. Mater 151: 794– 804.
- Veli S, Aly uz B (2007) Adsorption of copper and zinc from aqueous solutions by using natural clay. J. Hazard. Mater 149: 226–233.
- Wang H, Tian Z, Jiang L, Luo W, Wei Z et al. (2017) Highly efficient adsorption of Cr(VI) from aqueous solution by Fe3+ impregnated biochar. J. Dispersion Sci. Technol. 38: 815-825.
- Weng CH, Tsai CZ, Chua SH, Sharma YC (2007) Adsorption characteristics of copper(II) onto spent activated clay. Sep. Puri.Tech 54: 187–197.
- WHO (2008) Guidelines for drinking-water quality. Recommendations. (3rd edtn), World Health Organisation, Geneva.
- 31. Yen TF (2007) Chemical process for environmental engineering. Imperial college Press, London.