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Chromium and nickel removal from industrial wastewater using Tunisian clay

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ABSTRACT

In this study, illitic Tunisian (MOM R) clay was applied for the removal of Cr(III) and Ni(II), from industrial wastewater. The considered adsorbent (MOM R) was collected from Jebel El Hamma, Lower Cretaceous age. To characterize the adsorbent structures, infrared spectroscopy and X-ray diffraction techniques were used. The effects of agitation time, adsorbent quantity, pH, initial metal ion concentration, and temperature on the removal of these metals were studied. In order to study the adsorption isotherm, two equilibrium models, the Freundlich and Langmuir isotherms, were analyzed. The estimated optimum pH of chromium (III) ion retention for the considered adsorbents was 2.13 and 6.43 for nickel (II). The equilibrium data were analyzed using the Langmuir and Freundlich isotherms. The adsorption capacities of Cr(III) were 7.751 mg/g and 62.5 mg/g Ni(II). The effect of temperature on the adsorption phenomenon was also investigated. The results indicated that adsorption is an endothermic process for chromium and nickel ions removal. This study demonstrates that the considered adsorbent can be used as an alternative emerging technology for water treatment without any side effect.

Keywords: Adsorption; Isotherms models; Tunisian clay; Heavy metals; Wastewater treatment

1. Introduction

Heavy metal ions have become an ecotoxicological hazard of prime interest and increasing significance, because of their accumulation in living organisms [1]. Both Ni(II) and Cr(III) are present in effluents of a large number of industries. People often suffer from allergy due to exposure to nickel-containing materials.

The chronic toxicity of chromium to humans and the environment has been well documented. Different industrial applications use various forms of chromium, such as chromite, ferrochromium, chromium

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metal, chromite refractory bricks, chromite foundry sands, chromic acid, and other chromium compounds, while the main industrial applications of chromium and its compounds included non-ferrous and ferroalloys, refractories, and chemicals (metal finishing and corrosion control, leather tanning and finishing, pigments, wood preservative, etc.). This element occurs in aqueous systems in both the trivalent form (Cr^{3+}) the hexavalent form (chromate CrO_4^{2-} and dichromate $Cr_2O_7^{2-}$), whereas Cr(VI) has long been recognized as a toxic substance to animal and plants, Cr(III) is considered to be less toxic, though its elimination from contaminated waters is also of a primarily necessity in industrialized countries [2,3].

Nickel is a toxic heavy metal that is widely used in silver refineries, electroplating, zinc base casting, and storage battery industries [4]. The effects of Nickel have also been well documented [5]. For example, a high concentration of nickel (II) causes lung, nose, and bone cancer. It is, therefore, essential to remove Ni (II) from industrial wastewater.

Hence, the removal of chromium and nickel from water and wastewater is assumed important for the protection of the environment against the contamination of their components by heavy metals. The conventional methods for heavy metal removal from water and wastewater [6] include oxidation, reduction, precipitation, membrane filtration, ion exchange [7], and adsorption. Among all, adsorption is highly effective and economical. Though the use of commercial activated carbon is a well-known adsorbent for the removal of heavy metals from water and wastewater [8], the high cost of activated carbon limits its use as an adsorbent in developing countries. Hence, several research workers used different low-cost adsorbents such as coconut coir pith [9], sawdust [10], sludge ash [11], banana pith [12], activated phosphate rock [13], vermiculite [14], and montmorillonite [15].

Mineral clay can adsorb 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 SiO^- and AlO^- groups at the clay particle edges [16]. 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 Cr(III) and Ni(II) ions removal from industrial wastewater by adsorption on illite-rich clay named MOM R. The advantages of this process include low-cost, simplicity, high quality, ease of scale-up, and good reproducibility. MOM R characterization was performed and its applicability in heavy metal ions removal was evaluated in the view of operating variables on the adsorption and adsorption isotherms as well as the adsorption thermodynamics.

2. Materials and methods

2.1. Adsorbent

The raw clay (MOM R) used in this study was collected from the chain of South chotts. It was sampled in the El Hamma region. It is early Hauterivian–Barremian age (Fig. 1).

2.2. Adsorbate

The wastewater tested in this investigation was obtained from the outlet of an industrial wastewater treatment plant. The various characteristics of industrial wastewater are shown in Table 1.

2.3. 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. 2. 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 MOM R specific surface area (m^2/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 MOM R.

The X-ray diffraction analysis indicated that the raw clay MOM R is mainly composed of illite (48%) associated to kaolinite (18%), smectite (4%), quartz (14%), and dolomite (16%) (Table 2).

The chemical analysis showed that the main constituents of MOM R clay are silica (42.1%), alumina (17.9%), and iron oxides (7.36%) (Table 3). The LOI is

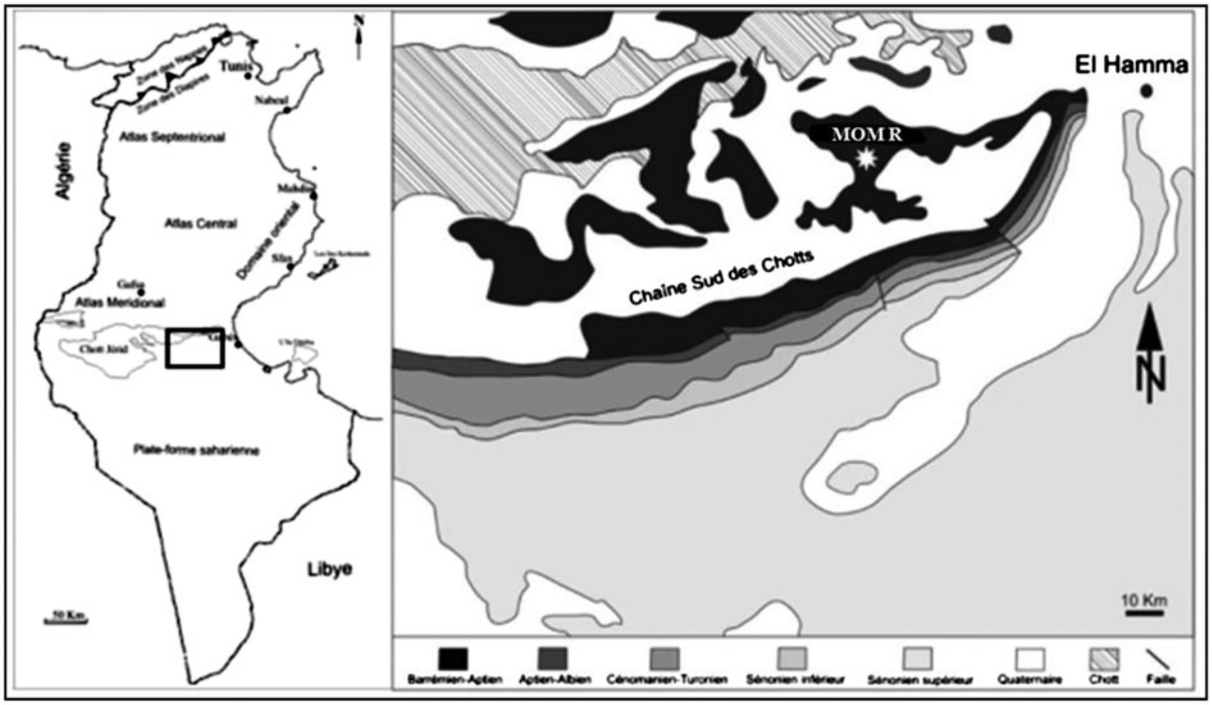

Fig. 1. Localization of the studied mineral clay deposit (El Hamma area) [17].

Table 1
Physico-chemical caracteristics of influent

Physicochemical parameters	Range	Mean ± SD
PH	1.54–3.2	2.23 ± 0.4
TSS (mg/L)	5.2–25	14.98 ± 4.42
EC (ms/S 25 °C)	8–19.8	13.19 ± 3.05
DCO (mg/L)	119–1.300	662.36 ± 338.68
DBO_5 (mg/L)	10–82	30.33 ± 18.62
Ni (mg/L)	16.2–291	125 ± 59.17
Cr (mg/L)	4.75–570	167.21 ± 120.06
Cu (mg/L)	2.01–43.45	21.82 ± 13.72
Zn (mg/L)	2–40	16.00 ± 13.03

14% (Table 3). It is mainly attributed to the loss of H_2O from clay minerals, especially smectite, and CO_2 originating from the decomposition of dolomite.

The BET surface area of MOM R sample was found to be $125.58\,m^2/g$.

The infrared absorption spectrum (Fig. 3) of raw MOM R showed that absorption bands at $3{,}628\,cm^{-1}$ and $3{,}400\,cm^{-1}$ was assigned to the stretching vibration of surface hydroxyl groups $Al^{-}OH$ and $Si^{-}OH$, respectively. Additionally, its spectrum contained weak bands at $1{,}650\,cm^{-1}$ attributed to the vibration of organic groups (COO^{-}). The bands appeared at 912 and $798\,cm^{-1}$ corresponding to dioctahedral smectite and quartz. On the other hand, a significant amount of kaolinite was revealed by the absorption bands intensity at 3.700 and $696\,cm^{-1}$. The bands appeared at 1.022, 530, and $470\,cm^{-1}$ corresponding to Si–O–Al, Si–O–Al, and Si–O–Mg, respectively.

3. Effect of various operating parameters on chromium and nickel removal

3.1. Effect of adsorbent amount

The influence of the amount of MOM R adsorbent (0.75–25 g/100 mL) on Ni(II) Cr(III) removal at constant values of initial metal concentration (raw effluent), contact time (60 min), and temperature (25 °C) is shown in Fig. 4. The results showed that the removal of nickel and chromium increased rapidly to

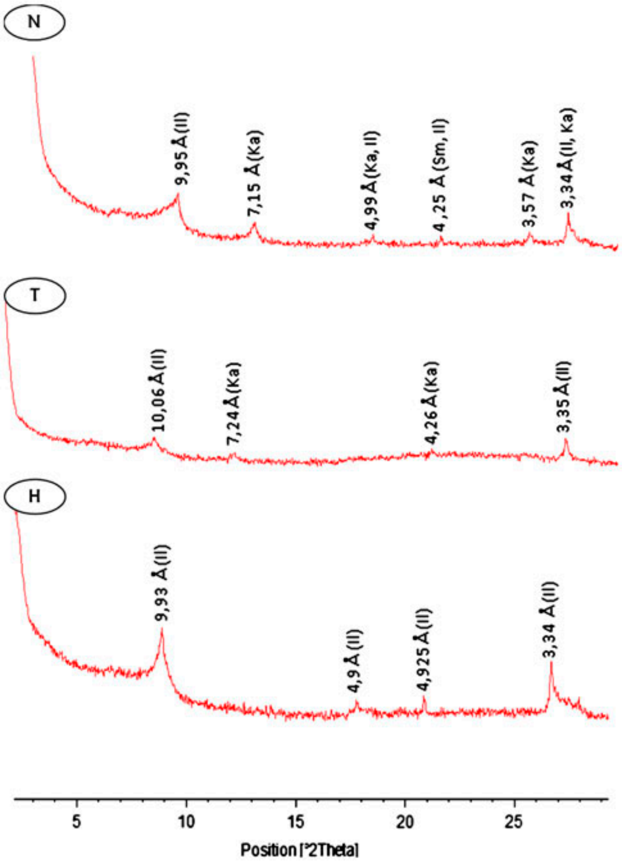

Fig. 2. XRD spectrum of oriented aggregates of MOM R sample.

83 and 82%, respectively, until an adsorbent dose of 5 g/100 mL and moderately beyond this value. This was an expected result since as the adsorbent dose increased, the number of adsorbent sites increased; therefore, these amounts attached more ions to their surfaces [17].

3.2. Effect of pH

The influence of pH on the removal of Ni(II) and Cr(III) ions by MOM R sample was investigated. In the present work, nickel and chromium adsorption was studied in the pH range of 2.17–7.57 with a constant clay amount of 2.5 g/100 ml of effluent and a shaking time of 120 min.

The results presented in Fig. 5 reveal that the adsorption of nickel increases from 91 to 95.7% with an increase in solution pH from 2.17 to 6.43 and then decreases rapidly at pH 7.57. The effect of pH can be explained in terms of pzc (point of zero charge) of the adsorbent MOM R equal to 6.94 [18]. Above 6.94, adsorbent surface is a negatively charged MOM R; therefore, adsorption percentage progressively increases from 2.13 to 6.19 pH by electrostatic attraction. Below pzc adsorption decreases due to electrostatic repulsion between the positively charged surfaces of adsorbent and cationic metal Ni. Due to the precipitation of some Cr(III) ions, the influence of initial pH on Cr(III) removal may be explained as follows: at pH 2.13 adsorption Cr(III) decreases. This is due to a competition between the ionic form of chromium (Cr^+) and the precipitated form ($Cr(OH^+)_3$). Furthermore, above the load pzc adsorbent and metals will be incompatible. The percentage of the adsorbed Cr(III) is constant at pH 2.13.

3.3. Effect of shaking time

The time-dependent behavior of chromium and nickel adsorption was studied by varying the contact

Table 2
Mineralogical composition of MOM R sample clay

Sample MOM R	Total rock mineralogy (%)				
	Clay minerals			Non clay minerals	
	Illite	Kaolinite	Smectite	Dolomite	Quartz
	48	18	4	16	14

Table 3
Chemical composition of MOM R sample clay

SiO_2 (%)	Al_2O_3 (%)	Fe_2O_3 (%)	TiO_2 (%)	CaO (%)	MgO (%)	Na_2O (%)	K_2O (%)	P_2O_5 (%)	LOI (%)
42.1	17.9	7.36	0.86	6.55	6.4	0.41	4.15	0.14	14

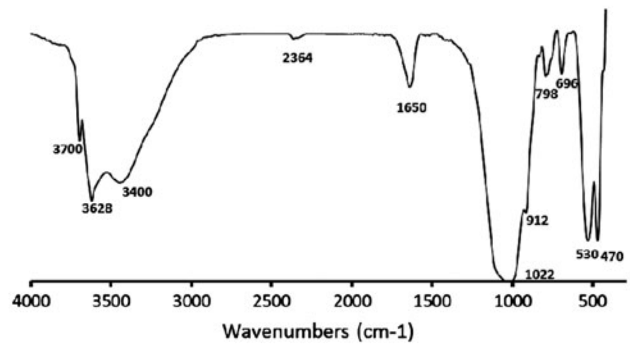

Fig. 3. FT-IR spectra of MOM R.

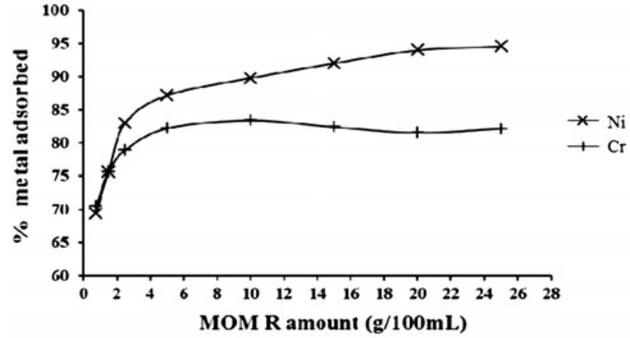

Fig. 4. Effect of adsorbent amount on Ni(II) and Cr(III) adsorption.

time between the adsorbate and adsorbent in the range 1–120 min. The MOM R sample dose was 2.5 g/100 mL, and the solution pH was fixed at 6.43 for nickel and 2.17 for chromium. The data showed that the adsorption of nickel and chromium ions on MOM R was very fast (Fig. 6). According to the experimental results of several authors [19,20] 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 nickel and chromium 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.

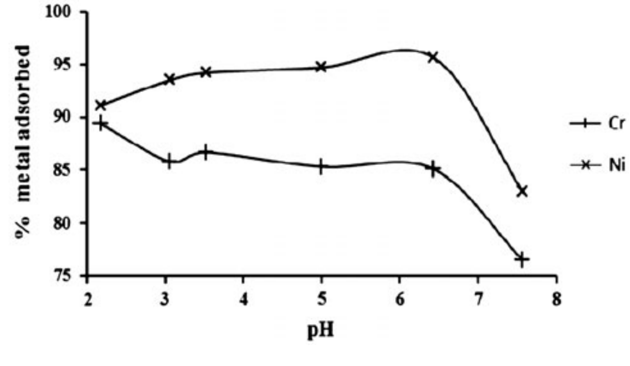

Fig. 5. Effect of pH Ni(II) and Cr(III) adsorption.

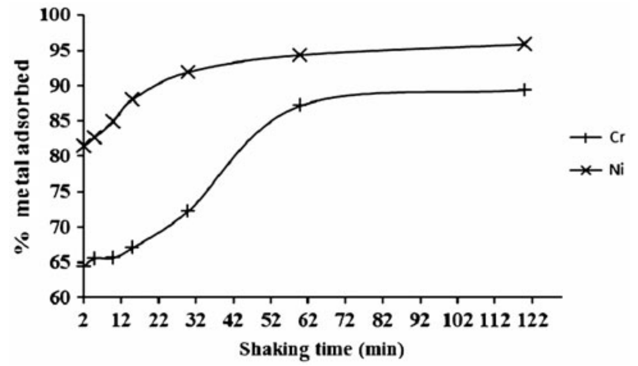

Fig. 6. Effect of shaking time on Ni(II) and Cr(III) adsorption.

4. Adsorption isotherm

Nickel and chromium ions adsorption isotherms obtained for mineral clay adsorbents are shown in Fig. 7. These isotherms represent the adsorption behavior of Ni(II) and Cr(III) ions on the MOM R adsorbents as a function of increasing aqueous nickel and chromium concentration, for a contact time of 60 min.

The Freundlich isotherm model used for nickel and chromium adsorption (Fig. 8) 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 Eq. (1):

$$Q = K_f C_e^{1/n} \tag{1}$$

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:

$$\log Q = \log K_f + \frac{1}{n} \log C_e \tag{2}$$

Table 4 indicates that there is a slight deviation from linearity using the Freundlich isotherm model for describing Cr(III) adsorption (R^2 equal to 0.98). The model gives a poor presentation for Ni(II) adsorption

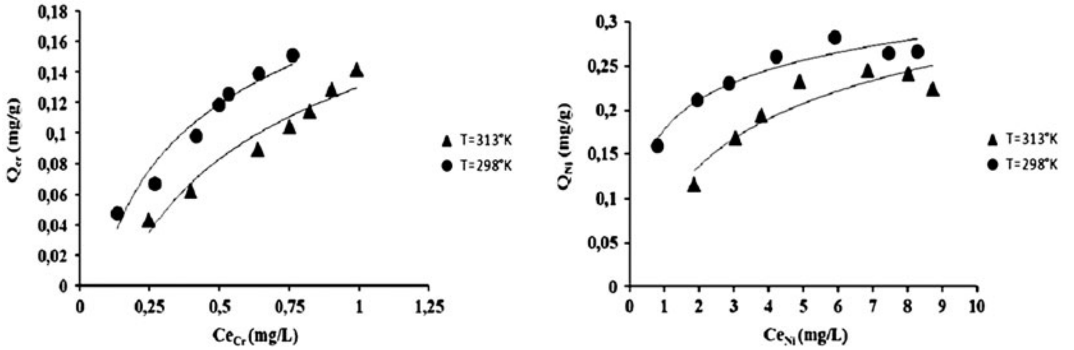

Fig. 7. Equilibrium isotherms for Ni(II) and Cr(III) ions removal by MOM R (2.5 g adsorbent/100 mL effluent, $T = 25$ and 40°C, pH 2.17 and 6.43 for Cr and Ni respectively).

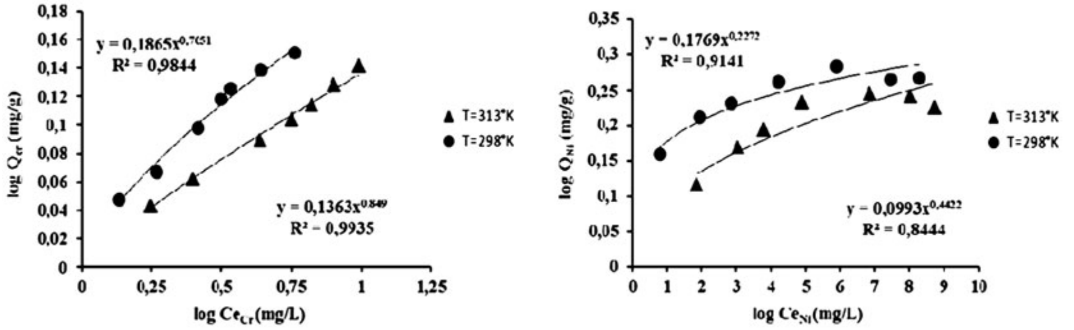

Fig. 8. Freundlich isotherms for the adsorption of Ni(II) and Cr(III) at $T = 25$ and 40°C on MOM R.

behavior (R^2 equal to 0.84). Freundlich parameters (K_f and n) indicate whether the nature of adsorption is either favorable or unfavorable [21]. The intercept is an indicator of adsorption capacity, and the slope is an indicator of adsorption intensity. In the two adsorption systems, values obtained of $1 < n < 10$ imply favorable adsorption. The K_f values, reported in Table 2, can be used to indicate the relative adsorption capacity of the system [22].

The results of nickel and chromium ions adsorption onto MOM R (Fig. 9) 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:

$$\frac{C_e}{q_e} = \frac{1}{Qb} + \frac{C_e}{Q} \tag{3}$$

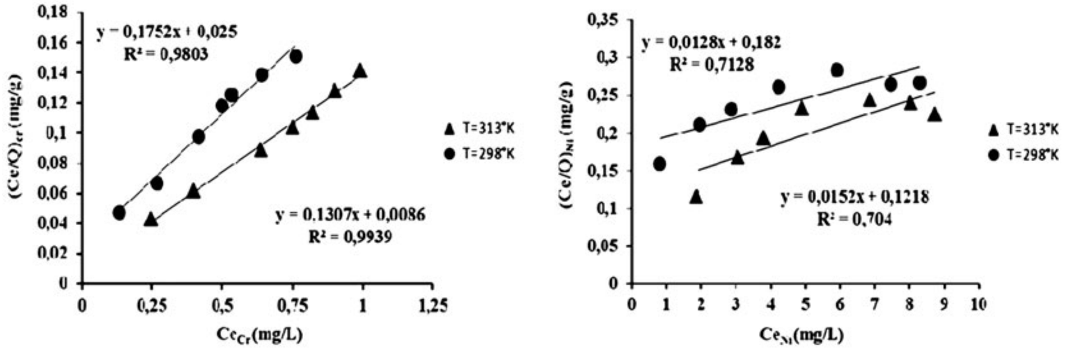

Fig. 9. Langmuir isotherms for the adsorption of Ni(II) and Cr(III) at $T = 25$ and 40°C on MOM R.

Table 4
Freundlich and Langmuir constants for Cr (III) and Ni (II) adsorption on MOM R

Metals	T (K)	Langmuir constants			Freundlich constants		
		b (L/mg)	Q (mg/g)	R^2	K_f	$1/n$	R^2
Ni (II)	298	0.12	65.79	0.70	0.1	0.44	0.84
	313	0.07	78.12	0.71	0.18	0.23	0.91
Cr (III)	298	7.00	5.81	0.98	0.19	0.70	0.98
	313	15.19	7.65	0.99	0.14	0.85	0.99

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).

Table 4 indicates that the Langmuir equation gives a fairly good application for chromium adsorption with a regression coefficient, R^2 equal to 0.98. The Langmuir isotherm gives a poor presentation for nickel adsorption behavior at 298 K (R^2 equal to 0.70). Using the Langmuir model, the maximum adsorption capacity at 298°K for the metals can be estimated as: Ni (65.790 mg/g) and Cr (5.813 mg/g). The adsorbent (MOM R) can remove the two metal ions with a higher affinity for Ni(II).

5. Adsorption thermodynamic parameters

In order to explain the effect of temperature on the adsorption thermodynamic parameters, standard Gibbs free energy ($\Delta G°$), standard enthalpy ($\Delta H°$), and standard entropy ($\Delta S°$) were determined. The adsorption process of metal ions can be summarized by the following reversible process which represents a heterogeneous equilibrium. The equation given below was used to determine the Gibbs free energy of adsorption ($\Delta G°$) [22,23].

$$\Delta G = -RT \ln b \tag{4}$$

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:

$$\ln b = \frac{\Delta S}{H} - \frac{\Delta H}{RT} \tag{5}$$

When ln b is plotted against $1/T$, a straight line with slope $\Delta H/R$ and intercept $\Delta S/R$ 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 5. 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, the negative value of ΔG° decreased with an increase in temperature, indicating that the spontaneous nature of Ni(II) and Cr(III) adsorption was inversely proportional to the temperature. Positive values of ΔH suggest the endothermic nature of the Cr(III) adsorption on MOM R. The negative value of ΔH suggests the exothermic nature of the adsorption of Ni(II) on MOM R. The positive values of ΔS reflect the affinity of MOM R for Ni(II) and Cr(III) and show the increasing randomness at the solid/liquid interface during the sorption of metal ions on MOM R.

Table 5
Thermodynamic parameters for the adsorption of Cr (III) and Ni (II) at various temperatures on MOM R

T (K)	Chromium			Nickel		
	ΔG° (kJ/mol)	ΔS° (kJ/mol)	ΔH° (kJ/mol)	ΔG° (kJ/mol)	ΔS° (kJ/mol)	ΔH° (kJ/mol)
298	−11.832	0.149	32.175	−2.071	0.0692	−22.406
313	−14.446	0.149	32.175	−0.772	0.0692	−22.406

6. 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:

1. The mineralogical and chemical analyzes showed that the types of natural material used were illite kaolinite.
2. The adsorption of heavy metals depended on the solution pH. Maximum retention of chromium and nickel ions occurred at around; pH (Ni) 6.43, pH (Cr) 2.13, respectively, shaking time 60 min, adsorbent amount 2.5 g/100 mL, and temperature 40˚C.
3. For the adsorption isotherms of chromium and nickel ions, both Langmuir and Freundlich equations were fitted to experimental data satisfactorily.
4. These results led to classify the Tunisian illite kaolinite of El Hamma region as a new low-cost adsorbent of some well-known adsorbents for wastewater cleanup.

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