



Contribution to the removal study of Co^{2+} ions by acid-activated clay from Maghnia (Algeria): equilibrium and kinetic studies

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ABSTRACT

A sample of clay, bentonite from Maghnia (N.W. Algeria) was treated (acid-activated) and used as adsorbent for the removal of Co^{2+} ions from aqueous solutions. The effect of acid treatment, shaking time, pH of aqueous solution, metal concentration and adsorbent amount was studied. The sorption kinetics of Co^{2+} have been analysed by Lagergren pseudo-first order and pseudo-second order kinetic models. The experimental results indicated that the best fit is obtained with the pseudo-second order kinetic model. The experimental equilibrium adsorption data were tested for the Freundlich and Langmuir equations. Results indicate that the order fit is Freundlich > Langmuir.

Keywords: Clay; Removal; Acid-treatment; FT-IR; Adsorption; Kinetics; Pseudo-second order; Langmuir; Freundlich; Co^{2+} ; Ni^{2+}

1. Introduction

Cobalt is present in the terrestrial crust and its abundance is of about 23 ppm [1]. It is used in the manufacture of economic and strategic interest tools (ceramic, alloys with steel...). The hold of conscience of the problem of the inorganic pollutants, essentially the heavy metals, in waters destined to the human consumption, drove us to examine the possibility of elimination of the cobalt by adsorption onto Algerian clay (a bentonite from Maghnia, N.W. Algeria) in aqueous solution. Numerous studies showed that the adsorption of the cobalt by treated and modified clays was of interest [2–5]. The heavy metals, non biodegradable, are endowed with particular chemical properties that confer them toxicity to the human being and the living organisms (animal and plant reign). Among these metals,

the cobalt is present in the surface soil and its average concentrations remain lower than 0.2 mg l^{-1} in the industrial liquid sewages [6]. During the last years, numerous methods for removing pollutants from water and wastewater are well developed as the chemical precipitation, the ion exchange, the electrolysis, the membranes processes and the adsorption method [7–9]. In the last few years, works achieved in our Laboratory (Laboratoire d'Electrochimie-Corrosion, Métallurgie et Chimie Minérale de la Faculté de Chimie –USTHB) show good potentiality for Algerian clay to be used as adsorbent for organic and inorganic pollutants in aqueous solutions [7,9–18].

The purposes of this work are to study the influence of the pH of the solutions on the removal of Co^{2+} , the effect of shaking time, the effect of the initial concentration of the Co^{2+} ions, the effect of mass of adsorbent onto acid-activated clay, a low-cost material, a bentonite clay from Maghnia (N.W. Algeria).

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2. Materials and experimental method

2.1. Clay adsorbent

The clay, a bentonite from Maghnia (N.W. Algeria) was obtained from the Algerian bentonite Company (ENOF), Algeria. The clay was treated (acid-activated) before using it as adsorbent.

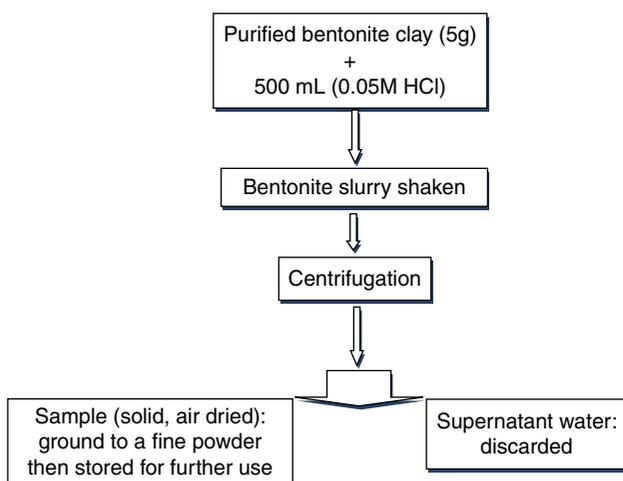
This material clay has been treated, characterized and extensively used as adsorbent for the removal of organic and inorganic pollutants from aqueous systems [11,15,19–21].

2.2. Reagents

All chemicals were purchased in analytical reagent grade and were used as delivered. These were obtained from Carlo Erba (NaOH, 98%), Merck (HCl, $d = 1.18$, 37%) and Panreac ($\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$, 99.5%). The elements standard solutions used were prepared with distilled water.

2.3. Preparation and acid treatment of bentonite clay

The commercial clay was purified using a sedimentation method [22]. In this method, 5g of clay were dispersed in 500 ml distilled water and shaken overnight on mechanical shaker (Janke type, Hunkel Ika. Werk, KS 500). The resulting clay slurry was then left to stand or 2 h to allow sedimentation of silica and other heavy impurities. The suspension was then centrifuged and the supernatant water discarded. The restrained sample was air dried and reacted with a 0.05 M HCl solution. The acid-activated bentonite was centrifuged, air dried and ground to fine powder then stored for further use, Scheme 1.



Scheme 1. Schematic diagram for the procedure of purification and acid-treatment of bentonite (adapted from Van Olphen, 1963).

2.4. Analytical method

The concentrations of Co^{2+} were analyzed by an Analyst 700 Perkin-Elmer type flame atomic absorption spectrometer (SAA) equipped with deuterium background corrector. All measurements were carried out in air/acetylene flame in the range of 0.2–3.0 mg l^{-1} at 240.7 nm. The removal of metal ions was calculated as:

$$\text{Removal \%} = \left(\frac{C_i - C_e}{C_i} \right) \times 100 \quad (1)$$

where C_i and C_e are the initial and equilibrium metal ions concentrations, respectively.

2.5. Effect of pH on the removal of Co^{2+}

A series of adsorption experiments were carried within a pH range of 1–9, in 100 ml Erlenmeyer flasks by mixing 1g of acid-activated bentonite with 10 mg l^{-1} of aqueous solution of Co^{2+} . The pH of metal ion solutions was adjusted with either 0.1 M HCl or 0.1 M NaOH. The samples collected were then analyzed by SAA.

2.6. Effect of shaking time on the removal of Co^{2+}

For the study of the effect of shaking time on the removal of Co^{2+} , 1g of acid-activated bentonite in 10 mg l^{-1} of aqueous solution of Co^{2+} was used. The removal experiments were carried at time intervals between 5 and 120 min and their pH adjusted to 5 ± 0.01 either 0.1 M HCl or 0.1 M NaOH. The samples collected were then analyzed by SAA.

2.7. Effect of mass on the removal of Co^{2+}

In this part of our work, a series of adsorption experiments were carried within acid-activated bentonite mass range of 0.1–5 g, in 100 ml Erlenmeyer flasks with 10 mg l^{-1} of aqueous solution of Co^{2+} . The shaking time and the pH of metal ion solutions were 60 min and 5 ± 0.01 , respectively.

2.8. Effect of initial concentration of Co^{2+} on the removal

A series of adsorption experiments were carried within initial concentration range of 5–100 mg l^{-1} , in 100 ml Erlenmeyer flasks with 1 g of acid-activated bentonite. The shaking time and the pH of metal ion solutions were 60 min and 5 ± 0.01 , respectively.

2.9. Adsorption equilibrium study

The adsorption experiments were carried out at room temperature ($26 \pm 2^\circ\text{C}$) using 100 ml Erlenmeyer

flasks containing 50 ml of 5–100 mg l⁻¹ of Co²⁺ and 1 g of acid-activated bentonite for 1 h. The pH of metal ion solutions was adjusted to 5 ± 0.01. After agitation, the suspensions were centrifuged and the supernatant kept for Co²⁺ analysis.

Differences between concentration in the initial C_i (mg l⁻¹) and equilibrium C_e (mg l⁻¹) solutions were used to calculate the quantity adsorbed q_t (mg g⁻¹) in mmol (1 g)⁻¹ of acid-activated bentonite, using the following mass-balance equation:

$$q_t = \frac{C_i - C_e}{m} \times V \quad (2)$$

v is the volume of aqueous solution (l) and m is the mass of acid-activated bentonite (g) used. The experimental equilibrium adsorption data were tested for the Langmuir and Freundlich equations.

2.9.1. Langmuir equation

The standard Langmuir equation is:

$$\frac{C_t}{Q_{ad}} = \frac{1}{Q^0 \cdot b} + \frac{C_t}{Q^0} \quad (3)$$

where Q_{ad}: quantity adsorbed (mg g⁻¹ in mmol 1g⁻¹); Q⁰: maximum adsorption capacity (mg g⁻¹). C_t: is the concentration of Co²⁺ in liquid phase at time t (mn) in (mg L⁻¹); b: Langmuir constant.

2.9.2. Freundlich equation

$$\log Q_{ad} = \log K_F + n \cdot \log C_t \quad (4)$$

where K_F (mg g⁻¹) and n: Freundlich constants; C_t: is the concentration of Co²⁺ in liquid phase at time t (mn) in (mg L⁻¹); Q_{ad}: quantity adsorbed (mg g⁻¹).

2.10. Adsorption kinetic models

The sorption kinetics of Co²⁺ have been analysed by Lagergren pseudo-first order and pseudo-second order kinetic models.

2.10.1. Pseudo-first order equation (Lagergren equation)

The pseudo-first order kinetic model is obtained as follows:

$$\frac{dq_t}{dt} = k_1(q_e - q_t) \quad (5)$$

When rearranged, integrated and linearized it gives:

$$\ln(q_e - q_t) = \ln q_e - k_1 t \quad (6)$$

where q_t: is the amount of Co²⁺ adsorbed at time t (mn) in (mg g⁻¹); q_e: is the amount of Co²⁺ adsorbed at equilibrium (mg g⁻¹); k₁: is the rate constant of the pseudo-first order for adsorption of metal ions (g mg⁻¹ mn⁻¹).

2.10.2. Pseudo-second order equation

The pseudo- second order kinetic model is obtained as follows:

$$\frac{dq_t}{dt} = k_2(q_e - q_t)^2 \quad (7)$$

When rearranged, integrated and linearized it gives:

$$\frac{t}{q_t} = \frac{1}{k_2 \times q_e^2} + \frac{1}{q_e} t \quad (8)$$

where q_t: is the amount of Co²⁺ adsorbed at time t (mn) in (mg g⁻¹); q_e: is the amount of Co²⁺ adsorbed at equilibrium (mg g⁻¹); k₂: is the rate constant of the pseudo-second order for adsorption of metal ions (g mg⁻¹ mn⁻¹);

3. Results and discussion

3.1. Effect of pH on the removal of Co²⁺ ions

An early study in our Laboratory has shown that the equilibrium of adsorption behavior of heavy metals is reached for a contact time of a range: 30–90 min, [7]. The pH effect on the removal of Co²⁺ ions was investigated within the range from 1 to 9, (Fig. 1). It is found that the removal increased gradually in acidic solutions within the pH range of 1–5 and then becomes constant within the pH range of 5–9. At low pH values, the effect of H₃O⁺ ions on surface of bentonite clay, could hinder the access of metal ions, by repulsive forces, to the surface functional groups, [23].

However, with the increasing pH, the concentration of H₃O⁺ decreases and more of the metal ions could reach the clay surface and adsorb on it. The percentage removal, which is strongly depended on pH values, reach 90% at pH = 5. Thus, the pH 5 was selected for all further experimental studies of cobalt.

3.2. Effect of shaking time on the removal of Co²⁺

The effect of shaking time on the removal of Co²⁺ ions, Fig. 2, was studied in the range of 5–120 min. This removal attains saturation within 5 min and 20 min for acid-activated clay (0.05M and 1M HCl) and 0.5M HCl),

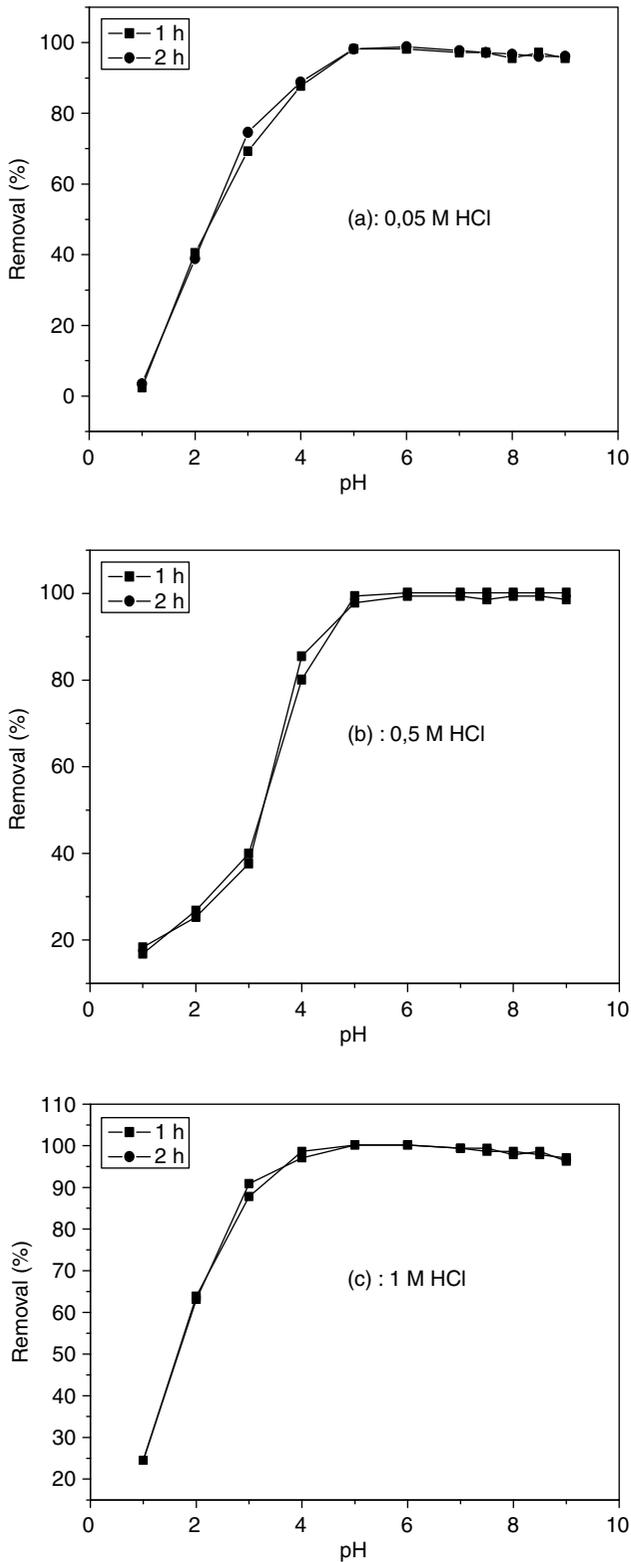


Fig. 1. Removal of Co^{2+} onto acid-activated (0.05, 0.5 and 1 M HCl) clay as a function of pH ($[\text{Co}^{2+}]$: 10 mg l^{-1} ; mass of acid-activated clay: 1 g; shaking time 1 h and 2 h; T: 25°C).

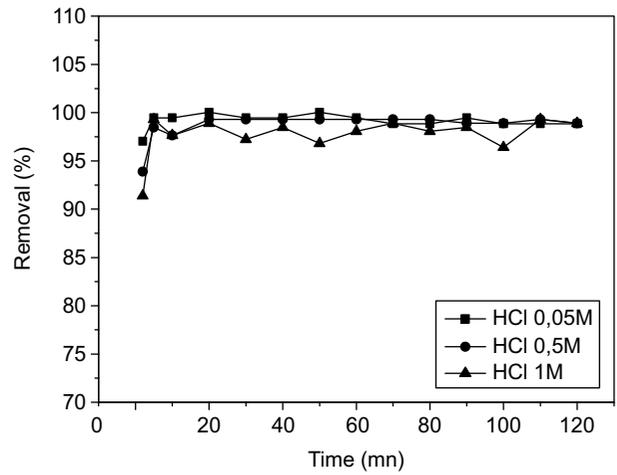


Fig. 2. Removal of Co^{2+} onto acid-activated clay (0.05, 0.5 and 1 M HCl) as a function of shaking time ($[\text{Co}^{2+}]$: 10 mg l^{-1} ; pH: 5; mass of acid-activated clay: 1g; T: 25°C).

respectively. Then, it was slightly decreasing to reach equilibrium within 60 min. The maximum adsorption was 98%. Similar behavior was reported elsewhere on the effect of shaking time on the removal of Pb^{2+} , [7]. However 1h was fixed as the optimum shaking time, Fig. 2.

3.3. Effect of mass of acid-activated clay on the removal of Co^{2+}

The removal of Co^{2+} increased with the acid-activated clay amount (0.1–5 g). This removal became constant beyond masses greater than 0.5 g. This increase may be associated with the increase of available sites on the clay surface upon increasing the amount of acid-activated clay [23]. The optimum removal was 99%, Fig. 3.

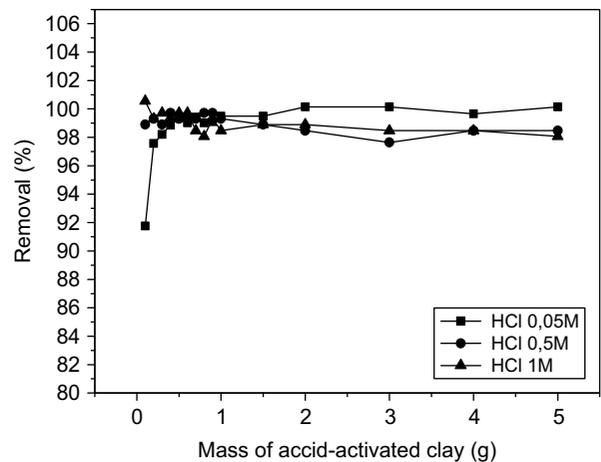


Fig. 3. Removal of Co^{2+} as a function of acid-activated clay mass (0.05, 0.5 and 1 M HCl) ($[\text{Co}^{2+}]$: 10 mg l^{-1} ; pH: 5; shaking time: 1 h; T: 25°C).

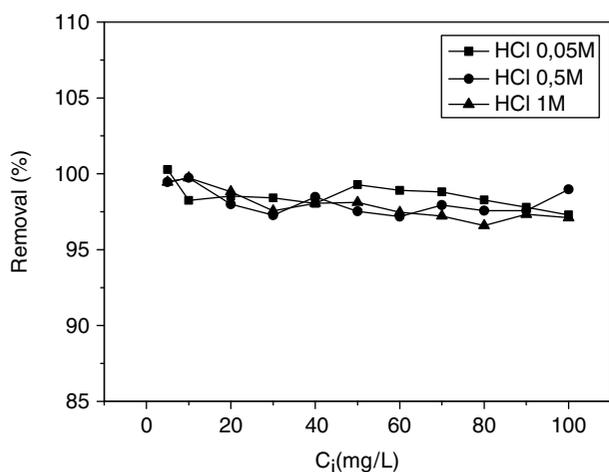


Fig. 4. Removal of Co²⁺ onto acid-activated clay (0.05, 0.5 and 1 M HCl) as a function of initial metal concentration (pH: 5; mass of acid-activated clay: 1 g; shaking time: 1 h; T: 25°C).

3.4. Effect of initial concentration of Co²⁺ ions

The removal of Co²⁺ ions on acid-activated clay as a function of initial concentration in the range 5–100 mg l⁻¹ was investigated at pH = 5 (Fig. 4). As seen in this figure, the removal was constant and higher than 70% for 100 mg l⁻¹. However, this percentage removal decreasing, after the initial concentration exceeds 100 mg l⁻¹, to reach 2% for 1000 mg l⁻¹. This behaviour observed for Co²⁺ ions might be explained by the availability of sites.

4. Adsorption isotherm

The adsorption isotherms for Co²⁺ sorption onto acid-activated clay were obtained at various metal

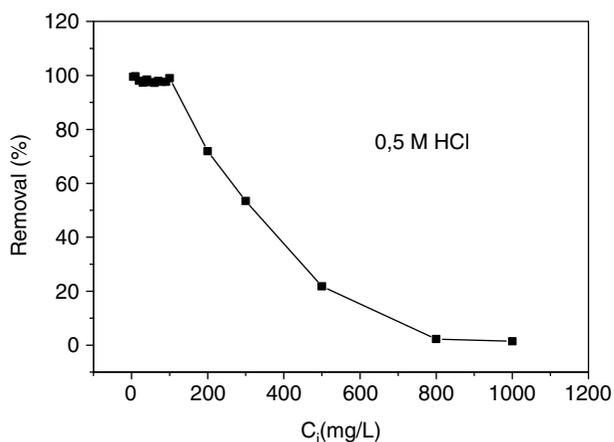


Fig. 5. Removal of Co²⁺ onto acid-activated clay (0.5 M HCl) as a function of initial metal concentration: 10–1000 mg l⁻¹ (pH: 5; mass of acid-activated clay: 1 g; shaking time: 1 h; T: 25°C).

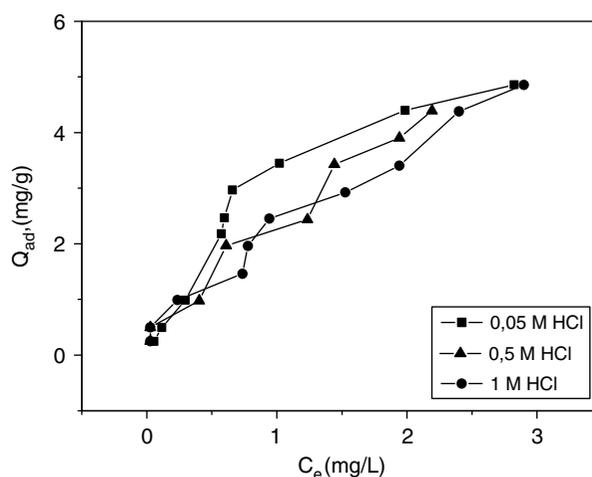


Fig. 6. The adsorption isotherm of Co²⁺ onto acid-activated clay (0.05, 0.5 and 1 M HCl) at equilibrium (pH: 5; mass of acid-activated clay: 1 g; shaking time: 1 h; T: 25°C).

concentrations from 5 to 100 mg l⁻¹, while keeping all other parameters constants (shaking time, solution pH, acid-activated clay amount at room temperature). The isothermal relationship between the equilibrium concentration of Co²⁺ ions in the solid and liquid phases is shown in the following Fig. 5. The isotherms were constructed by plotting the amounts sorbed Q_{ad} versus the concentration remaining in solutions C_e . The plot of $Q_{ad} = f(C_e)$, Fig. 6, shows that the increase, in the quantity adsorbed Q_{ad} of Co²⁺ onto acid-activated clay, with increasing of the initial concentration of Co²⁺ ions. This plot, according to Gilles's model, is of a "S" Type, [24].

5. Adsorption isotherm models

In order to represent the equilibrium adsorptive behaviour and a satisfactory description of the equation state between the two phases composing the adsorption system, two kinds, Langmuir and Freundlich equations, of several isotherms equations (Langmuir, Freundlich, Temkin, Dubinin-Radushkevich) were tested to fit the experimental data, Figs. 7a and b. The linear plots of the Langmuir and the Freundlich equations indicate that the equilibrium sorption data are satisfactorily fitted in the order: Freundlich > Langmuir for Co²⁺ ions. The value of n at equilibrium is 0.76, Table 1, representing favourable adsorption and suggests a physical mechanism with weak adsorption bond of Van der Waals forces.

6. Adsorption kinetic models

The Lagergren plots of $\ln(q_e - q_t) = f(t)$ for pseudo-first order kinetics according to Eq. (6).

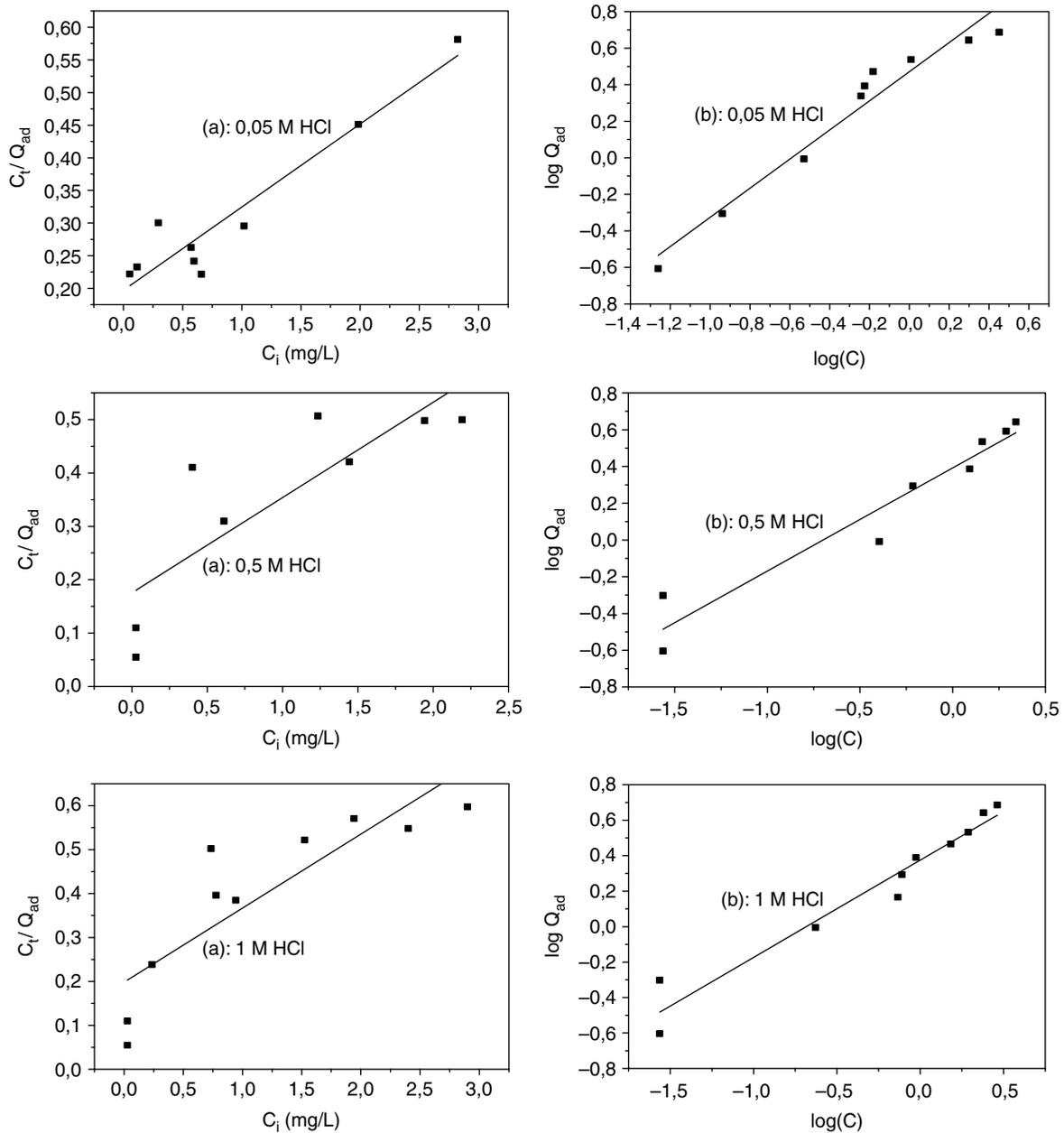


Fig. 7. Langmuir (a), Freundlich (b) isotherms for Co^{2+} onto acid-activated clay (0.05, 0.5 and 1 M HCl) (pH: 5; mass of acid-activated clay: 1 g; shaking time: 1 h; T: 25°C).

Table 1
Langmuir and Freundlich constants

Acid-activated clay (HCl)	Freundlich			Langmuir		
	N	K (mg g^{-1})	R^2	q_m (mg g^{-1})	b (l mg^{-1})	R^2
0.05 M	0.76	2.94	0.96	6.85	0.17	0.93
0.5 M	0.56	2.46	0.93	5.62	0.031	0.66
1 M	0.55	2.37	0.95	5.95	0.032	0.72

These plots, Fig. 8, were not linear ($R^2 = 0.34$) which yielded $k_1 = 7.05 \times 10^{-3}$. However the pseudo-first order mechanism is not appropriate to describe the experimental data.

The pseudo-second order kinetics was tested by plotting t/q_t versus t according to Eq. (8).

Pseudo-second-order kinetic model was developed by Ho for the sorption systems of divalent metal ions [25].

The pseudo-second-order model is based on the assumption that the rate-limiting step may be chemical

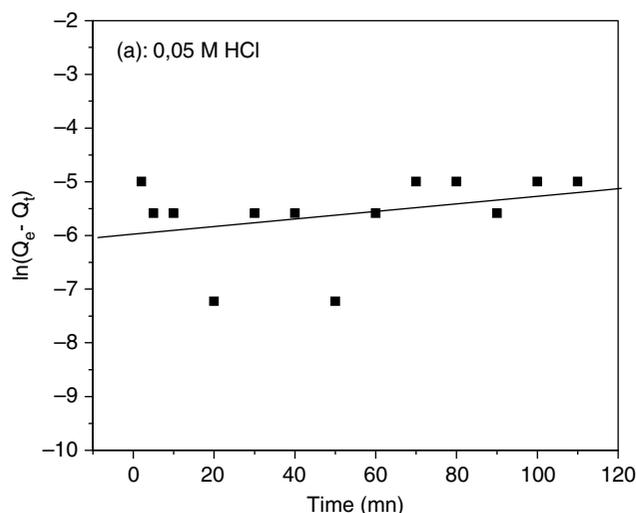


Fig. 8. Linear plot of pseudo-first order model: adsorption of Co^{2+} ions onto acid-activated clay (0.05, 0.5 and 1 M HCl).

sorption or chemisorptions involving valency forces through sharing or exchange of electrons between sorbent and sorbate [26].

This model includes all courses of adsorption, such as diffusion of external liquid membrane, surface adsorption, intra-particle diffusion which can provide real, complete and reliability adsorption mechanism for metal adsorption onto clay [27].

In our case, for the systems studied, that is, the adsorption of Co^{2+} ions onto acid-activated clay, the pseudo-second order provides the best correlation of the experimental data and it is in agreement with chemisorptions being the rate-controlling step. The plots, Fig. 9, were linear ($R^2 = 0.99$, Table 2). The experimental results indicated that the best fit is obtained with the pseudo-second order kinetic model.

7. Competitive adsorption-desorption of Co^{2+} and Ni^{2+} ions

7.1. Adsorption

For the study of the adsorption of Co^{2+} and Ni^{2+} ions onto acid-activated clay, the pH value of the suspensions prepared as described above and adjusted. The final pH value was five. After the equilibrium period (1 h), the suspensions were centrifuged and filtered, then Co^{2+} and Ni^{2+} ions were analyzed in the filtrate by AAS.

7.2. Desorption experiments

For the study of desorption, samples previously reacted with Co^{2+} and Ni^{2+} ions same concentrations were used. At the end of the adsorption period (1 h), the

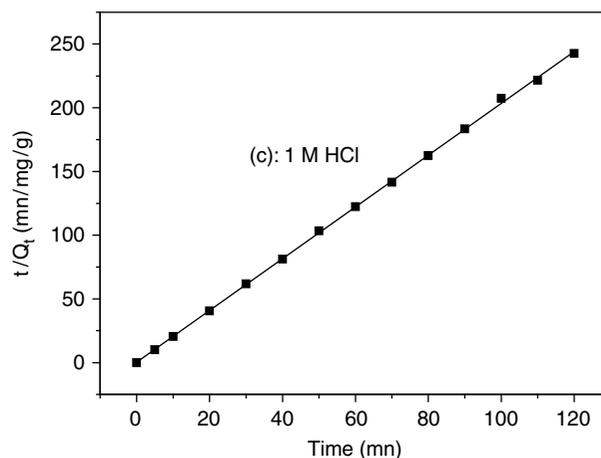
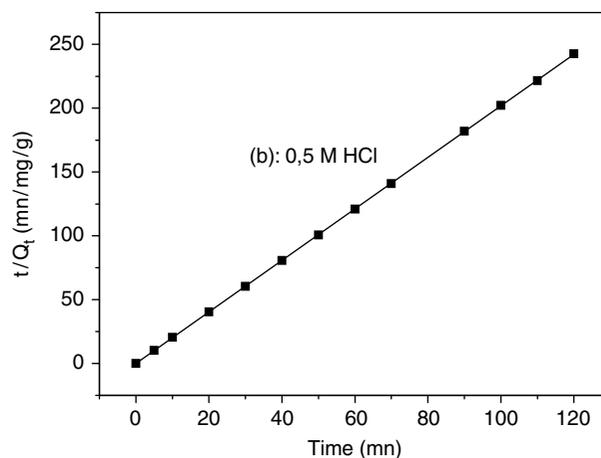
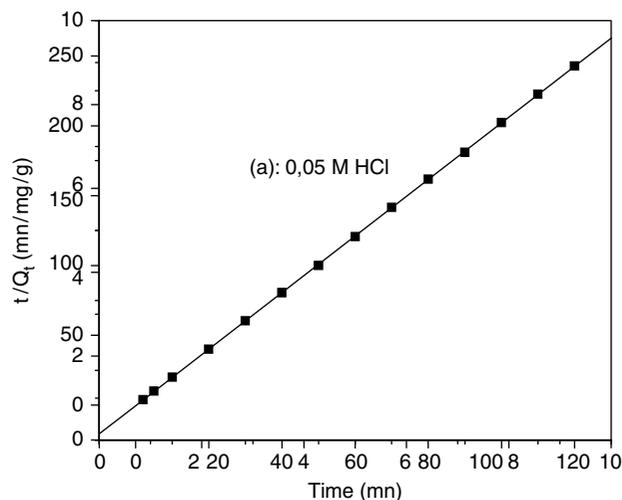


Fig. 9. Linear plot of pseudo-second order model: adsorption of Co^{2+} ions onto acid-activated clay (0.05, 0.5 and 1 M HCl).

samples were resuspended and treated as in the adsorption experiments: the pH value of these solutions was adjusted to two and the samples were shaken for 1 h. The desorption steps were repeated two times. Adsorption-desorption, experimental results are shown in Fig. 10

Table 2
Pseudo-first order and pseudo-second order constants

Acid-activated clay	Pseudo-first order			Pseudo-second order		
	Q_e	K_1	R^2	Q_e	K_2	R^2
0.05 M HCl	393.06	7.05×10^{-3}	0.34	0.494	1.47	0.99
0.5 M HCl	0.008	8.2×10^{-3}	0.15	0.495	0.25	0.99
1 M HCl	0.012	4.4×10^{-3}	0.03	0.492	9.42	0.99

and gathered in Tables 3 and 4. This result suggests a strong affinity of Co^{2+} and Ni^{2+} ions to acid-activated clay surfaces. The experimental behavior was the same as that obtained using 0.05, 0.5 and 1 M HCl.

7.3. Competitive adsorption-desorption of Co^{2+} and Ni^{2+} ions

After adsorption-desorption of Co^{2+} and Ni^{2+} ions separately, a competitive adsorption-desorption experimental

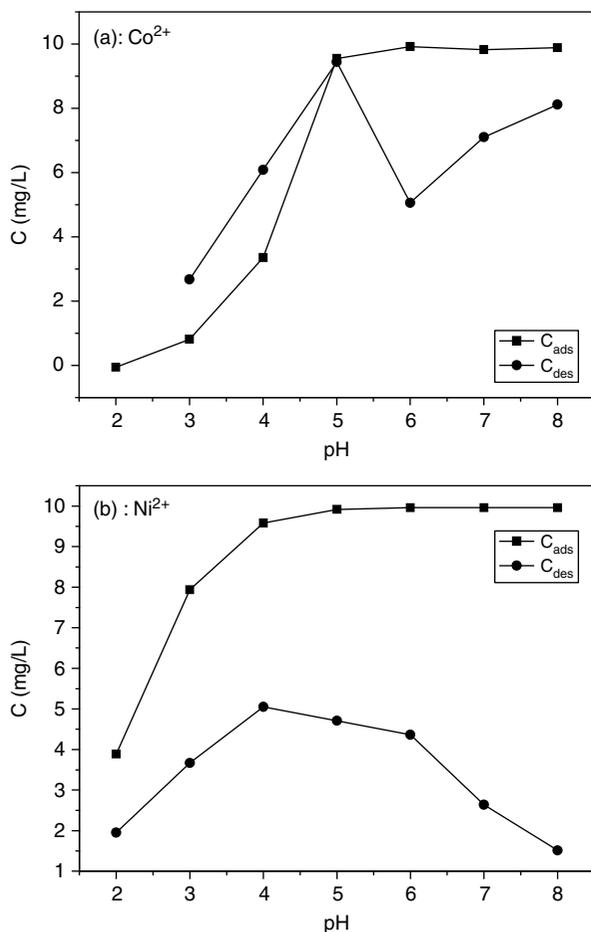


Fig. 10. Adsorption (ads.) and desorption (des.) of Co^{2+} (a) and Ni^{2+} (b) onto acid-activation of clay (0.5 M HCl) as a function of pH.

Table 3

Adsorption (ads.) and desorption (des.) of Co^{2+} onto acid-activation of clay (0.5 M HCl), $[\text{Co}^{2+}] = 10 \text{ mg l}^{-1}$, $\text{pH}_{\text{ads}}: 5$, $\text{pH}_{\text{des}}: 2$

Acid-activation clay (HCl)	0.05 M	0.5 M	1 M
C_{ads} (mg l^{-1})	9.78	9.54	9.82
C_{des} (mg l^{-1})	5.52	9.44	7.86

Table 4

Adsorption (ads.) and desorption (des.) of Ni^{2+} onto acid-activation of clay (0.5 M HCl), $[\text{Ni}^{2+}] = 10 \text{ mg l}^{-1}$, $\text{pH}_{\text{ads}}: 5$, $\text{pH}_{\text{des}}: 2$

Acid-activation clay (HCl)	0.05 M	0.5 M	1 M
C_{ads} (mg l^{-1})	9.84	9.92	9.81
C_{des} (mg l^{-1})	5.05	4.71	7.12

Table 5

Competitive adsorption (ads.) and desorption (des.) of Co^{2+} and Ni^{2+} as a function of pH and acid-activation of clay. $[\text{Ni}^{2+}] = 10 \text{ mg l}^{-1}$, $\text{pH}_{\text{ads}}: 5$, $\text{pH}_{\text{des}}: 2$

Acid-activation clay (HCl)	0.05 M		0.5 M		1 M	
	C_{ads}	C_{des}	C_{ads}	C_{des}	C_{ads}	C_{des}
Co^{2+}	9.90	7.28	9.28	9.03	9.28	8.45
Ni^{2+}	9.84	5.40	9.39	8.51	9.84	7.47

work of Co^{2+} and Ni^{2+} ions was undertaken and the results are gathered in Table 5. The adsorption is at the same level for both Co^{2+} and Ni^{2+} ions. However, the desorption of Co^{2+} ions is more important.

8. Conclusions

Acid-activated bentonite clay from Maghnia (N.W. Algeria) can be used as an effective adsorbent for the removal of Co^{2+} from aqueous solutions. The effective solution pH 5 for 60 min as contact time required for the maximum removal 90%. This means that acid-activated bentonite clays are excellent for practical applications. The experimental results indicated that the best fit is obtained with the pseudo-second order kinetic model. The adsorption isotherm experiment indicates that the Freundlich isotherm is a better fit than the Langmuir.

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