Co^{2+} removal from wastewater by a low-cost adsorbent

Hayet ASSAMEUR[1] and Makhlouf BOUFATIT[1]*

Abstract — A sample of bentonite from Maghnia (N.W. Algeria) was treated with HCl (0,05M; 0,5M and 1M) and characterized by powder X-ray diffraction, FT-IR spectroscopy and elemental analysis. The acid-activated bentonite was employed as adsorbent for Co^{2+} ions from aqueous solutions by mean of batch experiments. The simultaneous effect of treatment, shaking time and pH was studied. The results showed that the effective pH was 5 and the removal efficiency of Co^{2+} by acid-activated bentonite could reach 90-98 %, when the initial concentration of metal ions 10 mg / L and shaking time 20 mn and 60 mn. Two isotherm equations due to Freundlich and Langmuir models were applied to describe equilibrium isotherms for the adsorption of Co^{2+}. 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 Algerian clay had significant potential for removing Co^{2+} from wastewater using adsorption method.

Keywords — Acid treatment, Bentonite, Co^{2+}, DRX, FT- IR, Kinetics, Removal, Wastewater

1 INTRODUCTION

The pollution by heavy metals became currently a big challenge and a concern as for the quality of water and the environment in general [1]. The Cobalt, a very poisonous element, is used mainly in economic and strategic area as metallurgy, electronics and the nuclear processes. The limit of tolerance for Co (II) and its toxicity has been fixed as LD50 (Lethal Dose 50) [2]. 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 [3-13]. Some studies achieved in our Laboratory show good potentiality for Algerian clay to be used as adsorbent for organic and inorganic pollutants in aqueous solutions [4, 5, 14-16]. The purpose of this work was to study the simultaneous influence of an acidic treatment, the role of the pH and the effect of shaking time on the removal of Co (II) from aqueous systems onto Algerian bentonite clay and its application in the case of inorganic effluents.

1. Université des Sciences et de la Technologie Houari Boumediène (U. S. T. H. B.), Faculté de Chimie, Laboratoire d'Electrochimie-Corrosion, Métallurgie et Chimie Minérale, B.P.: 32, El-Alia, Bab-Ezzouar, Alger 16111, Algeria. Tel / Fax: + 213 21 24 73 11
* Corresponding author: E-mail: maboufatit@yahoo.com ; mboufatit@usthb.dz

2 MATERIALS AND METHOD

2.1 Reagents and solutions

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 (CoCl$_2$ 6H$_2$O, 99.5%). The elements standard solutions used were prepared with distilled water.

2.2 Preparation of acid-activated bentonite

The clay used in this work is a bentonite type from Maghnia (N.W. Algeria). It was kindly supplied by the Algerian bentonite Company ENOF. The commercial clay was purified using a sedimentation method [17], treated with different acid solutions (0.05M, 0.5M, 1M HCl). Then the acid-activated bentonite was used as adsorbent for the removal of Co^{2+}.

2.3 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 at 240.7 nm. The removal of metal ions was calculated as:

$$\text{Removal \%} = (\frac{C_i - C_e}{C_i}).100 \qquad (1)$$

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

2.3 Adsorption kinetic models

The sorption kinetics of Co^{2+} have been analysed by Lagergren pseudo-first order and pseudo-second order kinetic models.

2.3.1 Pseudo-first order equation (Lagergren equation)

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

$$\frac{dq_t}{dt} = k_1 (q_e - q_t) \qquad (2)$$

When rearranged, integrated and linearized it gives:

$$\ln\left(q_e - q_t\right) = \ln q_e - k_1 t \qquad (3)$$

Where

q_t: is the amount of Co^{2+} adsorbed at time t (min) in (mg/g);

q_e: is the amount of Co^{2+} adsorbed at equilibrium (mg/g);

k_1: is the rate constant of the pseudo-first order for adsorption of metal ions (**g/mg/min**).

2.3.2 Pseudo-second order equation

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

$$\frac{dq_t}{dt} = k_2 (q_e - q_t)^2 \qquad (4)$$

When rearranged, integrated and linearized it gives:

$$\frac{t}{q_t} = \frac{1}{k_2 \times q_e^2} + \frac{1}{q_e} t \qquad (5)$$

Where

q_t: is the amount of Co^{2+} adsorbed at time t (min) in (mg/g);

q_e: is the amount of Co^{2+} adsorbed at equilibrium (mg/g);

k_2: is the rate constant of the pseudo-second order for adsorption of metal ions (**g/mg/min**).

3 Resultats and discussion

3.1 Characterization of acid-activated bentonite

The surface properties of raw and acid-activated bentonite were characterized by Fourier Transform Infrared spectra (FT-IR) and X-ray diffraction (XRD).

3.1.1 XRD analysis
XRD patterns were obtained from Philips PW 1730 diffractometer equipped with anode using Cu-Kα □radiation (40 kV, 30 mA). XRD analysis (Fig.1)

showed that there was no obvious difference in the crystal structure of the raw and acid-activated bentonite (which was used in the experiments). The reflexions of all samples were exactly the same except the disappearance of the reflexion centred at $2\theta = 2.6$ and 5 in the acid-activated bentonite (0.05M; 0.5M and 1M HCl) spectrum.
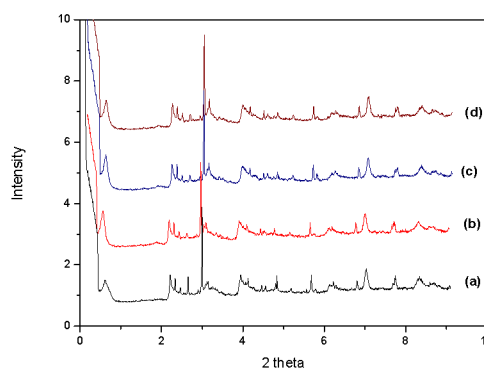

Fig. 1. X-ray diffractograms of bentonite (a- raw and acid-activated with HCl: b- 0.05M; c- 0.5M; d- 1M HCl)

3.1. 2 Infrared Spectroscopy Study

The characteristic bands of bentonite and the detailed vibrational frequencies with possible assignments being given are obtained from studies reported earlier [16, 18-20]. All products, Fig. 2(a, b, c, d) exhibit bands which might be ascribed to the stretching frequencies of the OH functional group of co-ordination water or due to stretching vibrations of Si-O, Si-O-Si, OH attached to (Al^{3+}, Fe^{3+} and Mg^{2+}) groups and the Silica Quartz impurities.

3. 1. 2. 1 OH functional group

The intense bands at 3200-3600 cm^{-1}, might be ascribed to the stretching frequencies of the OH functional group of co-ordination water and of the hydration OH stretching. The absorption band at the 1600-1800 cm^{-1} range can be attributed to both OH stretching vibration and $\delta(H_2O)$ deformation.

3. 1. 2. 2 Si–O, Si-O-Si Si-O-M and M-OH (M = Al, Mg, Fe) groups

The bands between 1200 and 500 cm^{-1} in all samples are due to stretching vibrations of Si-O, Si-O-Si, OH attached to (Al^{3+}, Fe^{3+} and Mg^{2+}) groups and the Silica Quartz impurities, These are centred at 1040 cm^{-1}, 915 cm^{-1}, 750 cm^{-1}, 590 cm^{-1} and 523 cm^{-1} and 418.3 cm^{-1}, respectively.
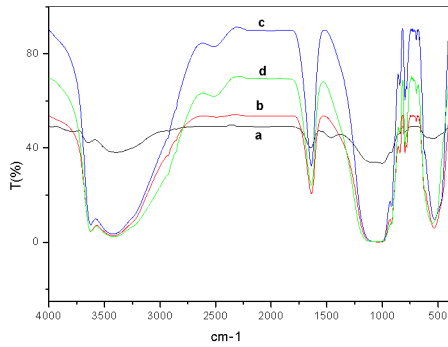
Fig. 2. IR Spectra of bentonite (a- raw and acid-activated with HCl: b- 0.05M; c- 0.5M; d- 1M HCl)

3.1- Effect of pH

The pH effect was investigated as the first parameter within the range from 1 to 9 (Fig. 3). This figure shows that the removal of Co^{2+} ions strongly depended on pH values. It is increasing gradually in acidic solutions within the pH range of 1-5 to reach 96% as maximum and then becomes constant within the pH range of 5-9. In fact, adsorption of Co^{2+} ions onto acid activated bentonite could be masked at pH values higher than 5. At low pH values, the surface of acid activated bentonite be closely associated with hydronium ions (H_3O^+) which hinder the access of metal ions, by repulsive forces, to the surface functional groups However, with the increasing pH, the concentration of H_3O^+ decreases and more of the metal ions could reach the clay surface and adsorb on it, [21].
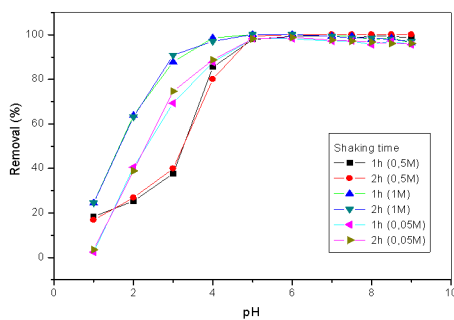

Fig. 3. Removal of Co^{2+} onto acid-activated bentonite as a function of pH (HCl: 0.05M, 0.5M, 1M; $[Co^{2+}]$:10 mg.L^{-1}; shaking time: 1h and 2h; mass of acid-activated bentonite: 1g ; T : **ambiante**)

3.2- Effect of shaking time

The effect of shaking time on the removal of Co^{2+} ions is shown in Fig. 4. According to this figure, the removal increases with the increasing of shaking time, in the range of 5–120 min, to reach

equilibrium within 20 min. Maxima adsorptions were 98% for both 0.05M, 0.5M and 1M HCl acid-activated bentonite.
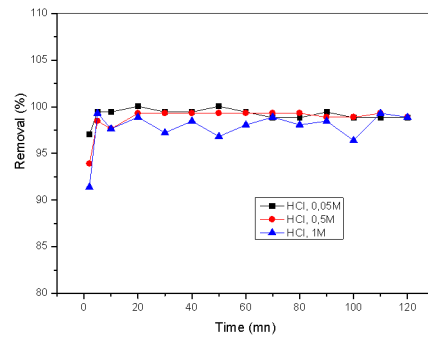

Fig. 4. Removal of Co^{2+} onto acid-activated bentonite as a function of shaking time (HCl: 0.05M, 0.5M, 1M; $[Co^{2+}]$: 10 mg.L^{-1}; pH :5 ; mass of acid-activated bentonite :1g T: **ambiante**)

4- Adsorption kinetic models

The Lagergren plots of $\ln (q_e - q_t) = f(t)$ for the pseudo-first order kinetics according to the following equation:

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

These plots were not linear (R^2 = 0.34, 0.15, 0.03, Table 1) and the pseudo-first order mechanism is not appropriate to describe the experimental data.

The pseudo- second order kinetics was also tested by plotting t/q_t versus t according to the following equation:

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

The plots were linear (R^2 = 0.99, Table 1).
The results indicated that the best fit is obtained with the pseudo-second order kinetic model.

Table 1. Pseudo-first order and Pseudo-second order constants

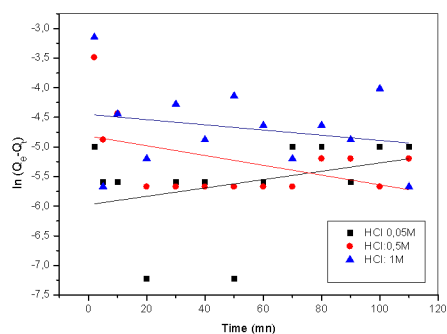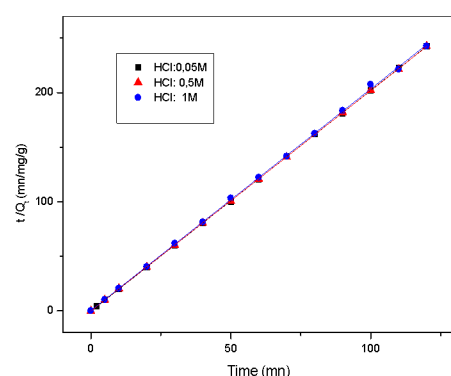| HCl (M)	Pseudo-first order			Pseudo-second order		
	Qe	K_1	R^2	Qe	K_2	R^2
0.05	$2.6.10^{-3}$	7.10^{-3}	0.34	0.49	1.47	0.99
0.5	$8.2.10^{-3}$	-8.10^{-3}	0.15	0.50	0.25	0.99
1	12.10^{-3}	-4.10^{-3}	0.03	0.49	9.42	0.99

Fig. 5. Linear plot of pseudo-first order

Fig. 6. Linear plot of pseudo-second order

Conclusions

The experimental results indicated that:

- The 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 for the removal was 5.
- The contact time required, for the maximum removal (90%), was 1h.
- The best fit is obtained with the pseudo-second order kinetic model.
The availability and the low-cost of this bentonite clay make it a good candidate in adsorption processes for use in wastwater treatment and purification.

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