# Kinetic and thermodynamic study of the adsorption of cobalt on the beet pulp

S. Elanza*, A. Lebkiri, E.H. Rifi, J. Hmimou, M. Lebkiri, Y. Essaadaoui

**Abstract**— In this work, we have valorized the beet pulp (BP) in the removing of metal ions $Co^{2+}$ from aqueous solutions.   The kinetic study shows that the extraction equilibrium of $Co^{2+}$ ions by the BP is reached after 80 min and the extraction process is expressed by the second-order kinetic. The effect of the concentration of $Co^{2+}$ and the initial pH on the removal efficiency shows that the binding capacity increases with increase in the $pH_i$ and the concentration of metal ions. The thermodynamic and mathematical modeling study of the adsorption of $Co^{2+}$ ions on the BP, shows that the ad-sorption process is favorable and chemisorption. The      negative values of $\Delta G^0$ show that the adsorption process occurs spontaneously and the positive values of $\Delta H^0$ show that the process is endothermic. Also the positive values of $\Delta S^0$ indicate increasing the randomness at the solid / liquid interface during the adsorption of $Co^{2+}$ ions on the PB.

**Keywords** — Adsorption, cobalt, beet pulp, extraction kinetics, modeling, thermodynamic study, chemisorption

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## 1 INTRODUCTION

The Heavy metals present in of effluents at high contents are considered toxic because of their adverse effects on fauna, flora and man. The heavy metals are not biodegradable and can accumulate in the food chain [1].

Specific and effective techniques have been employed for the removal of toxic metals from aqueous solutions, which may be industrial effluent or contaminated namely: The liquid-liquid extraction [2-5], the liquid-gel extraction [6-13], the solid   liquid - extraction [14-18], the membrane separation [19-22], the exchange of ions [23-26], precipitation, flotation.

In these recent years, the use of natural materials like fixing agents has expanded greatly, particularly due to their low cost and their strong ability to bind many metal ions [27-32].

With the aim to use a material less costly and harmless to the environment, we studied the extraction of metal ions $Co^{2+}$ by

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the beet pulp.

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## 2 Materials and methods

### 2.1 Material used

The beet pulp is the dry matter that remains after the extrac-tion of sugar contained in sugar beet. Its proportion in the sugar beet is 5.5% [33].

The beet pulp is consisting mainly of the cellulose, the hemicellulose and the pectin. The glucose is the precursor the cellulose, the hemicellulose of the beet pulp is a copolymer contains the xylose, the mannose, the glucose and galactose. The pectins are composed of several types of patterns whose main constituent is the galacturonic acid.

The beet pulp was dried in air, under the action of  solar rays, then crushed and sieved a view to obtaining homogeneous materials for experimental achievements and the fraction of particle size of very small diameter.

### 2.2 Preparation of metal solutions

The cobalt solutions are prepared by dissolving of    hydrated salt of cobalt chloride ($CoCl_2$, $5H_2O$) in   distilled water. The pH of each solution was adjusted by the hydrochloric acid (HCl) and sodium hydroxide (NaOH) using a glass electrod combined at pH-meter of type EUTECH: pH510 instrument.

### 2.3 Protocol experimental

The liquid-solid extraction of metallic cations $Co^{2+}$ by the beet pulp (BP) was carried out by contacting a volume of 100 ml of the aqueous phase, of concentration equal to 20 ppm, with a

mass of 0.5 g of BP stirred in beakers at 25 °C until extraction equilibrium. The pH of each solution is adjusted to 5.5. The extractant matrix was previously introduced into a small sachet of filter paper closed by a wire.

The extraction kinetics of $Co^{2+}$ ion represents the evolution of the quantity of the metal fixed on the extractant matrix with time. Each sample was diluted with distilled water and assayed to determine the final concentration of the remaining metal at extraction equilibrium and calculated the yield (R %) and extraction capacity (q).

The extraction yield R% is calculated using the following formula:

$$R\% = (Co - Ce)\ 100/Co$$

The extraction capacity at time t is defined by the following formula:

$$q_t\ (mg/g) = (Co - Ct)\ V/m$$

Co: initial concentration of metal (ppm). Ct: residual concentration of metal at time t (ppm).

$C_t$: residual concentration of metal at time t (ppm).

V: volume of the metallic solution (l).

m: mass of the support extractant introduced in solution (g)

## 2.4 method of analysis

In this work, the dosage of metal solutions of cobalt is performed in the laboratory of the phosphate office cherifian (OCP) by the technique of atomic absorption spectrometry at flame. The Spectrometer used is of type novAA 350.

## 3 Results and discussions

### 3.1 Extraction kinetics

For establish the equilibrium extraction of the ions $Co^{2+}$ with beet pulp (BP), we followed with time the change in binding capacity of $Co^{2+}$ (q) on the BP. The results obtained are shown in the Fig 1. The analysis of this curve shows that the equilibrium of extraction of $Co^{2+}$ to the BP is reached after 80 min and the maximum capacity at equilibrium ($q_e$) is of the order of 2.1 mg / g, and the extraction yield is about 52.5%.
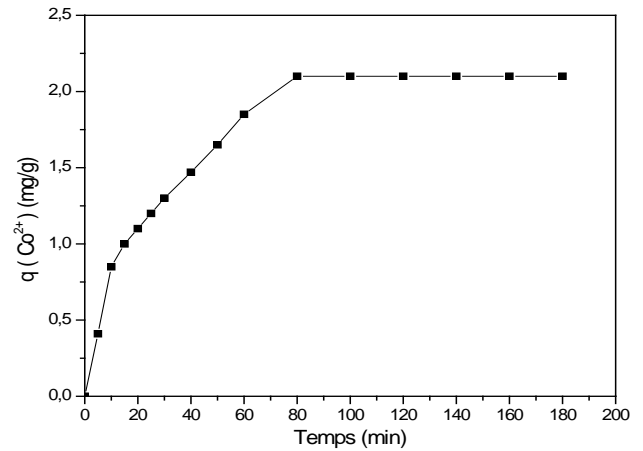


Fig. 1: Effect of contact time on the removal capacity of $Co^{2+}$ by the BP

### 3.2 Effect of the initial pH

To study the evolution of the quantity extracted of $Co^{2+}$ by the BP with of the initial pH imposed on the aqueous solution. We prepared of metal solutions at different pH: 4; 5; 6; 7; 7.3; 7.5. The results obtained are the subject of the Figure 2. The analysis of the curve obtained shows that the quantity of $Co^{2+}$ fixed on the beet pulp increases with the increase in the pHi imposed at the metal solutions.

Indeed, the increase in pH causes the dissociation of the ionizable functional groups of surface, which increases the negative charge of surface and attracts the metal cations in solution. Also, the competition of the $H^+$ protons in solution with the $Co^{2+}$ cations for the same sites of fixing is weakened considerably as pH increases.
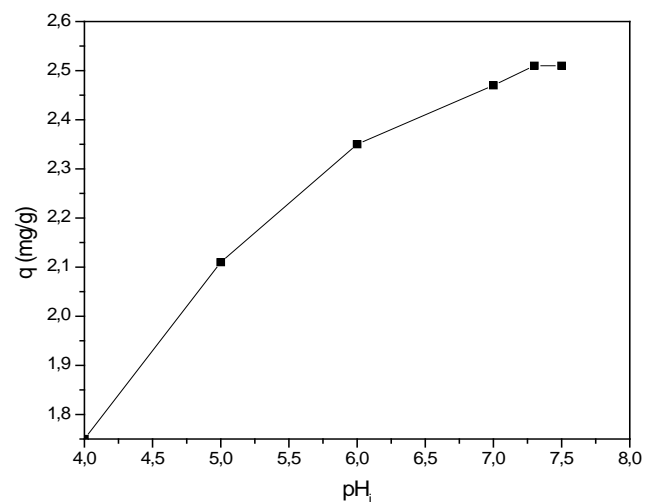


Fig. 2: Effect of initial pH on the removal capacity of $Co^{2+}$ by the PB

### 3.3 Kinetic models

Three kinetic models are studied to describe the cobalt adsorption phenomenon on the beet pulp: the first-order model, the second-order model and the Elovich model.

### 3.3.1 The first order kinetics

The kinetic model of first order is expressed by the equation of Lagergren [34].

$$dq/dt = K_1(q_e - q_t)$$

After integration between t = 0 and t, qt = 0 and qt we obtain the linear form:

$$Ln\,(q_e - q_t) = ln\,q_e - k_1 t$$

The course of the curve ln (q_e - q_t) = f (t) (Fig 3) gives a straight line with the slope equal -k_1 and the ordinate at the origin equal to ln (q_e).

$q_t$ and $q_e$ : The extraction capacities at time t and the extraction equilibrium

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$k_1$ (min$^{-1}$): speed constant of the process of extraction of the first order.
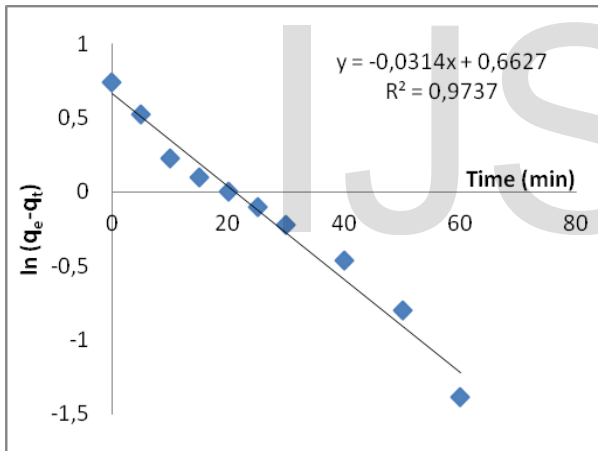


Fig. 3: Curve of the linear form of the first order kinetic model

After integration between t = 0 and t, qt = 0 and qt we obtain the linear form:

$$t/q_t = 1/K_2 q_e^2 + t/q_e$$

The course of the curve t/qt = f (t) (Fig.4) gives a straight line with the slope equal $1/q_e$ and intercept equal to $\frac{1}{K_2 q_e^2}$.

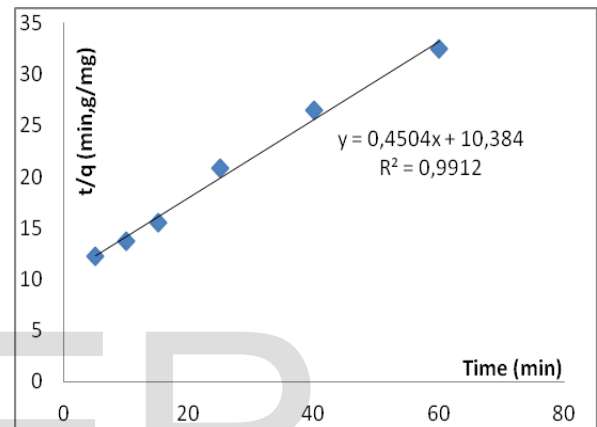k2 (g min-1mg-1): speed constant of the extraction process of the second order.



Fig. 4: Curve of the linear form of the second order kinetic model

The table1 gathers the correlation coefficients (R$^2$), and the constant kinetics of extraction for the two models.

Table 1:  kinetic parameters of extraction for the two models

The results in this table show that the correlation coefficient R$^2$ given by the second order kinetic model (0.9912) is greater than the first order (0.9737), also the binding capacity calculated at equilibrium (qe cal) for the second-order kinetic mod-

| First order kinetics | | | | Second order kinetics | | | |
|---|---|---|---|---|---|---|---|
| K_1 (min$^{-1}$) | R$^2$ | q_e exp (mg.g$^{-1}$) | q_e cal (mg.g$^{-1}$) | K_2 (g mg$^{-1}$min$^{-1}$) | R$^2$ | q_e exp (mg.g$^{-1}$) | q_e cal (mg.g$^{-1}$) |
| 0.0314 | 0.9737 | 2.1 | 1.94 | 0.0195 | 0.9912 | 2.1 | 2.22 |

### 3.3.2 The second order kinetics

The kinetic model of second order is expressed by the equation of HO and MCKAY [35].

$$dq/dt = K_2(q_e - q_t)^2$$

el is very close to the experimental binding capacity at equilibrium (qe exp), therefore we can deduce that the extraction kinetics of Co2 + by BP is expressed by the second order kinetic. These results imply that the chemisorption mechanism may play an important role in the removal of $Co^{2+}$ by the beet pulp.

### 3.3.3. Kinetic model of Elovich

The kinetic model of Elovich was also applied to the experimental results. This model is one of the most used models to verify and describe the adsorption of chemisorption.
The kinetic model of Elovich is expressed by the following equation **[36].**

$$dq_t/ = \alpha \exp(\beta q_t)$$

After integration of this equation we obtain the following linear form:

$$q_t = 1/\beta \ln(\alpha\beta) + 1/\beta \ln t$$

The course of the curve $q_t = f(\ln t)$ gives a straight line with the slope equal $1/\beta$ and intercept equal to $1/\beta \ln(\alpha\beta)$.

The constant $\alpha$ (mg g-1 min-1) is the initial adsorption rate and $\beta$ (mg g-1) is the constant of desorption related to the extent of the surface coverage and the activation energy for chemisorption.

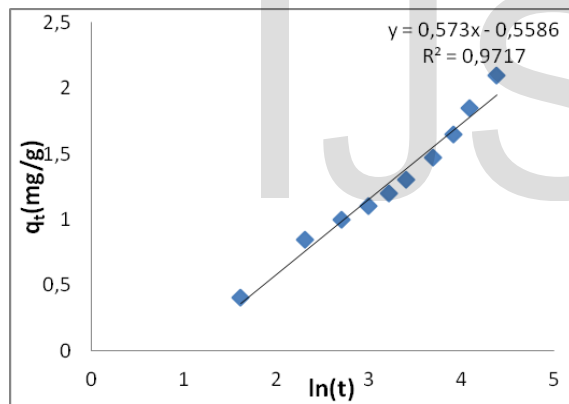The results of the curve $q_t = f(\ln t)$ are shown in the Fig 5.

Fig. 5: Curve of the linear form of the kinetic model of Elovich

The constants $\alpha$ and $\beta$, and the correlation coefficient $R^2$ are summarized in the table 2:

Table 2: Parameters of the kinetic model of Elovich

| $\alpha$(mgg-1 min-1) | $\beta$(g mg-1) | $R^2$ |
|---|---|---|
| 0.216 | 1.745 | 0.9717 |

The value of $R^2$ is close to unity, $R^2 > 0.97$, which probably means that the adsorption of $Co^{2+}$ on the BP is chemisorption, this type confirming the kinetic model of the second order.

### 3.4 Effect of concentration of $Co^{2+}$

The effect of the initial concentration of $Co^{2+}$ on the binding capacity was studied by varying the initial concentrations of the metal ions $Co^{2+}$ between 20ppm and 400 ppm. The figure (6) shows the evolution of the metal binding capacity of $Co^{2+}$ as a function of the initial concentration. The quantity of $Co^{2+}$ fixed to the BP increases with the increase of the initial concentration and reached a maximum value of 2.53 mg /g at a concentration of 250 ppm of $Co^{2+}$.
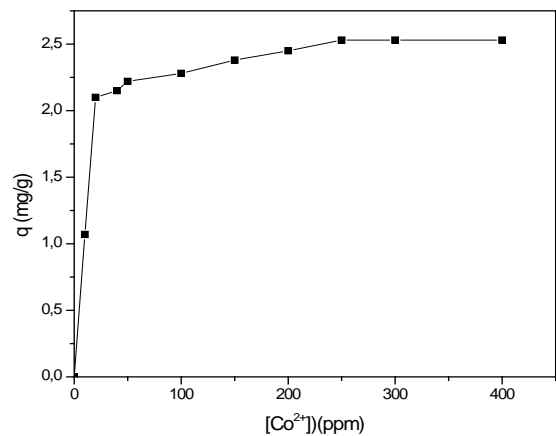
**Fig. 6:** Effect of $[Co^{2+}]_i$ on the binding capacity on the BP

### 3.5 Models of adsorption isotherms

The adsorption isotherms are defined as the set of states of adsorption equilibrium at a given temperature. The table 3 summarizes the different expressions of the main adsorption models namely: The model of Freundlich, the Langmuir model and model Temkin.

Table 3: Models of adsorption isotherms

| Model | Freundlich | Langmuir | Temkin |
|---|---|---|---|
| Equation | $q_e = K_F C_e^{1/n}$ | $q_e = (q_m k_L ce)/1+k_L ce$ | $q_e = (RT/b) \ln(AC_e)$ |
| Linear form | $\ln q_e = \ln K_F + 1/n \ln C_e$ | $C_e/qe = 1/k_L q_m + c_e/q_m$ | $q = B \ln A + B \ln C_e$ |
| Reference | **[37]** | **[38]** | **[39]** |

$K_F$ and n are constants related to the Freundlich adsorption capacity and the adsorption intensity, $q_m$ is the quantity necessary to cover the entire surface with a monolayer of adsorbed substance, b is the constant energy of adsorption and KL is the constant of the Langmuir isotherm.
$R_L$ is the Langmuir separation factor or the equilibrium parameter was used to give an indication of the adsorption. $0 < R_L < 1$ the adsorption is favorable, $R_L > 1$ the adsorption is unfavorable, $R_L = 0$ the adsorption is irreversible and $R_L = 1$ the adsorption is linear.
$R_L$ is determined by the following relationship: $R_L = 1/1 + K_L C_0$

With $C_o$ (mg / g) is the initial concentration, and $K_L$ is the Langmuir constant.

The curves of linear forms of adsorption isotherms of three models are shown in Figures 7; 8 and 9, and the parameters of isotherms of Freundlich, Langmuir and Temkin are summarized in the table 4.
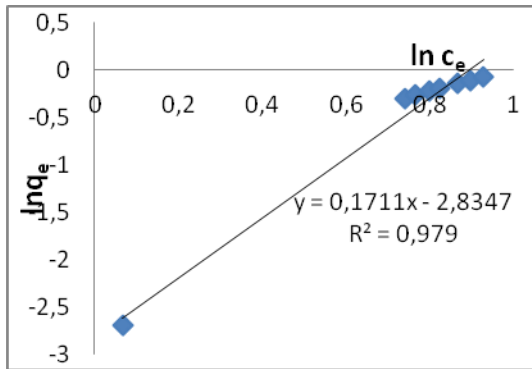


Fig. 7: Adsorption isotherm of $Co^{2+}$ on the PBB according to the model of Freundlich
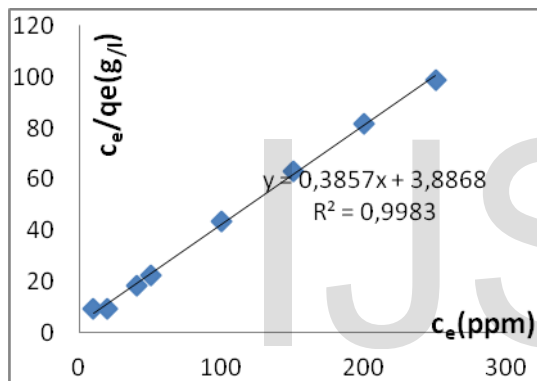


Fig. 8: Adsorption isotherm of $Co^{2+}$ on the PBB according to the model of Langmuir
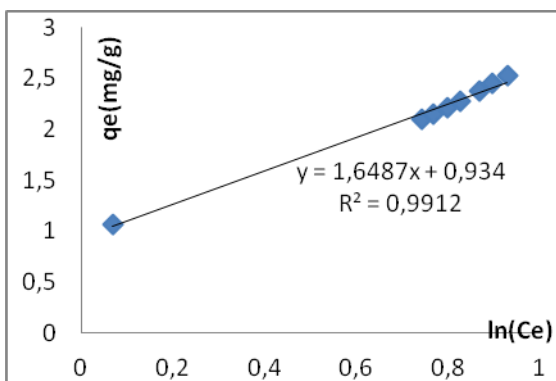


Fig. 9: Adsorption isotherm of $Co^{2+}$ on the PBB according to the model of Temkin

Table 4: The isotherms Parameters of Freundlich, Langmuir and Temkin

| Model of Freundlich | | | |
|---|---|---|---|
| 1/n | $K_F$ | $R^2$ | |
| 0.17 | 0.58 | 0.979 | |
| Model of Langmuir | | | |

| $q_{m\ cal}$ | $q_{m\ exp}$ | $K_L$ | $R_L$ | $R^2$ |
|---|---|---|---|---|
| 2.59 | 2.53 | **0.1** | 0.038 | 0.9983 |

| Model of Temkin | | | |
|---|---|---|---|
| A | B | b | $R^2$ |
| 1.76 | 1.65 | 5.819 | 0.9912 |

The modeling of the experimental results shows that the correlation coefficients $R^2$ given by the models of Freundlich, Langmuir and Temkin are closed to the unity, as the maximum binding capacity calculated ($q_m$) required to cover the entire surface with a monolayer is equal to 2.59 mg / g, this value is very closed to the experimental maximum capacity which is of the order of 2.53mg / g. these results show that the adsorption is monolayer and chemisorption. Also, the factors, $R_L$ = 0038 and 1 / n = 0.17 shows that the adsorption is favorable.

## 4 Thermodynamic study of the adsorption of $Co^{2+}$ ions on the BP

The thermodynamic parameters, such as the Gibbs free energy ($\Delta G°$), the enthalpy ($\Delta H°$) and the entropy ($\Delta S°$) were calculated using the following equations:

$$\Delta G° = - RT\ Ln\ Kc$$

$$Kc = C_a/C_e$$

$$\Delta G° = \Delta H° - T\Delta S°$$

$$LnK_c = \Delta S°/R° - \Delta H°/RT$$

$Kc$ is the equilibrium constant; Ca is the concentration in the solid phase at equilibrium (mg $L^{-1}$). Ce is the concentration in the solution at equilibrium (mg $l^{-1}$), R is the ideal gas constant (8.314J $mol^{-1}$ $K^{-1}$). $\Delta H°$ and $\Delta S°$ were obtained from the slope and intercept of $LnK_c$ versus 1 / T. the temperature (T) used are: 25 ° C (298K), 36 ° C (309k), 45 ° C (318K).

The results of the thermodynamic study of the adsorption of metal ions $Co^{2+}$ on the PBB are shown in the figure 10.

Table 5: the thermodynamic parameters of the adsorption of $Co^{2+}$ on the BP

| T ($^0$K) | $\Delta G^0$ (KJ $mol^{-1}$) | $\Delta H^0$ (KJ $mol^{-1}$) | $\Delta S^0$ (J $mol^{-1}k^{-1}$) | $R^2$ |
|---|---|---|---|---|
| 298 | -1,398 | | | |
| 309 | -2,031 | 11.281 | 38.57 | 0.996 |
| 318 | -2,457 | | | |

The results of the thermodynamic study of the adsorption of metal ions $Co^{2+}$ on BP, show that the values positive of $\Delta H^0$ which indicates the endothermic nature of the adsorption. Also, the negative values of the $\Delta G^0$ show that the adsorption process was spontaneous. The variation of entropy ($\Delta S^0$) is a measure of disorder. The transformations spontaneous go in the direction of an increase in disorder. In our case, the positive values of $\Delta S^0$ indicate the increased randomness in the solid / liquid interface during the adsorption of metal ions $Co^{2+}$ on the BP.

## 5 Conclusion

The extraction of cobalt from aqueous solutions diluted by the beet pulp was studied. The kinetic study shows that the extraction equilibrium of $Co^{2+}$ ions by the BP is reached after 80 min and the extraction process is expressed by the second-order kinetic. The effect of the concentration of $Co^{2+}$ and the initial pH on the removal efficiency shows that the binding capacity increases with increase in the $pH_i$ and the concentration of metal ions. The thermodynamic and mathematical modeling study of the adsorption of $Co^{2+}$ ions on the BP, shows that the adsorption process is favorable and chemisorption. The negative values of $\Delta G^0$ show that the adsorption process occurs spontaneously and the positive values of $\Delta H^0$ show that the process is endothermic. Also the positive values of $\Delta S^0$ indicate increasing the randomness at the solid / liquid interface during the adsorption of $Co^{2+}$ ions on the PB.

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