

Adsorption of cobalt from aqueous solutions onto Bark of Eucalyptus

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Abstract: In this work, we used the bark of eucalyptus grafted with acrylic acid (EAA) as an adsorbent for removing of Co^{2+} ions from aqueous solutions. EAA was characterized using Fourier Transformed Infrared Spectroscopy (FTIR), X-Ray diffraction (XRD), and bohemian method. The bulk density and the zero-charge point (p_{zch}) were also determined. The results showed that eucalyptus grafted with acrylic acid (EAA) is rich in COOH and OH groups and p_{zch} is acidic. We also valorized the Bark of Eucalyptus (EB) in the removing of Co^{2+} ions from aqueous solutions. The kinetic study showed that the extraction equilibrium of Co^{2+} ions by EB is reached after 40 min and the extraction process is expressed by the second-order kinetic model. The effect of Co^{2+} concentration and initial pH on the removal efficiency showed that the binding capacity increases with increasing in the pH, and the concentration of Co^{2+} ions and the maximum capacity is 55.55 mg/g. The mathematical modelling study of the adsorption of Co^{2+} ions on the BE showed that the adsorption process follows the Langmuir model. The kinetics of desorption is 8 times faster than the extraction and our material is regenerated with higher performance.

Keywords: Adsorption, Bark of Eucalyptus, Cobalt, Wastewater treatment, Isotherm adsorption.

Introduction

Cobalt is a relatively rare element that is essential for human health since it is a part of vitamin B12¹. However, higher concentrations of Co^{2+} are detrimental to human health, resulting in paralysis, diarrhoea, lung irritations and bone defects². Hence, a large variety of materials were explored to remove Co^{2+} from aqueous solution: vermiculite³, zeolites⁴, sepiolite⁵, and kaolinite⁶. To the best of our knowledge, there has not been much study on the adsorption behavior and mechanism of Co^{2+} on Bark of Eucalyptus (EB). In spite of the presence of numerous depollution techniques such as membrane systems, coprecipitation, ion-exchange resins, and electro dialysis are still very expensive⁷. Adsorption is an efficient technique used in the removal of dyes, odor, organic pollutants and inorganic heavy metal ions from industrial wastewater. Various sorbents are used in the adsorption process including activated carbon, agricultural wastes, chitosan, and bark of eucalyptus. Activated carbon is the most widely used adsorbent due to its excellent adsorption efficiency for organic and inorganic pollutants, but its use is inadequate due to its high cost⁸⁻¹¹. However, the fight against metallic pollution has stimulated the search for clean technologies and particularly processes by using natural supports and fewer costs

for the removal of heavy metals from the industrial wastewater. Several studies have been recently developed for the elimination of heavy metals by plants^{7,12-15}, more particularly by the eucalyptus bark¹⁶⁻²⁰. In this regard, our work is based on trying to use a material based on eucalyptus bark because of its availability and its richness in compounds capable of fixing heavy metals (cellulose, hemicellulose, and Lignin). The chemical modification of eucalyptus bark can greatly increase the binding capacity of heavy metals. Among the possible treatments, there is the chemical modification of bark through the grafting of acrylic acid²¹⁻²³ or formaldehyde crosslinking^{24,25}. These treatments have the particular aim of reducing the hydrophilicity of wood and stabilizing it dimensionally. In this study, we grafted eucalyptus bark with acrylic acid and applied it to the decontamination of aqueous solutions loaded with Cobalt ion (II). The studied sorbent in this work is characterized by different techniques such as FT-IR, DRX, and MEB-EDX.

Materials and methods

Sorbent

The preparation of eucalyptus camaldulensis bark used as sorbent has been described in our

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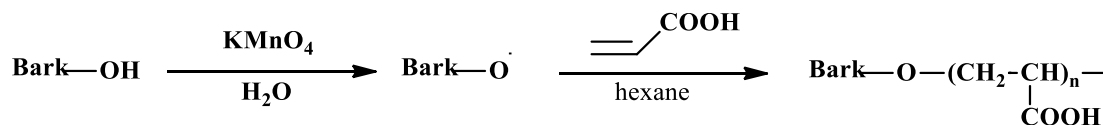
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previous study²⁶⁻²⁸. The copolymerization reaction of the bark of eucalyptus with acrylic acid was done with two steps: preliminary oxidation of the wood

leading to the formation of macro-radicals and then copolymerization with acrylic acid.

The reaction scheme adopted for the grafting of acrylic acid on eucalyptus bark is as follows.



Characterization of the material

The eucalyptus bark was characterized by different methods: the surface function has been defined by the Boehm method²⁹⁻³³, which corresponds to the acid-base titration of the surface functional groups. The determination of acidic oxygen surface functions is based on their neutralization by bases of increasing strength (NaHCO₃, Na₂CO₃, and NaOH) and the dosage of the basic oxygen functions of the surface is carried out by hydrochloric acid. The various materials (raw and treated eucalyptus bark with acid acrylic) were analyzed by Fourier Transform Infrared (FTIR) spectroscopy which was performed by using a VERTEX 70 type apparatus in the wavelength ranging from 400 to 4000 cm⁻¹; the spectral resolution is 4.0 cm⁻¹. The pellets were prepared from an intimate mixture of sieved samples (1 mg) and potassium bromide (100 mg) under a pressure of 4.5 10⁸ Pa. The powder samples were scanned using an X-ray diffractometer type XPERT-3, the wave number and the scanning degree are ranging between 0-4000cm⁻¹ and 0-50° respectively. The analysis of these materials (raw and treated eucalyptus bark) with DRX was on a continuous scanning mode using a monochromatic Kalpha radiation of copper (CuKα-radiation) (λ = 0.154 nm) at 35 kV and 30 mA. Scanning electron microscopy (SEM) and Energy Dispersive X-ray (EDAX) analysis of eucalyptus treated with acrylic acid (EAA) beads surface in order to characterize the surface morphology and texture of EAA beads in the absence and the presence of Co (II), the scanning electron microscopy and energy dispersive X-ray analysis were performed using VEGA3 TESCAN.

Adsorption and desorption procedures

The extraction experiments were realized by adding the given quantity of adsorbent with 100 mL of aqueous solution with known cobalt ion concentration in a 250 mL beaker. The pH of the solutions was adjusted by adding negligible volumes of 0.1 or 0.01 M HNO₃ or NaOH. The flask was intermittently stirred for an adequate period and

temperatures, depending on the purpose of the experiment. After each extraction test, the solution was filtered by using a cellulose nitrate filter paper with a diameter of 0.45 μm, and finally, the obtained solutions were analyzed to measure the different concentrations of Co²⁺ by inductively coupled plasma atomic emission (ICP-AES) spectrophotometry. The detection limits for Co²⁺ was 0.001 mg/L. The relative standard deviation of every test result was less than 3%.

For the desorption experiments, the bark of eucalyptus was added to 100 mL solution of 0.1 M HNO₃ at 25 °C to reach adsorption equilibrium.

The amount of sorption at equilibrium, q_e (mg g⁻¹), was calculated by (Eq.1):

$$q_e = \frac{(C_0 - C_e)V}{m} \quad (1)$$

The adsorption efficiency of cobalt fixed by the bark of eucalyptus is calculated from (Eq. 2):

$$R\% = \frac{C_0 - C_e}{C_0} \times 100 \quad (2)$$

Where C₀ and C_e (mg L⁻¹) are the initial and equilibrium liquid phase concentrations of metal, respectively. V (L) is the volume of the solution and m (g) is the mass of the dry used sorbent. All chemical products were purchased from Sigma-Aldrich (France) with a high quality.

Results and Discussion

Characterization of the material

Table 1 summarizes the different characteristics of crude eucalyptus bark (EB) and grafted eucalyptus bark with acrylic acid (EAA) while the chemical composition (the percentage of holocellulose, lignin, and extractable materials) of crude eucalyptus bark was determined according to TAPPI (the Technical Association of the Pulp and Paper Industry) standards³⁴.

Table 1. Physico-chemical characteristics of Eucalyptus bark before and after chemical treatment.

Material	Humidity (%)	Mineral materials (%)	pH _{zch}	Apparent density (g/cm ³)	Holocellulose (%)	Lignine of klason (%)	Extractable material (%)
EB	5.19	14.92	4.25	0.75	57	26	4.03
EAA	4.81	1.51	3.60	0.77	-	-	-

The determination results of materials surface functions by the Boehm method are illustrated in

Table (2).

Table 2. Surface functions of materials with different states.

Material	functions carboxyl (mmol/g)	functions lactones (mmol/g)	functions phenols (mmol/g)	Total of functions acids (mmol/g)	functions basic (mmol/g)
EB	0.09	0.12	0.45	0.66	0.00
EAA	0.57	0.14	0.55	1.26	0.00

At first, it is found that the surface chemistry of material is slightly affected by the performed chemical treatment (grafted the acrylic acid into the bark of eucalyptus). On one hand, the Eucalyptus bark (raw and treated) has an acidic character ($\text{pH} < 5$), which can be explained by the presence of acid functions and the absence of basic functions on the surface of both of materials. The results in Table 2 show a clear increase of carboxyl functions in the surface of the adsorbent after treatment of the eucalyptus bark with acrylic (0.57 mmol/g).

The spectra, which are obtained by infrared analysis (FTIR) of the raw and treated eucalyptus bark samples (EB, EAA), are shown in (Figure 1). Characteristic vibration bands were assigned to different chemical functions in accord with the literature data. The FTIR spectra of EB and EAA had almost the same form, but the treated bark with acrylic acid (EAA) had an increased intensity. All infrared spectra reveal the presence of a broad band at 3400 cm^{-1} which corresponds to the stretching vibrations of OH bond of the aromatic and aliphatic phenol structures (lignin and cellulose group) with the exception of the treated bark with Acrylic acid (EAA). There is an important increase of EAA spectra intensity due to the grafting by the acrylic

acid. The band which is about 2930 cm^{-1} corresponds to the asymmetric elongation of the cellulose C-H bond. As for the band located at 2850 cm^{-1} , it corresponds to the symmetrical elongation vibration of the C-H bond of the methoxy groups of the lignin. The peak at 1720 cm^{-1} characterizes the (C = O) valence vibration of carboxylic acids and/or esters of xylans present in hemicelluloses³⁵. For the compound which is treated with acrylic acid, this same peak appears with a marked increase in intensity due to the appearance of the carboxylic acids C = O bond of the acrylic acid grafted onto the bark. Furthermore, the band which is observed around 1630 cm^{-1} corresponds to the C = C deformation of the aromatic cycles of the lignins. The bands observed at 1380 cm^{-1} and 1230 cm^{-1} are attributed to the ν (C-O) vibration of the methoxy groups of lignin and the bond which is formed by the action of formaldehyde on cellulose (C-O-C). The band which is around 1159 cm^{-1} in the bark spectrum treated with acrylic acid corresponds to the elongation of the C-O bond of the acid group because of the grafting of the acid functions on the eucalyptus bark. The peak around 1030 cm^{-1} corresponds to the valence vibrations of the C-O and C-O-C bonds of cellulose³⁶.

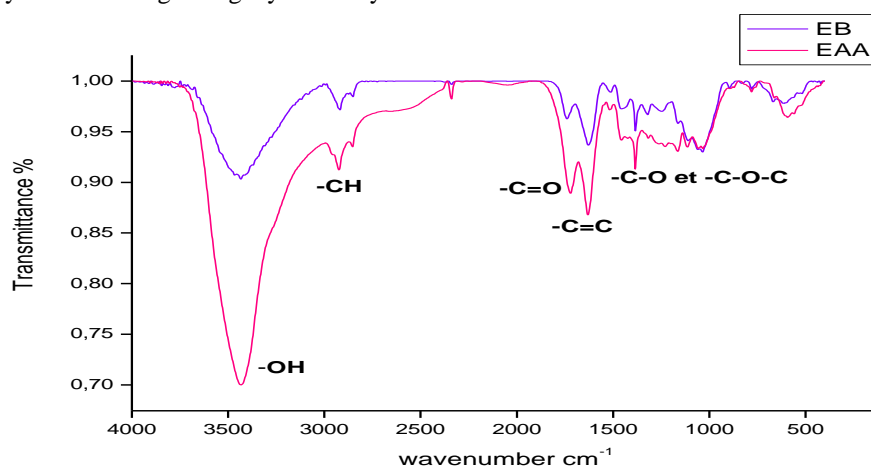


Figure 1. FTIR spectra of rough (EB) and modified (EAA) Eucalyptus bark

The X-ray diffraction patterns of the rough and modified eucalyptus bark samples are shown in Fig.2. Based on the literature and the Fig. 2, it appears that all the samples have the characteristic shape of a native cellulose correspond of two peaks

showed in the Fig. 2 of lignocellulosic materials with a clear domination of the amorphous form³⁷⁻³⁹ explained with the absence of the peaks along the spectrum.

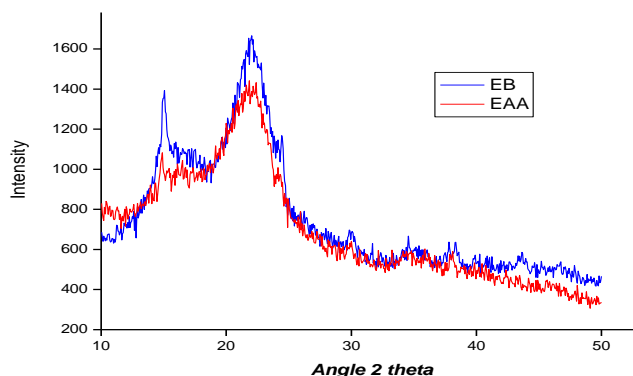
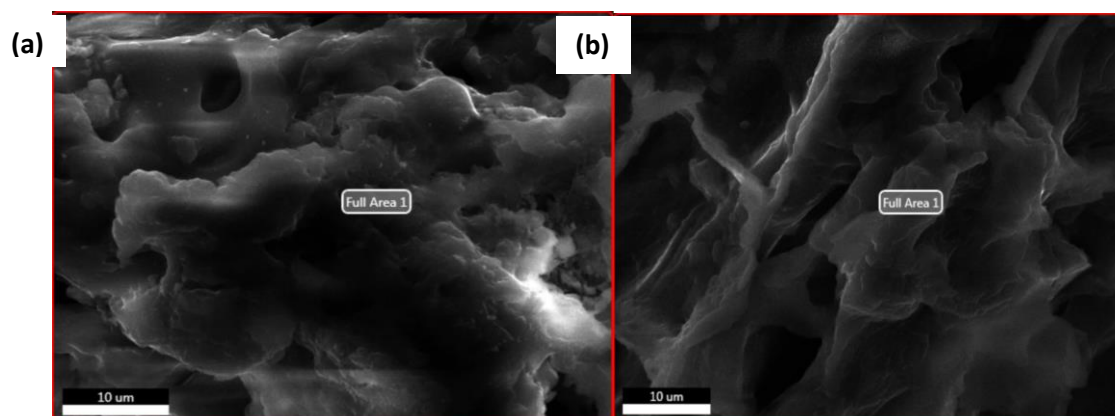


Figure 2. X-ray diffraction patterns of both the raw and the treated Eucalyptus bark.

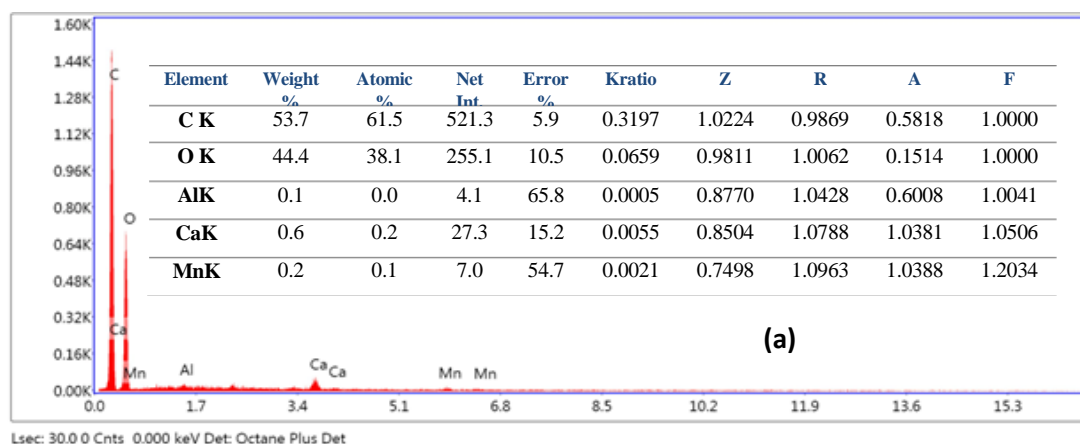
Figure 3 (a) and (b) show the SEM of EAA before and after cobalt attachment, respectively. It can be concluded that the surface of prepared EAA consists of layers and pores, which can increase the total surface area, and allows more attachment for Co^{2+} . The layers and pores can be seen in Fig. 3(a) which is available for active adsorption of contaminants, while Fig. 3 (b) depicts the adsorbed cobalt onto these pores.

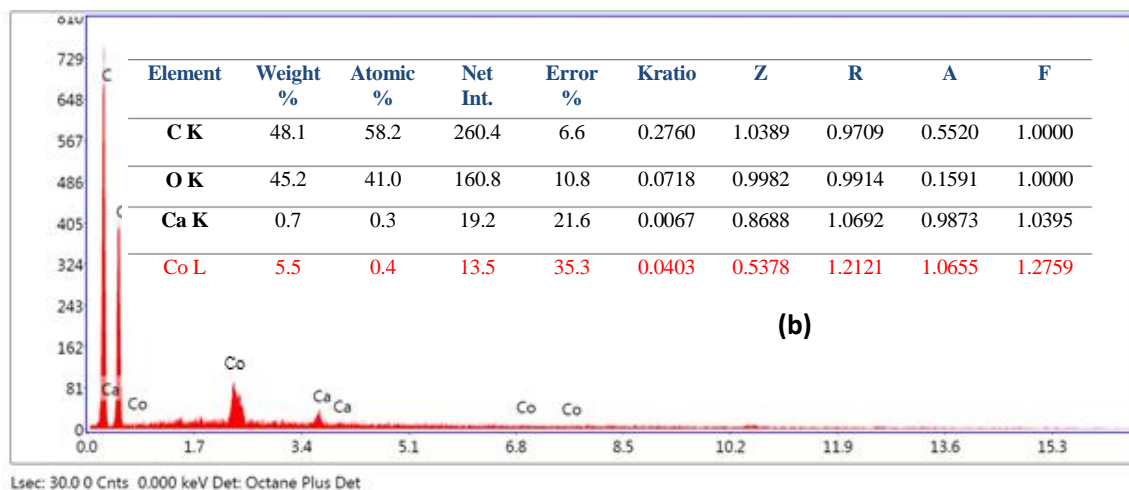
Figures 4 show the EDS spectrographs of EAA adsorbent before and after adsorption. Figures 4 (a)

shows the elemental analysis of EAA, indicating no peak for Co ions. The elemental analyses of EAA after adsorption are shown in Fig. 4 (b). The appearance of small peaks for cobalt in these spectra confirms the adsorption of cobalt on the prepared adsorbent. The cobalt percentage of the EAA after adsorption of cobalt (Fig.4 (b)) is higher than that of the EAA spectra before adsorption of Co(II) in Fig.4 (a), which indicates more attachment of cobalt on EAA.



Figures 3. (a) SEM of EAA before adsorption and (b) SEM of EAA after adsorption





Figures 4. (a) EDS of EAA before adsorption and (b) EDS of EAA after adsorption of Co(II)

Kinetics of adsorption

The kinetics of adsorption describes the contact time required to attain the extraction equilibrium by studying the simultaneous evolution of the concentration of Co^{2+} versus time (Figure 5) and the variation of the aqueous solution pH. The concentration of cobalt ions decreased from 20 to 4.8 mg/L through four hours. The extraction equilibrium

is reached after 40 minutes with an adsorption amount equal to 15.2 mg/g. The pH of the Co^{2+} solution during the kinetic study decreased in a fast way during the first minutes and then stabilize indicate the equilibrium of extraction. The pH value decreased from 5 to 3.6. The decrease in pH indicates that the adsorbent releases protons in order to fix the Co^{2+} ions.

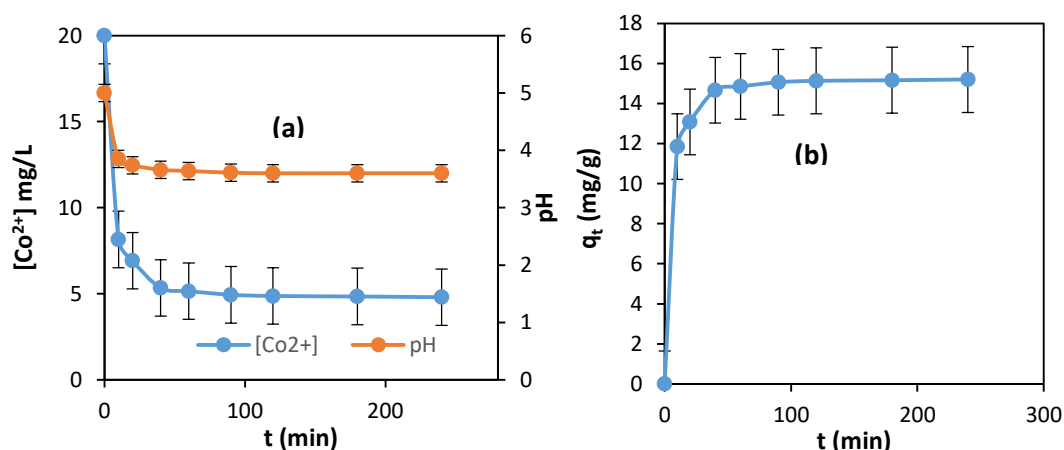


Figure 5. Variation of the Co^{2+} concentration and pH solution versus time (a), and the adsorption amount of Co^{2+} ions onto EAA at different contact time (b).

Effect of initial pH of the aqueous solution

It is well known that pH is an important factor for heavy metal adsorption. In this study, the pH was in the range of 2-7 to prevent precipitation of Co^{2+} in the form of metal hydroxides. The relationship between the initial pH values and the amounts of Co^{2+} adsorbed on the EAA is shown in Figure 6. It is found that the adsorption amount increases as the pH of the solution increase at pH less than 4, which is attributed to the fact that the active sites of the EAA are protonated and the surface of the sorbent charged positively. Therefore, the formation of bonds between active sites and metal ions is difficult because of the repulsive forces between them. When

$\text{pH} \geq 4$, the adsorption capacity of Co^{2+} increased slightly with increasing pH and afterwards remains constant, this can be explained by the surface becoming more and more negatively charged, so the attractive forces become more important between the metal ions and the support. Therefore, the pH ranging from 4 to 7 could be considered as the favorable pH in the adsorption process, or the maximum value of the adsorption amount is 16 mg/g at $\text{pH} = 6$. Thus, the optimum pH for Co^{2+} adsorption is 6, which was selected for the following experiments. The increase of the extraction capacity with the increase of the pH can be due to the release of two protons to capture Co^{2+} according to the equilibrium following:

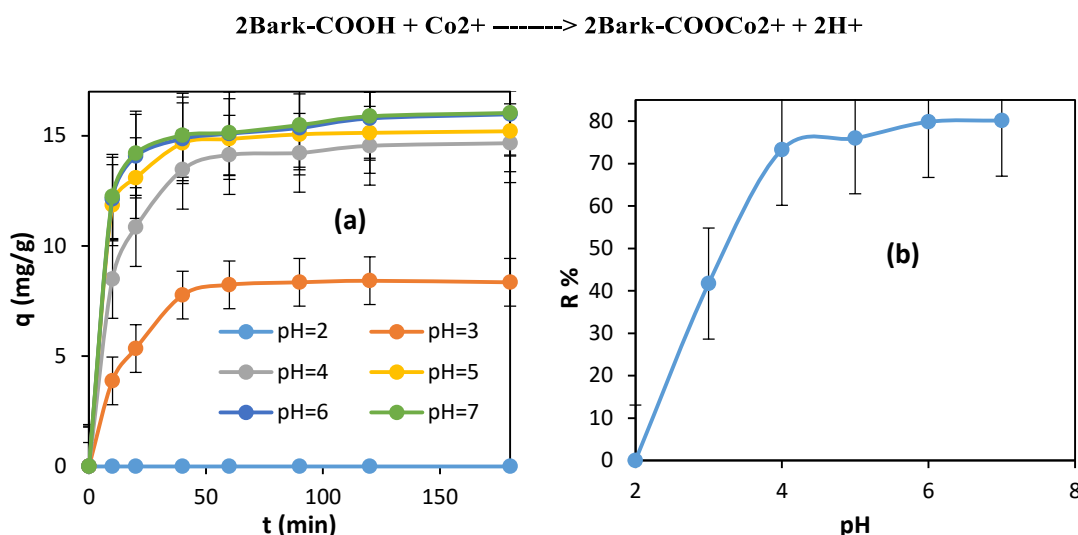


Figure 6. Effect of initial pH on the adsorption amount versus time of Co^{2+} (a) and adsorption efficiency of Co^{2+} versus initial pH by EAA (b).

Effect of initial concentration of cobalt ions

The initial concentration of the metal has an important influence on the retention capacity of the adsorbent. In order to study its effect, the following values were considered: 20, 40, 60, 80, 100 and 200 ppm. The obtained results were shown in Figure 7. The adsorption amount increases with the increase in the initial concentration of Co^{2+} . However, at high

concentrations, the driving force, due to the higher concentration gradient, and the adsorption amount of Co^{2+} (q_t), is greater, which causes adsorbent saturation⁴⁰. Accordingly, it can be concluded that the treated eucalyptus bark is an efficient adsorbent at low and high concentrations of cobalt ions from aqueous solutions.

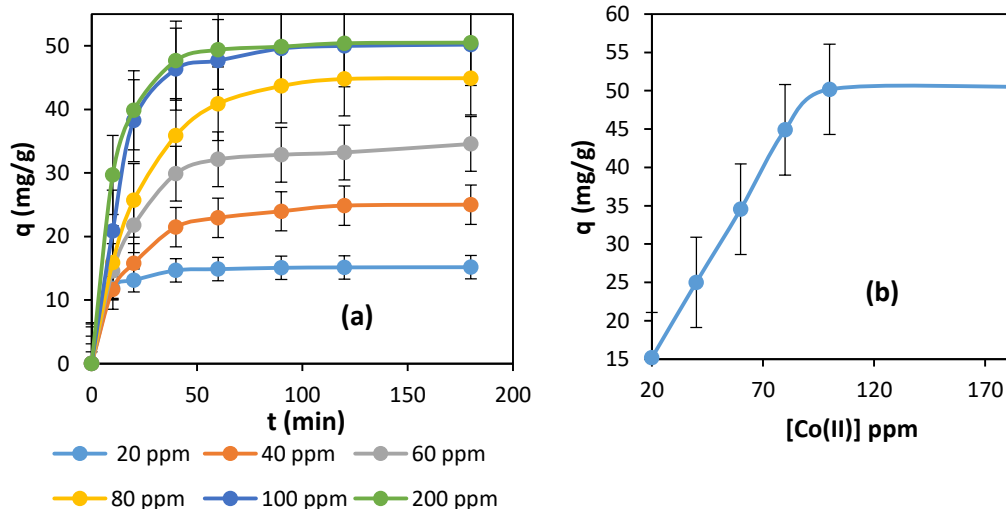


Figure 7. Effect of the initial concentration on the capacity of extraction of Co^{2+} versus time (a) and the adsorption amount versus initial concentration of Co^{2+} by EAA (b).

Effect of adsorbent mass on extraction

In this study, quantities of increasing EAA (0.02, 0.05, 0.07, 0.1, 0.2, 0.3, 0.4, 0.5, and 0.6 g) were plunged into 100 ml of each aqueous solution of Co (II), with a concentration equal to 20 ppm. The pH of each solution was set at 5.5. According to the results of Figure 8, it can be seen that the adsorption efficiency of the Co^{2+} ions increases progressively as the mass of the support contacted with the metal

solution increases and as a result, the contact surface becomes larger. Moreover, the availability of the active sites responsible for the metal ions complexation increases. An optimum efficiency of $\geq 97\%$ is obtained at a mass of 0.2 g. Consequently, it can be concluded that under the used operating conditions, a mass of 0.2 g of the support is sufficient to purify a metallic solution of Co^{2+} with a concentration equal to 20 ppm.

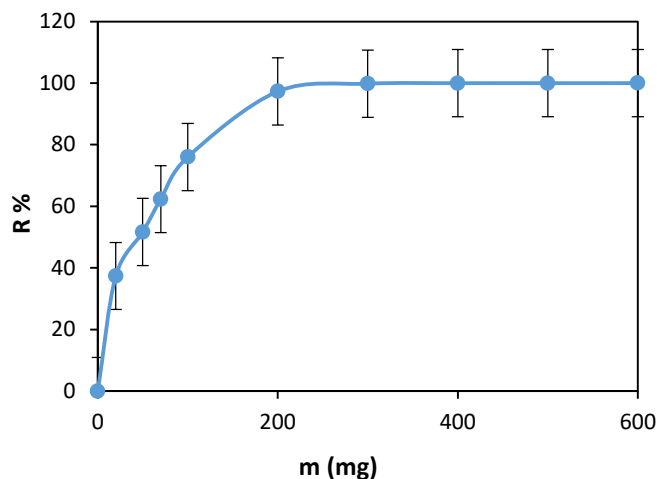


Figure 8. Effect of EAA mass on the adsorption efficiency of Co^{2+} .

Regeneration and desorption studies

The used EAA was regenerated by using 0.1 M HNO_3 solution. The procedure involved in using 100 ml of 0.1 M HNO_3 to desorb any cobalt ions on the EAA at room temperature for 5 min. The regenerated EAA was then used again after washing with water at the predetermined optimum conditions. The results (Table 3) showed that the change in the

removal efficiency of EAA after the first sorption step and subsequent use after regeneration was negligible. Therefore, being cheap and easily regenerated without losing its efficiency toward cobalt removal, EAA seems to be promising biosorbent to treat industrial wastewater streams that contaminated with cobalt.

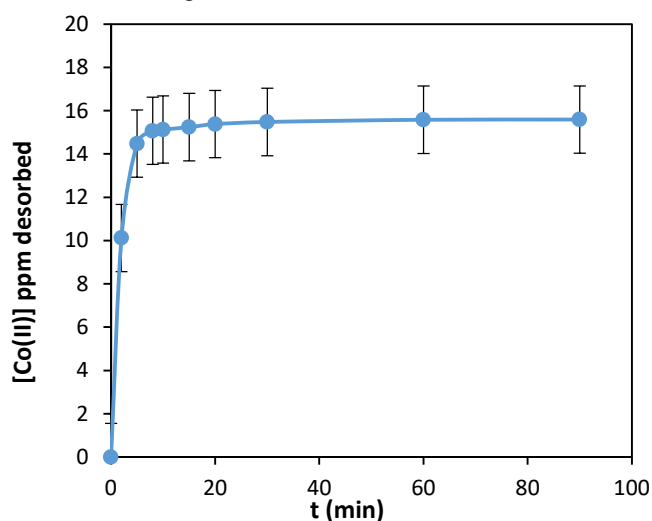


Figure 9. Desorption results of cobalt removal from aqueous solution by EAA (parameters: $m = 0.1$ g, $[\text{Co(II)}] = 500$ ppm, temperature = 25 ± 0.5 °C, contact time 90 min)

Table 3. Regeneration results of cobalt removal from aqueous solution by EAA (parameters: $m = 0.1$ g, $[\text{Co(II)}] = 500$ ppm, temperature = 25 ± 0.5 °C, contact time 90 min).

	Removal efficiency %
First run	71.6
1 st Regeneration	71.01
2 nd Regeneration	69.97
3 rd Regeneration	69.91

Adsorption isotherms

Adsorption isotherms characterize the equilibrium relationship between the amounts of adsorbed ions by adsorbents and its equilibrium concentration in the solution⁴¹⁻⁴⁴. There are several isotherms for analyzing experimental adsorption

equilibrium data. The equation parameters of these isotherms often provide some insight into the adsorption mechanism⁴⁵.

In order to identify the retention mechanism for the initial concentrations ($C_0 = 20$ to 200 mg/L), and

isotherms that represent better the adsorption of Co(II) ions on the eucalyptus bark (EAA), two theoretical models were tested on the obtained

experimental results, namely Freundlich and Langmuir.

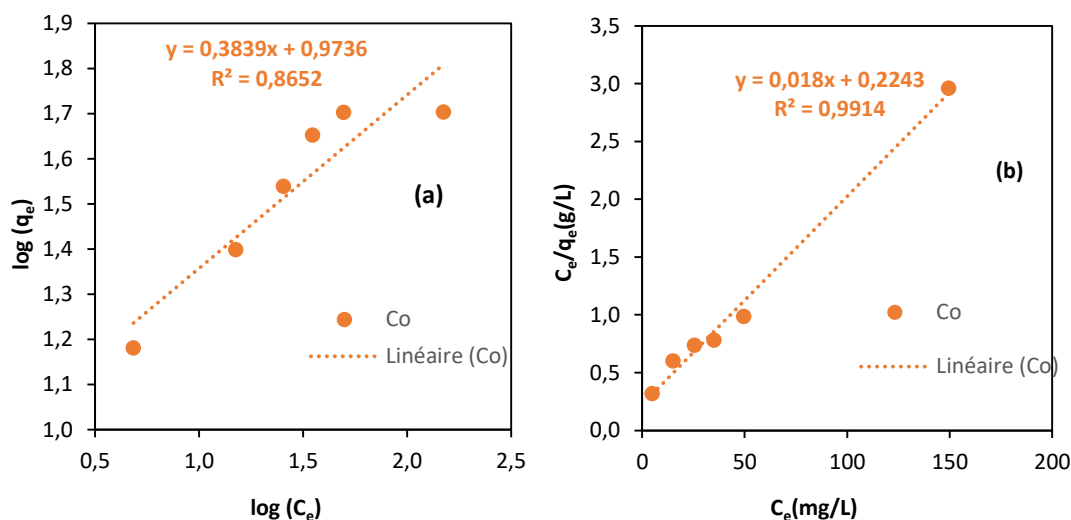


Figure 10. The adsorption isotherm modelling by Freundlich (a) and Langmuir (b).

From the graphical representation of each isotherm (Figure 10 and Table 4), which have given the correlation factors as well as the constants of each model, it is evident that the Co(II) ion retention mechanism is represented by Langmuir isotherm which has the highest correlation factor, compared to

another model. Thus, according to Langmuir theory, the adsorbent solid has a limited adsorption capacity (q_m), all active sites are identical, which implies that they can complex only one solute molecule (monolayer adsorption) also there are no interactions between the adsorbed molecules.

Table 4. Kinetic constants and correlation factors of different adsorption isotherms of Co (II) on EAA.

Type of isotherm	Constants		Equations
Freundlich	K_f ($\text{mg}^{1-n} \cdot \text{l}^n \cdot \text{g}^{-1}$)	2.6474	$\ln q_e = \ln K_f + n \ln C_e$
	n_f	0.3893	
	R	0.8652	
Langmuir	q_m (mg/g)	55.55	$C_e/q_e = C_e/q_m + 1/(q_m K_L)$
	K_L (L/mg)	0.46	
	R	0.9914	

K_f : Freundlich adsorption constant.

q_m : maximum adsorption capacity (mg / g).

K_L : Langmuir constant.

R: coefficient of linear regression.

C_e : Co^{2+} concentration at equilibrium.

q_e : equilibrium binding capacity.

Validation of kinetic models

The kinetic data obtained for the adsorption process were analyzed using the two most common models, Lagergren pseudo first order and pseudo second order. The Co(II) concentration that used in this study was 20 ppm.

The validity of the Lagergren equation is first tested by plotting $\ln(q_e - q_t)$ as a function of time (t). From the equation representative of pseudo-second-order kinetics and its linear form, the rate constant k_2

can be calculated graphically by plotting t/q_t as a function of time (t).

The linear regression data of various models are shown in Table (5). According to the obtained values, the correlation coefficients close to unity, it can be concluded that the cobalt retention kinetics are described better by the pseudo-second-order model than the pseudo first model. Therefore, the adsorption process depends on the ions concentration onto the adsorbent surface in accordance with chemisorption nature.

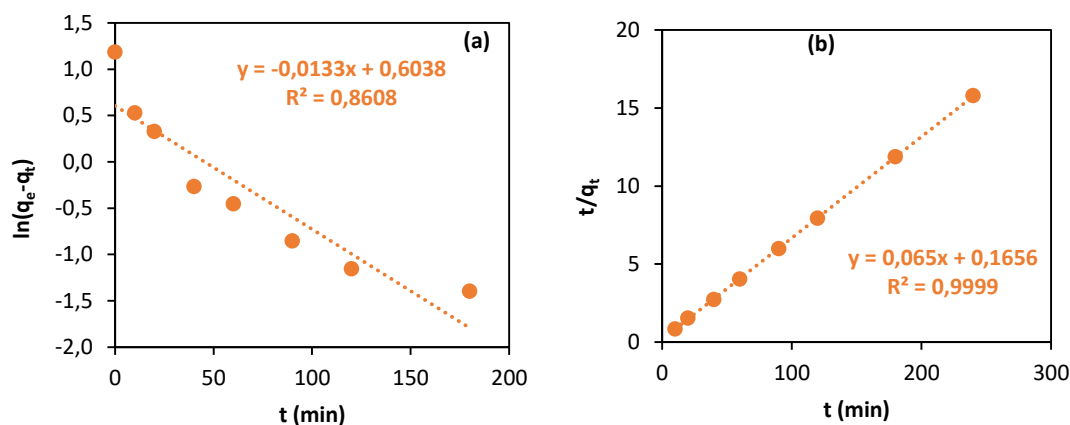


Figure 11. Linearization of the retention kinetics of cobalt of the pseudo-first-order (a) and pseudo-second-order (b).

Table 5. Kinetic models Parameters studied for cobalt.

	Lagergen pseudo1 st order		Pseudo 2 nd order	
Constants	$k_1(\text{min}^{-1})$	0.07187	$k_2(\text{g} \cdot \text{mg}^{-1} \cdot \text{min}^{-1})$	0.0956
	$q_e(\text{mg/g})$	4.25	$q_e(\text{mg/g})$	19.64
	R^2	0.83448	R^2	0.99998
Equations	$\text{Ln}(q_e - q_t) = \text{Ln}q_e - K_1 t$		$t/q_t = t/q_e + 1/(K_2 q_e)^2$	

K_1 : pseudo first order constant.

K_2 : pseudo-second order constant.

K_{int} : intra-particle diffusion constant.

C: constant (mg/g).

Comparative study

Table 7 shows various studied adsorbents used previously for the removal of Co (II). It is found that the bark adsorption capacity of the modified

Eucalyptus is among the highest capacities, which makes it among the suitable adsorbents for the removal of metals from actual wastewater facilities.

Table 7. The adsorption amount of cobalt ions by different natural adsorbents.

Adsorbent	Adsorption capacity (mg/g)	Reference
Modified <i>Eucalyptus bark</i> (EAA)	55.55	Present study
Apricot stone activated carbon (ASAC)	30.030	46
Pest moss treated with HNO ₃	25.510	46
Pest moss treated with NaOH	35.210	46
Hectorite particles	2.650	47
Roasted date pits	6.280	48
Hazelnut shells	13.88	48
Attapulgate	0.635	49
Bentonite	0.619	49
Kaolin	0.560	49

Conclusion

The chemical modification of Eucalyptus bark makes it possible to influence the microstructure of the lignocellulosic material, which leads to a change in the surface functions properties of the material (grafting of the COOH functions). These results were verified by FTIR, Bohemian method and XRD. The adsorption of Co(II) by eucalyptus bark was evaluated, the best adsorption efficiency was

recorded at pH = 5.5 and 0.2 g of EAA. The adsorption equilibrium is reached in about 40 min. The adsorption capacity increased with increasing initial concentration and reached 55.55 mg/g. The kinetic measurements showed that the process follows the pseudo-second-order model and isotherm adsorption showed that the Langmuir model is the best model to describe the adsorption process. The kinetics of desorption is 8 times faster

than that of adsorption and the prepared adsorbent is regenerated with higher performance.

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