

Biosorption of Co (II) ions from aqueous solutions using selected local *Luffa Cylindrica*: Adsorption and characterization studies

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Abstract

The present study is concerned with the removal of Cobalt (II) from aqueous solution by adsorption onto low cost adsorbent. *Luffa Cylindrica* as adsorbent, (LC) was investigated in batch adsorption system. LC was characterized by Scanning Electron Microscopy (SEM) and Brunauer-Emmett-Teller (BET) surface area analyzer. The sorption of Co (II) ions by LC was subjected to equilibrium, thermodynamics and kinetic studies and was carried out by considering the effects of pH, effect of mass and particles size of the biosorbent, initial metal ions concentration, contact time and temperature. BET surface area of LC was 46.396 m²/g. The optimum conditions for maximum adsorption were attained at pH 6 and LC mass is 1.5 g with particle size is < 0.08 mm and contact time is 60 min. The pseudo-second-order rate equation described the Kinetic data well. The process is chemisorptive and controlled by the pseudo-second-order. Adsorption parameters were determined using both Langmuir and Freundlich isotherms, but the experimental data were better fitted to the Langmuir equation than to Freundlich equation, with correlation coefficients above 0.99 which indicates the adsorption is monolayer adsorption with maximum adsorption capacity for Co(II) was 2.53 mg/g.

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1. Introduction

Metal elements are, in different forms, always present in the environment. In the form of traces, they are necessary or even indispensable to living beings [1]. On the other hand, at a relatively high concentration; they have a greater or lesser degree of toxicity [2]. In general, heavy metal ions are toxic, non-biodegradable, and tend to be accumulated in vital human organs, where they can act progressively over a long period through food chains. The determination of trace heavy metal ions in environmental samples has received increasing attention. Some trace elements are essential to man, whose daily requirement is only a few milligrams. However, if ingested in high levels, this can be harmful to human health. Thus, the elemental composition is essential to ensure food quality [3]. Cobalt is an essential trace element that has an important role in many bodily functions. It is toxic in large amounts and chronic ingestion of Co in the daily diet can cause toxic effects [4]. Toxicological effects of cobalt include vasodilatation, flushing and cardiomyopathy in humans and animals [5]. There is great interest in the determination of trace levels of Co in environmental investigations because cobalt affects living species as complexed Vitamin B12 [6]. Various techniques have been applied for the removal of heavy metals from water. This includes membrane filtration, ion exchange and chemical precipitation [7]. These techniques are costly. Adsorption has been proposed as a cost-effective method for water decontamination. Activated carbon is widely used as an adsorbent for water treatment. It is effective to sequester metal ions from water environment. However, activated carbon is relatively expensive [8, 9]. Adsorption is considered one of the important methods used for the removal of heavy metals [10-13]. Comparing to the other purification and separation methods, adsorption-as a wastewater treatment process-has demonstrated its efficiency and economic feasibility and has gained importance in industrial applications [14, 15], as elimination of heavy metal cations from aqueous solution by selecting the suitable adsorbents under optimum operation conditions [16]. One of the advantages of natural adsorbents is that, they are easily applicable because of their adaption to several conditions as pH, temperature, pressure and agitation. Besides, these materials are cheap and highly efficient. So, development of alternative adsorbent materials featuring high availability, high adsorption capacities and feasibility is required [17]. *Luffa Cylindrica*, LC, mainly consists of cellulose, hemicelluloses and lignin; of composition (60%, 30% and 10% by weight, respectively) [18]. Cellulose structure consists of monomeric unit of a β -D-glucopyranose linked through 1,4-glucosidic linkage. Cellulose is renewable, cheap and low in density, exhibits better processing flexibility and is a biodegradable material. Cellulose is a highly functionalized, linear stiff chain homopolymer, characterized by its hydrophilicity, chirality, biodegradability and broad chemical modifying capacity [19]. Because of its unique structure, LC has been used as an efficient adsorbent or as a carrier for immobilization of some microalgal cells for the removal of water pollutants [20]. In this study, we have used the *Luffa Cylindrica*, an agricultural waste abundantly available in the south of Algeria (Laghouat region) as an adsorbent to remove Cobalt (II) from the water. We consider in the first stage : the characterization of *Luffa Cylindrica*, in a second stage the adsorption study of the system kinetics of a Cobalt / fiber to determine the equilibrium constant of adsorption, We later studied step two comparative models (Langmuir model and Freundlich) were tested for the adsorption isotherms obtained.

2. Materials and methods

2.1. Preparation of *Luffa Cylindrica* and Solutions

Luffa Cylindrica was obtained from a local farmland in Laghouat region (Algeria) is used in this study. This material was cut into small pieces and washed several times with double distilled water in order to eliminate the impurities such as the sand and dust. After that, the material was dried at 105 °C for 180 min to evaporate the humidity. The obtained material was ground using a grinder of type Janke and Kunkel IKA labortechnik to improve its specific area. Finally, the powder was sieved at different diameters up to 0.5 mm (diameter uses less than 0.08 mm) [21]. Aqueous solutions

of copper were prepared from Cobalt (II) sulphate heptahydrate ($\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$) obtained from (BIOCHEM Chemopharma). Stock solutions of 1000 mg/L for Co(II) were prepared, by dissolving desired amount of ($\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$) in 500 mL of distilled water. After, different concentrations of solutions were prepared by appropriate dilution of the stock solution. Before mixing these solutions with the adsorbent, test solutions with pH values ranging from 1 to 8 (to permit a determination of the optimum pH for adsorption) by dropwise addition of 0.1 N sodium hydroxide, NaOH or 0.1 N hydrochloric acid, HCl (pH was measured using pH meter, ORION model 420A) Thermo Scientific). The ranges of initial concentrations of Cobalt (II) prepared from stock solutions varied from 10 to 100 mg.L^{-1} .

2.2. Characterization of adsorbent

The surface area BET of the LC sample was determined using NOVA 1000e (Surface Area & Pore Size Analyzer) manufactured by Quantachrome Instruments USA. Krypton gas was used in conducting single-point surface area measurements. Liquid Nitrogen was used in setting the adsorption of Nitrogen gas by the samples. The LC was degassed at 100 °C for 30 minutes and was cooled to liquid Nitrogen temperature. The surface area of the sample under measurement was then read from the display-meter. The value of the surface area recorded was then converted to specific surface area (m^2/g) by dividing the reading on the display by the weight of the *Luffa cylindrical* sample. The characterization was realized to explore the structure of the material. The surface morphology of the material was carried out using Scanning Electron Microscope (SEM) model JEOL JSM-6363LV.

2.3. Biosorption studies

The adsorption experiments were carried out by batch process 1.5 g of biosorbent was placed in Erlenmeyer flasks with 100 mL solution of metal ions of desired concentration. The entirety was agitated during a certain time at 300 rpm. Once the operation time had elapsed, the liquid phase was taken out, and then filtered through filter paper (Double Boxing rings 102) and final concentration of metal ion was determined in the filtrate by atomic absorption spectrometry (AAS). The amount of metal ions adsorbed at equilibrium per unit mass of biosorbent was determined according to the following equation:

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

Where, m is the mass of adsorbent (g), V is the volume of the solution (L), C_0 is the initial concentration of metal (mg/L), C_e is the equilibrium concentration of the adsorbate (mg/L) in solution and q_e is the metal quantity adsorbed at equilibrium (mg/g). For the calculation of cobalt rate adsorption (R), the following expression was used:

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

2.4. Kinetic Studies

The kinetic equations, which are, pseudo first-order (3), pseudo-second order (4):

Table 1: Kinetic Adsorption Models.

Kinetic model	Equation
Pseudo-First-Order [22]	$\log(q_e - q_t) = \log q_e - K_1 t / 2.303$ (3)
Pseudo-Second-Order [23]	$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t$ (4)

2.5. Modeling

Freundlich equation

In the case of dilute solutions, adsorption of the solute in many cases follows the Freundlich equation based on the assumption that the number of existing sites associated with a given free energy decreases exponentially with free energy. This equation is empirical [24].

$$q = k_F C_e \frac{1}{n} \quad (5)$$

Where k_F and n depend on the temperature of the adsorbent and the adsorbates, n varies from 0.8 to 2.

The linearization of equation (5) provides:

$$\ln(q) = \ln(k_F) + \frac{1}{n} \ln(C_e) \quad (6)$$

Langmuir model

Langmuir adsorption considered as a chemical phenomenon (surface of the solid is homogeneous adsorbed molecules do not interact between them and they can form at most a single layer of molecules on the surface of the solid) [24]. θ is the fraction of surface covered by adsorbed molecules and $(1-\theta)$ the uncovered portion. The net amount accumulated during the adsorption-desorption written:

$$\frac{dq}{dt} = k_a (1 - \theta) C_e - k_d \theta \quad (7)$$

At equilibrium $\frac{dq}{dt} = 0$, or of

$$\theta = \frac{K L C_e}{1 + K L C_e} \quad (8)$$

Combining the previous equations gives:

$$\frac{q}{qm} = \frac{K L C_e}{1 + K L C_e} \quad (9)$$

Linearization of equation (9) gives:

$$\frac{1}{q} = \frac{1}{qm K L C_e} + \frac{1}{qm} \quad (10)$$

3. Results and discussion :

3.1. Characterization of the adsorbent material

The surface area of LC, as determined by the BET method was found to be 46.396 m²/g. The surface area of the Luffa Cylindrica had a much higher surface area than the Luffa used in other study (The Specific surface area was 0.28 m²/g). Application of LC in natural form as Biosorbent to Removal of Divalent Metals from Aqueous Solutions - Kinetic and Equilibrium Study [25]. Scanning electron microscopy (SEM) of the LC biosorbent was taken in order to verify the presence of macropores in the structure of the fiber. In the micrographs presented in Figure1 is observed the fibrous structure of Luffa cylindrica, with some fissures and holes, which indicated the presence of the macroporous structure, which facilitates the fixation of different pollutants into its pores. This specific perforated surface is consisted by the fibers containing in these kinds of materials.

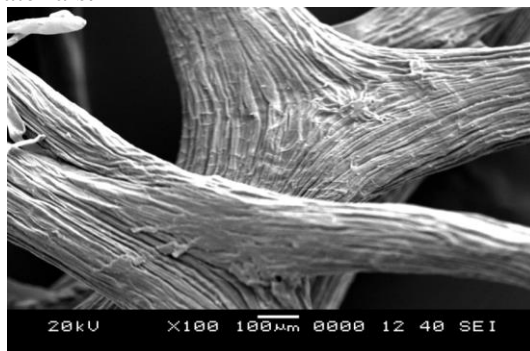


Figure 1. SEM picture of Luffa Cylindrica sample.

3.2. Optimization of adsorption parameters

The optimization of different adsorption parameters such as pH of solution, Co (II) concentration, and dose and particles size of LC at different time intervals was carried out for Co (II) onto LC.

Effect of pH:

The pH of the solution has a significant impact on the uptake of heavy metals since it determines the surface charge of the adsorbent and the degree of ionization and speciation of the adsorbate [26]. The influence of pH solution on iron adsorption onto LC is carried out at pH range of 1-8 and shown in Figure 2. The maximum adsorption of Co (II) is attained at pH = 6 (2.557 mg/g). At pH range of 1-5, there are many positive charges on the surface of LC, these charges which are attributed to the presence of H^+ are competed with Co (II) cations and hampered their adsorption, giving a large static repulsion force. As the pH is increased, the active sites which are increased the negative charge density on the LC surface would be exposed. These negative charge are increased the attraction of metallic ions with positive charge and allowed the adsorption onto the LC surface. In this study, these Cobalt cations at around pH 6 would be expected to interact more strongly with the negatively charged binding sites in the biosorbent. As a result, the optimum pH for Cobalt adsorption was found at pH of 6 and the other adsorption experiments were performed at this pH value.

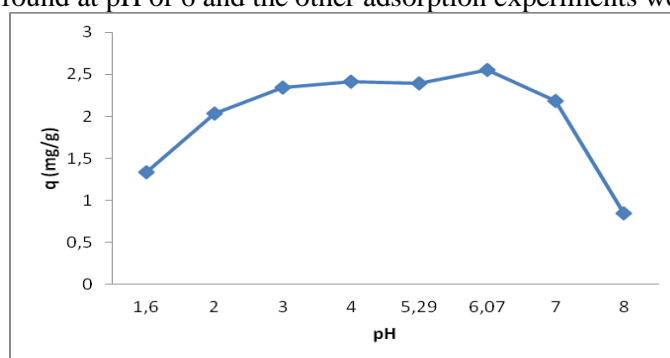


Figure 2. Effect of pH on cobalt adsorption onto LC at ($C_0 = 100$ mg/L, $m = 1.5$ g, $T = 25$ °C, contact time = 90 min and agitation rate = 300 rpm).

Effect of particles size:

The diameter of the adsorbent is an important parameter. Indeed, when the LC has a smaller diameter, the specific exchange surface will be higher, which improves the adsorbent capacity. It has been shown by previous work that the adsorption capacity is affected by the size of the adsorbent particles [27]. The effect of LC granulometry on the adsorption of Cobalt at an initial concentration of 100 ppm to different LC granules was studied. LC particle diameters used between 0.5 to 0.08 mm gave the metal reduction ratios shown in the Figure 3.

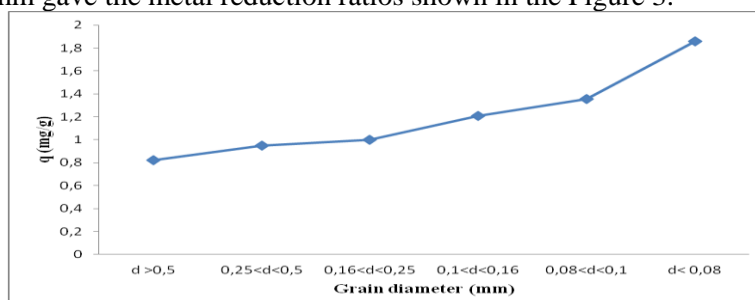


Figure 3. Effect of the diameter of biosorbent particle (dp) on cobalt adsorption onto LC at ($C_0 = 100$ mg/L, pH = 6, $m = 1.5$ g; $T = 25$ °C, contact time = 90 min and agitation rate = 300 rpm).

From the Figure 3, it can be seen that the adsorption increases proportionally with the decrease in LC diameters. Indeed between 0.8233 to 1.86 mg/g, the reduction rate of Co(II) increases until $dp < 0.08$ mm. This can be explained by the fact that small particles have a larger surface area than large particles. Therefore, it can be deduced that the optimum particle size is < 0.08 mm.

Effect of adsorbent weight:

The act of LC adsorbent mass on Cobalt adsorption at an initial concentration of 100 mg/L was studied. The masses of LC used between 0.1 to 7 g gave reduction rates presented in the Figure 4.

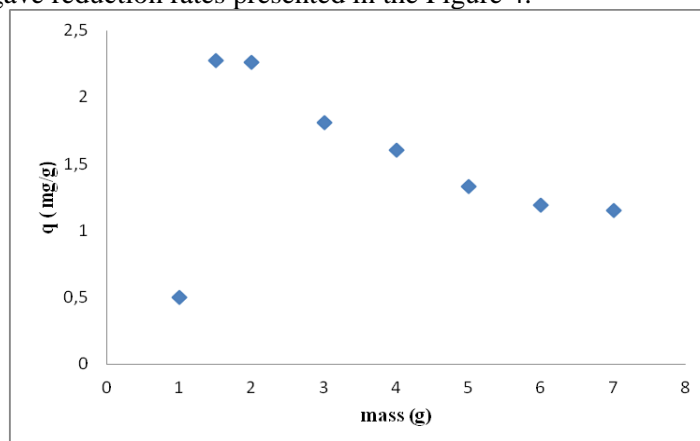


Figure 4. Effect of adsorbent weight on cobalt adsorption onto LC at ($C_0 = 100$ mg/L, pH = 6, $T = 25$ °C, contact time = 90 min and agitation rate = 300 rpm).

It is observed that the adsorption increases proportionally with the mass of LC. Indeed between 0 and 1.5 g, the reduction rate of Co (II) increases to an optimum value of 2.27 mg/g at 1.5 g. After, we have a decrease in the elimination efficiency is involved saturation. It can be deduced that the optimal mass is 1.5 g.

Effect of initial concentration and contact time:

Contact time is an important parameter for determining the equilibrium time required for the sorption of metal ions on a sorbent as it is directly proportional to amount of metal ions removed from aqueous solution. The Figure 5 represents the evolution of the amount adsorbed as a function of the initial concentration and the contact time.

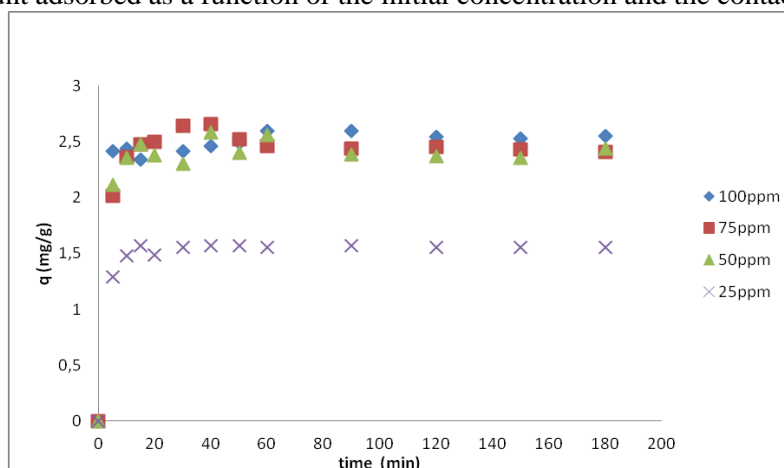


Figure 5. Effect of contact time cobalt ions adsorption onto LC at ($C_0 = 100$ mg/L, pH = 6, $m = 1.5$ g, $T = 25$ °C, contact time = 3 h and agitation rate = 300 rpm).

Examining the curves in Figure 5, we can say a priori, that the initial concentration has a clear influence on the adsorption rate of Co (II) on LC. The amount adsorbed is even higher than the initial concentration is high. The kinetics carried out at different initial concentrations (10 to 100 mg/L) made it possible to suggest that the adsorption process is governed by three essential steps, transfer of the cobalt molecules through the liquid solution surrounding the outer surface of the adsorbent and transfer of solutes through the pores of the solid particles to the active sites "internal diffusion" and the attachment of Co (II) particles to the sites LC assets. It is observed that the adsorbed quantity increases from 1.57 mg/g for $C = 25$ ppm up to 2.54 mg/g for $C = 100$ ppm. The optimal contact time is 60 min.

Effect of temperature :

Temperature is an indicator for the adsorption nature whether it is an exothermic or endothermic process. As mentioned by [28], increasing temperature may decrease the adsorptive forces between the phenol species and the active sites on the adsorbent surface as a result of decreasing adsorption efficiency [29]. The effect of temperature on the removal percent of Co(II) was studied in the temperature range of 10–40 °C as shown in Figure 6.

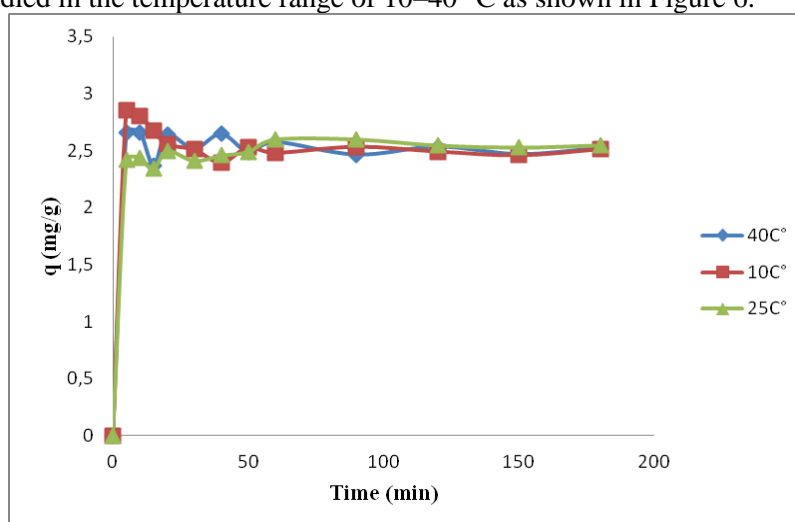


Figure 6 . Effect of temperature on cobalt adsorption onto LC at ($C_0 = 100$ mg/L, $m = 1.5$ g, $pH = 6$, contact time = 90 min and agitation rate = 300 rpm).

From the curve shown in the figure 6, we note that the absorption of cobalt is not affected by temperature change.

3.3. Kinetic studies:

In the kinetic models, it is normally assumed that the overall rate of adsorption is exclusively controlled by the adsorption rate of the solute on the surface of the adsorbent, and the intraparticle diffusion and external mass transport can be neglected. Moreover, it is considered that the adsorption rate of a solute on the surface can be represented in the same manner as the rate of a chemical reaction [30]. The adsorption kinetics is commonly modeled with the pseudo-first-order [31] and pseudo-second order [32]. The experimental results of the Co uptake, q_t , versus time were fitted to the above mentioned models by the method of nonlinear regression. The results are shown in Table 2 and Figure 7 and Figure 8. According to the linear regression results of the two models tested (Figure 7 and 8), and according to the correlation coefficients corresponding to the experimental results (Table 2), the kinetics would be governed earlier by the pseudo-second-order model. It can also be deduced that the process governing the adsorption on the surface of the LC would be a chemisorption which would imply forces and exchanges of electrons between the adsorbent and the adsorbate.

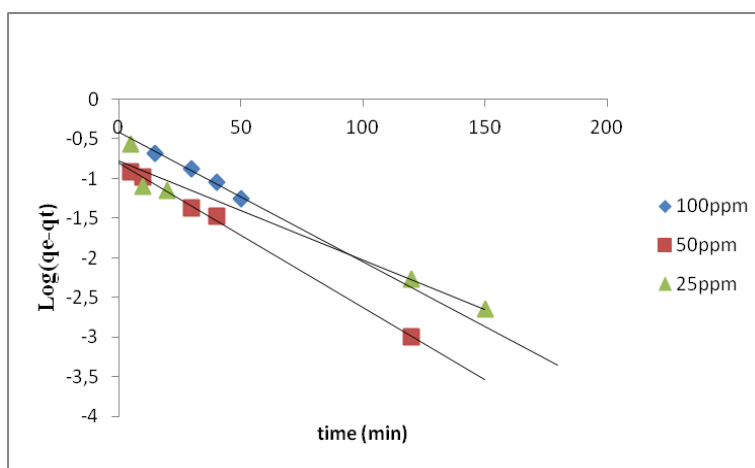


Figure 7. Kinetics of adsorption of pseudo first order.

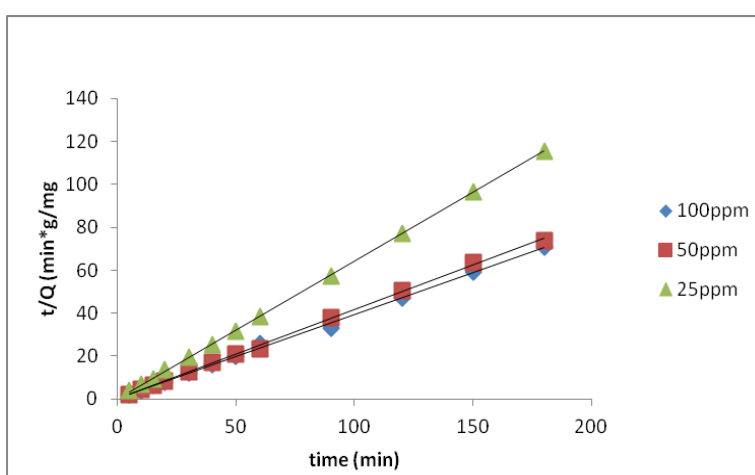


Figure 8. Kinetics of adsorption of pseudo second order.

Table 2. *Parameters of the two kinetic models studied.*

Model	Parameters	25 ppm	50 ppm	100 ppm
Experimental	qe, exp (mg/g)	1.558	2.383	2.5466
Pseudo first order	K_1 (min^{-1})	0.0285	0.0419	0.0375
	R^2	0.9592	0.9989	0.9863
	qe, cal (mg/g)	0.165	0.158	0.384
Pseudo second order	K_2 ($\text{g.mg}^{-1}.\text{min}^{-1}$)	2.480	1.752	0.3543
	R^2	0.9999	0.9991	0.9981
	qe, cal (mg/g)	1.560	2.406	2.560

3.4. Adsorption isotherm :

In order to examine the possibility of modeling the experimental results obtained, two highly applied adsorption models were tested: the Langmuir and Freundlich models. The use of the linear equations of these two models with the

experimental results obtained, gives the graphical or isothermal representations corresponding to the adsorption of Co (II) (Figures 9 and 10) and Table 3 gives the kinetic and correlation constants of these two types of isotherms tested.

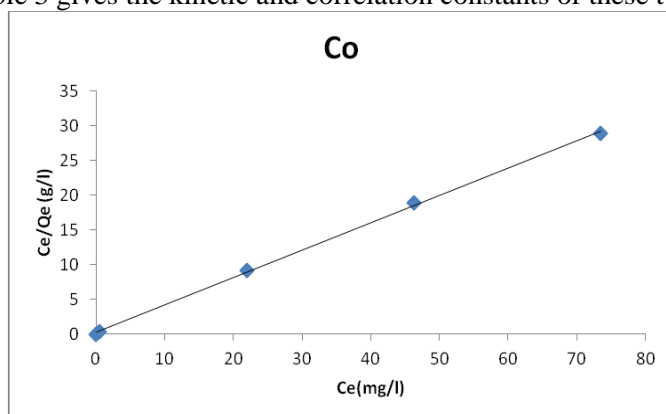


Figure 9. Adsorption isotherms according to the Langmuir model.

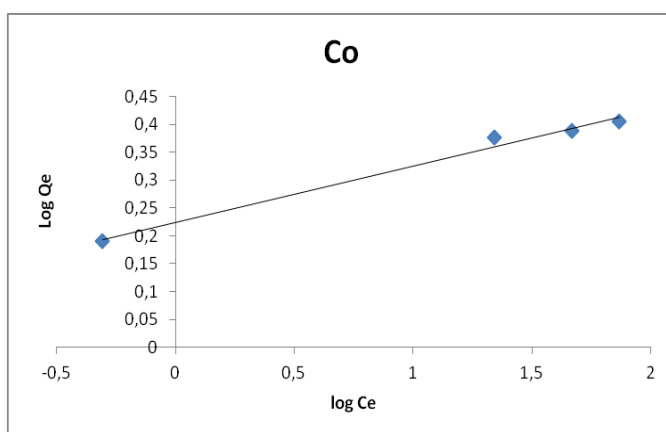


Figure 10. Adsorption isotherms according to the Freundlich model.

Table 3. The kinetic and correlation constants deduced from Co(II) adsorption isotherms on LC.

Model	Parameter	
Langmuir	q_m (mg.g ⁻¹)	2.5323
	K_L (L/mg)	1.6365
	R^2	0.9993
Freundlich	$1/n$	0.1011
	K_F (mg/g)	1.2522
	R^2	0.9880

The kinetic constants and correlation coefficients deduced from these isotherms (Table 3) Suggested that the corresponding model is that of Langmuir. This assumes that adsorption of Co (II) on LC is in monolayers. On the other hand, the Freundlich constant (n) found indicates that the adsorption is favorable for Co(II) on the LC, because the values of n obtained satisfy the condition of heterogeneity ($1 < n < 10$ and $0 < 1/n < 1$) required by the model.

Table 4. Comparison of adsorption capacities for Co(II) sorption by various adsorbents.

Adsorbents	Adsorption capacity (mg/g)	Source
The activated carbon from apricot stone with H ₃ PO ₄	111.11	[33]
<i>Bacillus cereus</i> biomass	68.10	[34]
The oxygenated apatite (OA)	32,2	[35]
Activated carbon prepared from hazelnut shells	13.88	[36]
palygorskite	8.88	[37]
LC	2.5323	Present work

4. Conclusion

In this study, an attempt to add value to waste material by developing an eco-friendly method for removing Co²⁺ ions from wastewater was conducted. Adsorption studies were developed and evaluated. These studies demonstrated that pH, sorbent dose, effect of masse and particles size, contact time and concentration are significant factors in adsorption. The maximum removal of cobalt was attained at pH 6, LC dose of 1.5 g using cobalt concentration of 100 mg/L. The average BET surface area of LC was 46.396 m²/g. The adsorption equilibrium data obeyed the Langmuir isotherm. The adsorption capacity (q₀) calculated from the Langmuir isotherm was 2.53 mg/g, indicating monolayer adsorption on a homogenous surface. The adsorption kinetic was described well by the pseudo-second-order model, *Luffa cylindrica* was proposed as cheap, easily available and efficient method for removal of heavy metals from the environment. Thus, local raw materials could be used to prepare an adsorbent with a good and favorable adsorptive capacity.

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