

IDENTIFICATION OF NEW SORBENT MATERIALS FOR CADMIUM REMOVAL FROM AQUEOUS SOLUTIONS

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ABSTRACT

This study compares the abilities of four low-cost materials: eucalyptus bark, maize leaves, grape bunch and banana peel to remove cadmium from synthetic aqueous solutions. Kinetic data and equilibrium sorption isotherms were measured in batch conditions. Kinetics of cadmium sorption was contact time, initial cadmium concentration and sorbent type dependent. The results also showed that the kinetics of cadmium sorption were described by a pseudo-second order rate model. The cadmium uptake of these low-cost materials was quantitatively evaluated using sorption isotherms. Results indicated that the Langmuir model gave a better/an acceptable fit to the experimental data than the Freundlich equation within the concentration range studied. A high cadmium sorption was observed by these materials. The eucalyptus bark was the most effective to remove cadmium ions with a maximum sorption capacity about 99.50 mg/g followed by grape bunch (75.59 mg/g), banana peel (69.44 mg/g) and maize leaves (57.84 mg/g).

Keywords: cadmium; removal; sorption; low-cost materials.

INTRODUCTION

Cadmium is attracting wide attention of environmentalists as one of the most toxic heavy metals. The major sources of cadmium release into the environment by waste streams are electroplating, smelting, alloy manufacturing, pigments, plastic, battery, mining and refining processes (Holan et al. [1], Volesky et al. [2], Chong & Volesky [3]). Cadmium has been well recognized for its negative effect on the environment where it accumulates readily in living systems. Adverse health effects due to cadmium are well documented and it has been reported to cause renal disturbances, lung insufficiency, bone lesions, cancer and hypertension in humans (Hutton & Symon [4], Nriagu [5]). Current technologies for cadmium removal from wastewater such as: precipitation, ion exchange and adsorption lack a sufficiently high affinity and selectivity to reduce residual cadmium to the levels dictated by ever more stringent government regulations (Singh et al. [6], Yin & Blanch [7], Sadowski et al. [8]). This situation has in recent years led to a growing interest in

the application of biomaterials technology for removal of trace amounts of toxic metals from dilute aqueous wastes. Recently, Bailey et al. [9] reviewed a wide variety of low cost sorbents for the removal of heavy metals. A low cost sorbent is defined as one which is abundant in nature, or is a by-product or waste material from another industry. Among the various resources of biological wastes, agricultural wastes (e.g., stems, peels, husks, leaves, fruit shells, ...etc) have been demonstrated to remove metal ions in aqueous solutions (Tee & Khan [10]; Scott [11], McKay & Porter [12], Sun & Shi [13], Al-Asheh & Duvnjak [14], Meunier et al. [15], Sekhar et al. [16], Özer et al. [17], Wang & Qin [18]).

This work studies the possibility of using a certain biological wastes: eucalyptus bark, maize leaves, grape bunch and banana peel as inexpensive sorbent materials for the removal of cadmium from synthetic aqueous solutions. These materials are abundantly available through our country and the world. The present study reports their sorption potential through kinetics tests and sorption isotherms, in batch conditions. The experimental data of cadmium sorption kinetics for each sorbent tested were fitted by two models namely: first-order and pseudo- second-order models. Those of cadmium sorption equilibrium for each material tested were fitted by either the Langmuir or Freundlich equations.

MATERIALS AND METHODS

In this work, four agricultural and forestry waste by-products: eucalyptus bark, maize leaves, grape bunch and banana peel have been employed as low-cost sorbent materials in the removal of cadmium from synthetic aqueous solutions. Except banana peel (banana imported from Equator - South of America), all other wastes were collected from the region of BENSEKRANE in Tlemcen - ALGERIA, in the form of large flakes, cut and sun/air dried at ambient temperature. They were used after the following preliminary treatment: 10 g of each dried material were added to 2 L of distilled water in a beaker agitated vigorously by a magnetic stirrer at ambient temperature of $25 \pm 1^\circ\text{C}$ for 4 hours, then filtered, continuously washed with distilled water until constant pH to remove the surface adhered particles and water soluble materials, and oven-dried overnight at 80°C for 24 hours after filtration. Each sorbent material was crushed and sieved to have a particles size of 0.1 - 3.15 mm for further batch sorption experiments.

Cadmium solutions of desired concentration were prepared from $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ (Windor Laboratories Limited), by dissolving the exact quantities of cadmium salts in distilled water. All chemicals were commercial products used without purification.

1- Uptake Kinetics

The initial solution metal concentration was 100 mg/L for all experiments except for that carried out to examine the effect of the initial concentration of cadmium. For metal removal kinetic studies, 0.6 g of dried sorbent material was contacted with 0.3 L

of metal solutions in a beaker agitated vigorously by a magnetic stirrer using a water bath maintained at a constant temperature of 25 ± 1 °C. In all cases, the working pH was that of the solution and was not adjusted. The residual cadmium concentration in the aqueous solution at appropriate time intervals was obtained by using a Cd^{2+} - ion selective electrode technique. The electrode used for measurement of cadmium was Orion Model 9448 and was used in conjunction with Orion Model reference electrode and an Orion Model 710A meter, which provided readings accurate to ± 0.1 mV. For the measurement of pH, an Orion Model 9107 combination electrode, with the aforementioned meter, was used. pH readings were monitored to $+ 0.01$ unit. For certain experiments, this cadmium concentration was also done using a Perkin Elmer Model 2280 atomic absorption spectrophotometer. No differences in the results obtained by these two methods of analysis were observed. The metal uptake q_t (mg metal ion /g dried sorbent) was determined as the difference between the initial and time concentrations of metal in the aqueous solution.

All studies were carried out in duplicate and the average results are presented in this work. Preliminary experiments had shown that cadmium sorption losses to the container walls were negligible.

2- Uptake Isotherms

The equilibrium isotherms were determined by contacting a constant mass 0.1 g of sorbent material with a range of different concentrations of cadmium solutions: 1-2000 mg/L. The mixtures were agitated in a series of beakers with equal volumes of solution 50 ml for a period of 24 hours at room temperature 25 ± 1 °C. The contact time to reach equilibrium was previously determined by kinetic tests using the same conditions. The reaction mixture pH was not controlled after the initiation of experiments. After shaking the flasks for 24 hr, the final pH was measured. The equilibrium concentration of free cadmium was obtained by using a Cd^{2+} - ion-selective electrode technique and the cadmium loading by sorbent material was calculated.

RESULTS AND DISCUSSION

All batch sorption experiments reported here were investigated at natural initial pH value of solution < 7 , because insoluble cadmium hydroxide starts precipitating at higher pH values, making true sorption studies impossible.

1 - Uptake Kinetics of Metal

1.1- Effect of contact time: According to Figure1, for initial cadmium concentration of 100 mg/L, the kinetics of cadmium removal by the sorbent materials used present a same shape characterized by a strong increase in cadmium sorption initially followed by a slow increase until equilibrium is reached. The necessary time to reach this equilibrium is about: 3h respectively for maize leaves and banana peel, 4h for grape

bunch and 6h for eucalyptus bark, and, an increase of removal time to 24 hours doesn't show notable effects. The capacities of cadmium sorption at equilibrium are: 30.20 mg/g for eucalyptus bark, 23.40 mg/g for grape bunch, 20.50 mg/g for banana peel and 17.50 mg/g for maize leaves corresponding to a removal of about 61.63, 44.57, 40.20 and 32.71 % respectively of initial cadmium solution.

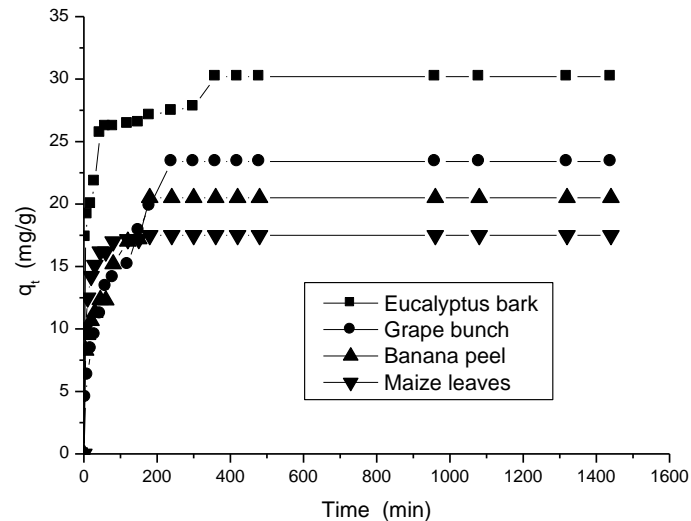


Figure 1: Kinetics of cadmium sorption by low-cost materials. Initial cadmium concentration: 100 mg/L.

As shown in Fig.2, during the course of cadmium removal by each of these sorbents, we noticed a decrease in the value of the initial pH of solutions for the first times of contact solution – sorbent material until to reach a state of equilibrium: $\Delta\text{pH} = \text{pH}_{\text{init}} - \text{pH}_{\text{eq.}} = 1.04$ (eucalyptus bark), 1.08 (grape bunch), 0.9 (banana peel) and 0.07 units (maize leaves). The same tendency was observed for cadmium sorption by other natural wastes used as sorbent materials (Benaïssa [19]).

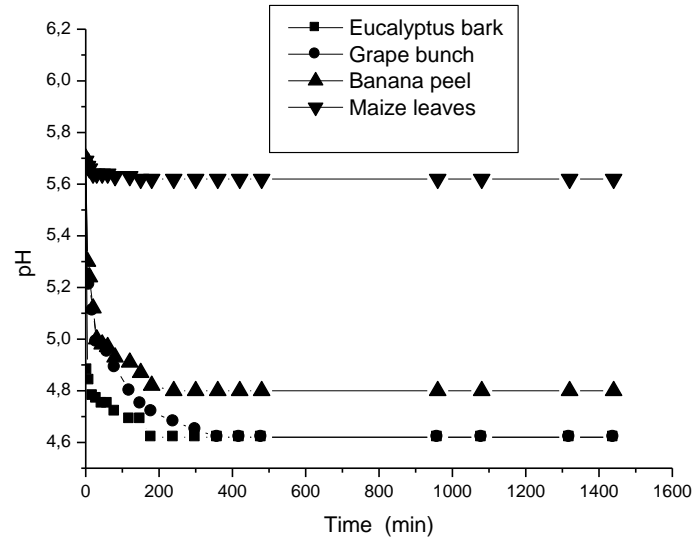


Figure 2: pH profiles of cadmium sorption by low-cost materials

In order to investigate the reason for the initial pH decrease, preliminary experiments performed with each of the sorbent materials tested in distilled water under the same conditions were carried out. As shown in Fig. 3, except in the case of maize leaves, initial pHs exhibited a decrease during the first times of contact solution-sorbent followed by a state of equilibrium: this decrease can be interpreted by a possible release of H_3O^+ ions into the solution from the sorbent surface.

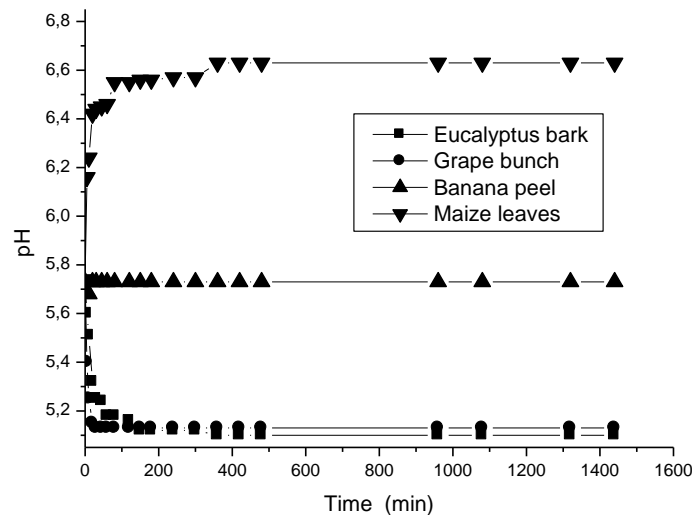


Figure 3: pH profiles of a distilled water in the presence of sorbent materials.

The kinetics of cadmium sorption by these sorbents can be modelled using by the first-order rate equation of Lagergren (25) and the pseudo-order rate equation (Ho [21]; Ho & McKay, [22]) shown below as Eqs. (1)-(2), respectively:

$$\log(q_e - q_t) = \log q_e - k_L \cdot t/2.3 \quad (1)$$

$$t/q_t = 1/k \cdot q_e^2 + t / q_e \quad (2)$$

where k_L is the Lagergren rate constant of sorption (min^{-1}) and k the pseudo second-order rate constant of sorption ($\text{g} \cdot \text{mg}^{-1} \cdot \text{min}^{-1}$); q_e and q_t are the amounts of metal sorbed ($\text{mg} \cdot \text{g}^{-1}$) at equilibrium and at time t , respectively. For an initial cadmium concentration of 100 mg/L, the different values of constants from the slopes and intercepts of linear plots of $\log(q_e - q_t)$ vs. t , and t/q_t vs. t , respectively (see Figures 4 and 5) are summarized in the Table 1.

Only, the pseudo second –order reaction rate model adequately described the kinetics of cadmium sorption with high correlation coefficients ($R^2 > 9985$) compared to those of the first-order rate model ($R^2 < 0.9581$). The values of q_e obtained from the fitting to the pseudo second-order reaction rate model are very similar to the experimental values obtained from the sorption kinetics at equilibrium: consequently, it was further used to describe all the kinetics of cadmium sorption by the sorbent materials tested.

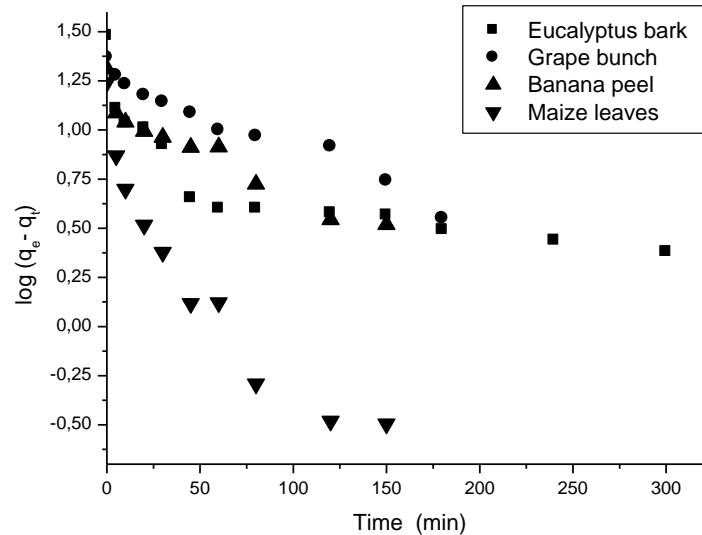


Figure 4: First-order rate kinetics plots for cadmium sorption by various sorbent materials.

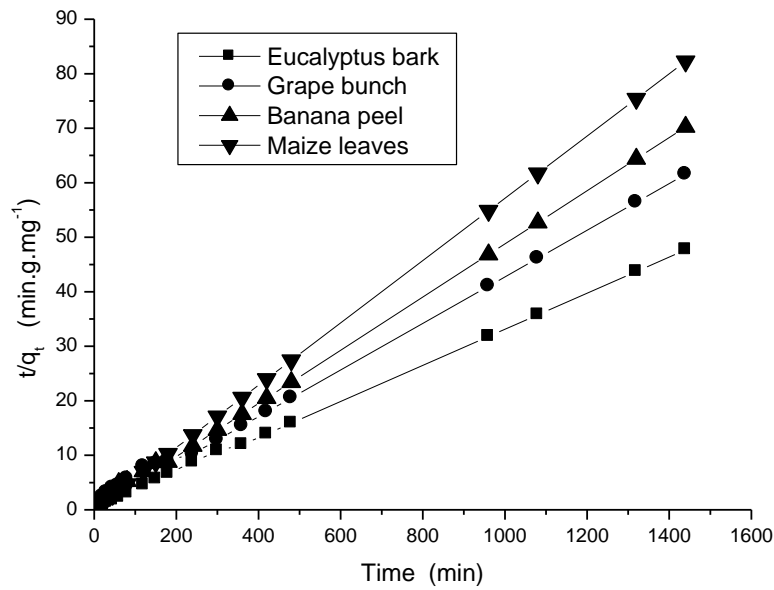


Figure 5: Pseudo second-order rate kinetics plots for cadmium sorption by various sorbent materials.

Table 1: Models rate constants for cadmium sorption kinetics by sorbent materials at $C_0 = 100$ mg/g.

Sorbents	$q_{eexp.}$ (mg/g)	q_{ecal} (mg/g)	$k_L \cdot 10^2$ (min^{-1})	R^2	$q_{ecal.}$ (mg/g)	$k \cdot 10^3$ ($\text{g} \cdot \text{mg}^{-1} \cdot \text{min}^{-1}$)	R^2
Eucalyptus bark	30.20	10.37	0.62	0.6467	30.52	2.53	0.9997
Maize leaves	17.50	6.65	2.46	0.8651	17.55	20.03	1
Grape bunch	23.40	19.26	0.88	0.9583	24.20	1.15	0.9985
Banana peel	20.50	13.78	1.06	0.9076	20.86	2.63	0.9994

1.2- Effect of initial cadmium concentration: Several experiments were also undertaken to study the effect of varying the initial cadmium concentration on the cadmium sorption kinetics. The results obtained indicated that the curves have the same shape (see Fig. 6 as a typical example).

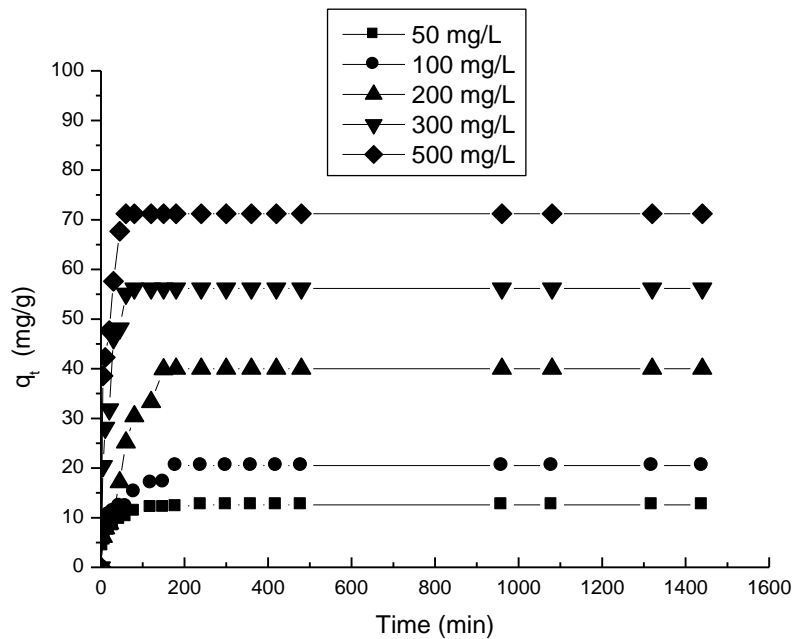


Figure 6: Effect of initial cadmium concentration on the kinetics of cadmium sorption by banana peel as a typical example.

From the results obtained at equilibrium, the necessary time to reach equilibrium is variable in the range of 1-6 h depending on the type of sorbent material used. Except for grape bunch, for all other sorbent materials, this time decreases as the initial cadmium concentration increases. We also notice that the amounts of cadmium sorbed at the equilibrium increase with the initial cadmium concentration. This is a result of the increase in the driving force the concentration gradient, as an increase in the initial cadmium ion concentrations [17].

During the phenomenon of cadmium removal, we also noticed the same trend observed previously about the evolution of initial pH value of solutions for all studied initial cadmium concentrations (see Fig. 7 as a typical example), without reaching the pH value of cadmium precipitation.

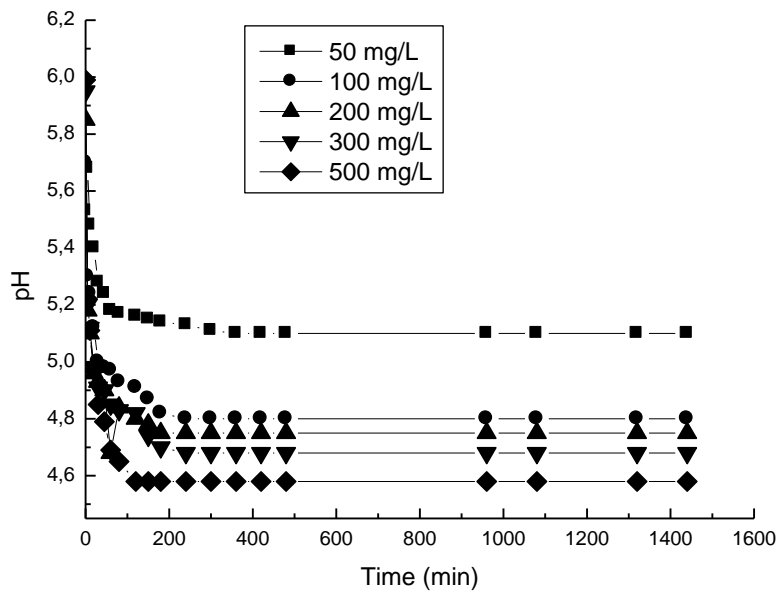


Figure 7: pH profiles of cadmium sorption by banana peel as a typical example.

When the previous data were only fitted to the pseudo second-order rate equation, straight lines (Fig. no shown here) were obtained with high correlation coefficients ($R^2 > 0.999$) indicating that the process follows a pseudo second-order kinetics (See Table 2). For all sorbents tested, the equilibrium cadmium sorption capacity, q_e , increases with the increase in the initial cadmium concentration. The values of q_e obtained from the fitting to the pseudo second-order reaction rate model are very similar to the experimental values obtained from the sorption kinetics at equilibrium. In general, an increase in initial cadmium concentration doesn't lead to a clear tendency in the variation of rate constant values.

Table 2: Pseudo second-order rate constants for cadmium sorption kinetics by various sorbent materials: influence of initial cadmium concentration.

Eucalyptus bark				
Initial Cd ²⁺ concentration C _o (mg/L)	q _e exp. (mg/g)	q _e cal. (mg/g)	k.10 ³ (min ⁻¹ .g / mg)	R ²
50	17.24	17.30	14.25	0.9999
100	30.20	30.52	2.53	0.9997
200	56.00	56.79	1.25	0.9997
300	62.50	62.85	3.12	0.9999
500	75.50	75.64	6.47	0.9999
Maize leaves				
Initial Cd ²⁺ concentration C _o (mg/L)	q _e exp. (mg/g)	q _e cal. (mg/g)	k.10 ³ (min ⁻¹ .g / mg)	R ²
50	16.50	17.08	1.58	0.9989
100	17.50	17.55	20.03	1
200	31.50	31.81	3.33	0.9998
300	52.30	52.69	2.80	0.9998
500	52.50	52.63	8.43	?
Grape bunch				
Initial Cd ²⁺ concentration C _o (mg/L)	q _e exp. (mg/g)	q _e cal. (mg/g)	k.10 ³ (min ⁻¹ .g / mg)	R ²
50	15.25	15.30	21.27	0.9999
100	23.40	24.20	1.15	0.9985
200	45.20	45.77	1.77	0.9996
300	60.20	60.39	5.46	0.9999
500	67.50	67.70	4.92	0.9999
Banana peel				
Initial Cd ²⁺ concentration C _o (mg/L)	q _e exp. (mg/g)	q _e cal. (mg/g)	k.10 ³ (min ⁻¹ .g / mg)	R ²
50	12.59	12.70	8.67	0.9999
100	20.50	20.86	2.63	0.9994
200	40.00	41.34	0.74	0.9976
300	56.17	56.43	4.04	0.9999
500	71.20	71.43	5.16	0.9999

2- Equilibrium of Sorption

To study equilibrium of cadmium removal by these sorbent materials, sorption isotherms of sorption with no initial pH control of solution were measured. As shown

in Fig. 8, the isotherms obtained for cadmium sorption are of L type according to the classification of Giles et al.[23] and analogous to Langmuir’s type according to the classification of Brunauer et al.[24] for solid-gas adsorption.

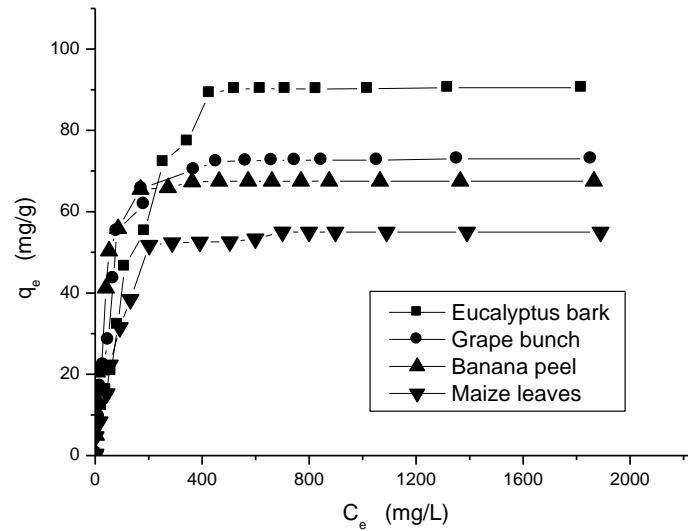


Figure 8: Isotherms of cadmium sorption by various sorbent materials at 25 °C.

To describe sorption isotherms of ions from aqueous solutions, there are a few models in the literature. The use of biological materials is an enormous complicating factor, i.e. the uptake process is a complex one. The utilization of a model has value in comparing different biomaterials under different operating conditions and rests solely on the adequacy between the observed experimental tendencies and the shape of the mathematical laws associated to this model. Among the models available, the Langmuir [25] and Freundlich [26] sorption models are commonly used to fit experimental data when solute uptake occurs by a monolayer sorption. They can provide information on metal-uptake capacities and differences in metal uptake between various species (Kapoor and Viraraghavan [27]). These models were tested in the present work.

The Langmuir model has the form:

$$q_e = q_m K_L C_e / (1 + K_L C_e) \tag{3}$$

which may be linearized as follow:

$$C_e/q_e = 1/K_L q_m + C_e/q_m \tag{4}$$

The Freundlich model has the form:

$$q_e = K_F C_e^n \tag{5}$$

which may be linearized by taking logarithms as follow:

$$\ln q_e = \ln K_F + n \cdot \ln C_e \quad (6)$$

where: q_e is the amount of metal ion sorbed at equilibrium per g of sorbent (mg/g); C_e the equilibrium concentration of metal ion in the solution (mg/L); q_m , K_L are the Langmuir model constants; K_F , n the Freundlich model constants. If the equation of Langmuir is valid to describe our experimental results, it must verify the linearized shape of the basis equation, in system of coordinates C_e/q_e vs. C_e , that will permit us to obtain the constants q_m and K_L from the intercept and slope. The q_m values provide a measure of the maximum sorption capacity, q_{max} , in such a system. The maximum sorption capacity is a useful criterion in assessing which of the four low-cost adsorbent materials has the greatest uptake. If the equation of Freundlich is also verified, we must obtain a straight line in the system of coordinates $\ln q_e$ vs. $\ln C_e$, the slope and the intercepts to the origin give K_F and n respectively. The models parameters determined by least squares fit of the experimental data (see Figures 9 and 10) have been calculated and are listed in Table 3. According to the values of regression coefficient, it appears that Langmuir model better fit the experimental results over the experimental range than the Freundlich model. From the values of q_m obtained with the Langmuir model, a high cadmium sorption by these sorbent materials was observed in the following order: eucalyptus bark (99.50 mg/g) > grape bunch (75.59 mg/g) > banana peel (69.44 mg/g) > maize leaves (57.84 mg/g). These differences of cadmium uptake are due to the properties of each sorbent material such as structure, functional groups and surface area [17].

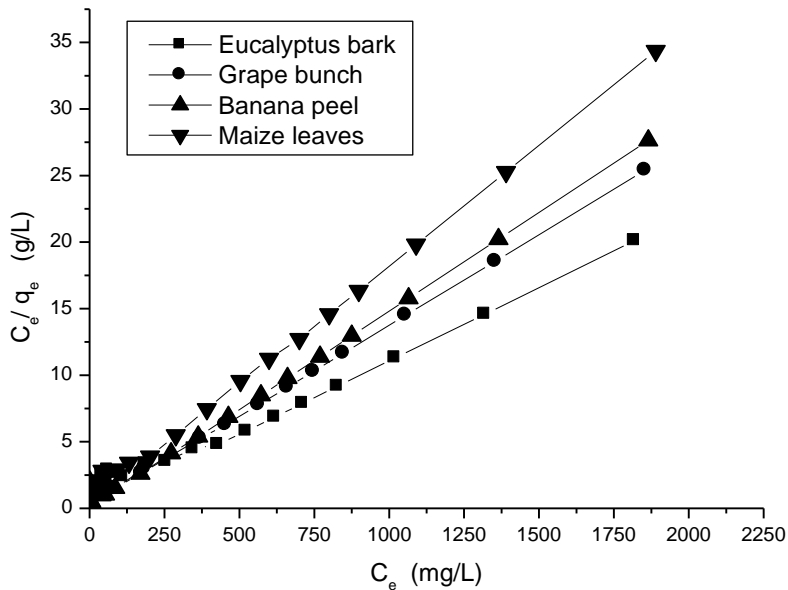


Figure 9: Langmuir plots for cadmium sorption by various sorbents at 25 °C

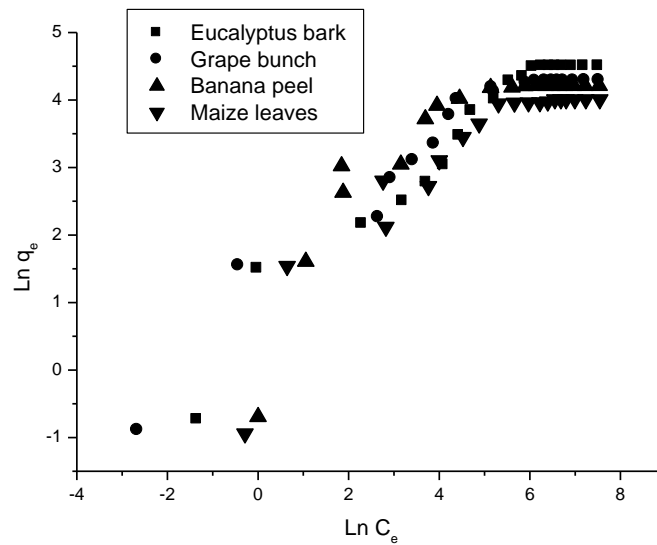


Figure 10: Freundlich plots for cadmium sorption by various sorbents at 25 °C

Table 3: Parameters of Langmuir and Freundlich sorption isotherms.

Langmuir model			
Sorbent material	q_{\max} (mg/g)	K_L (L/mg)	R^2
Maize leaves	57.84	0.016	0.9969
Banana peel	69.44	0.032	0.9971
Grape bunch	75.59	0.024	0.9979
Eucalyptus bark	99.50	0.009	0.9869

Freundlich model			
Sorbent material	K_F	n	R^2
Maize leaves	2.00	0.520	0.8412
Banana peel	3.71	0.470	0.7294
Grape bunch	3.63	0.477	0.9088
Eucalyptus bark	2.30	0.563	0.9393

For comparison, these sorption capacities are considerably higher than some sorbent materials reported in literature such as: natural zeolites as Clinoptilolite (23 mg/g) (Curovic et al. [28]), ion exchange resins as Duolite GT-73 (66 mg/g) (Volesky et al. [29]) and Granulated activated carbon (7.87 mg/g) (Ramos et al. [30]) although this direct comparison is difficult due to the varying experimental conditions used in these studies. The applicability of these models should be considered as a mathematical representation of the sorption equilibrium over a given metal-ion concentration range.

The mechanistic conclusions from the good fit of the models alone should be avoided. At this stage, we have not enough information about the mechanism of cadmium sorption by these sorbents. According to many researchers, the sorption of metals by these kinds of materials might be attributed to their proteins, carbohydrates, and phenolic compounds that have carboxyl, hydroxyl, sulfate, phosphate, and amino groups that can bind metal ions (Al-Asheh and Duvnjak [14]; Meunier et al. [15]; Villaescusa et al. [31]; Adler et al. [32]). It is also possible that the metal bind to different kinds of sites. Metal sorption consists of several mechanisms that quantitatively and qualitatively differ according to the metal species in solution and the origin and processing of the sorbent (Villaescusa et al. [31]).

The essential characteristics of the Langmuir isotherm can be expressed in terms of dimensionless constant separation factor or equilibrium parameter, R_L [33], which is defined as:

$$R_L = 1 / (1 + K_L C_0) \quad (7)$$

According to the value of R_L , the isotherm shape may be interpreted as follows:

Value of R_L	Type of sorption
$R_L > 1$	Unfavourable
$R_L = 1$	Linear
$0 < R_L < 1$	Favourable
$R_L = 0$	Irreversible

The calculated R_L value versus initial cadmium concentration at 298 K was represented in Fig. 11. It was observed that at these experimental conditions, cadmium sorption by dried sunflower leaves was found to be more favourable at higher initial cadmium concentrations.

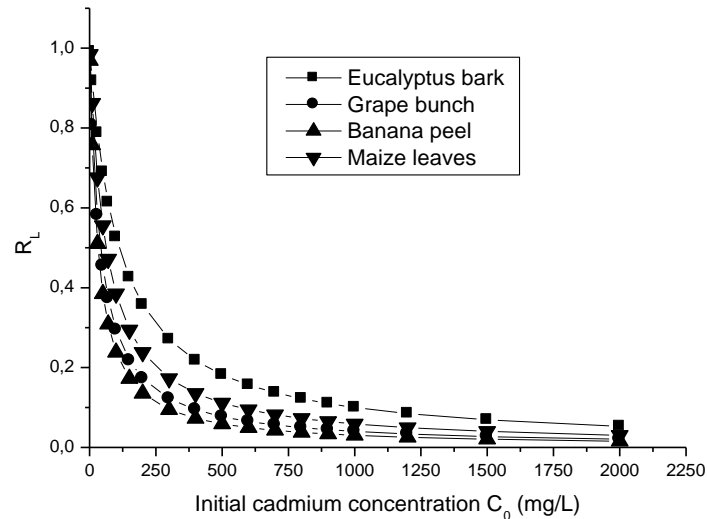


Figure 11: Separation factor for cadmium sorption by sorbent materials at 25 °C

CONCLUSION

This work shows the interest of a concept based on the waste to treat another waste or to resolve an environmental problem. The results obtained confirm that the low-cost materials tested can remove cadmium ion from aqueous solution. The sorption performances are strongly affected by parameters such as: contact time, initial cadmium concentration and sorbent material type. The amount of cadmium sorbed by these materials used increased with the increase of the initial cadmium concentration. The results showed that the kinetics of cadmium sorption were described by a pseudo-second order rate model. A good fitting of cadmium sorption equilibrium data was obtained with Langmuir model in all the range of concentrations studied. From these results, high maximum cadmium sorption capacities are observed with these materials. The highest removal of cadmium ions is obtained with eucalyptus bark. However, we have not enough information about the mechanism of cadmium sorption by these sorbent materials. Additional work will be required in order to determine the sorption of other metal ions, to optimise the overall process and to identify the different functional groups responsible for the metal ion binding.

Acknowledgements

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