

REMOVAL OF CADMIUM IONS BY SORPTION FROM AQUEOUS SOLUTIONS USING LOW-COST MATERIALS

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ABSTRACT

The efficiency of four low-cost sorbent materials namely peas husk, broad bean husk, medlar peel and fig leaves, for removing cadmium ions from aqueous solutions, in single systems, has been investigated in batch mode. Kinetic data and equilibrium sorption isotherms were measured. Kinetics of cadmium sorption was contact time, initial cadmium concentration and sorbent type dependent. For a given sorbent, the amount of cadmium sorbed increased with the increase of contact time and initial cadmium concentration. The kinetics of cadmium sorption were well described by a pseudo-second order rate model. Cadmium uptake of each sorbent tested was quantitatively evaluated using sorption isotherms. Results indicated that Langmuir model gave an acceptable fit to the experimental data. The broad bean husk was the most effective to remove cadmium ions with a maximum sorption capacity about 147.71 mg/g followed by peas husk (118.91 mg/g), fig leaves (103.09 mg/g), and medlar peel (98.14 mg/g), under the experimental conditions tested here.

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

INTRODUCTION

In the field of environmental pollution, there are few subjects that, during recent years, have been developed as rapidly as the study of toxic metals. The contamination of water by toxic heavy metals is a world-wide environmental problem. Cadmium, in particular, has received a great deal of attention due to its highly toxic nature and its tendency to accumulate in the tissues of living organisms. This metal is a non essential and non-beneficial element for plants, animals and humans. The main sources of cadmium in streams are effluents from industries such as electroplating, smelting, paints, alloy manufacturing, pigments, plastics, battery, zinc mining and refining processes (Holan et al. [1], Volesky et al. [2], Chong & Volesky [3]). Because of its high toxicity, most countries include cadmium among the "priority pollutants" requiring suitable treatment prior to discharge into the environment. At present, a variety of physicochemical processes such as precipitation, ion exchange, adsorption, etc... are employed to treat cadmium-containing effluents. The selection of a particular

treatment technique depends notably on a number of factors, e.g. waste type and concentration, other constituents, level of clean-up required and economics. However, these technologies are generally practical and cost-effective only with concentrated wastewater, and are ineffective when applied to low strength wastes with heavy metal ions concentrations less than 100 mg/L, Volesky [4]. This situation has in recent years led to a growing interest in the application of waste materials of biological natural origin for removal of trace amounts of toxic metals from dilute aqueous wastes. Recently, Bailey et al. [5] 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. A number of natural materials (agricultural/forestry wastes) and by-products have been studied in the literature for their capacity to remove cadmium from aqueous solutions, such as eucalyptus bark (Benaïssa [6], Ghodbane et al. [7]), banana peel (Benaïssa [6], Memon et al. [8]), almond peel (Benaïssa [6], bunch grape (Benaïssa [6]), bagasse sugar [9], sawdust [10], rice husk [11], spent grain [12], pine bark [13], rice polish [14], tree fern [15], modified corn cobs [16], etc. Therefore, there is a need for the search of low cost and easily available biomaterials, which can remove cadmium. The suitability of different types of low-cost materials to remove heavy metal ions, the mechanism involved and the factors governing the sorption are still not fully understood clearly.

The aim of this work is to report the results of a feasibility study using four biological natural wastes: peas husk, broad bean husk, medlar peel and fig leaves as inexpensive sorbent materials for the removal of cadmium ions from synthetic aqueous solutions, in single systems. 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. These fundamental data will be useful for further applications in the treatment of practical waste or process effluents. The effect of various experimental parameters such as: contact time, initial cadmium concentration and sorbent type on the kinetics of cadmium sorption was studied. The experimental sorption kinetic data were analysed using two common models namely first-order rate and pseudo second-order rate equations. In order to obtain information about the maximum sorption capacities for comparison between the sorbents tested, the known model of Langmuir was selected to analyse the experimental data of cadmium sorption equilibrium for each sorbent tested. The results obtained may contribute to a better understanding or application of the sorption phenomena at the liquid/solid interface.

MATERIALS AND METHODS

1- Materials and metal solution

In this work, four agricultural by-product wastes namely: peas husk, broad bean husk, medlar peel and fig leaves have been employed as low-cost sorbent materials in the removal of cadmium from aqueous solutions. All these wastes were collected in spring (peas husk and medlar peel), summer (broad bean husk) and autumn 2001 (fig leaves)

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 as sorbent materials after the following treatment: 10 g of each sorbent material were contacted with 2 L of distilled water in a beaker agitated vigorously (at a speed of 400 rpm) by a magnetic stirrer at ambient temperature of $25\pm 1^\circ\text{C}$ during 4 h, then filtered, continuously washed with distilled water until constant pH to remove the surface adhered particles and water soluble materials, and oven-dried at 80°C for 24 h after filtration. These materials were crushed and sieved to have particles of size 0.80 – 1.60 mm with a predominant size 0.50-0.80 mm for all sorbents except fig leaves (> 0.125 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.

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

2- 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 kinetics 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 $25\pm 1^\circ\text{C}$. 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. Based on the ready availability of this electrode in our laboratory, this method was chosen. 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.

Most experiments 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.

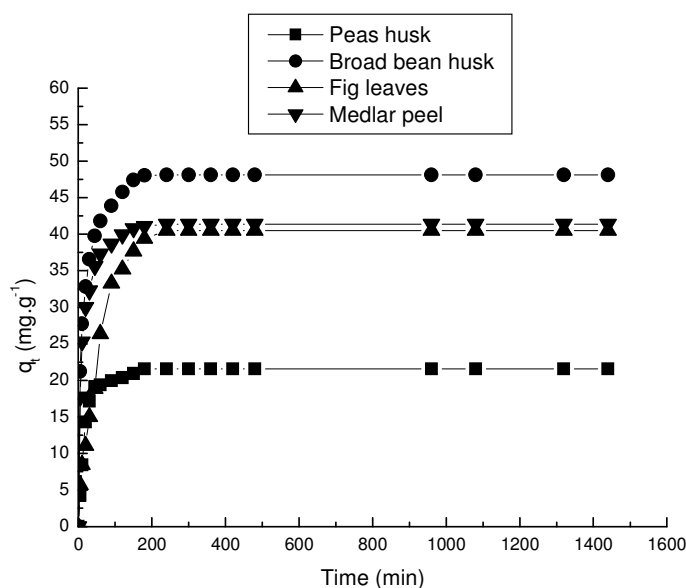
3- Uptake isotherms

The equilibrium isotherms were determined by contacting a constant mass 0.1 g of each sorbent material with a range of different concentrations of cadmium solutions: 5 – 1000 mg/L. The mixtures were agitated in a series of beakers with equal volumes of solution 50 mL for a period of 24 h at room temperature 25 ± 1 °C. This contact time to reach equilibrium is efficient to avoid any pseudo equilibrium and was previously determined by kinetics tests using the same conditions. The mixture pH was not controlled after the initiation of experiments. At equilibrium, the final pH was measured. The equilibrium cadmium concentration was obtained by using a Cd^{2+} -ion-selective electrode technique and the cadmium loading by each sorbent material was calculated.

RESULTS AND DISCUSSION

1 – Sorption kinetics

The initial solute concentration of an effluent is important since a given mass of sorbent material can only remove a fixed amount of solute. According to Fig. 1, for an 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 sorbent type dependent: 3 h for medlar peel, peas husk and broad bean husk respectively, and, 4 h for fig leaves. The amounts of cadmium sorbed at equilibrium are: 48.12 mg/g for broad bean husk, 41.38 mg/g for medlar peel, 40.51 mg/g for fig leaves and 21.58 mg/g for peas husk corresponding to a removal of about 96, 83, 81 and 43 % respectively of initial cadmium solution.



**Figure 1: Kinetics of cadmium sorption by different sorbent materials.
Initial cadmium concentration: 100 mg/L**

During the course of cadmium sorption by each of sorbents tested, a change in the initial pH value of the solution was observed, as shown in Fig. 2. Except fig leaves, for all other sorbents, the initial pH of solution slightly decreased. In order to investigate the reason for the initial pH changes, additional experiments were performed with each of these sorbents tested in distilled water under the same conditions as previously. As shown in Fig. 3, medlar peel, initial pHs exhibited a slight increase that can be interpreted as a possible fixation of H_3O^+ ions by the negative groups present on the sorbent surface. Concerning its decrease in cadmium solution, it can be interpreted as a possible release of H_3O^+ ions into the solution due to cadmium ions sorption.

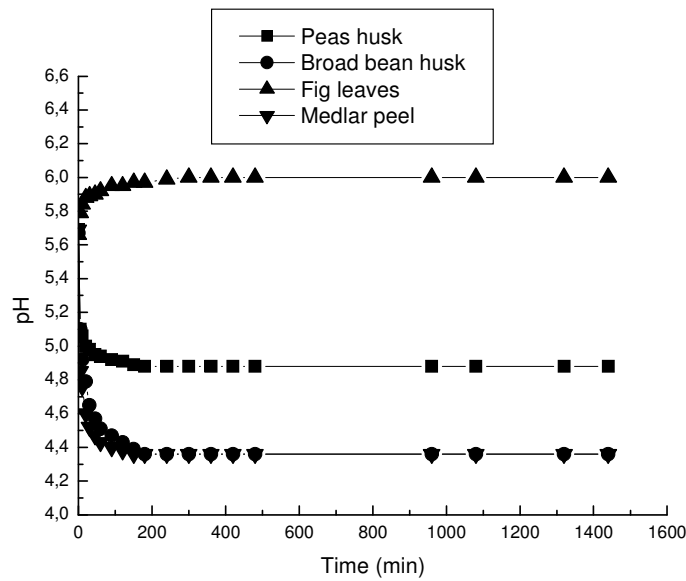


Figure 2: pH profiles of cadmium sorption by different sorbent materials
Initial cadmium concentration: 100 mg/L

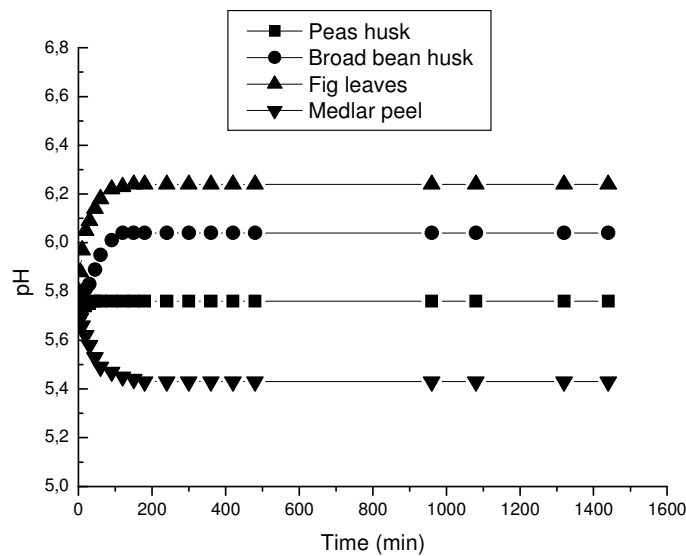


Figure 3: pH profiles of distilled water in the presence of different sorbent materials

The same tendencies were observed with other comparable systems sorbent - metal (Sekhar et al. [15], Ho [18]). Concerning fig leaves, the slight increase can be interpreted by a certain competition between cadmium ions and H_3O^+ ions for binding sites. Other authors have found the same trend in the removal of this ion or other ions by some other materials (Fiol et al. [19]; Villaescusa et al. [20]; Benguella & Benaïssa [21-23]; Benaïssa & Benguella [24]). At this stage, further investigations are required to understand the mechanisms involved in cadmium sorption by this type of complex materials.

To study the effect of initial cadmium concentration on the cadmium sorption kinetics, several experiments were also undertaken. For each sorbent tested, the results obtained indicated that the curves have the same shape (see Fig. 4 as a typical example).

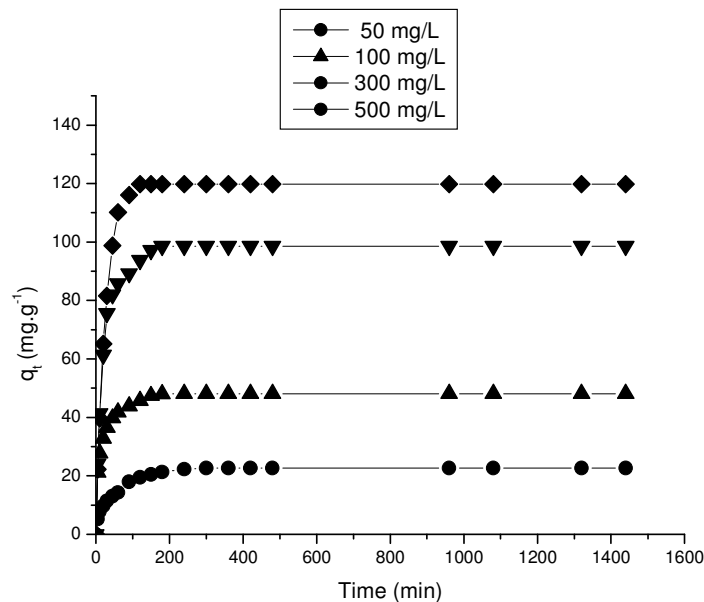


Figure 4: Effect of initial cadmium concentration on the kinetics of cadmium sorption by broad bean husk

From the results obtained at equilibrium and presented in Table 1, the necessary time to reach equilibrium is variable depending on the type of sorbent material used: broad bean husk (2-5 h), peas husk (1.5-3 h), fig leaves (2-6 h) and medlar peel (2-4 h). In general, this time decreases as the initial cadmium concentration increases. For all sorbents, the amount of cadmium sorbed at the equilibrium increases as the initial cadmium concentration increases. This is a result of the increase in the driving force the concentration gradient, as an increase in the initial cadmium ion concentrations (Özer et al. [25]).

During the kinetics experiments, for all sorbents tested, a decrease in the initial pH value of solution was observed for all studied concentrations (see Fig. 5 as a typical example), except for fig leaves (see Fig. 6).

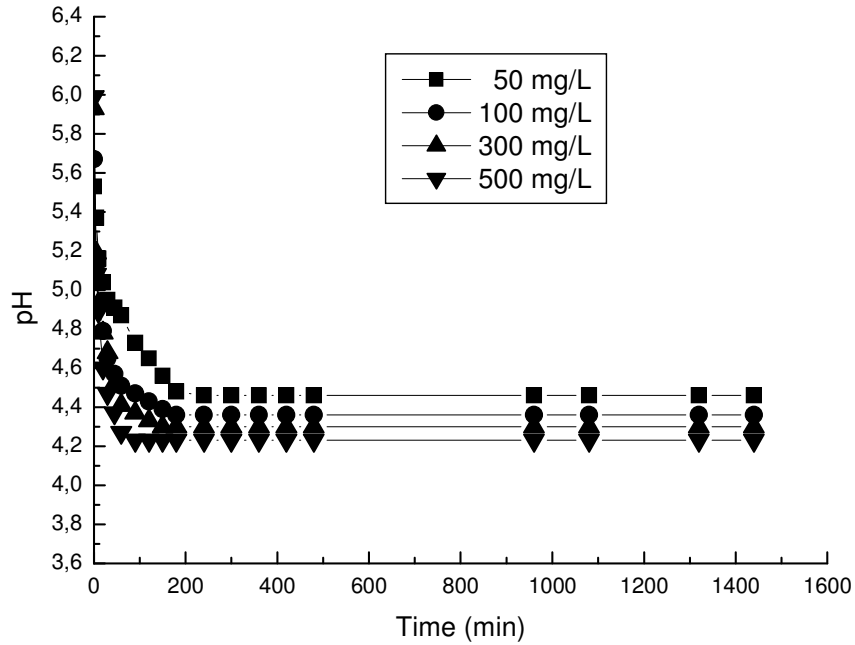


Figure 5: Effect of initial cadmium concentration on pH profiles of cadmium sorption by broad bean peel, as a typical example

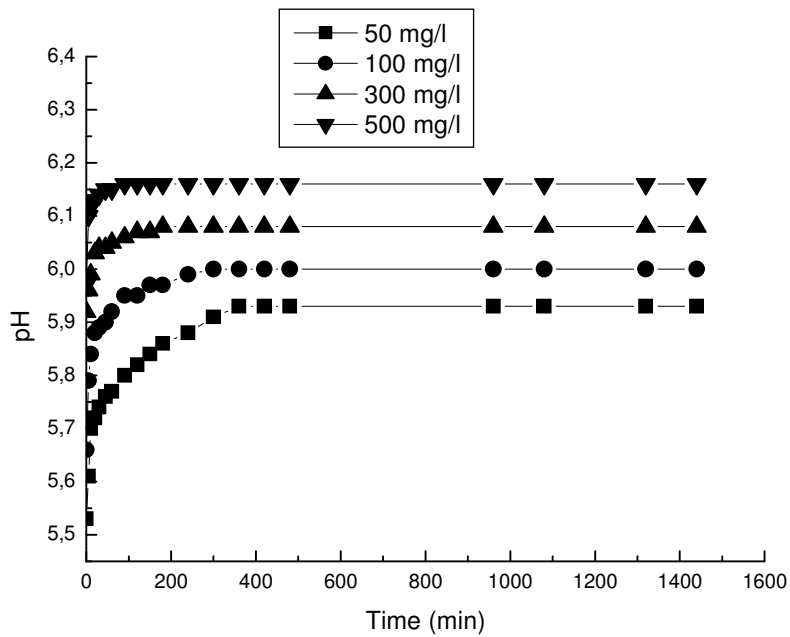


Figure 6: Effect of initial cadmium concentration on pH profiles of cadmium sorption by fig leaves

To analyse the kinetic data of cadmium sorption by each of sorbents tested under these experimental conditions, two common models from the literature namely: the first-order rate equation of Lagergren [26] and the pseudo second-order rate equation (Ho [27], Ho & McKay [28]) were chosen and shown below as Eqs. (1) and (2) in their linear forms, 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 obtained from the slopes and intercepts of linear plots of $\log (q_e - q_t)$ vs. t , and t/q_t vs. t , respectively (Figures not presented here) are summarized in the Table 1.

Table 1: Comparison of models for cadmium sorption kinetics by different sorbent materials at $C_0=100$ mg/g

Sorbent	First-order rate model				Pseudo second-order rate model		
	q_e exp. (mg/g)	q_e cal. (mg/g)	$k_L \cdot 10^3$ (min^{-1})	R^2	q_e cal. (mg/g)	$k \cdot 10^4$ ($\text{g} \cdot \text{mg}^{-1} \cdot \text{min}^{-1}$)	R^2
Fig leaves	40.51	42.63	18.88	0.9876	41.65	8.70	0.9988
Medlar peel	41.38	23.03	24.66	0.9866	41.58	49.0	0.9999
Broad bean husk	48.12	35.81	29.44	0.9266	48.40	35.06	0.9999
Peas husk	21.58	12.84	22.01	0.8886	21.74	61.86	0.9999

Only, the pseudo second –order reaction rate model adequately described the kinetics of cadmium sorption with high correlation coefficients ($R^2 = 0.9988-0.9999$) compared to those of the first –order rate model ($R^2 = 0.8886-0.9876$). The values of q_e obtained from the fitting to the pseudo second-order rate model are very similar to those obtained experimentally from the sorption kinetics at equilibrium: consequently, it was further used to describe all the kinetics of cadmium sorption by each of the sorbent materials tested. For all initial cadmium concentrations tested, straight lines (Fig. not 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 those obtained from the sorption kinetics at equilibrium: these confirm that the kinetic data obtained follow the

pseudo-second order kinetic model. In this model, all the steps of sorption such as: external diffusion, internal diffusion, and sorption are lumped together and it is assumed that the difference between the average solid phase concentration and the equilibrium concentration is the driving force for sorption, and that the overall sorption rate is proportional to the square of the driving force (Wu et al. [29]). In general, an increase in initial cadmium concentration led to a decrease in the rate constant values.

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

Fig leaves				
Initial Cd ²⁺ Concentration C _o (mg/L)	q _e exp (mg/g)	q _e .cal. (mg/g)	k.10 ⁴ (min ⁻¹ .g / mg)	R ²
50	21.86	22.45	15.56	0.9993
100	40.51	41.65	8.70	0.9988
300	73.32	73.85	18.54	0.9999
500	82.38	82.99	16.22	0.9999

Medlar peel				
Initial Cd ²⁺ Concentration C _o (mg/L)	q _e exp. (mg/g)	q _e cal. (mg/g)	k.10 ⁴ (min ⁻¹ .g / mg)	R ²
50	20.87	21.00	76.72	0.9999
100	41.38	41.58	49.00	0.9999
300	64.57	64.89	29.36	0.9999
500	82.35	82.71	27.00	0.9999

Broad bean husk				
Initial Cd ²⁺ Concentration C _o (mg/L)	q _e exp. (mg/g)	q _e cal. (mg/g)	k.10 ⁴ (min ⁻¹ .g / mg)	R ²
50	22.70	23.15	21.26	0.9996
100	48.12	48.40	35.06	0.9999
300	98.58	99.30	13.34	0.9999
500	119.83	120.92	10.16	0.9998

Peas husk				
Initial Cd ²⁺ Concentration C _o (mg/L)	q _e exp. (mg/g)	q _e cal. (mg/g)	k.10 ⁴ (min ⁻¹ .g / mg)	R ²
50	10.19	10.24	204.84	0.9999
100	21.58	21.74	61.86	0.9999
300	60.41	60.61	49.90	0.9999
500	74.11	74.40	36.70	0.9999

2- Sorption equilibrium

To study the equilibrium of cadmium sorption by each of these sorbent materials, isotherms of sorption at natural initial pH of solutions were measured. As shown in Fig. 7, for all sorbents tested, the amount of cadmium sorbed increases initially with the cadmium concentration at equilibrium but then reaches a certain saturation. The shape of these isotherms is of type-2 class L type (Langmuir type) according to Giles et al. [30] classification for sorption from solution, implying strong preferential sorption of cadmium ions. L2-type isotherms are usually associated with ionic solute adsorption 'e.g., metal cations and ionic dyes. Under the experimental conditions tested here. The response of each of the four sorbents tested is not similar: the broad bean husk is the most effective to remove cadmium ions followed by peas husk, fig leaves, and medlar peel, respectively.

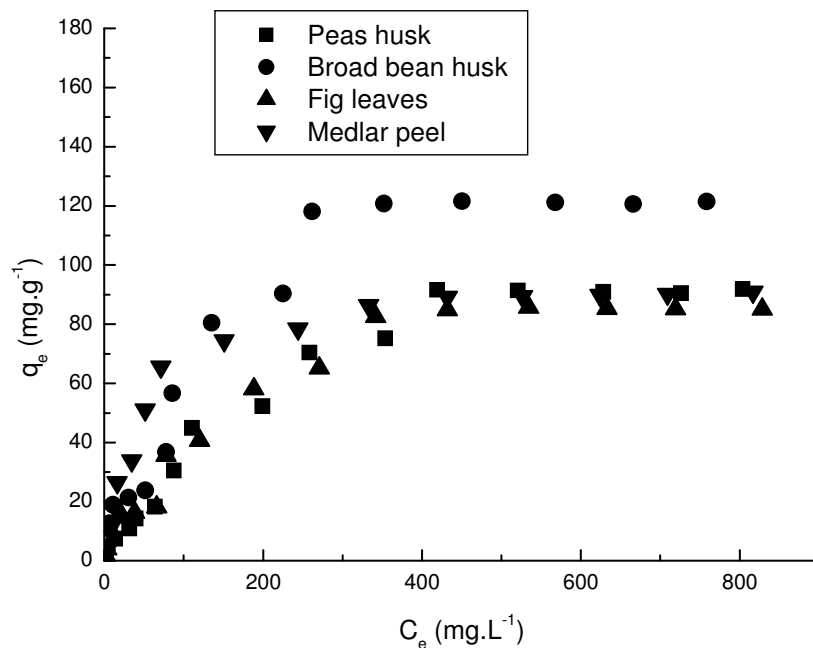


Figure 7: Isotherms of cadmium sorption by various sorbent materials at 25 °C

In order to optimise the design of a sorption system to remove pollutant from effluents, it is important to establish the most appropriate correlation for the equilibrium curve. Among the models available in the literature, the Langmuir [31] model is commonly used to fit experimental data when solute uptake occurs by a monolayer sorption. It can provide information on metal-uptake capacities and differences in metal uptake between various species (Kapoor and Viraraghavan [32]). It was used here to describe the cadmium sorption isotherms obtained. This modelling permits us to determine the maximal capacity of biosorption. The quality of the isotherm fit to the experimental data is typically assessed based on the magnitude of the correlation coefficient for the

regression; i.e. the isotherm giving an R^2 value closest to unity is deemed to provide the best fit. The Langmuir model has the form:

$$q_e = q_m K_L C_e / (1 + K_L C_e) \quad (3)$$

It may be linearized as follow:

$$C_e/q_e = 1/K_L q_m + C_e/q_m \quad (4)$$

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. 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 and it is a useful criterion in assessing which of the four low-cost adsorbent materials has the greatest uptake. The model parameters determined by least squares fit of the experimental data are listed in Table 3.

Table 3: Parameters of Langmuir model for cadmium sorption by different sorbent materials at 25 °C

Sorbent	q_{max} (mg/g)	K_L (L/mg)	R^2
Broad bean husk	147.71	0.008	0.9492
Peas husk	118.91	0.005	0.9142
Medlar peel	98.14	0.018	0.9982
Fig leaves	103.09	0.007	0.9546

Fig. 8 shows a graphical comparison of the experimental and calculated isotherms with these constants: it appears that Langmuir model acceptably fit the experimental results over the experimental range. 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: broad bean husk (147.71 mg/g) > peas husk (118.91 mg/g) > fig leaves (103.09 mg/g) > medlar peel (98.14 mg/g). Differences of metal uptake are due to the properties of each sorbent material such as structure, functional groups and surface area (Ozer et al. [25]).

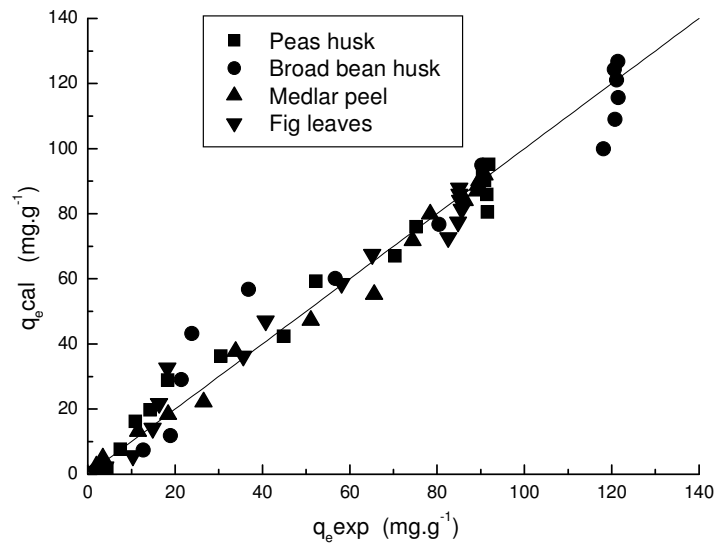


Figure 8: Comparison of Langmuir model with experiment for cadmium sorption by different sorbent materials

The applicability of this model 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, no information about the mechanism of cadmium sorption by these sorbents are available. According to many researchers, the sorption of metals by this kind of natural sorbent 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 [33]; Meunier et al. [34]; Villaescusa et al. [20]; Adler et al. [35]). 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. [20]. As shown in Table 4 for comparison, these sorption capacities obtained under these experimental conditions are considerably higher than those of other sorbent materials reported in literature, although this direct comparison is difficult due to the varying experimental conditions used in these studies.

Table 4: Comparison of maximum capacities of some sorbent materials for cadmium ions sorption, from the literature

Sorbent	q_m (mg/g)	Reference
Broad bean husk	147.71	This work
Peas husk	118.91	This work
Almond peel	103.20	(Benaïssa [6])
Fig leaves	103.09	This work
Eucalyptus bark	99.50	(Benaïssa [6])
Medlar peel	98.14	This work
Grape bunch	75.59	(Benaïssa [6])
Banana peel	69.44	(Benaïssa [6])
Duolite GT-73 (ion exchange resins)	66	(Volesky et al. [2])
Maize leaves	57.84	(Benaïssa [6])
Banana peel	35.52	(Memon et al. [8])
Clinoptilolite (natural zeolite)	23	(Curkovic et al. [36])
Chitin	14.71	(Benguella & Benaïssa [23])
Eucalyptus bark	14.53	(Ghodbane et al. [7])
Granulated activated carbon	7.87	(Ramos et al. [37])

CONCLUSION

This work shows the interest of a concept based on a waste to treat another waste or to resolve an environmental problem. The results obtained confirm that the low-cost materials tested can remove cadmium ions at different degrees from aqueous solution. The sorption performances are strongly affected by parameters such as: contact time, initial cadmium concentration and sorbent type. The amount of cadmium sorbed by these materials used increased with the increase of contact time and initial cadmium concentration. The kinetics of cadmium sorption was well described by a pseudo-second order rate model. An acceptable fitting of cadmium sorption equilibrium data was obtained with Langmuir model in all the range of concentrations studied. From these results, high maximum cadmium ions sorption capacities were observed with these materials: the highest cadmium ions sorption was obtained with broad bean husk. This experimental study is quite useful in developing an appropriate technology for designing a waste water treatment plant.

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