

Screening 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: peels of peas, broad bean, and medlar, respectively and fig leaves, to remove cadmium from 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 Langmuir model gave an acceptable fit to the experimental data. A high cadmium sorption was observed by these materials. The broad bean peel was the most effective to remove cadmium ions with a maximum sorption capacity about 147.71 mg/g followed by peas peel (118.91 mg/g), fig leaves (103.09 mg/g), and medlar peel (98.14 mg/g).
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1. Introduction

The presence of heavy metals in the aquatic environment is a source of great environmental concern (Rangsayatorn et al. [1]). 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. [2], Volesky et al. [3], Chong and Volesky [4]). Cadmium has been well recognized for its negative effect on the environment where it accumulates readily in living systems. 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. [5], Yin and Blanch [6], Sadowski et al. [7]). 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. [8] 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 and Khan [9]; Scott [10]; McKay and Porter [11]; Sun and Shi [12]; Al-Asheh and Duvnjak [13]; Meunier et al. [14]; Sekhar et al. [15]; Özer et al. [16]; Wang and Qin [17]).

This work studies the possibility of using certain biological wastes: peas, broad bean, medlar peels and fig leaves as inexpensive sorbents for the removal of cadmium from aqueous solutions. These materials are abundantly available through our country and the world. The present study reports their sorption potential through tests kinetics and sorption isotherms, in batch conditions. The experimental data of cadmium sorption equilibrium for each material tested were fitted by either the Langmuir and Freundlich equations and those of sorption kinetics by three models namely: first-order, pseudo second-order and second-order models.

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2. Materials and methods

In this work, four agricultural by-product wastes: peels of peas, broad bean, medlar, respectively and fig leaves have been employed as low-cost sorbent materials in the removal of cadmium from aqueous solutions. All these by-products were collected in spring (peels of peas and medlar, respectively), summer (broad bean peel) 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 initial pH value of solution <7 , because insoluble cadmium hydroxide starts precipitating at higher pH values, making true sorption studies impossible.

2.1. 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 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. 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.

2.2. 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: 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 $25 \pm 1^\circ\text{C}$. The contact time to reach equilibrium was previously determined by kinetics tests using the same conditions. The reaction mixture pH was not controlled after the initiation of experiments. After shaking the flasks for 24 h, 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.

3. Results and discussion

3.1. Uptake kinetics of metal

3.1.1. Effect of contact time

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 about: 3 h for medlar, peas and broad bean peels, respectively and 4 h for fig leaves. The amounts of cadmium sorbed at equilibrium are: 48.12 mg/g for broad bean peel, 41.38 mg/g for medlar peel, 40.51 mg/g for fig leaves and 21.58 mg/g for peas peel.

During the course of cadmium sorption by these materials, we noticed an evolution in the value of the initial pH of the solution presented in Fig. 2.

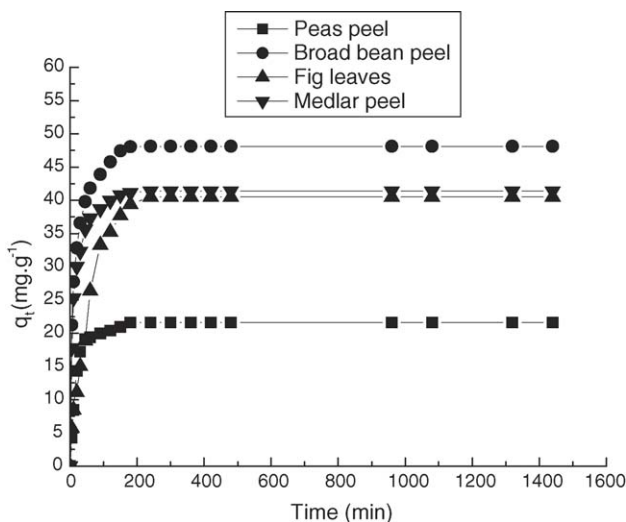


Fig. 1. Kinetics of cadmium sorption by sorbent materials (initial cadmium concentration: 100 mg/L).

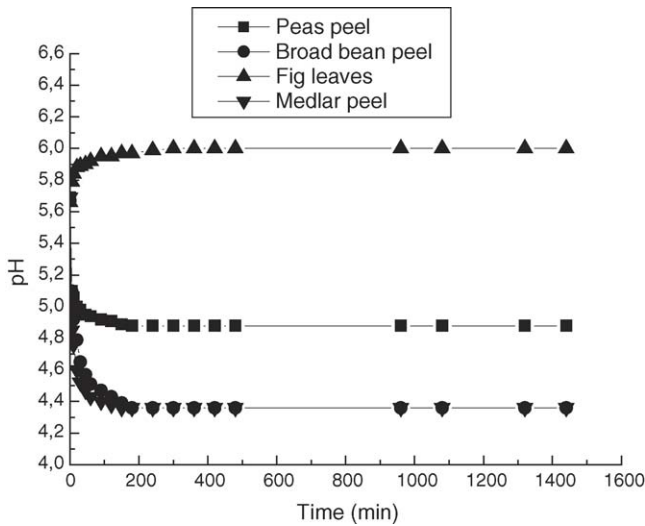


Fig. 2. pH profiles of cadmium sorption by sorbent materials.

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, 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 medlar leaves, initial pHs exhibited a slight increase that can be interpreted as a possible fixation of H_3O^+ by the negative groups present on the sorbent surface. Concerning the decrease in its value in the presence of cadmium ions, it can be interpreted as a possible release of H_3O^+ ions into the solution due to cadmium ions sorption.

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^+ 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 and Benaïssa [21–23]; Benaïssa and Benguella [24]). At this stage, further investigations are required to understand the mechanisms involved in cadmium sorption by this type of complex materials.

The kinetics of cadmium sorption by these sorbents can be modelled using the first-order rate equation of Lagergren [25], the pseudo second-order rate equation (Ho [26]; Ho and McKay [27]) and the second order rate equation shown below as Eqs. (1)–(3), respectively:

$$\log(q_e - q_t)/q_e = -k_L t/2.3 \tag{1}$$

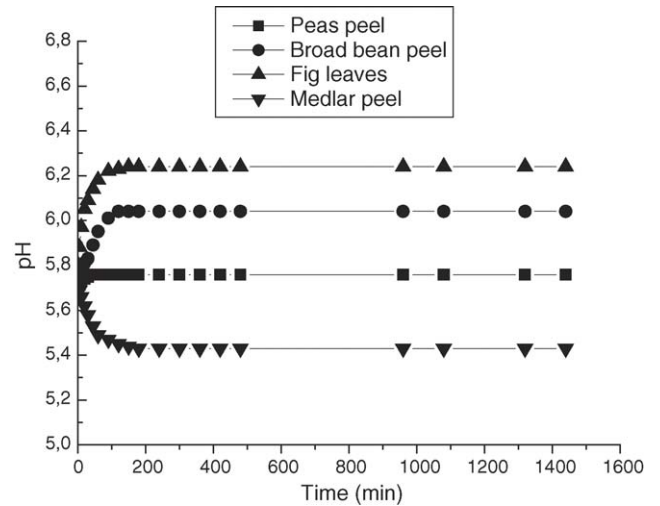


Fig. 3. pH profiles of a distilled water in the presence of sorbent materials.

$$\frac{t}{q_t} = \frac{1}{kq_e^2} + \frac{t}{q_e} \tag{2}$$

$$\frac{1}{q_e - q_t} = \frac{1}{q_e} + k' t \tag{3}$$

where k_L is the Lagergren rate constant of sorption (min^{-1}); k the pseudo second-order rate constant of sorption ($\text{g mg}^{-1} \text{min}^{-1}$) and k' the rate constant ($\text{g mg}^{-1} \text{min}^{-1}$); q_e and q_t are the amounts of metal sorbed (mg 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 $\log(q_e - q_t)/q_e$ versus t , t/q_t versus t and $1/(q_e - q_t)$ versus t , respectively (Figures not presented here) 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 ($R^2 > 0.999$): consequently, it was further used to describe all the kinetics of cadmium sorption by the sorbent materials tested.

3.1.2. 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 Figs. 4–7).

From the results obtained at equilibrium in Table 2, the necessary time to reach equilibrium is variable depending on the type of sorbent material used: this time decreases as the initial cadmium concentration increases. We also notice that the amounts

Table 1
Models rate constants for cadmium sorption kinetics by sorbent materials at $C_0 = 100 \text{ mg/L}$

Sorbents	$k_L \times 10^3 \text{ (min}^{-1}\text{)}$	R^2	$k \times 10^4 \text{ (g mg}^{-1} \text{min}^{-1}\text{)}$	R^2	$k' \times 10^3 \text{ (g mg}^{-1} \text{min}^{-1}\text{)}$	R^2
Fig leaves	18.88	0.9876	4.35	0.9988	3.60	0.7259
Medlar peel	24.66	0.9866	24.50	0.9999	15.21	0.7537
Broad bean peel	29.44	0.9266	17.53	0.9999	53.40	0.4473
Peas peel	22.01	0.8886	30.93	0.9999	9.04	0.9191

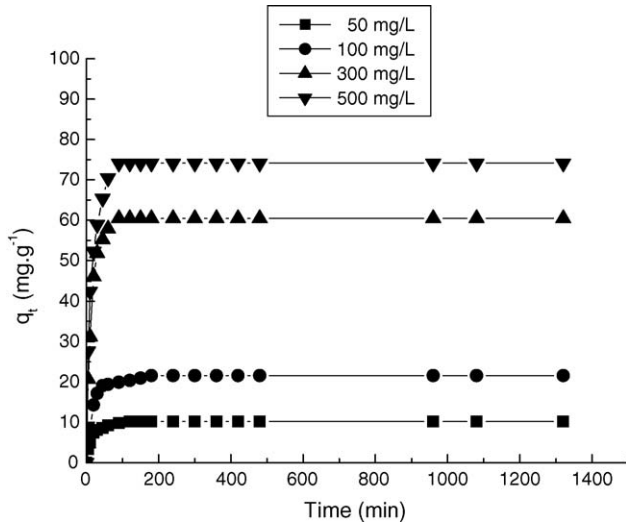


Fig. 4. Effect of initial cadmium concentration on the kinetics of cadmium sorption by peas peel.

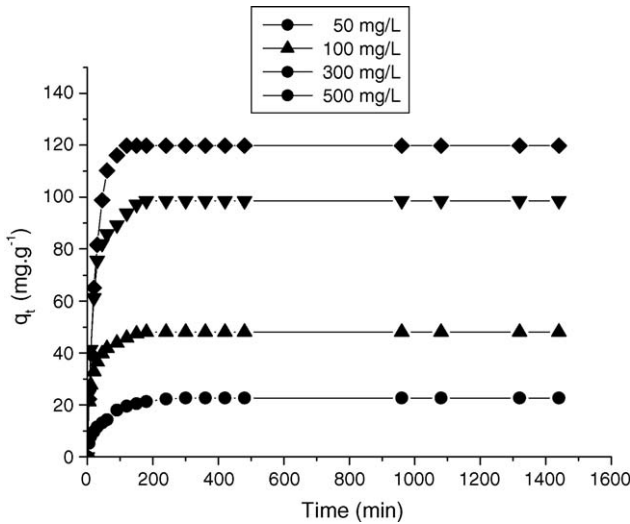


Fig. 5. Effect of initial cadmium concentration on the kinetics of cadmium sorption by broad bean peel.

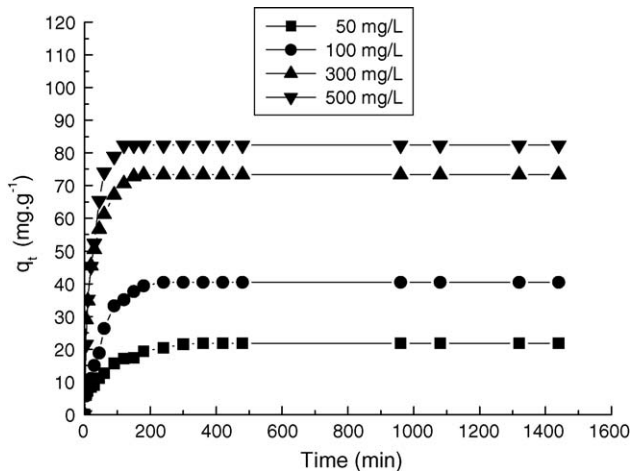


Fig. 6. Effect of initial cadmium concentration on the kinetics of cadmium sorption by fig leaves.

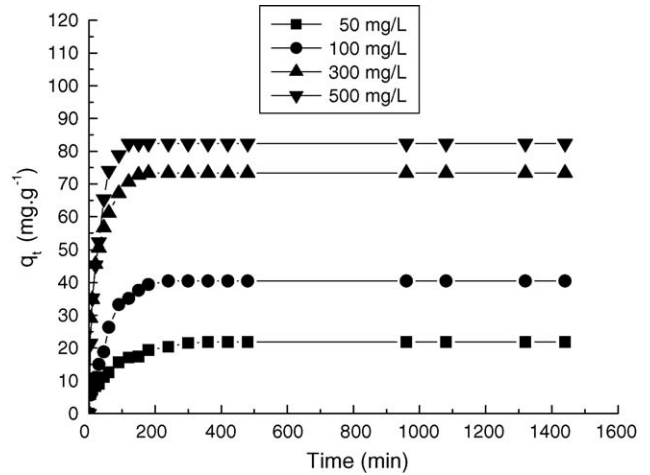


Fig. 7. Effect of initial cadmium concentration on the kinetics of cadmium sorption by medlar peel.

of cadmium sorbed at the equilibrium increases with the initial cadmium concentration.

During the kinetics experiments, except for fig leaves, we also noticed a slight decrease in the initial pH value of the solution for all studied concentrations (see Figs. 8 and 9).

When the previous data were only fitted to the pseudo second-order rate equation, 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 3). For all sorbents tested, the equilibrium sorption capacity, q_e , increases with an increase in the initial cadmium concentration. The values of q_e obtained from the fitting to the

Table 2

Experimental results obtained at equilibrium from the kinetics of cadmium sorption by different sorbent materials used: effect of initial cadmium concentration

Broad bean peel				
C_0 (mg/L)	50	100	300	500
pH _e	4.46	4.36	4.30	4.23
t_e (min)	300	180	180	120
q_e (mg/g)	22.7	48.1	98.6	119.9
Loss in sorbent weight (%)	5.4	9.0	3.5	5.6
Peas peel				
pH _e	4.89	4.88	4.80	4.76
t_e (min)	120	180	90	90
q_e (mg/g)	10.2	21.6	60.4	74.1
Loss in sorbent weight (%)	9.1	7.8	8.0	6.0
Fig leaves				
pH _e	5.93	6.00	6.08	6.16
t_e (min)	360	240	150	120
q_e (mg/g)	21.9	40.5	73.3	82.4
Loss in sorbent weight (%)	10.6	9.5	7.1	6.9
Medlar peel				
pH _e	4.36	4.36	4.28	4.20
t_e (min)	240	180	180	120
q_e (mg/g)	20.9	41.4	64.6	82.4
Loss in sorbent weight (%)	8.3	9.5	7.9	6.9

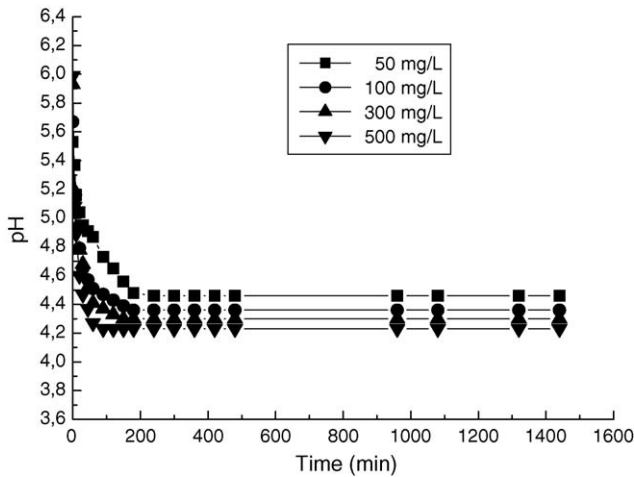


Fig. 8. pH profiles of cadmium sorption by broad bean peel as a typical example.

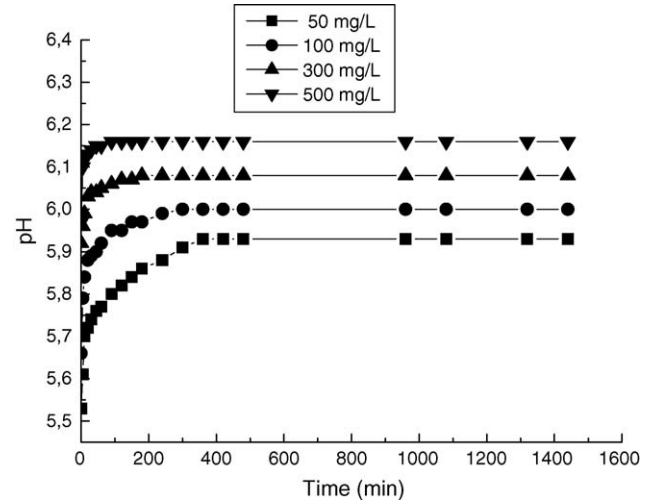


Fig. 9. pH profiles of cadmium sorption by fig leaves.

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 led to a decrease in the rate constant values.

3.2. Equilibrium of sorption

To study equilibrium of cadmium removal by these sorbent materials, isotherms of sorption with no initial pH control of

solution were measured. As shown in Fig. 10, the isotherms obtained for cadmium sorption are of Langmuir's type according to the classification of Brunauer et al. [28] and of L type according to the classification of Giles et al. [29].

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

Table 3

Pseudo second-order rate constants for cadmium sorption kinetics by various sorbent materials at initial cadmium concentration $C_0 = 100 \text{ mg/L}$

Fig leaves

Initial Cd^{2+} concentration C_0 (mg/L)	q_e cal (mg/g)	q_e exp (mg/g)	$k \times 10^4$ ($\text{min}^{-1} \text{ g/mg}$)	R^2
50	22.45	21.86	15.56	0.9993
100	41.65	40.51	8.70	0.9988
300	73.85	73.32	18.54	0.9999
500	82.99	82.38	16.22	0.9999

Medlar peel

Initial Cd^{2+} concentration C_0 (mg/L)	q_e cal (mg/g)	q_e exp (mg/g)	$k \times 10^4$ ($\text{min}^{-1} \text{ g/mg}$)	R^2
50	21.00	20.87	76.72	0.9999
100	41.58	41.38	49.00	0.9999
300	64.89	64.57	29.36	0.9999
500	82.71	82.35	27.00	0.9999

Broad bean peel

Initial Cd^{2+} concentration C_0 (mg/L)	q_e cal (mg/g)	q_e exp (mg/g)	$k \times 10^4$ ($\text{min}^{-1} \text{ g/mg}$)	R^2
50	23.15	22.70	21.26	0.9996
100	48.40	48.12	35.06	0.9999
300	99.30	98.58	13.34	0.9999
500	120.92	119.83	10.16	0.9998

Peas peel

Initial Cd^{2+} concentration C_0 (mg/L)	q_e cal (mg/g)	q_e exp (mg/g)	$k \times 10^4$ ($\text{min}^{-1} \text{ g/mg}$)	R^2
50	10.24	10.19	204.84	0.9999
100	21.74	21.58	61.86	0.9999
300	60.61	60.41	49.90	0.9999
500	74.40	74.11	36.70	0.9999

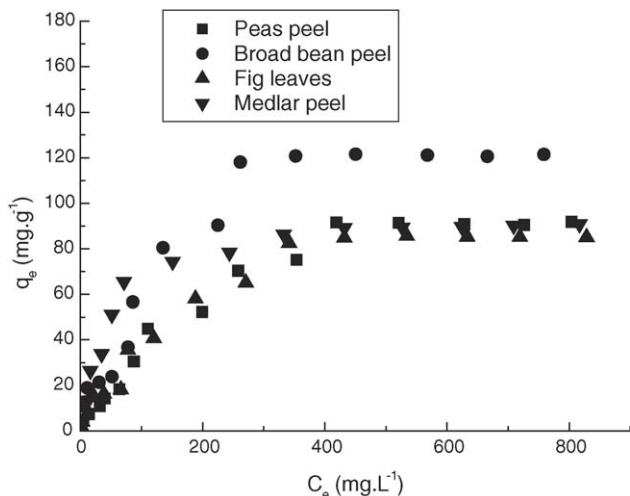


Fig. 10. Isotherms of cadmium sorption by various sorbent materials at 25 °C.

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 [30] and Freundlich [31] sorption models are commonly used to fit experimental data when solute uptake occurs by a monolayer sorption. They can provide informations on metal-uptake capacities and differences in metal uptake between various species (Kapoor and Viraraghavan [32]). These models were tested in the present work.

The Langmuir model has the form:

$$q_e = \frac{q_m b C_e}{1 + b C_e} \tag{4}$$

and the Freundlich model has the form:

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

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, b are the Langmuir model constants; K, 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 versus C_e , that will permit us to obtain the constants q_m and b 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 sorbent materials has the greatest

Table 4
Parameters of Langmuir and Freundlich sorption isotherms

Sorbent material	Langmuir model			Freundlich model		
	q_{max} (mg/g)	b (L/mg)	R^2	K	n	R^2
Broad bean peel	147.71	0.008	0.9492	2.59	0.634	0.9532
Peas peel	118.91	0.005	0.9142	2.31	0.571	0.9617
Medlar peel	98.14	0.018	0.9982	3.31	0.560	0.8871
Fig leaves	103.09	0.007	0.9546	2.17	0.588	0.9715

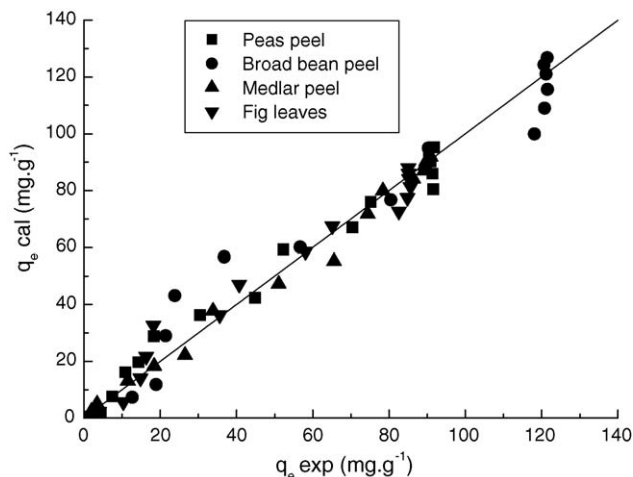


Fig. 11. Comparison of Langmuir model with experiment for cadmium sorption by different sorbent materials.

uptake. If the equation of Freundlich is also verified, we must obtain a straight line in the system of coordinates $Ln q_e$ versus $Ln C_e$, the slope and the intercepts to the origin give n and k , respectively. The models parameters determined by least squares fit of the experimental data have been calculated and are listed in Table 4.

Figs. 11 and 12 show graphical comparisons of the experimental and calculated isotherms with these constants: it appears that Langmuir 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 peel (1.31 mmol/g) > peas peel (1.06 mmol/g) > fig leaves (0.92 mmol/g) > medlar peel (0.87 mmol/g). For comparison, these sorption capacities are considerably higher than some sorbent materials reported in literature such as: natural zeolites as Clinoptilolite (0.21 mmol/g) [33], ion exchange resins as Duo-lite GT-73 (0.59 mmol/g) [34] and Granulated activated carbon (0.07 mmol/g) [35] although this direct comparison is difficult due to the varying experimental conditions used in these stud-

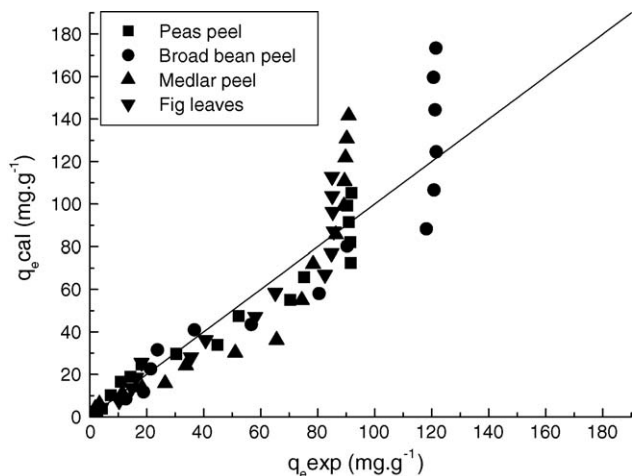


Fig. 12. Comparison of Freundlich model with experiment for cadmium sorption by different sorbent materials.

ies. 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 [13]; Meunier et al. [14]; Villaescusa et al. [20]; Adler et al. [36]). 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]).

4. Conclusions

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 type. The amount of cadmium sorbed by these materials used increased with the increase of the initial cadmium concentration. 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 sorption capacities are observed with these materials. The highest removal of cadmium ions is obtained with broad bean peel. However, we have not enough information about the mechanism of cadmium sorption by these sorbents. 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.

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