# 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: almond rinds, eucalyptus barks, maize leaves, grapes bunches and bananas rinds to remove cadmium from aqueous solutions. Kinetic data and equilibrium sorption isotherms were measured in batch conditions. Kinetics of cadmium sorption was time of contact and initial cadmium concentration dependent. The cadmium uptake of these low-cost materials was quantitatively evaluated using sorption isotherms. Results indicated that the Langmuir model gave a better fit to the experimental data than the Freundlich equation. A high cadmium sorption was observed by these materials. The sunflower leaves, were the most effective to remove cadmium ions with a maximum sorption capacity about 153.85 mg/g followed by almond rinds (104.60 mg/g), eucalyptus barks (99.30 mg/g), grapes bunches (75.64 mg/g), bananas rinds (69.35 mg/g) and maize leaves (57.84 mg/g). The results also showed that the kinetics of cadmium sorption were described by a pseudo-second order rate model

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

### 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. Biomaterials including agricultural waste (e.g., stems, leaves, fruit shells, etc...) have been demonstrated to remove certain chemicals species (Shi et al. [8]).

This work studies the possibility of using a certain biological wastes: almond rinds, eucalyptus barks, maize leaves, grapes bunches, bananas rinds and sunflower leaves as an inexpensive adsorbent 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 sorption isotherms and kinetics tests, 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 a pseudo-second-order model.

## MATERIALS AND METHODS

In this work, five agricultural waste by-products: almond rinds, eucalyptus barks, maize leaves, grapes bunches, bananas rinds and sunflower leaves have been employed as low-cost sorbent materials in the removal of cadmium from aqueous solutions. Except banana rinds imported from Equator (South of America), all other by-products were collected from different regions of Tlemcen-ALGERIA. They were used after a preliminary treatment. 10 g of dried material were added to 2 L of distilled water in a beaker agitated vigorously by a magnetic stirrer at ambient temperature of 25°C for 4 hours, then continuously washed with distilled water to remove the surface adhered particles and water soluble materials, and oven-dried overnight at 80°C for 24 hours after filtration. This material was crushed and sieved to have particles of heterogeneous size (0.1 - 3.15 mm) for further batch sorption experiments.

Cadmium solutions of desired concentration were prepared from $Cd(NO_3)_2.4H_2O$ (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 kinetics studies, 0.6 g of dried activated sludge or sunflower leaves was contacted with 300 mL 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 (mg metal ion /g dried sorbent) was determined as the difference between the concentrations before and after the sorption.

Preliminary experiments had shown that cadmium adsorption 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 ppm. 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 kinetics tests using the same conditions. The reaction mixture pH was not controlled after the initiation of experiments. After shaking the flasks for 24h, the final pH was measured. The final 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 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

According to Figure1, 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 maize leaves and bananas rinds, 4 h for almond rinds and grapes bunches and 6h for eucalyptus barks. The capacities of cadmium sorption at equilibrium are: 43.54 mg/g for sunflower leaves, 43.11 mg/g for almond rinds, 39.10 mg/g for sunflower leaves, 30.20 mg/g for eucalyptus barks, 23.40 mg/g for grapes bunches, 20.50mg/g for bananas rinds and 17.50 mg/g maize leaves to initial cadmium concentration of 100 mg/L.

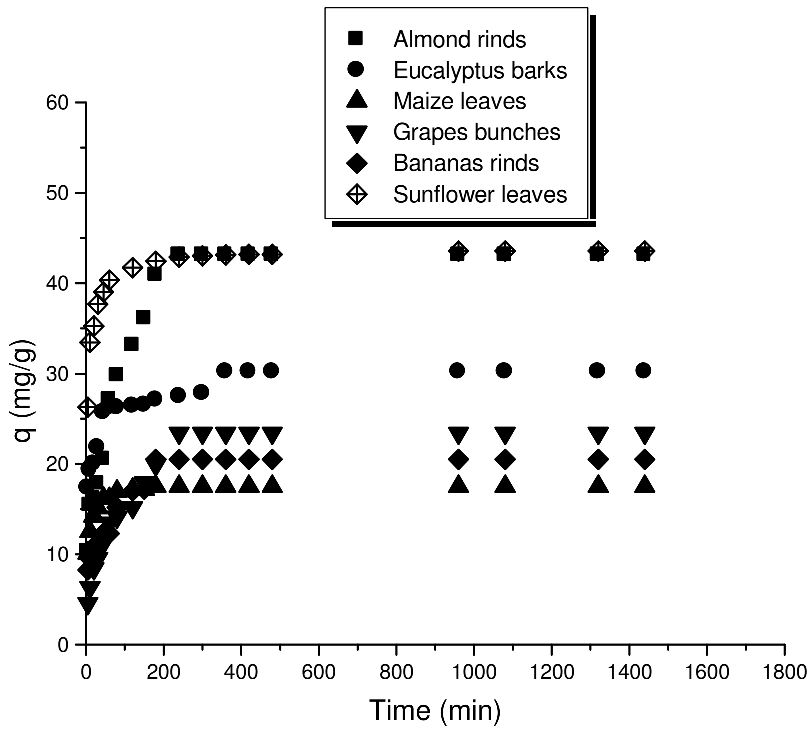


**Figure 1:** Kinetics of cadmium sorption by low-cost materials.
(initial cadmium concentration 100 mg/L; dose 2 g /L; initial pH of solution free; heterogeneous particle size 0.1 - 3.15 mm; agitation speed 400 rpm/min; T = 25 °C)

During the course of cadmium removal by these materials, we noticed an evolution in the value of the initial pH of the solution presented in Figure 2. This can be interpreted by a competition between cadmium ions and $H_3O^+$ for binding sites in the case of sunflower leaves, and, by a probable ion exchange phenomenon for the others. For the first phenomenon, as a result of this competition, only some of superficial groups become available to cadmium ions for sorption.

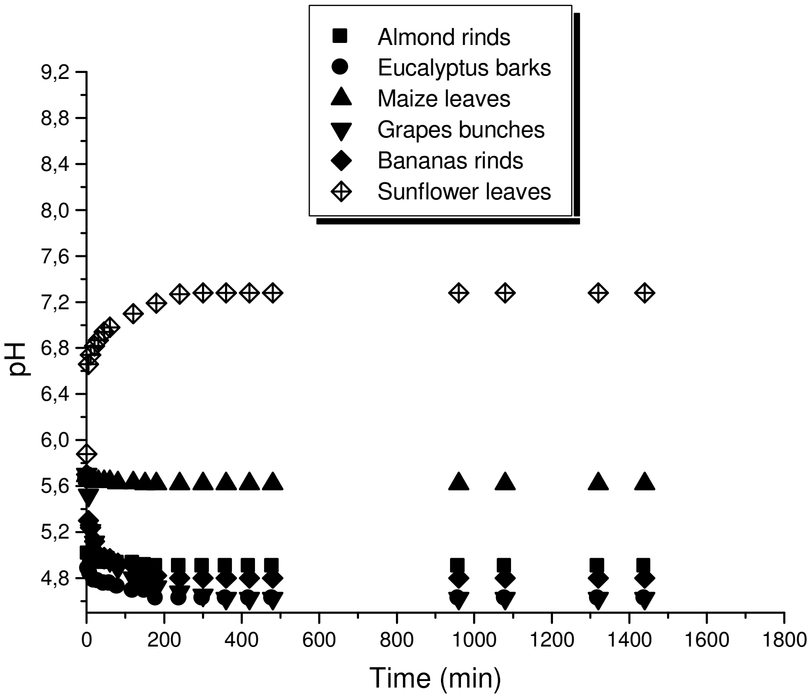


**Figure 2**: pH profiles of cadmium sorption by low-cost materials

The kinetics of cadmium sorption by activated sludge were modelled using a pseudo-second order rate equation developed by Ho & McKay [18]. The kinetic rate equation is:

$$t / q_t = 1/ 2K'q_e^2 + t / q_e \qquad (1)$$

where K' ($g.mg^{-1}.min^{-1}$) is the rate constant of sorption, $q_e$ and $q_t$ are the amounts of metal ion sorbed ($mg.g^{-1}$) at equilibrium and at time t, respectively ($mg.g^{-1}$) at equilibrium and at time t, respectively.

The K' values from the slopes and intercepts are summarized in the Table 1. The pseudo second –order reaction rate model adequately described the kinetics of cadmium sorption with high correlation coefficient (Figures no shown here).

**Table 1:** Pseudo second-order rate constants for cadmium sorption kinetics by various sorbent materials

| Sorbent material | K' ($min^{-1}.g$ / mg).$10^{+4}$ | $R^2$ |
|---|---|---|
| Maize leaves | 100 | 0.990 |
| Bananas rinds | 10 | 0.998 |
| Grapes bunches | 5.76 | 0.998 |
| Eucalyptus bark | 10 | 0.998 |
| Almond rinds | 4.42 | 0.998 |
| Sunflower leaves | 2.89 | 0.998 |

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 Figure 3 as a typical example).

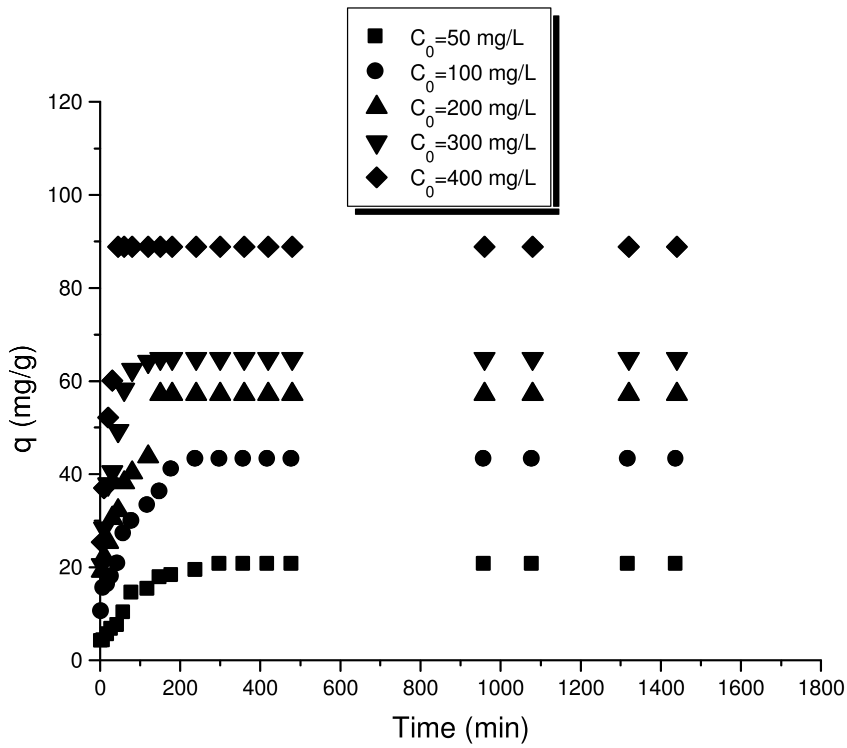


**Figure 3:** Effect of initial cadmium concentration on the kinetics of cadmium sorption by a almond rinds (as a typical example)

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 capacity of cadmium removal at the equilibrium increases with the initial cadmium concentration.

During the kinetics experiments, except for sunflower leaves, we also noticed a decrease of the initial pH value of the solution for all studied concentrations ( figures no shown here), without reaching the pH value of cadmium precipitation (see Table 2).

**Table 2**: Experimental results obtained at equilibrium from the kinetics of cadmium sorption by different sorbent materials used to different initial cadmium concentration.

**Almond rinds**

| $C_0$ (mg/L) | 50 | 100 | 200 | 300 | 500 |
|---|---|---|---|---|---|
| $pH_i$ | 5.50 | 5.66 | 5.82 | 5.92 | 5.97 |
| $pH_e$ | 4.94 | 4.90 | 4.88 | 4.82 | 4.78 |
| $t_e$ (min) | 300 | 240 | 150 | 120 | 45 |
| $q_e$ (mg/g) | 20.50 | 43.11 | 57.11 | 64.80 | 88.88 |

**Eucalyptus barks**

| | | | | | |
|---|---|---|---|---|---|
| $pH_i$ | 5.51 | 5.66 | 5.80 | 5.92 | 5.97 |
| $pH_e$ | 4.88 | 4.62 | 4.50 | 4.58 | 4.56 |
| $t_e$ (min) | 300 | 360 | 180 | 80 | 60 |
| $q_e$ (mg/g) | 17.24 | 30.20 | 56.00 | 62.50 | 75.50 |

**Maize leaves**

| | | | | | |
|---|---|---|---|---|---|
| $pH_i$ | 5.50 | 5.69 | 5.83 | 5.93 | 5.95 |
| $pH_e$ | 5.38 | 5.62 | 5.59 | 5.54 | 5.51 |
| $t_e$ (min) | 300 | 180 | 150 | 80 | 60 |
| $q_e$ (mg/g) | 16.50 | 17.50 | 31.50 | 52.30 | 52.50 |

**Grapes bunches**

| | | | | | |
|---|---|---|---|---|---|
| $pH_i$ | 5.53 | 5.70 | 5.85 | 5.95 | 5.97 |
| $pH_e$ | 4.70 | 4.62 | 4.60 | 4.55 | 5.55 |
| $t_e$ (min) | 120 | 240 | 120 | 120 | 80 |
| $q_e$ (mg/g) | 15.25 | 23.40 | 45.20 | 60.20 | 67.50 |

**Bananas rinds**

| | | | | | |
|---|---|---|---|---|---|
| $pH_i$ | 5.53 | 5.70 | 5.85 | 5.95 | 5.99 |
| $pH_e$ | 5.10 | 4.80 | 4.75 | 4.68 | 4.58 |
| $t_e$ (min) | 240 | 180 | 150 | 80 | 60 |
| $q_e$ (mg/g) | 12.59 | 20.50 | 40.00 | 56.17 | 71.20 |

**Sunflower leaves**

| $C_0$ (mg/L) | 60 | 100 | 200 | 300 | 500 |
|---|---|---|---|---|---|
| $pH_i$ | 5.72 | 5.88 | 5.68 | 5.68 | 5.73 |
| $pH_e$ | 7.83 | 7.28 | 7.24 | 7.02 | 7.00 |
| $t_e$ (min) | 240 | 240 | 420 | 420 | 360 |
| $q_e$ (mg/g) | 27.67 | 43.54 | 80.58 | 88.25 | 120.00 |

## 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 Figure 4, the isotherms obtained for cadmium sorption are of Langmuir's type according to the classification of Brunauer et al. [11] and of L type according to the classification of Giles et al. [12].

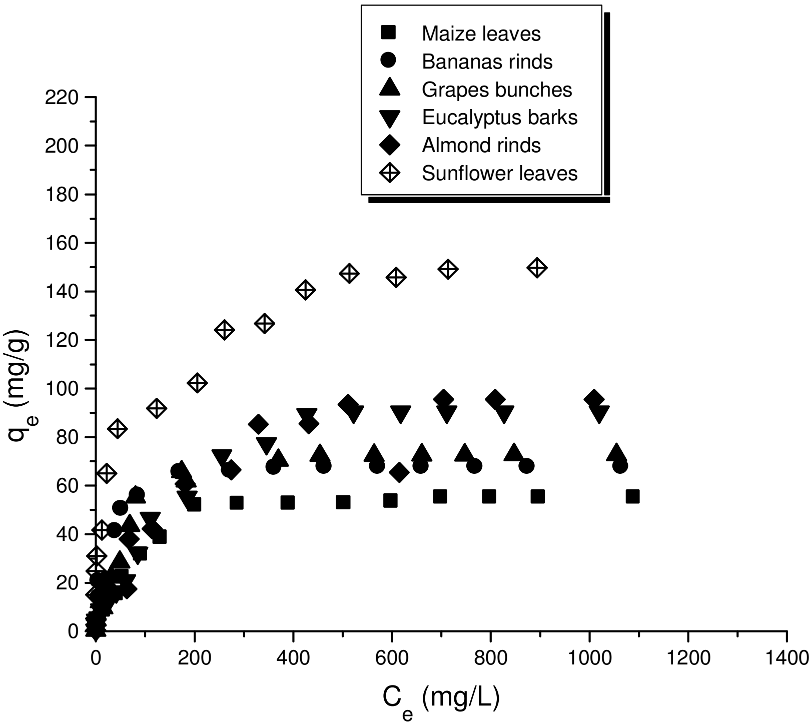


**Figure 4**: Isotherms of cadmium sorption by various sorbent materials at 25 °C.

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 [13] and Freundlich [14] sorption models are commonly used to fit experimental data when solute uptake occurs by a monolayer sorption. These models were tested in the present work. The Langmuir model has the form:

$$q = q_m \, b \, C_e / (1+bC_e) \qquad (2)$$

and the Freundlich model has the form:

$$q = KC_e^{\,n} \qquad (3)$$

where: q 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 Ce/q vs. $C_e$, that will permit us to obtain the constants $q_m$ and b from the intercept and slope. If the equation of Freundlich is also verified, we must obtain a straight line in the system of coordinates Ln q vs. Ln $C_e$, the slope and the intercepts to the origin give n and k respectively. Results of the modelling of isotherms of cadmium sorption by these sorbent materials, according to these models, are represented in Figures 5 and 6.

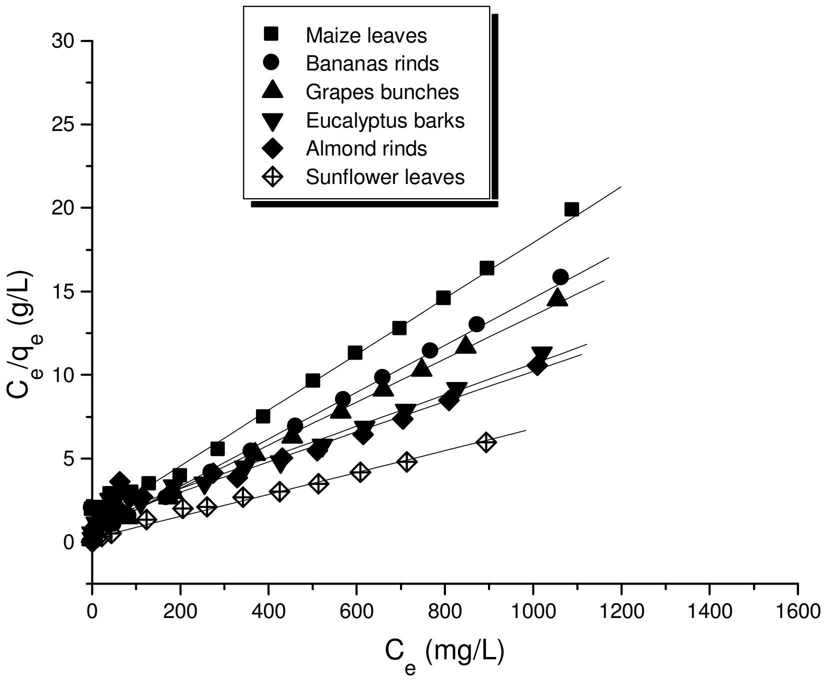


**Figure 5:** Linearised plot of Langmuir isotherm for cadmium sorption by sorbents materials.

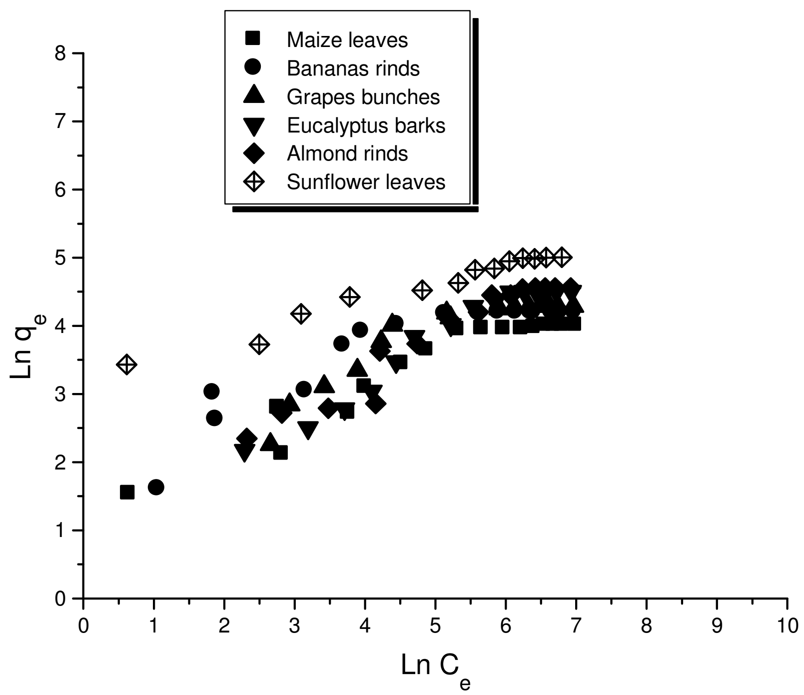


**Figure 6:** Linearised plot of Freundlich isotherm for cadmium sorption by sorbent materials

The linear plots of $C_e/q_e$ against $C_e$ for different adsorbents suggest the applicability of Langmuir isotherms for the present systems. The models parameters determined by least squares fit of the experimental data have been calculated and are listed in Table 4. The $q_m$ values provide a measure of the maximum adsorption capacity, $q_{max}$, in such a system. The maximum adsorption capacity is a useful criterion in assessing which of the five low-cost adsorbent materials has the greatest uptake.

**Table 4**: Parameters of Langmuir and Freundlich sorption isotherms.

**Langmuir model**

| Sorbent material | $q_{max}$ (mg/g) | b (L/mg) | $R^2$ |
|---|---|---|---|
| Maize leaves | 59.88 | 0.014 | 0.992 |
| Bananas rinds | 71.43 | 0.026 | 0.992 |
| Grapes bunches | 76.92 | 0.021 | 0.994 |
| Eucalyptus barks | 106.38 | 0.007 | 0.968 |
| Almond rinds | 111.11 | 0.008 | 0.951 |
| Sunflower leaves | 153.85 | 0.030 | 0.988 |

**Freundlich model**

| Sorbent material | K | n | $R^2$ |
|---|---|---|---|
| Maize leaves | 1.78 | 0.559 | 0.862 |
| Bananas rinds | 3.28 | 0.513 | 0.752 |
| Grapes bunches | 3.41 | 0.506 | 0.927 |
| Eucalyptus barks | 2.13 | 0.591 | 0.953 |
| Almond rinds | 3.41 | 0.517 | 0.953 |
| Sunflower leaves | 22.22 | 0.301 | 0.953 |

It appears that the Langmuir model best fits the experimental results over the experimental range with good coefficients of correlation. According to the coefficients of correlation, we deduct that the model of Freundlich is not adequate for modelling isotherms in all the studied concentrations domain. 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. In spite of the above limitations, these models can provide information on metal-uptake capacities and differences in metal uptake between various species (Kapoor and Viraraghavan [15]). From these results, a high cadmium sorption by these sorbent materials is observed. The highest removal of cadmium ions is obtained with sunflower leaves.

## CONCLUSION

The results obtained confirm that these low-cost materials can remove cadmium ion from aqueous solution. The sorption performances are strongly affected by parameters such as : contact time and initial cadmium concentration. The amount of cadmium removed by these materials used increased with the increase of these parameters at a specific time. A good fitting of cadmium sorption equilibrium data is obtained with Langmuir model in all the range of concentrations studied. From these results, high maximum cadmium sorption capacities are observed with both these materials. The highest removal of cadmium ions is obtained with sunflower leaves.

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