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Utilization of an agricultural waste material, melon (*Cucumis melo* L.) peel, as a sorbent for the removal of cadmium from aqueous phase

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ABSTRACT

Melon (*Cucumis melo L.*) peel, an agricultural solid waste material, was utilized as a novel non-conventional sorbent for the removal of cadmium from aqueous phase. The effects of sorbent dose, pH, ionic strength, temperature, stirring speed, initial concentration and contact time on the sorption of cadmium were evaluated. Results indicate an increase in uptake by the sorbent with increasing initial cadmium concentration, solution pH and contact time. The amount of cadmium sorption decreases with increasing temperature, ionic strength and sorbent dose. Mixing rates up to 400 rpm increase uptake, however, higher mixing rates result in insignificant enhancement of uptake compared to the dissipated energy. The equilibrium sorption data of cadmium by melon peel were analyzed by Langmuir, Freundlich and Temkin isotherm models. The results indicate that the Langmuir model provides the best correlation of the experimental data, with maximum monolayer sorption capacity of 81.97 mg g^{-1}. Pseudo-first-order, pseudo-second-order and intra-particle diffusion models were used to analyze the kinetic data obtained at different initial concentrations. Among the kinetic models studied, the pseudo-second-order model was the best applicable to describe the sorption of cadmium by melon peel. The results demonstrated that melon peel is very effective for the sorption of cadmium from aqueous solutions.

Keywords: Cadmium; Sorption; Melon peel; Kinetics; Equilibrium

1. Introduction

Industrial effluents containing heavy metals remain a serious environmental and sanitary problem. Cadmium is one of the toxic heavy metals and has received a great deal of attention. Cadmium has various applications in a variety of industrial processes. The major sources of cadmium release into the environment by waste streams are electroplating, smelting, alloy manufacturing, pigments, plastic, battery, mining and refining processes [1,2]. As a non-essential metal for human consumption, cadmium has an extremely long biological half-life (>20 years). Cadmium is among the most toxic metals and is known to cause renal dysfunction, bone degeneration, lung inefficiency, liver damage and hypertension in humans. US Environmental Protection Agency has also classified Cd(II) as group B1 carcinogen [3]. Cadmium has been designated as category I carcinogen by International Agency for Research on Cancer (IARC).

The removal of cadmium from contaminated water and wastewater is important in the protection of the environment and human health. Several technologies has been developed for the removal of cadmium from

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waters and wastewaters, such as chemical precipitation, oxidation or reduction, filtration, ion exchange, electrochemical treatment, reverse osmosis, membrane technology and evaporation recovery [4]. Most of these are ineffective or excessively expensive when the metal concentrations are less than 100 mg L^{-1} [1].

Adsorption process using commercial activated carbons is very effective for removal of cadmium from wastewater, but its high cost has motivated the search for alternatives and low-cost sorbents. An economic sorbent is defined as one which is abundant in nature, or is a by-product or waste from industry and requires little processing [5]. The use of unconventional sorbents has the following features: (i) it can be obtained abundant locally and cheaply. Most of them are readily utilized; (ii) less operation cost in terms of maintenance and supervision are required for the unconventional adsorption systems; (iii) utilization of industrial solid waste for the treatment of industrial wastewater is helpful not only to the environment, but also to reduce the disposal cost [6]. A number of agricultural and forest wastes and by-products have been studied in the literature for their capacity to remove cadmium from aqueous solutions, such as bagasse sugar [7], sawdust [8], rice husk [9], spent grain [10], pine bark [11], eucalyptus bark [12], rice polish [13], tree fern [14], modified corn cobs [15], wheat bran [16,17], fruit peels [18] etc.

In this investigation, the aptitude of melon peel for the removal of cadmium from aqueous solutions was examined. Melon, *Cucumis melo L.*, is an herbaceous annual plant originating of Africa, appertaining to the Cucurbitaceous family, largely cultivated for its edible fruit. Melon is a fruit of economic importance in both Algeria and the world. The world production of melon rises to 26.7 million tons. Due to the high consumption of melon, enormous amounts of the peels (as waste products) are disposed, causing a severe problem in the community. For an environmental viewpoint, the utilization of this agricultural waste as a low-cost sorbent for the removal of cadmium is recommended.

The aim of this work was to explore the feasibility of using melon peel, an agricultural waste, for removal of cadmium from aqueous solutions. The effects of various operating parameters such as initial cadmium concentration, solution pH, temperature, stirring speed, ionic strength, sorbent dose and contact time on cadmium removal were investigated.

2. Materials and methods

2.1. Sorbent

Melons were purchased from a local market (Annaba, Algeria). They were first washed several times with distilled water to remove the surface adhered particles. Then they were manually peeled. Collected peels were washed with distilled water to remove the water soluble materials and oven-dried at 70°C until constant weight. The dried sample was grounded and sieved to obtain a particle size range of 0.5–2 mm. The resulted material was washed repeatedly with distilled water until the wash water contained no color. Finally, the sorbent was then completely dried in an air circulating oven at 70°C and stored in a desiccator until use.

2.2. Sorbate

Cadmium solutions of desired concentration have been prepared by dissolving the appropriate amount of its sulfate ($3CdSO_4(8H_2O$, Fluka) in distilled water. All chemicals used in this study were of analytical grade.

2.3. Sorption studies

Batch equilibrium studies were carried out by adding a fixed amount of melon peel (0.5 g) into flasks containing 500 mL of different initial concentrations (50–300 mg L^{-1}) of cadmium solution. The flasks were agitated in an isothermal water-bath at 400 rpm and 25°C for 180 min until equilibrium was reached. Aqueous samples were taken from the solutions and the sorbent separated by filtration then the concentrations were analyzed by atomic absorption spectrophotometry (Perkin-Elmer A310) for the concentration of cadmium. The amount of equilibrium sorption, q_e (mg/g), was calculated by:

$$q_e = \frac{(C_0 - C_e)V}{W}, \tag{1}$$

where C_0 and C_e (mg L^{-1}) are the liquid-phase concentrations of cadmium at initial and equilibrium time t, respectively, V (L) is the volume of the solution and W (g) is the mass of sorbent used.

The effect of melon peel dose on the amount of cadmium sorbed was studied by adding different amounts (0.1, 0.3, 0.5, 1 and 2 g) of sorbent into a number of flasks containing a definite volume (500 mL in each flask) of fixed initial concentration (100 mg L^{-1}) of metal solution without changing the solution pH at 25°C. The flasks were placed in a thermostatic water-bath and agitation was provided at 400 rpm. The cadmium concentrations were measured at equilibrium.

To study the effect of solution pH on cadmium sorption, 0.5 g of melon peel was agitated with 500 mL of cadmium solution of metal concentration 100 mg L^{-1} at 25°C and 400 rpm. The experiment was conducted at different pH values ranging from 3 to 6.

The solution pH was adjusted using 0.1 N H_2SO_4 or NaOH aqueous solutions.

The influence of ionic strength on the sorption of cadmium by melon peel was studied with a constant initial concentration of 100 mg L^{-1}, sorbent mass of 0.5 g, solution volume of 500 mL and temperature of 25°C. The ionic strength of the cadmium solution was modified using different dosages of K_2SO_4 (1–10 g L^{-1}).

The effect of temperature on the sorption of cadmium was studied by contacting 0.5 g of sorbent with 500 mL of metal solution of 100 mg L^{-1} initial concentration at different temperatures (25–45°C).

To investigate the effect of stirring speed on the sorption of cadmium, the initial metal concentration, sorbent mass and solution temperature were 100 mg L^{-1}, 0.5 g and 25°C, respectively. The stirring speed was varied from 0 (without stirring) to 600 rpm.

For kinetic studies, the procedures of kinetic experiments were basically identical to those of equilibrium tests. The aqueous samples were taken at preset time intervals, and the concentrations of cadmium were similarly measured. All the kinetic experiments were carried out without pH adjustment. The amount of sorption at time t, q (mg g^{-1}), was calculated by:

$$q = \frac{(C_0 - C)V}{W}, \tag{2}$$

where C (mg L^{-1}) is the liquid-phase concentration of cadmium at any time.

3. Results and discussion

3.1. Effect of initial concentration and contact time

The effect of initial concentration (50–300 mg L^{-1}) on the sorption of cadmium by melon peel at 25°C is shown in Fig. 1. It can be seen that the removal at different concentrations is rapid in the initial stages and gradually decreases during the progress of sorption until the equilibrium is reached. It was observed that an increase in initial cadmium concentration leads to an increase in the sorption of cadmium by melon peel. The amount of cadmium sorbed at equilibrium increased from 39.34 to 75.04 mg g^{-1} as the concentration was increased from 50 to 300 mg L^{-1}. The initial concentration provides an important driving force to overcome all mass transfer resistances of the cadmium between the aqueous and solid phases. As the initial cadmium concentration increased the equilibrium removal of cadmium decreased. This effect can be explained on the basis of the cadmium/sorbent ratio. At low metal/sorbent ratios, there are number of sorption sites in melon peel structure. As the metal/sorbent ratio increases, sorption sites are saturated, resulting in a decrease in the sorption efficiency.

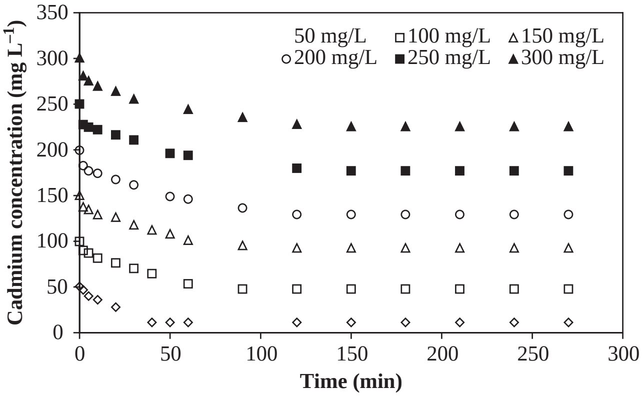

Fig. 1. Effect of initial concentration and contact time on the removal of cadmium by melon peel (conditions: 500 mL of cadmium solution, initial concentration 50–300 mg L^{-1}, sorbent mass: 0.5 g, stirring speed 400 rpm, pH 5, temperature 25°C).

It is also shown in Fig. 1 that for the initial cadmium concentrations of 50 and 100 mg L^{-1}, equilibrium is reached in about 40 and 90 min, respectively. For cadmium solutions with initial concentrations of 150 and 200 mg L^{-1}, equilibrium time of 120 min was required. At higher initial cadmium concentration (250 and 300 mg L^{-1}), the time necessary to reach equilibrium was 150 min. This is due to the fact that sorption sites took up the available metal ions more quickly at low concentration, but metal needed to diffuse to the inner sites of the sorbent for high concentration. However, the experimental data were measured at 180 min to make sure that full equilibrium was attained.

3.2. Effect of sorbent dose

In order to investigate the effect of sorbent dose on cadmium sorption, experiments were carried out at initial metal concentration of 100 mg L^{-1}, while the amount of sorbent added was varied from 0.1 to 2 g. Fig. 2 shows the effect of sorbent dose on the sorption of cadmium by melon peel. It was observed that the amount of cadmium sorbed decreased with the increase in sorbent dose. At equilibrium time, the sorbed amount increased from 15.81 to 84.30 mg g^{-1} for a decrease in sorbent mass from 2.0 to 0.1 g, respectively. The decrease in the amount of cadmium sorbed with increasing sorbent mass is due to the split in the flux or the concentration gradient between solute concentrations in the solution and on the sorbent surface. However, the removal of cadmium increases with an increase in sorbent dosage. The increase in cadmium removal was due to the increase of the available

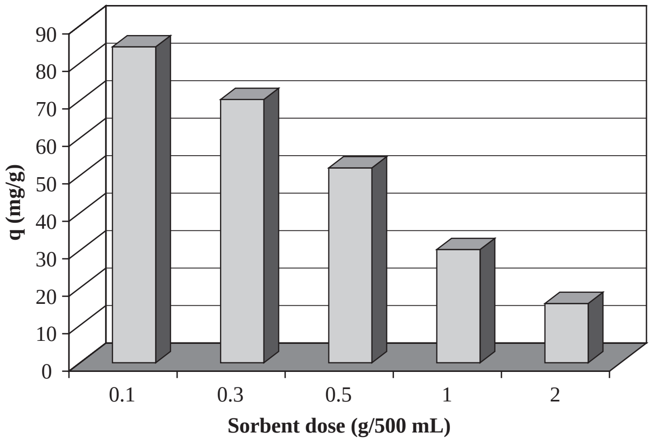

Fig. 2. Effect of sorbent dose on the sorption of cadmium by melon peel (conditions: 500 mL of cadmium solution, initial concentration 100 mg L^{-1}, sorbent mass: 0.1–2 g, stirring speed 400 rpm, pH 5, contact time 180 min, temperature 25°C).

sorption surface and availability of more sorption sites. At higher sorbent to cadmium concentration ratios, there is a very fast superficial sorption onto the sorbent surface that produces a lower metal concentration in the solution than when the material to metal concentration ratio is lower. This is because a fixed mass of sorbent can only sorb a certain amount of metal.

3.3. Effect of solution pH

Metal ion sorption by sorbents from aqueous solutions is depending on the pH of solution as it affects sorbent surface charge and degree of ionization. The concentration of the hydrolyzed cadmium species depends on the cadmium concentration and the solution pH. In this work, in order to avoid the precipitation in alkaline condition, the sorption of cadmium was carried out in acidic condition. For cadmium concentration of 100 mg L^{-1}, Cd^{2+} ions are the only ionic species present in the solution for pH $\leq$ 6 [12,17]. Fig. 3 illustrates the effect of initial pH on equilibrium uptake capacity of melon peel. The minimum sorption capacity was observed at strong acidic condition (pH 3). With the increase of solution pH, higher uptake of cadmium was occurred. The sorption capacity increased from 12.65 to 60.42 mg g^{-1} when pH increased from 3 to 6, respectively. The low cadmium sorption by melon peel at lower pH (3 and 4) is due to the strong competition of H^+ ions, because of their higher concentration and high mobility, causing a decrease in the amount of cadmium sorbed. Additionally, the solution pH influences the sorbent surface charge (melon peel PZC = 4.2). The surface charge of melon peel particles is positive at pH < PZC, is neutral at pH = PZC, and is negative at pH > PZC. There was strong resistance against the metal ions sorbed to the sorbent surface because the functional groups on the sorbent surface were highly protonated at strong acidic condition. At higher pH (5–6) > PZC, the melon peel particles surface become negatively charged, which enhances the positively charged cadmium cations (Cd^{2+}) through electrostatic forces of attraction.

3.4. Effect of ionic strength

Fig. 4 shows the effect of ionic strength (K_2SO_4) on the sorption of cadmium by melon peel. The obtained results put into evidence that the presence of salt provokes a dramatic decrease on metal uptake. Increasing the ionic strength of K_2SO_4 from 0 to 10 g L^{-1} result in a decrease of the amount of cadmium sorbed from 51.99

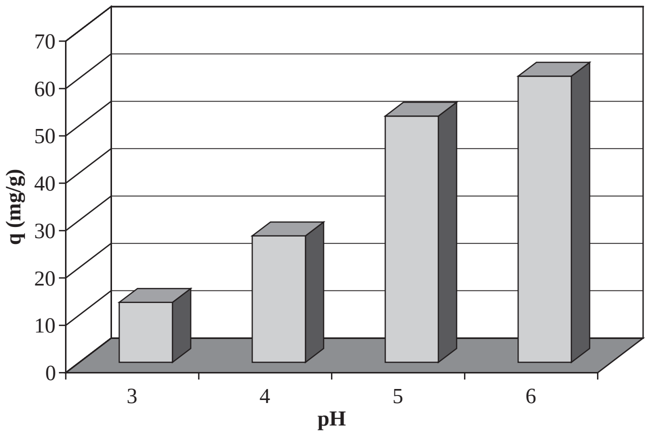

Fig. 3. Effect of solution pH on the sorption of cadmium by melon peel (conditions: 500 mL of cadmium solution, initial concentration 100 mg L^{-1}, sorbent mass: 0.5 g, stirring speed 400 rpm, pH 3–6, contact time 180 min, temperature 25°C).

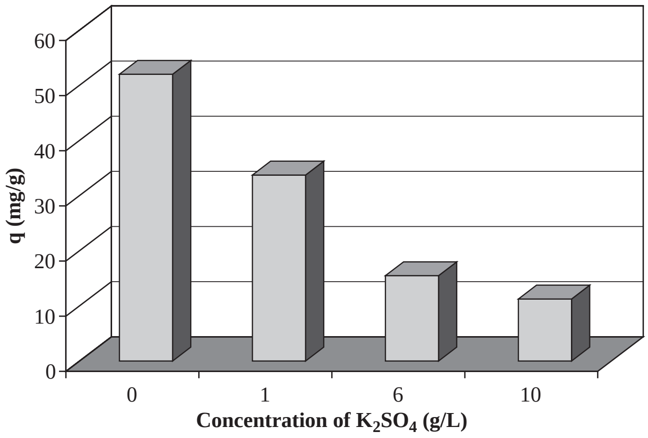

Fig. 4. Effect of ionic strength on the sorption of cadmium by melon peel (conditions: 500 mL of cadmium solution, initial concentration 100 mg L^{-1}, sorbent mass: 0.5 g, stirring speed 400 rpm, pH 5, contact time 180 min, temperature 25°C).

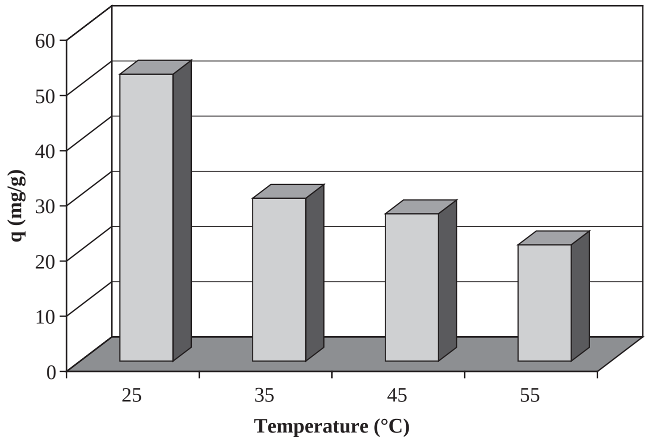

Fig. 5. Effect of temperature on the sorption of cadmium by melon peel (conditions: 500 mL of cadmium solution, initial concentration 100 mg L^{-1}, sorbent mass: 0.5 g, stirring speed 400 rpm, pH 5, contact time 180 min, temperature 25–55°C).

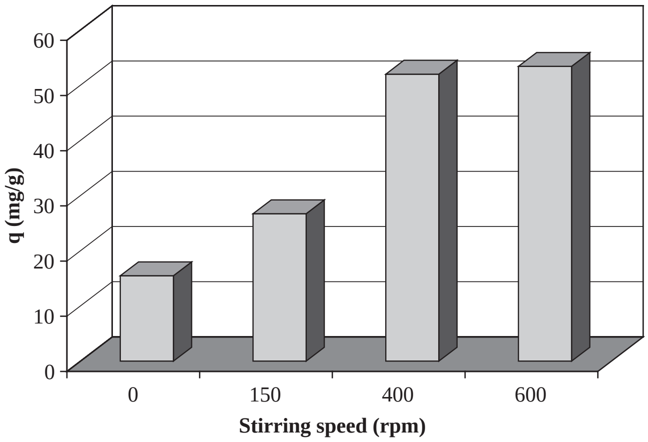

Fig. 6. Effect of stirring speed on the sorption of cadmium by melon peel (conditions: 500 mL of cadmium solution, initial concentration 100 mg L^{-1}, sorbent mass: 0.5 g, stirring speed 0–600 rpm, pH 5, contact time 180 min, temperature 25°C).

to 11.24 mg g^{-1}, respectively. The decrease in metal uptake could be due to competitive uptake of K^+ ions with cadmium cations. Additionally, the excess of K^+ cations may inhibit the approach of cadmium ions to the active sites of the sorbent. Another reason is the influence of the great ionic strength on the activity coefficient of cadmium, which reduce its transfer to the sorbent surface.

3.5. Effect of temperature

The effect of temperature on the sorption of cadmium by melon peel was investigated by varying the temperature from 25 to 55°C (Fig. 5). The sorption of metal ion was found to gradually decrease with the increase of temperature. The amount of cadmium sorption decreased from 51.99 to 21.08 mg g^{-1} when the temperature was increased from 25 to 55°C. This indicates that the sorption of cadmium by melon peel is an exothermic process. The decrease in sorption with the rise in temperature may be due to the weakening of sorptive forces between the active sites of the sorbent and sorbate species [19]. Additionally, this may be attributed to a relative increase in the escaping tendency of the solute from the solid phase to the bulk phase with the rise in temperature of the solution [20]. Temperature can affect several aspects of sorption: (i) the solute solubility; (ii) the swelling capacity of the sorbent; and (iii) the equilibrium position in relation with the exothermicity of the sorption phenomenon.

3.6. Effect of stirring speed

Fig. 6 shows the sorption of cadmium by melon peel at different stirring speed, ranging from 0 (without stirring) to 600 rpm. The amount of cadmium sorption capacity increased from 15.46 to 51.99 mg g^{-1} with increasing stirring speed from 0 to 400 rpm. This can be explained by the fact that increasing stirring speed reduced the film boundary layer surrounding particles, thus increasing the external film transfer coefficient and the driving force, and hence the sorption capacity. The change in the amount of cadmium sorption was insignificant compared to the dissipated energy when the stirring speed increases from 400 to 600 rpm.

3.7. Isotherm analysis

Sorption properties and equilibrium data, commonly known as sorption isotherms, describe how sorbate ions interact with sorbent particles and are thus critical in optimizing the use of solid materials. The analysis of the isotherm data by fitting them to different isotherm models is an important step to find the suitable model that can be used for design purpose. Three isotherms were tested for their ability to describe the experimental results, namely the Langmuir isotherm, the Freundlich isotherm and the Temkin isotherm.

Langmuir model [21], based on the assumption of ideal monolayer sorption on a homogenous surface, suggests a monolayer sorption, with no lateral interaction between the sorbed molecules. The linear form of Langmuir model is represented as follows:

$$\frac{C_e}{q_e} = \frac{1}{q_m} C_e + \frac{1}{b q_m}, \tag{3}$$

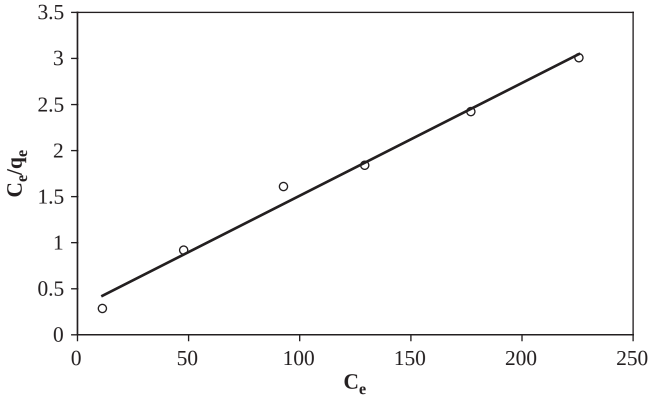

Fig. 7. Langmuir isotherm for the sorption of cadmium by melon peel at 25°C.

where C_e (mg L^{-1}) is the equilibrium concentration of the sorbate, q_e (mg g^{-1}) is the amount of sorbate per unit mass of sorbent, q_m (mg g^{-1}) and b (L mg^{-1}) are Langmuir constants related to sorption capacity and rate of sorption, respectively. The linear plot of specific sorption (C_e/q_e) against the equilibrium concentration (C_e) (Fig. 7) shows that the sorption obeys the Langmuir model. The Langmuir constants q_m and b were determined from the slope and intercept of the plot and are presented in Table 1. The determination coefficient value suggests that the Langmuir isotherm provides a good fit to the isotherm data.

The essential characteristics of the Langmuir isotherm can be expressed in terms of a dimensionless constant separation factor R_L that is given by Eq. (4) [22].

$$R_L = \frac{1}{1 + bC_0}, \tag{4}$$

Table 1
Isotherm parameters for the sorption of cadmium by melon peel at 25°C

Isotherm	Parameters
Langmuir	
b (L mg^{-1})	42.70×10^{-3}
q_m (mg g^{-1})	81.97
R^2	0.9876
Freundlich	
N	4.47
K_F ($mg^{1-\frac{1}{n}}L^{\frac{1}{n}}g^{-1}$)	22.41
R^2	0.9701
Temkin	
a_t (L mg^{-1})	1.76
b_t (J mol^{-1})	200.06
R^2	0.9413

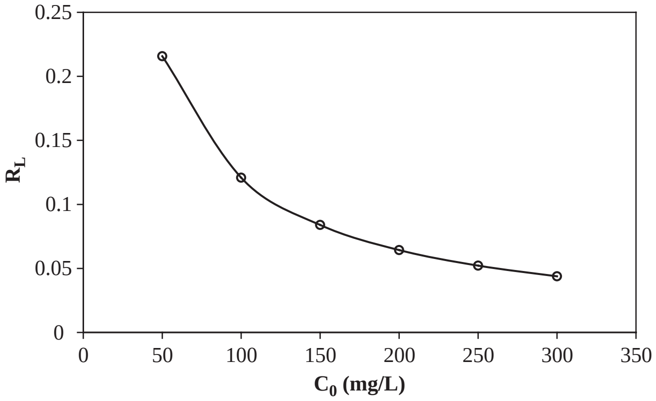

Fig. 8. Separation factor for the uptake of cadmium by melon peel at 25°C.

where C_0 (mg L^{-1}) is the initial concentration of sorbate and b (L mg^{-1}) is Langmuir constant. The parameter R_L indicates the nature of shape of the isotherm accordingly:

$R_L > 1$ unfavorable sorption
$0 < R_L < 1$ favorable sorption
$R_L = 0$ irreversible sorption
$R_L = 1$ linear sorption

The values of R_L versus initial cadmium concentration are presented in Fig. 8. It was observed that the value of R_L in the range of 0 to 1 at all initial metal concentrations confirms the favorable uptake of cadmium process. Also sorption was found to be more favorable at higher concentrations.

The Freundlich isotherm [23] is used for non-ideal sorption on heterogeneous surfaces. The heterogeneity is caused by the presence of different functional groups on the surface, and also by various mechanisms of sorbent–sorbate interactions. The linear form of the Freundlich isotherm is represented by the following equation:

$$\ln q_e = 1/n \, \ln C_e + \ln K_F, \tag{5}$$

where K_F ($mg^{1-\frac{1}{n}}L^{\frac{1}{n}}g^{-1}$) is roughly an indicator of the sorption capacity and n is the sorption intensity. Thus the constants can be determined as shown in Fig. 9. Values of K_F and n were determined as 22.41 and 4.47, respectively, at 25°C with R^2 of 0.9701. The magnitude of the exponent n gives an indication on the favorability of sorption. It is generally stated that values of n in the range 2–10 represent good, 1–2 moderately difficult, and less than 1 poor sorption characteristics [24]. The result shows that the value of n is greater than 2 indicating that the metal is favorably sorbed by melon peel. This is in agreement with the

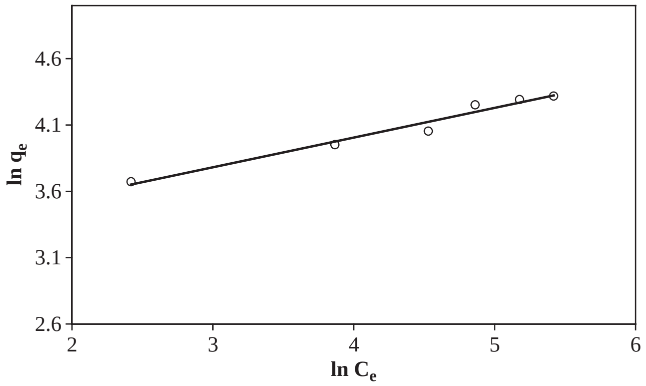

Fig. 9. Freundlich isotherm for the sorption of cadmium by melon peel at 25°C.

findings regarding to R_L value. The magnitude of Freundlich constant indicates good uptake of cadmium from aqueous solution.

The Temkin isotherm [25] is based on the assumption that the heat of sorption would decrease linearly with the increase of coverage of sorbent. The linear form of the Temkin equation can be described by

$$q_e = \frac{R_g T}{b_t} \ln a_t + \frac{R_g T}{b_t} \ln C_e, \tag{6}$$

where b_t (J mol^{-1}) is the Temkin constant related to the heat of sorption, a_t (L mg^{-1}) is the Temkin isotherm constant, R_g (8.314 J mol^{-1} K^{-1}) the gas constant and T (K) the absolute temperature. The sorption data can be analyzed according to Eq. (6). A plot of q_e versus ln C_e (Fig. 10) enables the determination of the constants a_t and b_t which are listed in Table 1. The determination coefficient of Temkin isotherm equation is lower than that obtained for the Langmuir and the Freundlich isotherms.

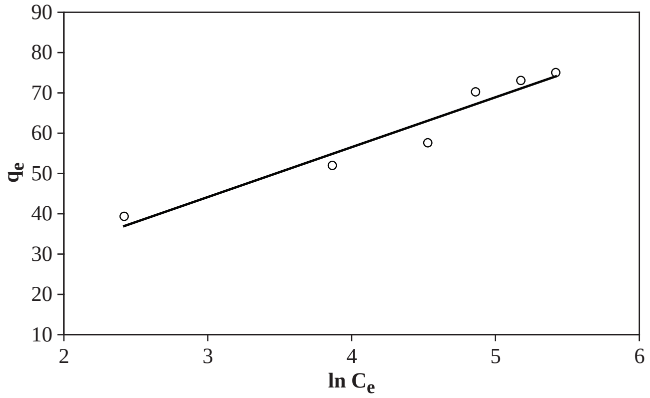

Fig. 10. Temkin isotherm for the sorption of cadmium by melon peel at 25°C.

Table 2
Comparison between different sorbents for their maximum uptake capacity of cadmium ions

Sorbent	pH	q_m (mg g^{-1})	References
Melon peel	5	81.97	This work
Caladium bicolor	5	73.62	[31]
Sawdust	5	68.79	[32]
Crab shell	5	33.72	[33]
Petiolar sheath palm	4	10.8	[34]

From Table 1 and in view of the values of determination coefficient, it can be concluded that the Langmuir isotherm model was more suitable for the experimental data than the Freundlich and the Temkin isotherms at 25°C and in the studied initial concentration range. This indicates that the sorption of cadmium by melon peel takes place as monolayer sorption on a surface with homogeneous distribution of active sites.

To assess the potential of melon peel, a comparative evaluation of the sorption capacities of various types of sorbents for the sorption of cadmium is shown in Table 2. It can be concluded that melon peel is very effective for this purpose. It should be noted that the values reported for cadmium removal capacity have only a relative meaning because of different experimental conditions.

3.8. Sorption kinetics

The kinetics of cadmium sorption by melon peel was studied with respect to different initial concentrations. Kinetic models are used to determine the rate of the sorption process. Three kinetic models: pseudo-first-order, pseudo-second-order and intraparticle diffusion models were used to investigate the sorption process of cadmium by melon peel. Lagergren proposed a method for sorption analysis which is the pseudo-first-order kinetic equation [26] in the form

$$\ln (q_e - q) = \ln q_e - K_1 t, \tag{7}$$

where K_1 (min^{-1}) is the pseudo-first-order rate constant, q_e (mg g^{-1}) is the amount of cadmium sorbed at equilibrium and q (mg g^{-1}) is the amount of cadmium on the surface of melon peel at any time.

Since $q = 0$ at $t = 0$, the initial rate of sorption can be calculated from Eq. (7) as follows

$$h_1 = K_1 q_e. \tag{8}$$

The values of K_1 and q_e can be determined by the slope of linear plots of ln(q_e – q) versus t (Fig. 11). The parameters of the pseudo-first-order model are summarized

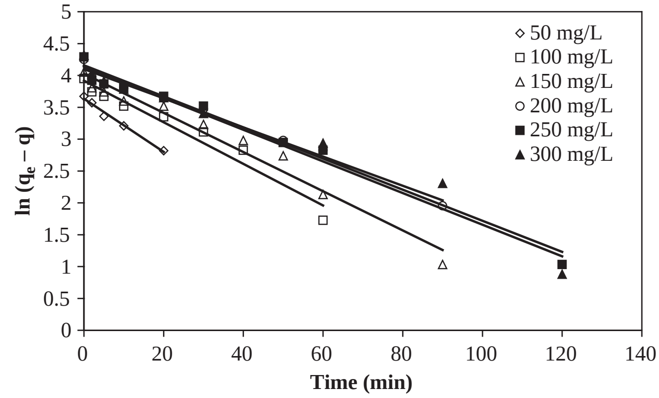

Fig. 11. The fitting of pseudo-first-order model for cadmium sorption by melon peel for different initial concentrations at 25°C.

in Table 3. The values of determination coefficient for the plots were in the range 0.9537–0.9852. However, although the coefficient of determination values are reasonably high, the calculated sorption capacity values obtained from this kinetic model do not give reasonable values compared with experimental sorption capacity. This finding suggested that the sorption process does not follow the pseudo-first-order sorption rate expression of Lagergren.

The sorption kinetics can also be described by the linearized form of the pseudo-second-order model [27,28]

$$\frac{t}{q} = \frac{1}{K_2 q_e^2} + \frac{1}{q_e} t, \tag{9}$$

where K_2 (g mg^{-1} min^{-1}) is the pseudo-second-order rate constant. The q_e and K_2 values can be calculated from the slope and intercept of the plots t/q versus t.

By plotting t/q against t for different initial cadmium concentrations (Fig. 12), a straight line was obtained in all cases and using Eq. (9) the pseudo-second-order rate constant (K_2) and q_e values were determined from the plots. The pseudo-second-order rate constants K_2 and the corresponding linear regression determination coefficients are given in Table 3. The determination coefficient values were found to be in the range 0.9942–0.9961. Moreover, the variations between the calculated q_e and experimental q_e were very minimal for this model. Therefore, it can be concluded that the pseudo-second-order kinetic model provided a better fit for the sorption of cadmium by melon peel at different initial cadmium concentrations compared to the pseudo-first-order model.

Since neither the pseudo-first-order equation nor the pseudo-second-order model can identify the diffusion mechanism, the kinetic results were further analyzed by the intraparticle diffusion model. The most commonly used technique for identifying the mechanism involved in the sorption process is by fitting an intraparticle diffusion plot. It is an empirically found functional relationship, common to the most sorption processes, where uptake varies almost proportionally with $t^{1/2}$ rather than with the contact time t. According to the theory proposed by Weber and Morris [29]:

$$q = K_{pd} t^{1/2} + C_{pd}, \tag{10}$$

where K_{pd} (mg g^{-1} min$^{-1/2}$) the rate parameter is obtained from the slope of the straight line of q versus $t^{1/2}$ (Fig. 13) whereas C_{pd} is the intercept of the plot which gives an idea about the thickness of boundary layer. The values of K_{pd}, C_{pd} and determination coefficient obtained for the plots are given in Table 4. The intercept of the plot gives an idea about the thickness of boundary layer, i.e., the larger the intercept, the greater the boundary layer effect. If intraparticle diffusion occurs, then q versus $t^{1/2}$ will be linear and if the plot passes through the origin, then the rate limiting

Table 3

Comparison of the parameters of the pseudo-first-order and pseudo-second-order models for the sorption of cadmium at various initial concentrations (conditions: 500 mL of cadmium solution, initial concentration 50–300 mg L^{-1}, sorbent mass: 0.5 g, stirring speed 400 rpm, pH 5, temperature 25°C)

C_0 (mg L^{-1})	$q_{e\ exp}$ (mg g^{-1})	Pseudo-first-order model				Pseudo-second-order model			
		K_1 (min^{-1})	$q_{e\ calc}$ (mg g^{-1})	h$_1$ (mg g^{-1} min^{-1})	R^2	K_2 (g mg^{-1} min^{-1})	$q_{e\ calc}$ (mg g^{-1})	h_2 (mg g^{-1} min^{-1})	R^2
50	39.34	0.0417	37.90	1.580	0.9852	2.116×10^{-3}	41.67	3.674	0.9961
100	51.99	0.0326	50.33	1.641	0.9537	0.983×10^{-3}	56.50	3.138	0.9950
150	57.61	0.0307	56.10	1.722	0.9692	0.810×10^{-3}	62.89	3.204	0.9942
200	70.25	0.0229	60.26	1.380	0.9832	0.676×10^{-3}	76.34	3.940	0.9944
250	73.07	0.0248	62.78	1.557	0.9809	0.695×10^{-3}	78.74	4.309	0.9948
300	75.04	0.0244	63.99	1.561	0.9603	0.735×10^{-3}	80.65	4.781	0.9961

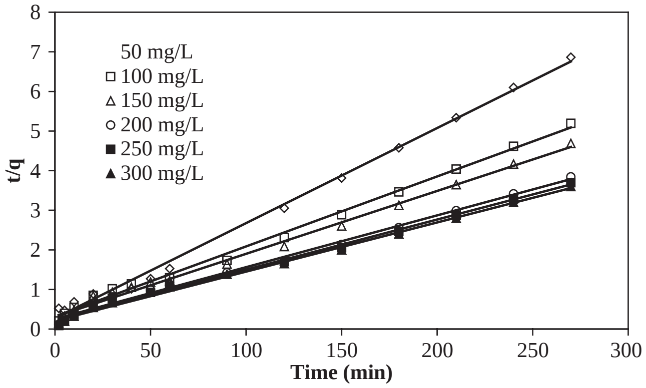

Fig. 12. The fitting of pseudo-second-order model for cadmium sorption by melon peel for different initial concentrations at 25°C.

process is only due to the intraparticle diffusion. Otherwise, some other mechanism along with intraparticle diffusion is also involved [30]. It can be seen from Fig. 13 and Table 4 that the regression was linear, but the plot did not pass through the origin, suggesting that sorption involved intraparticle diffusion, but that was not the only rate-controlling step. Other mechanisms may control the sorption rate.

4. Conclusion

The present study shows that melon peel can be used as a sorbent for the removal of cadmium from aqueous solutions. The sorption of cadmium was found to be dependent on initial concentration, sorbent dose, pH, temperature, ionic strength, stirring speed and temperature. Results indicate an increase in uptake by the sorbent with increasing initial cadmium concentration, solution pH and contact time. The amount of cadmium sorption decreases with increasing temperature, ionic strength and sorbent dose. Mixing rates up to 400 rpm increase uptake, however, higher mixing rates result in insignificant enhancement of uptake compared to the dissipated energy. The sorption kinetics can be predicted by pseudo-second-order kinetic model. Langmuir, Freundlich and Temkin isotherm models were used to interpret the sorption phenomenon of the sorbate. The equilibrium sorption data for cadmium was best represented by the Langmuir isotherm with maximum sorption capacity of 81.97 mg g^{-1}. It may be concluded that melon peel is an effective sorbent for the removal of cadmium from aqueous solutions.

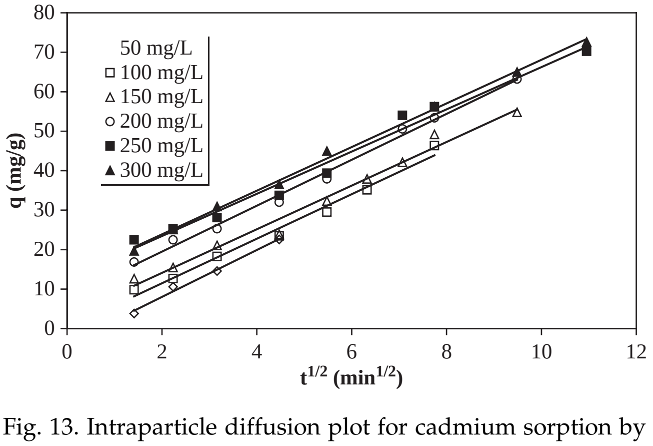

Fig. 13. Intraparticle diffusion plot for cadmium sorption by melon peel for different initial concentrations at 25°C.

Table 4
Intraparticle diffusion parameters and determination coefficients for the sorption of cadmium by melon peel at 25°C

C_0	K_{pd} (mg g^{-1} min$^{-1/2}$)	C_{pd}	R^2
50	5.95	–3.89	0.9891
100	5.64	0.18	0.9843
150	5.53	3.05	0.9826
200	5.82	7.86	0.9929
250	5.35	12.74	0.9804
300	5.53	12.82	0.9974

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References

[1] B. Volesky, Biosorption of heavy metals, CRC Press, 1990, Boca Raton, FL.

[2] J. Wase and C.F. Forster, Biosorbents for Metal Ions. Taylor & Francis, 1997, London.

[3] US Environmental Protection Agency, Integrated risk information system (IRIS) on cadmium. National Centre for Environment Assessment, Office of Research and Development, 1999, Washington, DC.

[4] S.H. Hasan, M. Talat and S. Rai, Sorption of cadmium and zinc from aqueous solutions by water hyacinth (*Eichchornia crassipes*), Bioresour. Technol., 98 (2007) 918–928.

[5] Z. Aksu and İ. Alper İşoğlu, Removal of copper (II) ions from aqueous solution by biosorption onto agricultural waste sugar beet pulp, Process Biochem., 40 (2005) 3031–3044.

[6] C.H. Weng and Y.F. Pan, Adsorption of a cationic dye (methylene blue) onto spent activated clay, J. Hazard. Mater., 144 (2007) 355–362.

[7] V.K. Gupta, C.K. Jain, A. Imran, M. Sharma and V.K. Saini, Removal of cadmium and nickel from wastewater using bagasse fly ash—a sugar industry waste, Water Res., 16 (2003) 4035.

[8] C.V. Taty-Costodes, H. Fauduet, C. Porte and A. Delacroix, Removal of Cd(II) and Pb(II) ions, from aqueous solutions, by adsorption onto sawdust of pinus sylvestris, J. Hazard. Mater., B105 (2003) 121–142.

[9] K. Upendra and B. Manas, Sorption of cadmium from aqueous solution using pretreated rice husk, Bioresour. Technol., 97 (2006) 104–109.

[10] K. S. Low, C. K. Lee and S. C. Liew, Sorption of cadmium and lead from aqueous solutions by spent grain, Process Biochem., 36 (2000) 59–64.

[11] S. Al-Asheh and Z. Duvnjak, Sorption of cadmium and other heavy metals by pine bark, J. Hazard. Mater., 56 (1997) 35–51.

[12] I. Ghodbane, L. Nouri, O. Hamdaoui and M. Chiha, Kinetic and equilibrium study for the sorption of cadmium(II) ions from aqueous phase by eucalyptus bark, J. Hazard. Mater., 152 (2008) 148–158.

[13] K.K. Singh, R. Rastogi and S.H. Hasan, Removal of cadmium from wastewater using agricultural waste ''rice polish'', J. Hazard. Mater., A121 (2005) 51–58.

[14] Y.S. Ho and C.C. Wang, Pseudo-isotherm for the sorption of cadmium ion onto tree fern, Process Biochem., 39 (6) (2004) 761–765.

[15] T. Vaughan and C.W. Seo, W.E. Marshall, Removal of selected metal ions from aqueous solutions using modified corncobs, Bioresour. Technol., 78 (2001) 133–139.

[16] L. Nouri and O. Hamdaoui, Ultrasonication-assisted sorption of cadmium from aqueous phase by wheat bran, J. Phys. Chem. A, 111 (2007) 8456–8463.

[17] L. Nouri, I. Ghodbane, O. Hamdaoui and M. Chiha, Batch sorption dynamics and equilibrium for the removal of cadmium ions from aqueous phase using wheat bran, J. Hazard. Mater., 149 (2007) 115–125.

[18] S. Schiewer and S.B. Patil, Pectin-rich fruit wastes as biosorbents for heavy metal removal: Equilibrium and kinetics, Bioresour. Technol., 99 (2008) 1896–1903.

[19] K.K. Pandey, G. Prasad and V.N. Singh, Use of wallastonite for the treatment of Cu (II) rich effluents. Water Air Soil Pollut., 27 (1986) 287–296.

[20] D.B. Singh, D.C. Rupainwar,G. Prasad and K.C. Jayaprakas, Studies on the Cd(II) removal from water by adsorption, J. Hazard. Mater., 60 (1998) 29.

[21] I. Langmuir, The adsorption of gases on plane surfaces of glass, mica and platinum, J. Am. Chem. Soc., 40 (1918) 1361–1403.

[22] K.R. Hall, L.C. Eagleton, A. Acrivos and T. Vermeulen, Pore and solid diffusion kinetics in fixed-bed adsorption under constant pattern conditions. Ind. Eng. Chem. Fundam., 5 (1966) 212–223.

[23] H.M.F. Freundlich, On the adsorption in solution, J. Phys. Chem., 57 (1906) 385–470.

[24] R.E. Treybal, Mass-transfer operations, 3rd edn., McGraw Hill, 1980.

[25] M.J. Temkin and V. Pyzhev, Recent modifications to Langmuir Isotherms, Acta Physiochim. USSR, 12 (1940) 217–222.

[26] S. Lagergren, About the theory of so-called adsorption of soluble substances, K. Sven. Vetenskapsakad. Handl., 24 (4) (1898) 1–39.

[27] Y.S. Ho and G. McKay, Sorption of dye from aqueous solution by peat, Chem. Eng. J., 70 (1998) 115–124.

[28] Y.S. Ho and G. McKay, The kinetics of sorption of divalent metal ions onto sphagnum moss peat, Water Res., 34 (2000) 735–742.

[29] W.J. Weber Jr. and J.C. Morris, Kinetics of adsorption on carbon from solution, J. Sanitary Eng. Div., 89 (1963) 31–59.

[30] V. Poots, G. McKay and J.J. Healy, The removal of acid dye from effluent using natural adsorbents: peat, Water Res., 10 (1976) 1061–1066.

[31] M. Horsfall and A.I. Spiff, Effect of metal ion concentration on the biosorption of Pb^{2+} and Cd^{2+} by Caladium bicolor (wild cocoyam), African J. Biotechnol., 4 (2005) 91–196.

[32] S.Q. Memon, N. Memon, S.W. Shah, M.Y. Khuhawar and M.I. Bhanger, Sawdust – a green and economical sorbent for the removal of Cd(II) ions, J. Hazard. Mater., 139 (2007) 116–121.

[33] D.S. Kim, The removal by crab shell of mixed heavy metal ions in aqueous solution, Bioresour. Technol., 87 (2003) 355–357.

[34] M. Iqbal, A. Saeed and N. Akhtar, Petiolar felt sheath of palm: a new biosorbent for the removal of heavy metals from the contaminated water, Bioresour. Technol., 81 (2002) 151–153.