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REMOVAL OF CADMIUM (II) FROM WATER BY ACTIVATED CARBON PREPARED FROM AVOCADO PEEL

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Abstract

The present work describes the biosorption potential of low cost and easily available avocado peel for the adsorptive removal of cadmium (II) metal. Avocado peel was treated chemically with ascorbic acid and physical treatment by increasing temperature to 500 °C. The adsorption behavior of avocado peel has been investigated as a function of appropriate equilibrium time, adsorbent dose, temperature, and pH in a batch system. Studies showed the modified peel is adsorbing more than non modified. The pH of aqueous solutions effects the heavy metals removal of cadmium. The maximum value of removal appeared at pH 5. The isothermal data of Cd (II) sorption conformed well to the Langmuir model. The equilibrium of removal of heavy metals was reached within 60 min. The removal process could be described by the pseudo-second-order kinetic model. In conclusion the activated carbon prepared from avocado peel is better than avocado peel only.

Keywords: biosorption, heavy metals, Activated carbon, avocado peel.

INTRODUCTION

Heavy metals released by a number of industrial processes in the environment are some of the major pollutants of soil, fish and water resources. The concentration of these contaminants must be decreased to meet any growing legislative standards and improved where feasible. Different physicochemical techniques for removing heavy metals from water include chemical precipitation, ion exchange, extraction, membrane processes, metal hydroxides; reverse osmosis, electrochemical treatment and adsorption are used. Most of these methods have several disadvantages, such as continuous input of chemicals, high cost, and toxic sludge generationor incomplete metal removal (Aydın *et al*, 2008 and Asgher & Bhatti, 2010,). Biosorption is the process of metal ions removal by biological materials and the biomaterials have been considered as potential sorbents for heavy metal removal, representing an important breakthrough (Chojnacka *et al.*, 2005). This technology, utilizing natural materials or industrial and agricultural wastes to remove heavy metals from aqueous media, offers cost-effective and an efficient alternative compared to usual chemical and physical remediation and decontamination methods. For improving their physicochemical property or enhancing their sorption capacity, some agricultural wastes had been subjected to various chemical modifications (Wong *et al.*, 2003, Shukla *et al.*, 2006, Anirudhan *et al.*, 2007 and Namasivayam & Sureshkumar, 2009).

Cadmium is a heavy metal with an extremely toxicity at very low concentrations. It has unknown required purpose in the body. Cadmium toxicity causes a lot of health problems including the main killer diseases like cancer, heart disease and diabetes. Cadmium replaces zinc in many metallo-enzymes and several of the symptoms of cadmium toxicity can be traced to a cadmium caused zinc lack (Sahmoun *et al.*, 2005). In this work, the potential of avocado peel to be used in the removal of Cd (II) from aqueous solutions was investigated. Studies have included the effect of pH, effect of mass of sorbent, time contact, sorption isotherms and kinetic of sorption.

MATERIALS AND METHODS

Preparation of the biosorbent.

Avocado peel was used as a biosorbent for the biosorption of cadmium (II). Before the start of all experiments, they were properly

cleaned with deionised water and dried at 70 °C for 5h, ground in mail and sieving to particle sizes 0.3-0.6 mm. After the sieving the materials was divided to two parts. The first part was used as it is without any modification. The second part was treated chemically by 1.0 M ascorbic acid in the ratio of 1:10 (sorbent: ascorbic acid, w/v) at room temperature for one day. Treated sorbent was washed by deionised water, dried at oven 105 °C then dried at 70 °C for 5hr and sieving to 70 μ m. Treated avocado peel was then covered with aluminum foil and placed in alumina crucible. The alumina crucible was capped with an alumina cover to prevent oxidation. The alumina crucible was placed in a furnace and heated up to carbonization temperature 500 °C with a heating rate of 10 °C/ min. After 2 hours, the furnace was switched of and cooled at room temperature.

Preparation of the Sorbate.

Stock solution of cadmium has been prepared by dissolving the appropriate amount of cadmium chloride, in distilled water. Solutions of the desired concentrations were obtained by proper dilutions of the stock solution with double distilled water.

Batch sorption experiments.

Different amount of sorbents were added to aqueous solution of heavy metals in 50.0 mL bottle at the room temperature. The shaker (Rosi 1000) for 5h was used. After equilibrium the suspension of the adsorbent was separated from solution by micro filter. For adjusting the initial pH of solutions after addition of the biosorbent Na OH and HCL (0.1N) were used.

Instrumental.

Atomic adsorption spectrometer (AAS) operating was used. Each measurement was repeated triplicate. The pH measurements were

measured with controlled pH analyzer. Shaker was used for all adsorption experiments.

RESULTS AND DISCUSSION

pH.

The pH value of the metal solution plays an important role in the whole sorption process and particularly on the sorption capacity. The effect of pH on adsorption was studied in the range of 1-6 pH that was not influenced by the metal precipitation. Adsorption of Cd (II) with the variation of pH is shown in Fig.(1).

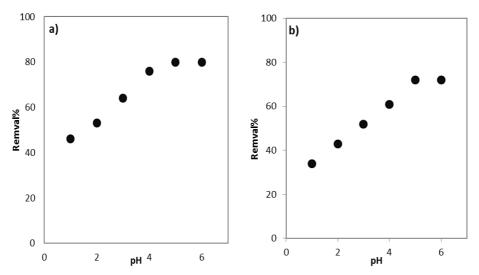


Fig. 1. Effect of pH on the amount sorbed of Cd (II) on to a) modified avocado peel b) non modified avocado peel

The results show that, the sorption is from 46 % to 74 % and from 34 % to 62 % for the modified and non-modified respectively. These results depict, that the pH significantly affects the extent of sorption by avocado peel. Any sorbent surface creates positive or negative charge on its surface. This charge is proportional to the pH of the solution, which surrounds the sorbent particles. The minimal values of the adsorption at law pH this may be due to competition between the protons and ions

release by absorbent of H^+ in the solution (Saeed *et al.*, 2005a and Saeed *et al.*, 2005b). This is because of their higher concentration and high mobility and partly to the fact that the solution pH influences the sorbent surface charge. At high pH values, the surface of sorbent particles may get negatively charged, which enhances the positively charged heavy metals cations through electrostatic forces of attraction.

Effect of sorbent mass.

The effect of a variation of sorbent mass on the sorption by avocado peel at room temperature $(25^{\circ}C)$ was studied in Fig. (2) by varying the sorbent amounts from 0.5 to 10 g/L.

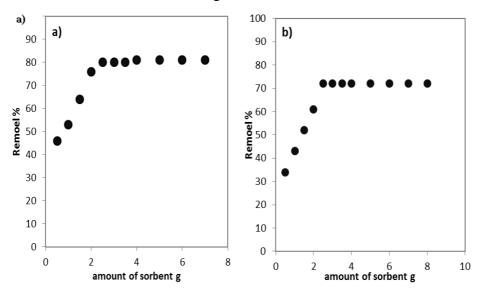


Fig. 2. Effect of the amount sorbent on the sorption process of Cd (II) on to a) modified avocado peel b) non modified avocado peel.

The adsorption of Cd (II) increases rapidly with an increase in the amount of sorbent due to greater availability of the surface area at higher concentrations of the adsorbents. A significant increase in uptake was observed when the dose was increased from 0.5 to 3.5 g/L. Any more addition of the adsorbent further than this did not cause any significant change in the adsorption (Preetha & Viruthagiri2007). From the results, it

is revealed that, within a certain range of initial metal concentration, the percentage of metal adsorption on sorbent is determined by the sorption capacity of the modified and non modified avocado peel from (44 -83 % and 36 -74 %,) respectively.

Sorption.

Adsorption from aqueous solutions involves concentration of solute on the solid surface. Sorption isotherms are usually determined under equilibrium conditions.

Freundlich.

The Freundlich isotherm is the first known equation explaining the sorption mechanism. This model is based on the assumption that the sorption process takes place by interaction of the molecules on the heterogeneous surfaces (Mahvi *et al.*, 2007). There is a logarithmic decline in the energy of biosorption with increase in the occupied binding sites. The non-linear equation is expressed as follows:

$$q_e = K_d C_e^{1/n}$$

Where: q_e = the amount of solute adsorbed per weight of adsorbent, C_e = the solute equilibrium concentration. K_d and 1/n= constants characteristic of the system. For linearization of the data, the Freundlich equation is written in logarithmic form:

$$\log q_{s} = \log K_{d} + \frac{1}{n} \log C_{s}$$

Plotting log q_e various log C_e a straight line is obtained with a slope of 1/n and log K_d is the intercept of log q_e at log (Ce=0), (Ce=1) (Fig.3).

	1/n	K _d	R ²
Modified	0.76	0.142	0.92
Non- modified	0.75	0.134	0.90

Table 1: Frendulich isotherm constants of removal of Cd (II) by avocado peel

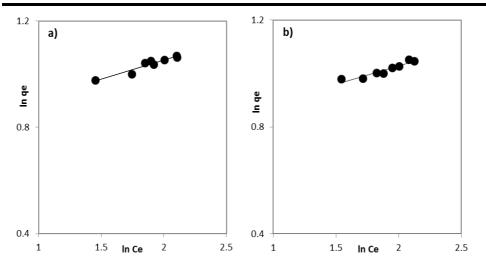


Fig. 3. Frendulich isotherm for adsorption of Cd (II) on to a) modified avocado peel b) non modified avocado peel.

High value of K_d indicate that the metal has been retained by the solid phase through sorption reactions, while low values of K_d indicate that large fraction of metal remains in solution. As shown in the table 1, K_d and 1/n of modified avocado peel are higher than non modified. Higher the value of 1/n will be the affinity between the water pollutant and the heterogeneity of the adsorbent sites. The 1/n value indicates the proportional distribution of energy sites and depends on the nature and strength of the adsorption process; for example, 1/n = 0.90 refers to the fact that 90% of the active adsorption sites have equal energy level (Lakshmi *et al.*, 2008).

Langmuir.

For adsorption from solution by solid adsorbents, Langmuir adsorption is expressed as:

$$q_{e} = \frac{bX_{m}C_{e}}{1 + bC_{e}}$$

Where X_m = the amount of solute adsorbed required for monolayer coverage of the surface,

b = a constant related to the heat of adsorption

This equation can be arranged in two forms namely:

$$\frac{1}{q_{\varepsilon}} = \frac{1}{x_m} + \left(\frac{1}{c_{\varepsilon}}\right) \left(\frac{1}{b X_m}\right)$$
(4)

and

$$\frac{c_e}{q_e} = \frac{1}{bX_m} + \frac{c_e}{X_m}$$
(5)

Table. 2. Langmuir isotherm constant of Cd (II) by avocado peel.

	b (L/mg)	X _m (mg/g)	\mathbf{R}^2
Modified	0.77	13.1	0.99
Non-modified	0.78	12.1	0.99

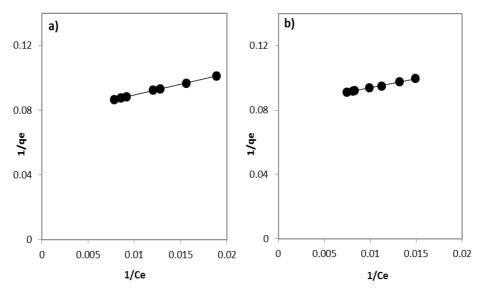


Fig. 4. Langmuir isotherm for adsorption of Cd (II) on to a) modified avocado peel b) non modified avocado peel.

By plotting C_e/q_e against C_e , a straight line is obtained having a slope $1/X_m$ and an intercept $1/bX_m$. By plotting $1/q_e$ versus $1/C_e$, straight line having a slope $1/bX_m$ and an intercept $1/X_m$ is obtained (Fig. 4).

The Langmuir isotherm equation was derived by assuming that there are only a fixed number of active sites obtainable for adsorption that only a monolayer is formed, and the adsorption is reversible and reaches an equilibrium condition. Therefore, it has been noted that, adsorption isotherms are of essential importance for the attributive of how molecules of pollutant interact with avocado peel surface, while the Freundlich isotherm does not predict saturation of solid surface by adsorbate (Gomes *et al.*, 2001). Most of the studies reported that the Langmuir isotherm is suitable for adsorption of heavy metals, which assume there is monolayer coverage. The experiments show that the Langmuir model fitted the results more than the Freundlich; therefore sorption follows the monolayer adsorption process.

Temkin isotherm.

The sorption data were analysed according to linear form of Temkin isotherm for the linear form of Temkin isotherm the qe is plotted against ln Ce the slope RT/b_t and the intercept RT/b_t ln A.

$$q_{\varepsilon} = \frac{RT}{b} \ln \left(AC_{\varepsilon} \right) (6)$$

A linear form of the Temkin isotherm can be expressed as:

$$q_{e} = \frac{RT}{b} \ln A + \frac{RT}{b} \ln C_{e}(7)$$

$$q_{e} = BlnA + BlnC_{e} (8)$$

Where $B = \frac{RT}{b}$, *T* is the absolute temperature (K), *R* is the universal gas constant (8.314 J/mol.K), *A* is the equilibrium binding constant (L/mg), and *b* is the variation of adsorption energy (kJ/mol). *B* is Temkin constant related to the heat of adsorption (kJ/mol). The Temkin adsorption isotherm model was chosen to evaluate the adsorption potentials of the adsorbent for adsorbates (Oliveira *et al.*, 2008).

The sorption data can be analyzed according to Eq. (7). Therefore, a plot of q_e versus ln C_e enables one to determine the constants A and B.

	A(L/mg)	b _t (Kj/mol)	\mathbf{R}^2
Modified	1.28	0.58	0.99
Non-modified	2.534	0.65	0.98

Table 3. Temkin isotherm constants of of Cd (II) by avocado peel.

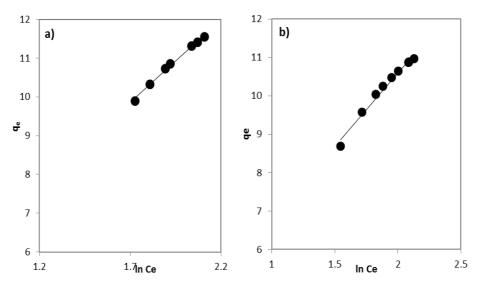


Fig. 5. Temkin isotherm for adsorption of Cd (II) on to a) modified avocado peel b) non modified avocado peel.

The values of the Temkin constants A and B were determined from Fig. (5) as shown in table (3). The correlation coefficient obtained showed that adsorption of Cd (II) also followed the Temkin model.

Kinetics Studies.

The rate of remove metal ions is of important significance for developing sorbent-based water technology. The necessary contact time to reach the equilibrium depends on the initial metals concentration and the sorption capacity, increases with the initial concentration in all cases. It can be shown the effect of contact time on the sorption of metals ions by avocado peel in Fig. (6).

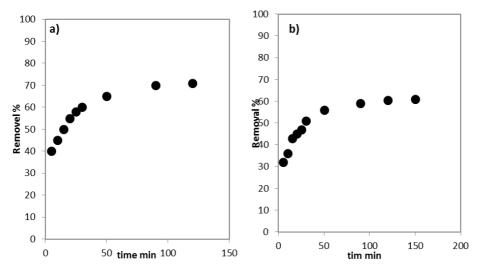


Fig. 6. The effect of time contact of Cd (II) on to a) modified avocado peel b) non modified avocado peel.

As seen from this figure, the contact time necessary to reach equilibrium is about 60 min and the amount of metals sorbed by avocado peel increases with time and, at some point in time, reaches a stable value beyond which no more is sorbed from solution. At this point, the sorbed amount of metals is in a state of dynamic equilibrium with the amount of the metals desorbing from the sorbent. The time necessary to reach this state of equilibrium of metals at the equilibrium time reflects the sorption capacity of the sorbent under the operating conditions (Nasernejad, *et al.*, 2005 and Krishnani *et al.*, 2008).

In order to investigate the controlling mechanism of the adsorption processes such as mass transfer and chemical reaction, the pseudo-firstorder and pseudo second- order equations are applied to model the kinetics of metals adsorption onto avocado peel.

To study the sorption kinetics of metal ions by sorbent the first order rate determined by the equation:

 $\frac{dq}{dt} = K_1(q_e - q_t) (9)$

Where q_e is the amount of adsorbed at equilibrium, q_t is the amount of adsorbed at any time t and K_1 is constant refers to sorption constant.

By making integrating at q=0 at t=0 and q_t=q_t at t=t

$$\log(q_e - q_t) = \log q_{e^{-\frac{K_1 t}{2.505}}}(10)$$

 Table 4.
 Pseudo-first-order kinetic parameters of Cd (II) by avocado peel.

	q _e (mg/g)	K_1 min ⁻¹	R ²
Modified	11.2	0.01	0.93
Non-modified	8.5	9x10 ⁻³	0.94

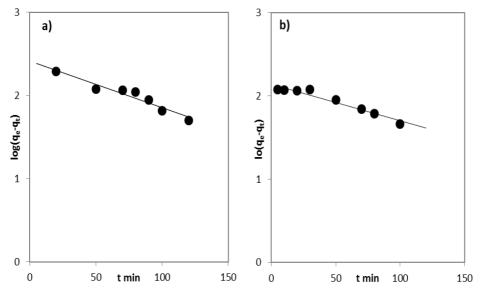


Fig. 7. shows pesudo first order kinetcs of Cd (II) on to a) modified avocado peel b) non modified avocado peel.

By plotting log (q_e-q_t) against t is straight line the slope is $K_1/2.303$ and intercept is log q_e . Where q_t and q_e are the adsorption capacity at time t (mg/g) and at equilibrium respectively, and k_1 (min⁻¹) is the pseudo-first order rate constant of the adsorption. This equation was applied to the present study. The rate constant k_1 and the correlation coefficients adsorption at different concentrations were calculated from the linear plots of log ($q_e - q_t$) versus t and the results were listed in (Table 4). From Fig. (7) the correlation coefficients of the pseudo-first-order kinetic model are low. For analyzed the data as pseudo-second-order which can describe by the Equation:

 $\frac{dq}{dt} = K_2 (q_e - q_t)^2 \ (11)$

Where K₂ is is rate constant (g/mg min)

$$\frac{dq}{(q_g - q_t)} = K_2 t \quad (12)$$

By integration this equation

$$\frac{t}{q} = \frac{1}{K_2 q_e^2} + \frac{1}{q_e} (13)$$

 Table 5. Pseudo-second-order kinetic parameters of Cd (II) by avocado peel.

	K^2 gmg ⁻¹ min ⁻¹	q _e mg/ g	\mathbf{R}^2
Modified	8.9x10 ⁻³	12.3	0.97
Non-modified	18.8x10 ⁻³	9	0.99

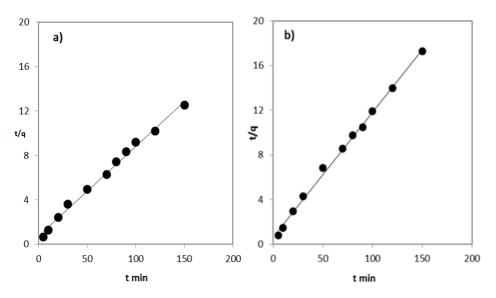


Fig. 8. Shows pesudo second first order kinetcs of Cd (II) on to a) modified avocado peel b) non modified avocado peel.

By plotting graph t/q versus t the slope is $1/q_e$ and intercepts $1/K_2$ q_e^2 . The plot of t/q versus t Fig. (8) should give a straight line if pseudo-second-order kinetics is applicable. q_e and k_2 can be determined from the slope and intercept of the plot, respectively.

At all initial concentrations studied, straight lines with very high correlation coefficients were obtained. The results showed that, Table (5), the adsorption of Cd (II) data was well represented by pseudo-second order. Kinetics results predicted that the effectiveness, suitability and applicability of pseudo-second order-kinetic model were more than that of pseudo-first order kinetic model and supported the assumption that the rate limiting step of adsorption on modified and non modified avocado peel may be chemical sorption or chemisorption. In chemisorption, the metal ions stick to the adsorbent surface by forming a chemical (usually covalent) bond and tend to find sites that maximize their coordination number with the surface (Cimino *et al.*, 2000 and Gholami *et al.*, 2006).

If the diffusion steps are slow, they become the rate-determining step in the binding to the active sites. The adsorption, in this case, is at random due to the existence of active sites with different energies (Chuah *et al.*, 2005). To determine the controlling rate of adsorption it can be the diffusion.

According to Boyd *et al* (1947) the effective particle diffusivity of metal ions can be calculated by the equation:

$$f(t) = \left[1 - exp\left(\frac{\pi^2 D_i t}{R^2}\right)\right]^{1/2} (14)$$

Where $F(t) = q_t/q_e$ is the fractional attainment of equilibrium at time t, D_i is the effective diffusion coefficient of adsorbates in the adsorbent phase (m²/s), r is radius of the adsorbent particle assumed to be spherical (m). By plotting ln [1/ (1–F(t))] versus t the slope will be $\pi^2 D_i / R^2$. The effective diffusivity is almost independent of C_o and the value of D_i largely depends on the properties of the adsorbent, and to some extent on the adsorbate . (Sirvastava *et al.*, 2007).

Reichenberg model.

The rate of sorption can be obtained from equation for the diffusion and mass transfer phenomena for the fast reaction, the sorption may be due to film diffusion.

If we applied the Reicherberg equation:

$$f(t) = \left(1 - \frac{6}{\pi^2}\right)e^{-BT}$$
(15)

The equation can be written:

 $B_t = -0.4977 [1 - f(t)] (16)$

The correlation is indicated that the sorption is film diffusion

By using $B_t = \frac{\pi^2 D_i}{R^2}$

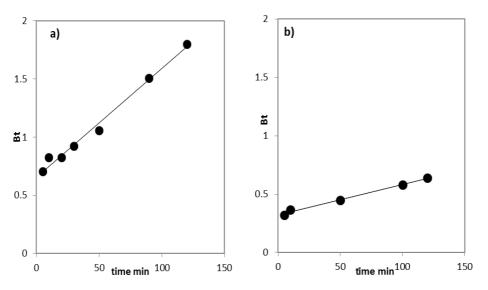


Fig. 9. Reicherberg isotherm for adsorption of Cd (II) onto a) modified avocado peel b) non modified avocado peel.

We can calculate D_i the effective diffusion coefficient (cm²/s). As shown in fig. (9) using equation applicable at F values, the blot of B_t versus t is linear deviate from origin. This means that, the adsorption is controlled by chemical reaction or external transport (film diffusion).

CONCLUSION

This study obviously propose that the use of avocado peel as biosorbents are much economical, effectual and more viable. They can be efficiently used to eliminate cadmium ions from aqueous solution. The various operational parameters observed during the process of investigations reveal that the contact time, sorbent mass, solution pH, and temperature govern the overall process of sorption. The sorption process followed pseudo-second-order rate kinetics. The Freundlich isotherm gives a worse fit of the equilibrium data. The biosorption performance of modified and non modified was also affected by initial amount of sorbent and contact time of the process. Better results were obtained at a contact time of 50 min and pH 5.

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إزالة عنصر الكادميوم من الماء بواسطة الكربون المعد من قشر الافوكادو إنجى صلاح الدين محمد الحداد

المعهد القومي لعلوم البحار والمصايد.

الملخص العربى

هذه الدراسه توصف قدره الامتصاص الحيوى لقشره الافكادو فى ازالة عنصر الكادميوم . فقد تمت معالجة قشره الافوكادو للحصول على الكربون كييميائيا بواسطه حمض الاسكروبيك و بزياده درجة الحراره. تم دراسه تاثير وقت تشبع و كمية الماده الماصه ودرجة الحمامضيه على قدره الامتصاصات الحيويه لإزالة عنصر الكادميوم. وجد ان درجة الحموضيه لها تاثير على عمليه الإزاله. وان اقصى كميه لإزالة عنصرالكادميوم عند درجة حموضه ^٥ . وقد اوضحت الدراسه ملائمة عمليه الامتصاص الحيويه لنموذج فروندليش و نموذج تمكين و لكن وجد ان النموذج الاكثر ملائمة هونموذج لانمجيور . ايضا وجد ان اقصى عملية إزاله تتم بعد اوزاله مى عليه الراسه الحركيه وجد انها تتبع النموذج الثانى للحركه الذى يؤيد ان عملية الإزاله هى علميه امتصاص كيميائيه. وفى النهايه فان قشره الافوكادو لها قدره على إزاله عنصر الكادميوم وان الكربون المعد من قشرة الافوكادو لديه تاثر اكبر على ازاله الكادميوم .