

## Use Of Palm Kernel Cake As Low Cost Biosorbent For The Removal Of Cadmium From Aqueous Solution

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**Abstract:** Heavy metals are a threat to human health and ecosystem. These days, great deal of attention is being given to green technologies for purification of water contaminated with heavy metal ions. Biosorption is one among such emerging technologies, which utilizes naturally occurring waste materials to sequester heavy metals from wastewater. Cadmium has hazardous impact on living beings; therefore, its removal through green and economical process is an important task. The aim of the present study is to utilize the locally available palm kernel cake as an biosorbent for cadmium removal from aqueous solution. Activated carbon prepared using from palm kernel cake was used for the experimental work. Batch experiments were performed at room temperature. The critical parameters studied were effects of pH, contact time, initial metal ion concentration and biosorbent dose on the biosorption of cadmium. The maximum biosorption was found to be 10.28 %. The kinetic data were found to best fit the pseudo-second order equation. High biosorption rates were obtained in the initial 30 min, and biosorption equilibrium was then gradually achieved in about 50 min. Biosorption increased with increase in pH for a range of 1 to 5. The equilibrium biosorption results closely followed the Langmuir isotherm. The values of constants were calculated from isotherms. The results indicated that activated palm kernel cake could be developed as a potential material to be used in green water treatment devices for removal of metal ions.

**Keywords:** Biosorption, activated palm kernel cake, cadmium, batch experiments, isotherms.

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### I. Introduction

Water pollution due to toxic heavy metals has been a major concern for scientists. Metals can be distinguished from other toxic pollutants, since they are non-biodegradable and can be concentrated and accumulated throughout the food chain and tissues. A variety of industries are responsible for the release of heavy metals into the environment through their effluents. Cadmium [Cd(II)] is a non-essential and a non-biodegradable metal ion which slowly accumulates in the body of living creatures, usually through food chain. It is one of the metals with the greatest potential hazard [1]. Cadmium enters in the water bodies through wastes generated from industrial processes such as casting of various cadmium alloy products, coating telephone cables, ceramics, metal electroplating, plastic manufacturing, metallurgical processes, industries of pigments and Cd/Ni batteries [2][3]. Cadmium is also found in domestic products like tobacco products, phosphate fertilizer, polyvinyl chloride (PVC) products, photo cells, petrol, oils, etc. [4].

Due to the toxicity and bioaccumulation of heavy metals various governmental agencies have imposed strict environmental legislations on waste water discharge. Government of India, has set Minimal National Standards (MINAS 2001) of 0.2 mg/l for Cd(II) for safe discharge of the effluents containing this metal ion into surface waters. Cd(II) is considered as a priority pollutant by the US Environmental Protection Agency. Environmental agencies set permissible limits for their respective levels in drinking water and other types of waters [5]. The permissible limit for Cd(II) as described by WHO is 0.005 mg/l (WHO 1971), this value is considered as the threshold for the protection of public health.

Cadmium is extremely toxic in relatively low dose [6]. It is an irritant to the respiratory tract. The harmful effects of cadmium include number of acute and chronic disorders [3]. "Itai-Itai" disease in Japan due to cadmium toxicity is well known. Cadmium is also responsible for kidney damage, renal disorder, high blood pressure, destruction of red blood cells [7], pulmonary emphysema, hypertension [8] and bone diseases

(osteomalacia, osteoporosis) [9]. Prolonged exposure to this pollutant can cause anemia and a yellow stain that gradually appears on the joints of the teeth.

There are several methods to treat the contaminated water; the selection of the treatment methods is based on the level of the waste and the cost of treatment [10]. Conventional methods for the removal of the heavy metal ions from wastewaters include chemical precipitation, electro flotation, ion exchange, reverse osmosis and biosorption onto activated carbon. These methods have been found to have certain limitations, since they often involve high capital and operational costs, incomplete removal [11] and may be associated with the generation of secondary waste which is again to be treated or to be safely disposed off [12].

Biosorption is very economical and effective process [13] [14]. Biosorption has advantages over the other methods because of its simple design with a sludge-free environment and can involve low investment in terms of both initial cost and land required. Activated carbon has been recognized as a highly effective biosorbent for the removal of heavy metal ion from the concentrated and dilute metal-bearing effluents [15] [16]. The high cost of activated carbon has prompted a search for cheaper substitutes. Many studies are recently devoted to use different biosorbent materials in processes involving the removal of Cd(II) ions from aqueous effluents with the aim of finding cheaper replacements for expensive conventional sorbent materials in different situations.

Natural materials that are available in large quantities and certain wastes from agricultural operations have potential to be used as low-cost biosorbents, as they represent unused resources, widely available and are environmentally friendly [17]. Many investigators have used inexpensive sorbent materials such as cassava waste [18], waste material [19], rice polish, and waste tea [20].

The efficiency of some plant materials to remove metals, which commonly occur in industrial effluents, has been studied. Among many biosorbents naturally available plant material can be used as an inexpensive method for metal ions removal from synthetic solutions and industrial effluents [21]. Olive cake [22], barley straw [23], Typha leaf powder [24], neem bark [25], mangosteen [26] coffee ground [27], peanut shell [28] plant material [14] has been used for such removals. The effects of factors such as contact time, pH and initial metal ion concentration were investigated [29] [1] [30] [31].

The use of activated carbon for biosorption of heavy metals has been emphasized recently, as it is considered to be a practically effective biosorbent for the removal of heavy metals at trace quantities [32]. Locally generated low cost materials have been tested in the production of activated carbon. Materials that are available in large quantities are wastes from agricultural operations [33]. Studies show that these materials have high carbon content and are effective as biosorbent in removing heavy metal pollutants from soil, water, air and has continued to increase over the years [34] [35]. Some of the materials used to prepare activated carbons include coconut husk and goat skin, hazel nut shells, rice husk and cashew nut shells [36] [37] [38] [39].

Present work deals with the evaluation of efficiency of activated palm kernel cake (PKC), which is the solid residue left behind after the extraction of oil from the kernels of the palm fruits. The global production of Palm Kernel Cake (PKC), a by-product of oil extraction from the nut of the palm tree, *Elaeis guineensis*, is ever increasing due to the tremendous growth of the oil palm industry in many parts of Asia and Africa (PORLA, 2000). World producers of palm kernel include Malayasia, Indonesia, Nigeria, Colombia, India, and Thailand. Palm trees are widely cultivated in the state of Andhra Pradesh, India. Several parts of the palm tree are efficiently used as sorbent in different forms for the removal of heavy metals [40] [41].

The low cost activated carbon prepared from palm kernel oil cake residue an agricultural waste is used for this work which has great potential to be used as biosorbent for heavy metals. Batch experiments were done to study the effects of variables such as contact time, pH, initial metal ion concentration and activated (PKC) dosage on Cd(II) removal. The applicability of different isotherm equations were tested by the data obtained and kinetics of biosorption was also studied. Process used in the present study is rather simple, cost-effective and easy to extrapolate at larger scale for a practical application of the removal of heavy metal ions.

## **II. Materials and Methods**

### **2.1 Preparation of the biosorbent**

In this work activated carbon was prepared from PKC. The cake was collected from the local palm oil distillery unit of Vizianagaram district in Andhra Pradesh, India. The cake was washed, sundried and heated in the oven for 12 hours at 55 °C. The dried PKC was carbonized in a muffle furnace at 800 °C for 2 hrs. The carbonized PKC was then soaked completely in a 25% concentrated solution of CaCl<sub>2</sub>, the gases that are formed due to exothermic reaction are allowed to escape for the first 3 min. and then covered with a lid for 24 hours. The sample is shifted to a drain tray where it is allowed to drain for 30 minutes and repeatedly washed with distilled water to remove traces of chemical. The washed sample is now placed in an oven for 2 hours at 110°C. The chemically activated carbon of PKC is then cooled and sealed in polythene bags to keep away from moisture and dust for further use.

## **2.2 Preparation of the metal solution**

Analytical reagent (AR) grade of chemicals were used for analysis. Appropriate amount of  $3\text{CdSO}_4 \cdot 8\text{H}_2\text{O}$  salts were dissolved in 1L of distilled water to prepare a stock solution of cadmium. The test solutions of cadmium ions were prepared by appropriate dilution of stock solution.

## **2.3 Batch biosorption studies**

Batch biosorption studies were carried out by adding known weight of activated PKC to a 50 ml solution of metal ion under different test conditions. The uptake capacity of Cd(II) was studied. The effect of solution pH, contact time, initial metal ion concentration and dosage of activated PKC were studied by varying any one of the process parameter and keeping the other parameters constant. The biosorption experiments of Cd(II) were conducted at  $30^\circ\text{C}$  in a thermostated rotary shaker at 120 rpm speed. The biosorbent was separated from the solution by filtration with Whatman filter paper number (0.45  $\mu\text{m}$ ). The residual metal ions were analyzed using an atomic biosorption spectrophotometer (nova 350 ®, Analytik Jena, Germany). Biosorption data obtained were applied for testing the applicability of different isotherms equations. Blank samples were also run under similar conditions. Each of the studies was conducted in triplicates and the mean value was used for calculations. The amount of Cd(II) sorbed per unit mass of the biosorbent was evaluated by using the following equations:

$$q_e = \frac{(C_0 - C_e) \times V}{W}$$

The percentage removal of Cd(II) was calculated as follows:

$$\% \text{ removal of Cd(II)} = \frac{C_0 - C_e}{C_0} \times 100$$

Where  $q_e$  is the amount of heavy metal ion adsorbed per unit weight of the biosorbent in mg/g, V is the volume of the solution treated in L,  $C_0$  is the initial concentration of metal ion in mg/L,  $C_e$  is the equilibrium metal ion concentration in mg/L and m is the mass of the biosorbent in grams.

## **2.4 Kinetics experiments**

In order to understand the biosorption kinetics on the process of biosorption, the agitation period was varied from 1 to 120 min using appropriate amount PKC in 50 ml of metal solution (10 g/l), without adjusting the pH. The samples were agitated on a rotary shaker. Samples were withdrawn from the solution at definite time intervals until equilibrium was reached. The residual metal ion concentration was calculated as mentioned earlier. Data obtained were applied to different kinetic equations.

# **III. Results and Discussions**

## **3.1 Effect of contact time on sorption efficiency**

The effect of contact time on the removal of Cd(II) biosorption on activated PKC was studied and the results were shown in the Fig.1. The data obtained from the biosorption of Cd(II) ions onto the activated PKC showed that the biosorption increased with increase in contact time. The biosorption of Cd(II) ions onto activated PKC was rapid for the first 30 min and equilibrium was nearly reached after 50 min. Hence, in the present work 50 min. was chosen as the equilibrium time. Generally the removal rate of sorbate is rapid initially, but it gradually decreases with time until it reaches equilibrium. The rate in percent of Cd(II) ions removal is higher in the beginning due to the large surface area of the biosorbent being available for the biosorption of the metals. As the surface sites become exhausted, the rate of uptake is controlled by the rate of transport from the exterior to the interior sites of the biosorbent particles [42]. It is also relevant that since active sorption sites in a system have a fixed number and each active sites can adsorb only one ion in a monolayer, the metal uptake by the sorbent surface will be rapid initially, slowing down as the competition for the decreasing availability active sites intensifies by the metal ions remaining in the solution [42]. Similar results for agitation time was observed with other biosorbents [43][44][45].

## **3.2 Effect of solution pH on sorption efficiency**

pH governs both the speciation of metals and the dissociation of active functional sites on the biosorbent [46]. It is one of the most important factors affecting metal biosorption onto sorbent, as hydrogen ions compete with the adsorbate [47]. This parameter is directly related with competition ability of hydrogen ions with metal ions to active sites on the activated PKC surface. Generally, metal biosorption involves complex mechanism of ion-exchange, chelation, biosorption by physical forces and ion entrapment inter and intrafibrillar capillaries and spaces of the structure of biosorbent. The effect of solution pH on the biosorption of Cd(II) ions onto activated PKC was evaluated within the pH range of 1-7 and the result is shown in Fig.2. Cd(II) removal

recorded its minimum values at pH 1. There was an increase in the percentage of Cd(II) removal with an increase in pH from 1 – 5 and showed marginal downward trend from pH 5. The maximum biosorption was found to be 83.55 % for Cd(II) ion at pH 5.

It may be due to the fact that active biosorption sites remain protonated at low pH, and become less available for metal ion biosorption. As pH increases, the concentration of H<sup>+</sup> ions decreases, hence they do not compete with metal ions on the biosorption sites, the more biosorbent surface with negative charge will easily attract the positively charged Cd(II) ions [48]. Optimum pH was found to be 5 for further experiments. At higher pH cadmium hydroxide starts precipitating from the solution, making actual biosorption studies impossible [49]. This result confirms the earlier report that the biosorption is pH-dependent [50]. Similar results of the same effect were observed for other biosorbents [51] [52][53].

### **3.3 Effect of initial cadmium ion concentration on sorption efficiency**

The Cd(II) uptake is particularly dependent on initial Cd(II) ion concentration. At low concentration values, Cd(II) ions are adsorbed at specific sites, while with increasing Cd(II) ion concentrations the specific sites are saturated with and exchange sites are filled. The different concentrations of Cd(II) ion solutions of 20, 50, 100, 150 and 200 mg/L were used and the experiments were performed at room temperature (30<sup>o</sup>C) with contact time of 50 min. Fig.3.shows the effect of metal concentration on the percent removal of Cd (II) ions. From the figure it was shown that the percentage Cd(II) ion biosorption decreased from 83.55 % to 44.9 % with the increment of initial Cd (II) ion concentration. At the lower Cd(II) ion concentration, the Cd(II) removal percentage was higher due to a large surface area of the activated PKC being available for the biosorption of Cd(II) ions. When the concentration of Cd(II) ion solution became higher, the Cd(II) removal percentage was lower because the available sites of the biosorption became less. At a higher initial Cd(II) ions concentration, the ratio of initial number of moles of Cd(II) ion to the available biosorption surface area was higher and as a result biosorption percentage was less. Identical effect for initial cadmium concentration was observed with other biosorbents [54][55]

### **3.4 Effect of activated PKC dosage on sorption efficiency**

The activated PKC dose is an important parameter because this determines the capacity of the activated PKC for a given initial Cd(II) ion concentration, Fig.4 shows the influence of activated PKC concentration on Cd(II) biosorption and it was examined by varying activated PKC dosage from 10 – 60 g/L while keeping the volume of Cd (II) ion solution constant at pH of 5. The percentage of Cd (II) ion removal steeply increases with the activated PKC dosage upto 20 mg/L. This result can be explained by the fact that the biosorption sites remain unsaturated during the biosorption whereas the number of sites available for biosorption sites increased by increasing the biosorbent dose. The maximum biosorption efficiency of Cd(II)ion onto activated PKC was found to be 85.1 % at activated PKC dosage of 20 g/L. There was a non-significant increase in the percentage removal of Cd(II) ion when the activated PKC increases beyond the 20 g/L. This suggests that after a certain dosage of biosorbent, the maximum biosorption is attained and hence the amount of ions remains constant even with further addition of dosage of biosorbent. Similar trend is reported for other biosorbents [56][57].

### **3.5 Effect of temperature on sorption efficiency**

Experiments were performed at different temperatures 20, 25, 30, 40, 60 and 90 <sup>o</sup>C at a concentration of 20 mg/L and pH of 5.0. The biosorption increased from 84% to 87.05% with the rise in temperature from 20 to 90 <sup>o</sup>C (Fig.5). The results showed that the sorption was endothermic in nature. Since sorbent is porous in nature and possibilities of diffusion of sorbate cannot be ruled out therefore, increase in the biosorption with the rise of temperature may be diffusion controlled which is endothermic process, i.e. the rise of temperatures favors the sorbate transport within the pores of the sorbent [58]. The increased sorption with the rise of temperature is also due to the increase in the number of the sorption sites generated because of breaking of some internal bonds near the edge of active surface sites of sorbent [59][60].

#### **3.5.1 Thermodynamic Parameters**

Thermodynamic parameters such as free energy ( $\Delta G^0$ ), enthalpy ( $\Delta H^0$ ) and entropy ( $\Delta S^0$ ) change of biosorption can be evaluated from the following equations [14,15]:

$$K_c = \frac{C_{Ae}}{C_e} \quad (3)$$

Where,  $K_c$  is the equilibrium constant and  $C_{Ae}$  and  $C_e$  (both in mg L<sup>-1</sup>) are the equilibrium concentrations for solute on the sorbent and in the solution, respectively. The  $K_c$  values are used in Eqs. (4) and (5) to determine the  $\Delta G^0$ ,  $\Delta H^0$  and  $\Delta S^0$ :

$$\Delta G^0 = -RT \ln K_c \quad (4)$$

The  $K_c$  may be expressed in terms of the  $\Delta H^0$  (K cal mol<sup>-1</sup>) and  $\Delta S^0$  (cal mol<sup>-1</sup> K<sup>-1</sup>) as a function of temperature:

$$\ln K_c = -\frac{\Delta H^0}{RT} + \frac{\Delta S^0}{R}$$

$$\log\left(\frac{q_e}{C_e}\right) = \frac{\Delta S^0}{R} - \frac{\Delta H^0}{RT} \quad (5)$$

Thermodynamic parameters such as free energy ( $\Delta G^0$ ), enthalpy ( $\Delta H^0$ ) and entropy ( $\Delta S^0$ ) are determined from the slope and intercept of the plots of  $\log(q_e/C_e)$  vs  $1/T$  Fig.6. The  $\Delta G^0$  values which were calculated using the biosorption of Cd(II) ion on activated PKC decreased, when the temperature was increased from 293 to 333 K which is shown in the figure. The process was thus endothermic in nature. The plot was used to compute the values of thermodynamic parameters. The value of enthalpy change ( $\Delta H^0$ ) and the entropy change ( $\Delta S^0$ ) recorded from this work are presented in Table 1. The Gibbs free energy  $\Delta G^0$  is small and negative but decreases with increase in temperature, indicating that the biosorption process lead to a decrease in Gibbs energy. The negative  $\Delta G^0$  value indicates that the process is feasible and spontaneous in the nature of biosorption; positive  $\Delta H^0$  value suggests the endothermic nature of biosorption and  $\Delta S^0$  can be used to describe the randomness at the activated PKC solution interface during the sorption. The thermodynamic parameters thus indicate that this biosorption process can be used for the removal of Cd(II) ions by activated PKC. A comparison of the thermodynamic parameters of other biosorbents are reported in Table 2.

### 3.6 Biosorption isotherm models

The analysis of the biosorption isotherms data by fitting them into different isotherm models is an important step to find the suitable model that can be used for design process. The experimental data were applied to the two-parameter isotherm models: Langmuir [65] and Freundlich [66].

An biosorption isotherm is characterized by certain constants; their values express the surface properties and affinity of the biosorbent. The experimental data for the uptake of cadmium ions were applied to both the Freundlich and Langmuir isotherm models as shown in Figs. 7 and 8, respectively. These Freundlich and Langmuir parameters compare well with those of other biosorbents that have been reported [1]. The values of the parameters show that activated PKC is a good biosorbent for the uptake of Cd(II) ions from aqueous solution.

The Langmuir expression is valid for monolayer biosorption onto a surface with finite number of identical sites (homogenous) without any interaction between adsorbed ions. The Langmuir expression or equilibrium ion removal is given by:

$$q_e = \frac{q_{\max} K_L C_e}{1 + K_L C_e} \quad (6)$$

Where  $q_e$  is Cd(II) ions concentration at equilibrium (mg/g);  $q_{\max}$ , maximum metal uptake per unit mass of activated PKC (mg/g) biosorption capacity;  $K_L$ , Langmuir constant (L/ $\mu$ g) related to energy of sorption;  $C_e$ , concentration of Cd(II) ions in aqueous phase. The values of  $q$  and  $K_L$  are the characteristics of the Langmuir model. They can be determined by linearizing equation (6).

$$\frac{C_e}{q_e} = \frac{1}{K_L q_m} + \frac{C_e}{q_m} \quad (7)$$

The  $K_L$  value, related to energy of biosorption, was used to evaluate the dimensionless parameter known as separation factor ( $R_L$ ) using the equation

$$R_L = \frac{1}{1 + K_L C_e}$$

where  $C_e$  is the equilibrium initial concentration ( $\mu$ g/L) of the adsorbate and  $K_L$  is the Langmuir equilibrium constant (L/ $\mu$ g).

The value of separation parameter  $R_L$  provides important information about the nature of biosorption. The value of  $R_L$  indicates the nature of Langmuir isotherm to be irreversible ( $R_L = 0$ ), favorable ( $0 < R_L < 1$ ), linear ( $R_L = 1$ ) or unfavorable ( $R_L > 1$ ).

The Freundlich expression is an empirical equation based on biosorption on a monolayer heterogeneous surface with interactions between adsorbed molecules and was used to estimate the biosorption capacity and intensity of metal ions towards the biosorbent.

Freundlich isotherm:

$$q_e = KC_e^{1/n} \quad (8)$$

Where, K is the Freundlich constant indicating the biosorption capacity and n is the Freundlich constant, indicating the biosorption intensity.

The above equation (8) is rearranged in linear form to give:

$$\log q_e = \log K + \frac{1}{n} \log C_e \quad (9)$$

Where, K and n are determined from the intercept and slope of the plot of  $\log q_e$  versus  $\log C_e$ .

### 3.6.1 Langmuir isotherm

The plot of  $C_e/q_e$  Vs  $C_e$  show that the experimental data fitted reasonably well to the linearised equation of the Langmuir isotherm over the whole Cd(II) ion range studied. The correlation coefficient was 0.9896,  $q_m$  and  $K_L$  were evaluated from the slope and intercept of the plot as 10.28 mg/g and 0.050 L/mg respectively. The essential characteristics of the Langmuir isotherm parameters can be used to predict the affinity between the sorbate and sorbent using separation factor or dimensionless equilibrium parameter, “ $R_L$ ”. The value of separation parameter  $R_L$  provides important information about the nature of biosorption.). The  $R_L$  was found to be 0.050 for concentration of 20 mg/L of Cd (II) which signifies favourable biosorption process.

### 3.6.2 Freundlich isotherm

The linear plot of  $\log q_e$  vs  $\log C_e$  Fig.8 showed that the Freundlich isotherm was also well representative for the Cd(II) ions removal by the activated PKC. The correlation coefficient was 0.9680.  $K_f$  and n were calculated from the slope of the Freundlich plot and were found to be 1.100 (mg/g) (1/mg)<sup>1/n</sup> and 0.461 respectively. The magnitude of  $K_f$  and n shows easy separation of heavy metal ion from wastewater and high biosorption capacity. The value of n, which is related to the distribution of bonded ions on the biosorbent surface, represents beneficial biosorption if it is between 1 and 10. The n value for activated PKC was found to be less than 1, indicating that biosorption of Cd (II) is unfavourable.

Table 3 gives isotherm parameters for both Langmuir and Freundlich isotherms. From linear correlation coefficients of the biosorption isotherm, it is noted that the Langmuir isotherm model exhibits a better fit to the sorption data of Cd(II) ions. The comparison of maximum monolayer biosorption onto various biosorbents was presented in Table 4. It shows that the activated PKC studied in this work has good biosorption capacity.

### 3.7 Biosorption kinetics

In order to investigate the controlling mechanism such as chemical reaction and mass transfer, the pseudo-first-order [74] and pseudo-second-order [75] were applied to model the kinetics of cadmium (II) biosorption onto activated PKC.

We attempted to analyze the biosorption data using pseudo first-order and pseudo second-order kinetic models. Lagergren pseudo-first-order model assumes that the rate of occupation of sorption sites is proportional to the number of unoccupied sites [76], i.e., rate of change of solute uptake with time is directly proportional to the difference in the saturation concentration and the amount of solid uptake with time. The general form of this model is expressed as

$$\frac{dq_t}{dt} = k_1(q_e - q_t)$$

$q_e$  and  $q_t$  are amount of adsorbate (mg/g) at time t and at equilibrium, respectively.  $k_1$  is the rate constant of pseudofirst-order biosorption. Integrated form of equation is

$$\frac{q_t}{q_e} = 1 - e^{(-k_1 t)}$$

It can be also written as

$$\log(q_e - q_t) = \log q_e - \frac{k_1 t}{2.303}$$

Linear plot of  $\log(q_e - q_t)$  versus t shows the applicability of pseudo-first-order kinetic model [77][78][79]. The rate constant  $k_1$  and equilibrium amount of metal ion  $q_e$  can be obtained from the slope and the intercept of plot. The pseudo-second-order model [79] is based on sorption capacity of solid phase.

$$\frac{dq_t}{dt} = k_2(q_e - q_t)^2$$

Where  $k_2$  is rate constant of pseudo-second-order biosorption ( $\text{g mg}^{-1} \text{min}^{-1}$ ). Integrated linear form of equation is

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (10)$$

This is the linear form of Ho second-order model. The plot of  $t/q_t$  versus  $t$  (Fig. 4) shows the kinetic data of biosorption of cadmium ions on the biosorbent. The good fit of kinetic data in second-order rate expression shows excellent linearity with high correlation coefficient  $R^2$ . The rate constant  $k_2$  and equilibrium amount of metal ion  $q_e$  can be obtained from the slope and the intercept of plot

### 3.7.1 The pseudo-first-order kinetic model

The biosorption of Cd(II) ion from an aqueous solution to activated PKC can be considered as a reversible process with equilibrium being established between the solution and activated PKC. According to Arivoli and Thenkuzhal [80] a plot of  $\log(q_e - q_t)$  versus time (min) is linear, if the pseudo-first order kinetics is obeyed. The plots for Cd(II) biosorption kinetics are represented in Fig.9. The values of kinetic constant ( $k_1$ ) were calculated from the slope of the plot. The calculated values of  $k_1$  and  $q_e$  for the initial concentration of 20 mg/l were 0.0495 and 0.405 mg/g respectively for activated PKC. The correlation coefficients for the pseudo-first order kinetic model are low. Moreover, a large difference of equilibrium biosorption capacity ( $q_e$ ) between the experiment and calculation was observed, indicating a poor pseudo first-order fit to the experimental data.

### 3.7.2 The pseudo-second-order kinetic model

The kinetic data were further analyzed using Ho's pseudo second-order kinetic model. This model is based on the assumption that the sorption follows second order chemisorption. The plot of  $t/q_t$  versus  $t$  (Fig.10) should give a straight line if pseudo-second-order kinetics is applicable and the parameters  $q_e$ , and  $k$  are determined to be 1.695(mg/g) and 0.391 ( $g\ mg^{-1}\ min^{-1}$ ) from the slope and intercept of the plot respectively. In addition, the calculated  $q_e$  values also agree with the experimental data in the case of pseudo-second-order kinetics. These suggest that the biosorption data are well represented by pseudo-second-order kinetics and thus support the assumption [79] that the rate-limiting step of Cd (II) ion onto activated PKC may be chemisorption. Kinetic parameters obtained for Cd (II) biosorption are presented in Table 5.

## IV. Figures and Tables

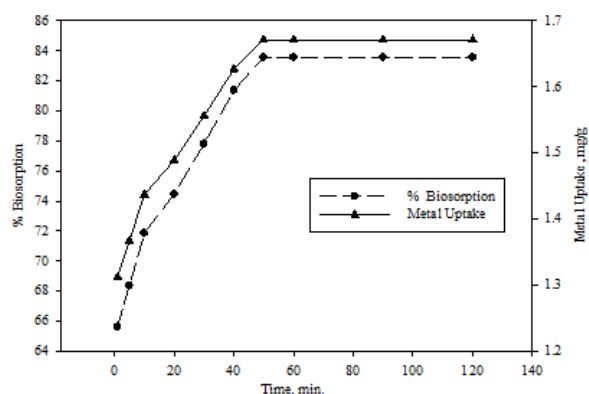


Fig. 1. Effect of agitation time on Cd(II) removal by activated PKC

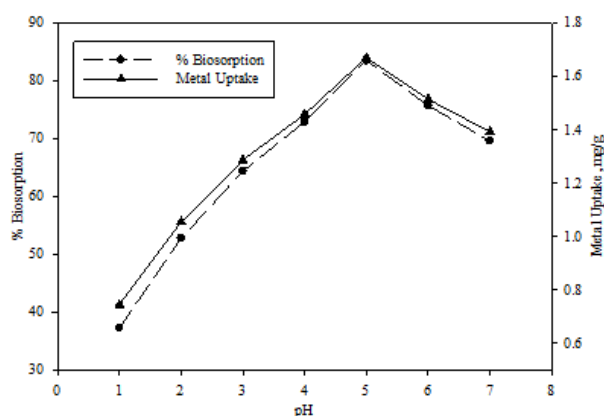


Fig.2. Effect of pH on Cd(II) removal by activated PKC

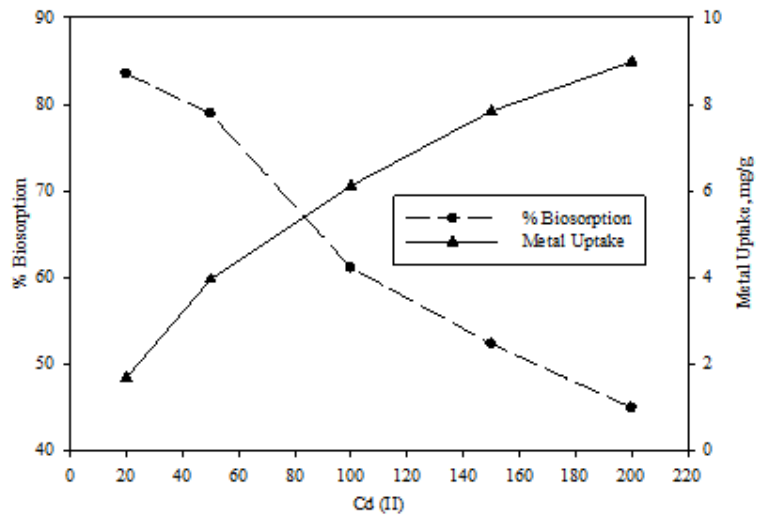


Fig. 3. Effect of initial cadmium concentration on Cd (II) removal by activated PKC

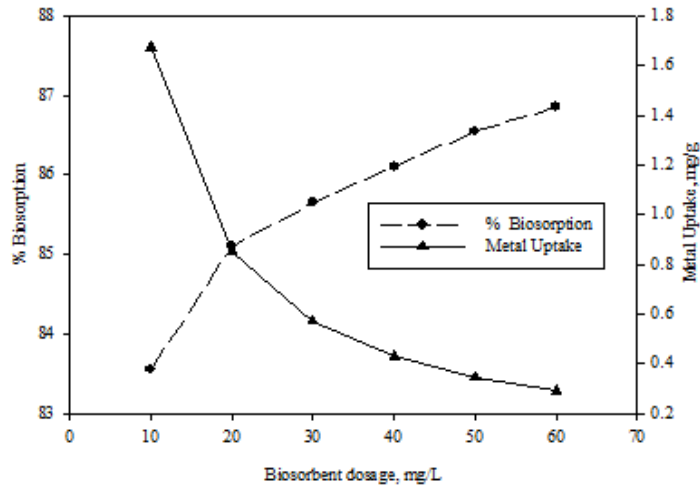


Fig.4. Effect of biosorbent dosage on Cd(II) removal by activated PKC

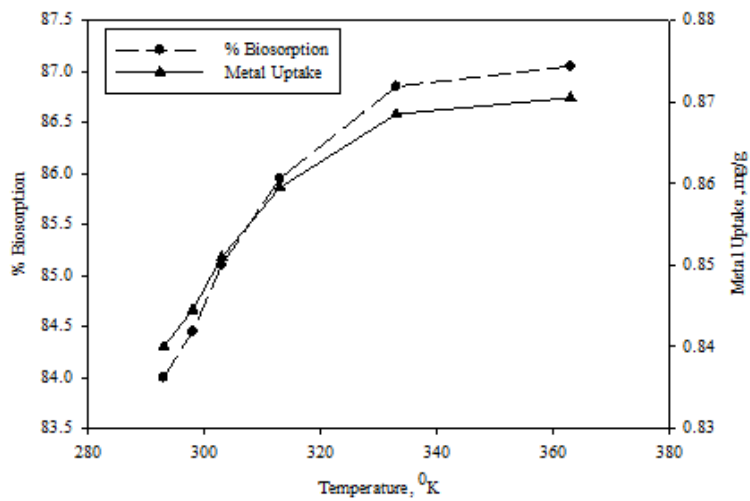


Fig. 5. Effect of temperature on Cd (II) removal by activated PKC



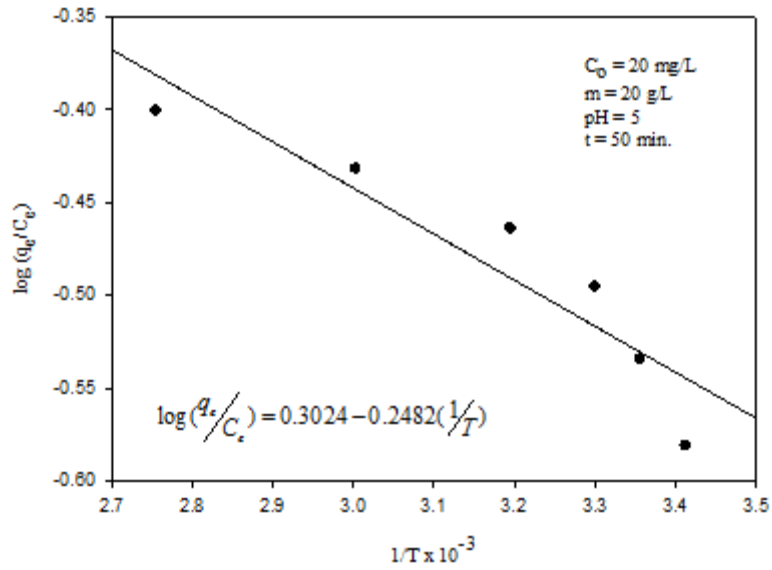


Fig. 6. Vant hoff plot for biosorption of cadmium by activated PKC

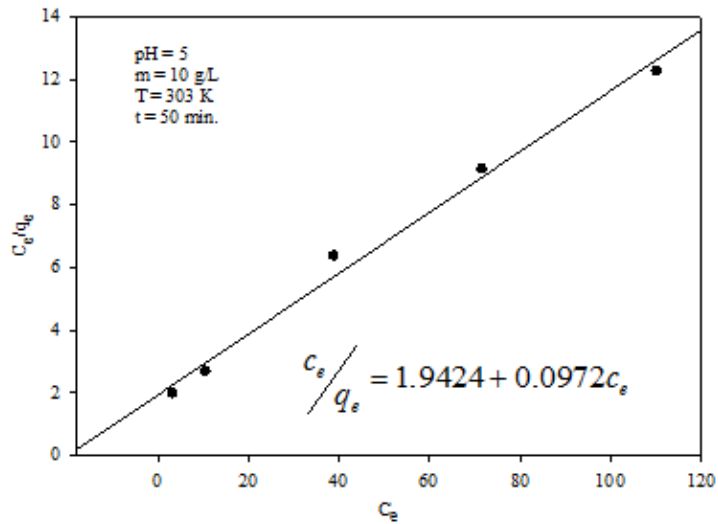


Fig.7. Langmuir isotherm for biosorption of Cd (II) by activated PKC

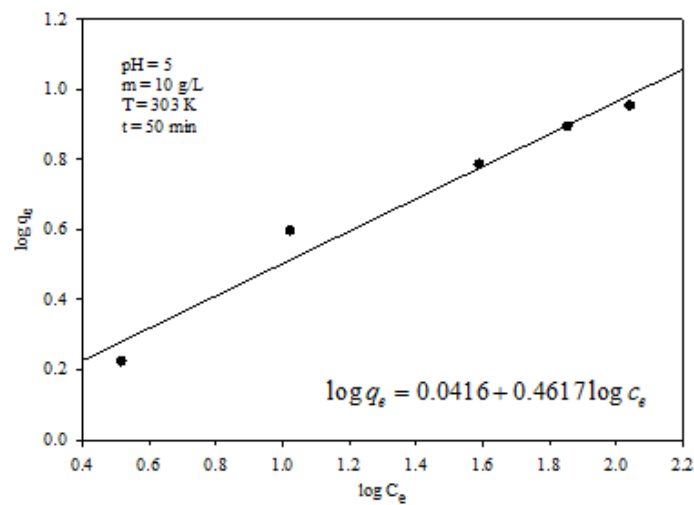


Fig.8. Freundlich isotherm for biosorption of Cd(II) by activated PKC

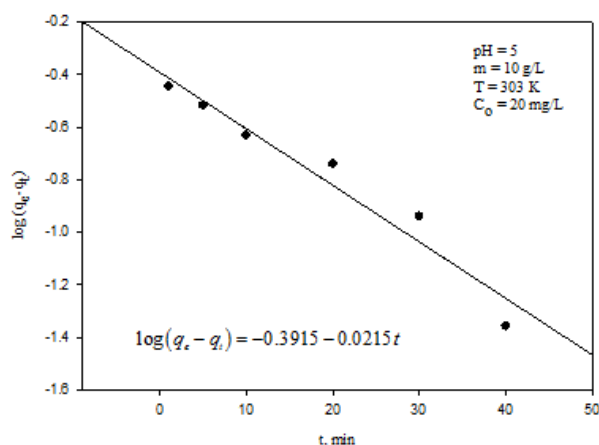


Fig. 9. Pseudo first order kinetics for Cd(II) biosorption by activated PKC

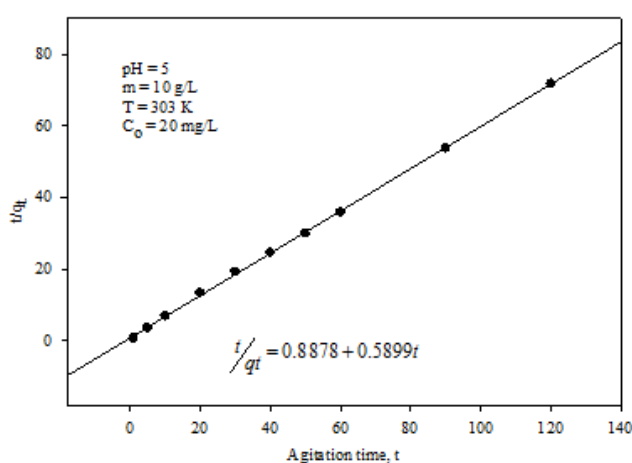


Fig.10. Pseudo second order kinetics for Cd(II) biosorption by activated PKC

| T, K | $\Delta G$ (kJ/mol) | $\Delta H$ (J/mol) | $\Delta S$ (J/mol/K) |
|------|---------------------|--------------------|----------------------|
| 293  | -1.691              | 4.7525             | 5.7590               |
| 298  | -1.711              |                    |                      |
| 303  | -1.749              |                    |                      |
| 313  | -1.807              |                    |                      |
| 333  | -1.923              |                    |                      |
| 363  | -2.097              |                    |                      |

Table 1. Thermodynamic parameters

| $\Delta G$ (kJ/mol) | $\Delta H$ (KJ/mol) | $\Delta S$ (KJ/mol/K) | Biosorbent                 | Reference |
|---------------------|---------------------|-----------------------|----------------------------|-----------|
| Negative            | 40.14               | 0.14                  | Rice Husk                  | [61]      |
| Negative            | -21.49              | 3.798                 | Dead Sargassum Sp. biomass | [62]      |
| Negative            | -13.089             | 38.288                | Hematite                   | [63]      |
| Negative            | 14.12               | -                     | Spent grain                | [64]      |

Table 2. Thermodynamic parameters of other biosorbents

| Freundlich |        |
|------------|--------|
| $K_f$      | 1.100  |
| $N$        | 0.461  |
| $R^2$      | 0.9680 |
| Langmuir   |        |
| $q_m$      | 10.28  |
| $K_L$      | 0.050  |
| $R^2$      | 0.9896 |
| $R_L$      | 0.5    |

Table 3. Isotherm model constants for cadmium biosorption

| Biosorbent                     | q (mg g <sup>-1</sup> ) | Reference     |
|--------------------------------|-------------------------|---------------|
| Rice husk                      | 2                       | [10]          |
| Sugarcane bagasse              | 24.7                    | [67]          |
| Tree fern                      | 16.3                    | [68]          |
| Green coconut shell            | 285.7                   | [69]          |
| Waste Chinese herb             | 17.5                    | [70]          |
| Olive cake                     | 65.4                    | [22]          |
| Exhausted olive cake           | 7.32                    | [71]          |
| Micro-particles of dried plant | 11-28                   | [72]          |
| Cashew nut shell               | 14.29                   | [73]          |
| Coffee grounds                 | 15.65                   | [27]          |
| Mangosteen                     | 3.15                    | [26]          |
| Activated palm kernel cake     | 12.224                  | Present study |

Table 4. Comparison of biosorption capacity of various biosorbents for Cd(II) ions

| Kinetic Model                | Parameter                     |
|------------------------------|-------------------------------|
| Pseudo-first order equation  | K <sub>ad</sub> = 0.0495      |
|                              | q <sub>e (Calc)</sub> = 0.405 |
|                              | q <sub>e (Expt)</sub> = 1.671 |
|                              | R <sup>2</sup> = 0.9483       |
| Pseudo-second order equation | k = 0.391                     |
|                              | q <sub>e (Calc)</sub> = 1.695 |
|                              | q <sub>e (Expt)</sub> = 1.671 |
|                              | R <sup>2</sup> = 0.9996       |

Table 5. Kinetic models and their parameters

## V. Conclusion

From the present investigation, we can conclude that the low-cost natural biosorbent activated carbon derived from palm kernel cake can efficiently remove cadmium ions present in the aqueous solution. The removal % of the cadmium ions was dependent on the pH, contact time, initial cadmium ion concentration and biosorbent dose. Results showed that biosorption was a pH-dependent process and the maximum biosorption occurs at pH 5. Equilibrium was attained in 50 min. Kinetic data were successfully described by a pseudo-second-order model. Biosorption isotherms were modeled using the Langmuir, Freundlich models. Based on the correlation coefficients, the Langmuir model adequately described the biosorption of Cd(II) under all examined conditions. All results showed that activated PKC is an attractive alternate low-cost biosorbent for removal of cadmium ion from aqueous solution. This activated carbon derived from palm kernel cake was found to be an effective, economical and environmentally friendly biosorbent for the removal of cadmium ions from aqueous solution and may potentially be used for removal of other heavy metal ions too.

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