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# APPLICATION OF METHYLGLYCINEDIACETIC ACID MODIFIED PODS OF PELTOPHORUM PTEROCARPUM AS GREEN ADSORBENT FOR REMOVAL OF CADMIUM (II) FROM AQUEOUS SOLUTION

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## ABSTRACT

Cumulative contamination of aquatic sources with large number of contaminants is not only threatening the aquatic biota but creating a worldwide shortage of recreational waters. Toxic heavy metals are considered as major pollutants that have direct effect on human health and animals. Third world countries are at high risk of water contamination due to lack of waste water treatment technologies. This study, therefore, investigates the potential ability of Methylglycinediacetic acid modified pods of *Peltophorum pterocarpum* (PpMGDA) to remove cadmium from aqueous solution. The influence of experimental parameters such as pH, contact time, temperature, adsorbent dose, agitation rate and initial cadmium ion concentration were optimized using batch systems. The biosorption mechanism of PpMGD Abiosorbent was well described by Langmuir isotherm ( $R^2 = 1$ ) and a pseudo second order kineticmodel ( $R^2 = 0.9986$ ), with a high regression coefficient. Thermodynamic study revealed that the biosorption of Cd(II) by using PpMGDA was endothermic, spontaneous and proceeded with increased randomness.

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## INTRODUCTION

Environmental pollution predominantly from heavy metals and minerals in the waste water is the most severe problem in India. Heavy metals such as chromium (Cr), arsenic (As), copper (Cu), lead (Pb), cadmium (Cd), mercury (Hg) and zinc (Zn) often be found in industrial wastewater and their discharge to the environment poses a serious threat due to their acute toxicity to aquatic and terrestrial life (Fergusson, 1990). As a result of increasing industrialization more heavy metals are being continually released to the environment and this has prompted environmental engineers and scientists to investigate methods by which heavy metal bearing wastewaters can be treated effectively and economically (Hossain et. al., 2012). Recently, considerable attention has been given to removal of heavy metals by biosorption, which is in simplest terms, a process of passive cations binding by biological material (Nouri et. al., 2001). The process of biosorption has many advantages over conventional treatment techniques including the selective removal of metals over a broad range of pH and temperature, its rapid kinetics of adsorption and desorption and low capital and operation cost (Ahluwalia and Goyal, 2007).

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Green adsorbents being economic and eco-friendly due to their unique chemical composition, availability in abundance, renewable, low in cost and more efficient are seem to be viable option for heavy metal remediation. These promising green adsorbents are used in the removal of metal ions either in their natural form or after some physical or chemical modification (Sud *et al.*, 2008). But, many studies have shown that the adsorption capacity of these adsorbents may be increased by their treatment with chemical reagents (Tarley *et al.*, 2004; Demirbas, 2008).

In present study, the application of Methylglycinediacetic acid modified pods of *Peltophorum pterocarpum* (PpMGDA) as a green adsorbent for removal of Cd(II) was investigated. The aim of the present work was to estimate various process parameters affecting the biosorption of Cd(II) metal such as solution pH, contact time, temperature, adsorbent dose, agitation rate and initial Cd(II) metal ion concentration. Adsorption isotherms (Langmuir, Freundlich, Dubinin-Kaganer-Radushkevich and Temkin) and kinetics models (Pseudo-first-order, Pseudo-second-order, Elovich and Weber & Morris Intraparticle diffusion) was employed to understand the probable biosorption mechanism. Thermodynamic studies was also carried out to estimate the standard Gibbs free change ( $\Delta G^0$ ), standard enthalpy change ( $\Delta H^0$ ) and standard entropy change ( $\Delta S^0$ ).

# **MATERIALS AND METHODS**

# Preparation of Chemicals and Reagents

All the chemicals and reagents used were of analytical reagent (AR) grade. Millipore water was used for all experimental work. The desired pH of the metal ion solution was adjusted with the help of 0.1 N HCl and 0.1 N NaOH.

# Preparation of Cadmium (II) synthetic waste water

1000 ppm of Cd(II) was prepared by dissolving 2.032 gm of cadmium chloride (CdCl<sub>2</sub>) in millipore water and the volume was made to the mark in a 1000 cm<sup>3</sup>volumetric flask using millipore water. Further desired working solutions of Cd(II) were prepared using appropriate subsequent dilutions of the stock solution.

# Preparation of Green Adsorbent

Pods of Peltophorum pterocarpum (Family: Leguminosae) were collected locally from Mumbai. It was washed with distilled water to eliminate the dust and other impurities. The washed green adsorbent was dried initially at room temperature for a week and then in an oven at 50 °C for 24 hrs and grounded in a mechanical grinder to form powder. The powder was sieved through 250 µm size sieve and stored in air tight container protect it from to Methylglycinediacetic acid modification of Peltophorum pterocarpum was carried out according to a similar method described by Zhu et. al., (2008). For the modification of green adsorbent by Methylglycinediacetic acid, 50 gm of pods of Peltophorum pterocarpum powder was added in 200 ml of 1 % MGDA and the mixture was heated at 50 °C for 2 hrs. The sample was filtered and the liquid fraction was discarded and dried in an oven at 60 °C for 24 hrs. After that, the temperature of an oven was raised up to 100 °C for 120 min. The dried MGDA modified green adsorbent was rinsed with double distilled water repeatedly to remove excess of MGDA. Finally the modified green adsorbent was dried in hot air oven at 60 °C for 48 hrs. The dried Methylglycinediacetic acid modified pods of Peltophorum pterocarpum (PpMGDA) adsorbent powder was stored in air tight container to protect it from moisture.

#### **Instrumentation Studies**

The pH of the solution was measured by using digital pH meter (Labline; Model: LSC-16). Rotary incubator shaker (Labtop; Model: LS1-125/R) was employed for the maintaining shaking condition along with temperature. The concentration of Cd(II) in the solutions before and after equilibrium was determined by measuring absorbance using Atomic Absorption Spectrophotometer (Agilent; Model: AA 240 FS).

## **Batch Biosorption Studies**

The batch adsorption method was employed to examine the biosorption of Cd(II) by PpMGDA. The method was used to determine the adsorption capacity, stability of adsorbent and optimum biosorption conditions. Different experimental conditions such as solution pH, contact time, temperature, adsorbent dose, agitation rate and initial Cd (II) ion concentration were optimized. The following equation was used to compute the percent removal (% Adsorption) of Cd (II) by the adsorbent,

% Adsorption = 
$$\frac{(c_i - c_e)}{c_i} \times 100$$
 (1)

Where,  $C_i$  and  $C_e$  are the initial concentration and equilibrium concentration of the cadmium (II) in mg/L.

The equilibrium adsorptive quantity  $(q_e)$  was determined by the following equation,

$$q_e = \frac{(C_i - C_e)}{w} \times V \tag{2}$$

Where,  $q_e$  (mg metal per g dry biosorbent) is the amount of Cd(II) biosorbed, V (in liter) is the solution volume and w (in gram) is the amount of dry biosorbent used.

Adsorption isotherm studies were systematically carried out by considering Langmuir isotherm, Freundlich isotherm, Dubinin-Kaganer-Radushkevich (DKR) isotherm and Temkin isotherm adsorption models. Determination of adsorption kinetics was studied with the help of Pseudo-first-order, Pseudo-second-order, Elovich and Weber & Morris intraparticle diffusion kinetics model.

## RESULTS AND DISCUSSION

# Study of Experimental Parameters

## Effect of pH

The adsorption of the Cd(II) ions mainly depends on the pH of the adsorption medium, which influences the surface charge of the adsorbent and degree of ionization of the adsorbate. The optimization of pH was done by varying the pH in the range of 2-10. The Fig. 1 indicates that the adsorption was found to increase up to maximum when pH was increased from 1 to 6. Further increase in pH leads to decrease in the % adsorption by PpMGDA. The optimum removal of Cd(II) was found to be at pH 6 (82.504 %).

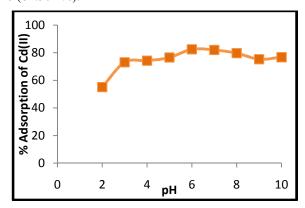


Fig 1 Effect of pH on Cd(II) biosorption by PpMGDA(Adsorbent dose: 0.5 gm/50 ml, Cd(II) concentration: 100 mg/L, Contact time: 90 minutes, Temperature: 30 °C, Agitation rate: 120 rpm)

## Effect of adsorbent dose

Fig. 2 shows the effect of adsorbent dose on the percentage removal of Cd(II). The percentage of Cd(II) ions adsorbed by PpMGDA increased from 35.073% to 84.794% with an increase in the weight of green adsorbent from 0.1 to 0.6 gm. This is attributed to increased adsorbent surface area and availability for more adsorption sites (Jadav *et al*, 2015; Rao *et al*, 2002).

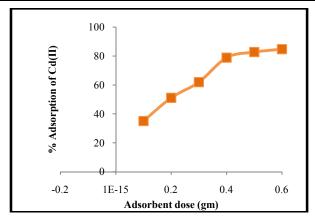


Fig 2 Effect of adsorbent dose on Cd(II) biosorption by PpMGDA (pH: 6, Cd(II) concentration: 100 mg/L, Contact time: 90 minutes, Temperature: 30 °C, Agitation rate: 120 rpm)

#### Effect of Initial Cadmium (II) ion Concentration

The experiment was conducted by maintaining the contact time at 90 minutes, pH 6, 0.5 gm of adsorbent dose (0.5 gm/50 ml), agitation rate 120 rpm and temperature at 30 °C. As can be seen in the Fig. 3 percentage removal of Cd(II) ions to some extent decreased with the increase in initial Cd(II) ions concentration by PpMGDA adsorbent.

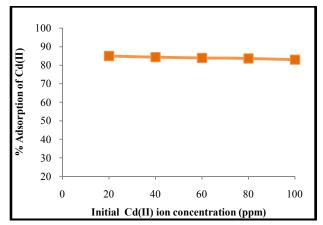
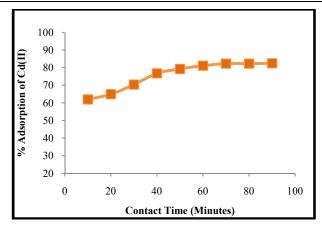


Fig 3 Effect of initial Cd(II) ion concentration on biosorption by PpMGDA (pH: 6, Adsorbent dose: 0.5 gm/50 ml, Contact time: 90 minutes, Temperature: 30 °C, Agitation rate: 120 rpm)

# Effect of Contact time

The effect of contact time on biosorption of Cd(II) ions by PpMGDA are shown in Fig. 4. There is a significant increase in the biosorption efficiency with time by PpMGDA. The maximum removal of Cd(II) was found to be 82.462 % after 90 minutes of contact time. This fast metal uptake from solution indicates that binding might have resulted from interaction with functional groups of the green adsorbent rather than diffusion (Sanusi *et al*, 2018).



**Fig 4** Effect of contact time on Cd(II) biosorption by PpMGDA (pH: 6, Adsorbent dose: 0.5 gm/50 ml, Cd(II) concentration: 100 mg/L, Temperature: 30 °C, Agitation rate: 120 rpm)

### Effect of Temperature

Fig. 5 illustrates Cd(II) sorption on PpMGDA at different temperatures. It can be inferred from the graph that an initial rise in temperature brings about a sharp increase in Cd(II) sorption from 10 °C to 50 °C. The optimum removal of Cd(II) was found to be 85.112 % at 50 °C temperature. Further increase in temperature showed slight drop in % Cd(II) removal at 60 °C.

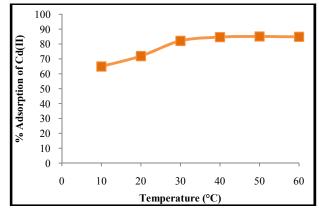
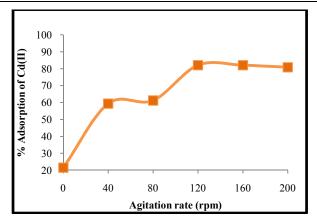


Fig 5 Effect of temperature on Cd(II) biosorption by PpMGDA (pH: 6, Adsorbent dose: 0.5 gm/50 ml, Cd(II) concentration: 100 mg/L, Contact time: 90 minutes, Agitation rate: 120 rpm)

## Effect of Agitation rate

Experiment was carried out by taking Cd(II) ion concentration 100 mg/L, adsorbent dose 0.5 gm/50 ml, pH 6, contact time of 90 minutes and temperature at 30 °C with varying agitation speed (0 – 200 rpm). The effect of agitation speed on the adsorption of Cd(II) ions is shown in Fig. 6. As agitation speed increased up to 120 rpm, adsorption capacity of PpMGDA for removal of Cd(II) also increased from 21.554 % to 82.077 %. Further increase in agitation speed resulted in significant decrease in removal efficiency of Cd(II) by PpMGDA.



**Fig 6** Effect of agitation rate on Cd(II) biosorption by PpMGDA (pH: 6, Adsorbent dose: 0.5 gm/50 ml, Cd(II) concentration: 100 mg/L, Contact time: 90 minutes, Temperature: 30 °C)

## Adsorption Isotherm Study

The results obtained from the biosorption of Cd(II) ions on PpMGDA was investigated using adsorption isotherm models: Langmuir, Freundlich, Dubinin-Kaganer-Radushkevich (DKR) and Temkin to describe the equilibrium between the metal ions sorbed on the biomass as shown in Table 1.

# Langmuir isotherm

The Langmuir equation, which is valid for monolayer sorption onto a surface of finite number of identical sites (Langmuir, 1918), is given by;

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

Where  $q_m$  is the maximum biosorption capacity of adsorbent (mg g<sup>-1</sup>). b is the Langmuir biosorption constant (L mg<sup>-1</sup>) related to the affinity between the biosorbent and biosorbate. Linearized Langmuir isotherm allows the calculation of biosorption capacities and Langmuir constants and is represented as:

$$\frac{1}{qe} = \frac{1}{q_m b c_e} + \frac{1}{q_m} \tag{4}$$

The linear plots of  $1/q_e vs 1/c_e$  is shown in Fig. 7 (a). The two constants b and  $q_m$  are calculated from the slope  $(1/q_m \cdot b)$  and intercept  $(1/q_m)$  of the line. The values of  $q_m$ , b and regression coefficient  $(R^2)$  are listed in Table 1.

# Freundlich adsorption isotherm

The Freundlich isotherm is based on the assumption that the adsorption occurs on heterogeneous surface of an adsorbent with interaction between the adsorbate molecules. Freundlich equation is represented by;

$$q = KC_e^{1/n} (5)$$

Where *K* and *n* are empirical constants which incorporating all parameters affecting the biosorption process such as, biosorption capacity and biosorption intensity respectively (Freundlich, 1906).

Linearized Freundlich adsorption isotherm was used to evaluate the sorption data and is represented as:

$$\log qe = \log K + \frac{1}{n} \log C_e \tag{6}$$

Equilibrium data for the adsorption is plotted as  $\log q_e vs \log C_e$ , as shown in Fig. 7 (b). The two constants n and K are calculated from the slope (1/n) and intercept  $(\log K)$  of the line, respectively. The values of K, 1/n and regression coefficient  $(R^2)$  are listed in Table 1.

# Dubinin-Kaganer-Radushkevich (DKR) adsorption isotherm

Linearized Dubinin-Kaganer-Radushkevich (DKR) adsorption isotherm equation is represented as;

$$lnq_e = \ln q_m - \beta \, \varepsilon^2 \tag{7}$$

Where  $q_m$  is the maximum biosorption capacity,  $\beta$  is the activity coefficient related to mean biosorption energy and  $\varepsilon$  is the polanyi potential (Dubinin, 1947), which is calculated from the following relation;

$$\varepsilon = RT \ln \left( 1 + \frac{1}{C_c} \right) \tag{8}$$

Equilibrium data for the adsorption is plotted as  $\ln q_e \text{vs } \epsilon^2$  as shown in Fig. 7 (c). The two constants  $\beta$  and  $q_m$  are calculated from the slope  $(\beta)$  and intercept  $(\ln q_m)$  of the line, respectively. The values of adsorption energy E was obtained by the following relationship,

$$E = \frac{1}{\sqrt{-2\beta}} \tag{9}$$

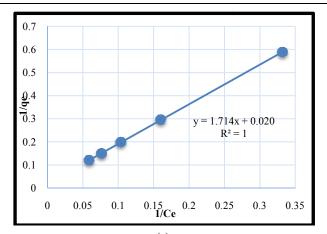
The E value was found to be 0.4082 KJ mol<sup>-1</sup>. The mean free energy gives evidence about biosorption mechanism whether it is physical or chemical biosorption. If the value of E is less than 8 KJ mol<sup>-1</sup>, then the biosorption process can be explained by physisorption mechanism, if E is between 8 and 16 KJ mol<sup>-1</sup>, the process is dominated by ion exchange mechanism, and if E> 16 KJ mol<sup>-1</sup>, the biosorption process is dominated by chemisorption (Olivieri and Brittenham, 1997). In the present work, E value (0.4082 KJ mol<sup>-1</sup>) which is less than 8 KJ mol<sup>-1</sup>, the biosorption of Cd(II) ions onto PpMGDA is of physical in nature.

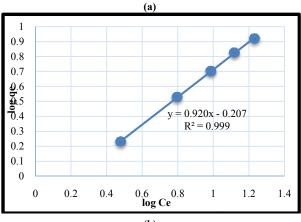
# Temkin Adsorption Isotherm

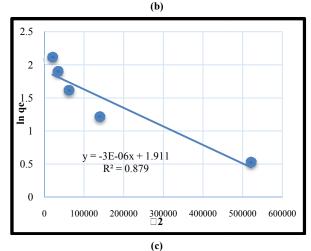
Linearized Temkin adsorption isotherm is given by the equation;

$$q_e = \frac{RT}{b_T} \ln A_T + \frac{RT}{b_T} \ln C_e \tag{10}$$

Where  $b_T$  is the Temkin constant related to heat of biosorption (J/mol) and  $A_T$  is the Temkin isotherm constant (L/g) (Temkin, 1940). Equilibrium data for the adsorption is plotted as  $q_e$ vs  $\ln C_e$  as shown in Fig. 7 (d). The two constants  $b_T$  and  $A_T$  are calculated from the slope  $(RT/b_T)$  and intercept  $(RT/b_T)$  in  $A_T$ ) of the line. The values of  $A_T$ ,  $b_T$  and regression coefficient  $(R^2)$  are listed in Table 1.







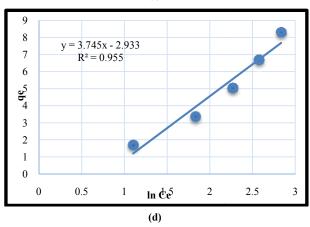


Fig 7 Adsorption isotherms (a) Langmuir, (b) Freundlich (c) DKR and (d) Temkin for Cd(II) biosorption by PpMGDA (pH: 6.0, Adsorbent dose: 0.5 gm/50 ml, Contact time: 90 minutes, Temperature: 30 °C, Agitation rate: 120 rpm)

#### Adsorption kinetics studies

Kinetic parameters of an adsorption process are crucial for the estimation of adsorption parameters, which in turn control the entire process of sorption, which are thus vital for designing sorption systems. The sorption kinetics of a system are controlled by different steps, including transfer of solute to the sorbent particle surface, transfer from the sorbent surface to the intra-particle active sites and retention these active sites via sorption, complexation or intra-particle precipitation phenomena (Shroff and Vaidya, 2011). To determine the controlling mechanism of the biosorption process, experimental data were scrutinized for pseudo-first-order equation (Lagergren, 1898), pseudo-secondorder equation (McKay et al, 1999), Elovich equation (Chien and Layton, 1980) and Weber & Morris intra-particle diffusion equation (Weber and Morris, 1963) which is presented below;

$$\ln(q_e - q_t) = \ln q_e - k_1 t \tag{11}$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \tag{12}$$

$$\ln(q_e - q_t) = \ln q_e - k_1 t \tag{11}$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \tag{12}$$

$$q_t = \frac{1}{\beta} \ln(\alpha \beta) + \frac{1}{\beta} \ln t \tag{13}$$

$$q_t = k_i t^{0.5} + c \tag{14}$$

$$q_t = k_i t^{0.5} + c (14)$$

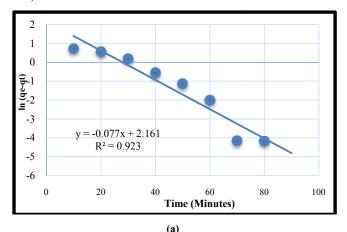
Where  $q_e$  (mg g<sup>-1</sup>) is the solid phase concentration at equilibrium,  $q_t$  (mg g<sup>-1</sup>) is the average solid phase concentration at time t (min),  $k_1$  (min<sup>-1</sup>) and  $k_2$  (g mg<sup>-1</sup> min<sup>-1</sup>) are the pseudo-first-order and pseudo-second-order rate constants, respectively. The symbols of  $\alpha$  (mg g<sup>-1</sup> min<sup>-1</sup>) and  $\beta$ (g mg<sup>-1</sup>) are Elovich coefficients representing initial biosorption rate and desorption constants, respectively.  $k_i$  ( mg  $g^{-1}$  min<sup>-1/2</sup>) is the intra-particle diffusion rate constant, c is intercept.

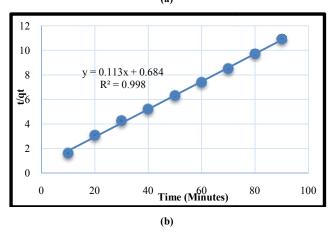
If the adsorption follows the pseudo-second-order model, a plot of  $\ln (q_e - q_t)$  against time t should be a straight line. Similarly,  $t/q_t$  should change lineally with time t if the adsorption process obeys the pseudo-second order model. If the adsorption process obeys Elovich model, a plot of  $q_t$ against lnt should be a straight line. Also a plot of  $q_t$  against  $t^{0.5}$  changes lineally the adsorption process obeys the Weber and Morris intra-particle diffusion model (Septhum et al, 2007).

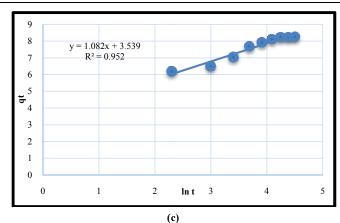
Biosorption of Cd(II) onto PpMGDA was monitored at different specific time interval and the Cd(II) removal was calculated from the data obtained. The pseudo-first-order model was plotted for  $ln (q_e-q_t)$  against t as shown in the Fig.8 (a). The values of  $k_l$  and  $q_e$  were estimated from the slope  $(k_l)$ and intercept (lnq<sub>e</sub>) of the plot and shown in Table 2. Pseudofirst-order model exhibited the correlation value ( $R^2 = 0.9235$ ) being lower than the correlation coefficient for the pseudosecond-order model. Kinetic biosorption for pseudo-first-order model occurs chemically and involves valency forces through ion sharing or exchange of electron between the biosorbent and the ions adsorbed onto it (Septhum et al, 2007; Jadav et al, 2015).

The pseudo-second-order model was plotted for  $t/q_t$  against t as shown in the Fig.8 (b). The values of  $q_e$  and  $k_2$  are calculated from the slope  $(1/q_e)$  and intercept  $(1/k_2 q_e^2)$  of the plot and values are shown in Table 2.Pseudo-second-order kinetic model revealed the strongest correlation ( $R^2 = 0.9986$ ). This finding indicates that Cd(II) biosorption follows in a monolayer fashion and which relies on the assumption that chemisorption or chemical adsorption is the rate-limiting step. Cd(II) reacts chemically with the specific binding sites on the surface of biosorbent (Jadav et al. 2015). The Elovich model was plotted for  $q_t$  against ln t as shown in the Fig. 8 (c). The values of  $\beta$  and  $\alpha$  are calculated from the slope  $(I/\beta)$  and the intercept  $(\ln (\alpha \beta)/\beta)$  of the plot and values are shown in Table 2. The Elovich model has been used with the assumption that the actual adsorption surface is energetically heterogeneous (Thomas and Thomas, 1947; Poojari and Bhalerao, 2018). The Elovich model showed a correlation coefficient ( $R^2 = 0.9525$ ).

The Weber & Morris intra-particle diffusion model was plotted for  $q_t$  against  $t^{0.5}$  as shown in the Fig. 8 (d). The value of  $k_i$  and c are calculated from the slope  $(k_i)$  and intercept (c) of the plot and values are shown in Table 2. The Weber and Morris intraparticle diffusion model showed a  $(R^2 = 0.9308)$  being lower than the correlation coefficient for the pseudo-second-order model. The intercept of the plot does not pass through the origin, this is indicative of some degree of boundary layer control and intra-particle pore diffusion is not only ratelimiting step (Weber and Morris, 1963; Poojari and Bhalerao, 2018).







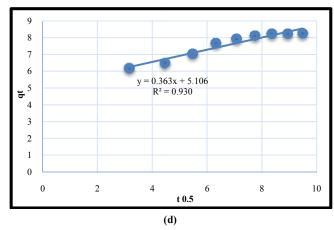


Figure 8 Adsorption kinetic models (a) pseudo-first-order, (b) pseudo-second-order (c) Elovich and (d) Weber and Morris intra-particle diffusion for Cd(II) biosorption by PpMGDA (pH: 6.0, Adsorbent dose: 0.5 gm/50 ml, Initial Cd(II) concentration: 100 mg/L, Temperature: 30 °C, Agitation rate: 120 rpm)

# Thermodynamic Studies

Thermodynamic parameters are imperative factors that determine the feasibility and spontaneity of an adsorption process. The equilibrium constant at various temperatures and thermodynamic parameters of adsorption can be estimated from the following equations;

$$K_{c} = \frac{c_{Ae}}{c_{e}}$$

$$\Delta G^{0} = -RT \ln K_{c}$$
(15)

$$\Delta G^0 = -RT \ln K_c \tag{16}$$

$$\Delta G^0 = \Delta H^0 - T \Delta S^0 \tag{17}$$

$$\Delta G^{0} = \Delta H^{0} - T\Delta S^{0}$$

$$\ln K_{c} = \frac{\Delta S^{0}}{R} - \frac{\Delta H^{0}}{RT}$$
(18)

Where  $K_c$  is the equilibrium constant,  $C_e$  is the equilibrium concentration in solution (mg/L) and  $C_{Ae}$  is the amount of Cd(II) biosorbed on the biosorbent per liter of solution at equilibrium (mg/L).  $\Delta G^{\circ}$ ,  $\Delta H^{\circ}$  and  $\Delta S^{\circ}$  are changes in standard Gibbs free energy (kJ/mol), standard enthalpy (kJ/mol) and standard entropy (J/mol K) respectively. R is the gas constant (8.314 J/mol K) and T is the temperature (K) (Catena and

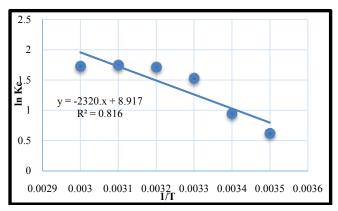
Table 1 Adsorption isotherm constants for Cd(II) biosorption by PpMGDA

Langmuir parameters		Freundlich parameters			DKR parameters				Temkin parameters			
$q_m$	b	$R^2$	K	1/n	$R^2$	β	$q_m$	E	$R^2$	$A_T$	$\boldsymbol{b}_T$	$R^2$
49.26	0.012	1	8.3215	-0.2074	0.9997	-3 x 10 <sup>-6</sup>	6.76	0.4082	0.8792	0.4570	672.52	0.9552

Table 2: Adsorption kinetics data for Cd(II) biosorption by PpMGDA

Pseudo-first-order model			Pseudo-second-order model			Elovich model			Intra-particle diffusion model		
$q_e$	$k_{I}$	$R^2$	$q_e$	$k_2$	$R^2$	α	β	$R^2$	Ki	С	$R^2$
8.6815	1.7825	0.9235	8.8496	0.0186	0.9986	28.477	0.9237	0.9525	0.3635	5.1063	0.9308

The values of  $\Delta H$  °and  $\Delta S$ ° were determined from the slope and the intercept from the plot of lnKc versus I/T (Fig. 9). The values of equilibrium constant (Kc), Gibbs free energy ( $\Delta G$ °), the standard change in entropy ( $\Delta S$ °) and the standard change in enthalpy ( $\Delta H$ °) were represented in Table 3. The value of standard Gibbs free energy change ( $\Delta G$ °) is small and negative and indicates the spontaneous nature of the biosorption. The values of  $\Delta G$ ° were found to decreases as the temperature increases, indicating more driving force and hence resulting in higher biosorption capacity. The value of  $\Delta H$ ° was positive, indicating the endothermic nature of the biosorption of Cd(II) onto PpMGDA. The positive value of  $\Delta S$ ° shows an affinity of biosorbent and the increasing randomness at the solid-solution interface during the biosorption process (Sharma and Bhalerao, 2018).



**Fig 9** Plot of *lnKc* against *1/T* for determination of thermodynamic parameters for Cd(II) biosorption by PpMGDA (pH: 6.0, Adsorbent dose: 0.5 g/50 mL, Cd(II) concentration: 100 mg/L, Contact time: 90 minutes, Agitation rate: 120 rpm)

**Table 3** Thermodynamic parameters of Cd(II) biosorption by PpMGDA

Sr. No.	Temperature	*	Кс	$-\Delta G^{\theta}$	$\Delta H^{\theta}$	$\Delta S^{\theta}$	
	(°C)	(K)		(KJ/mol)	(KJ/mol)	(J/mol)	
1	10 °C	283	1.8538	1.4523			
2	20 °C	293	2.5660	2.2955			
3	30 °C	303	4.5982	3.8433	19.2901	74.1401	
4	40 °C	313	5.5270	4.4490	19.2901	/4.1401	
5	50 °C	323	5.7168	4.6818			
6	60 °C	333	5.6063	4.7727			

# **CONCLUSION**

this study, the potential application Methylglycinediacetic acid modified pods of Peltophorum pterocarpum (PpMGDA) toward the removal of Cd(II) ions in aqueous solution was investigated. The adsorption characteristics of Cd(II) onto PpMGDA was found to be influenced by pH, contact time, temperature, adsorbent dose, agitation rate and initial cadmium ion concentration of the system. The adsorption equilibrium data obtained for removal of Cd(II) ion onto the adsorbents studied showed best fit to the Langmuir isotherm. The adsorption kinetic data fitted a pseudo-second-order model well. Thermodynamic study revealed that the biosorption process for removal of Cds(II) by using PpMGDA was endothermic, spontaneous and proceeded with increased randomness. Hence the obtained results are indication that the Methylglycinediacetic acid modified pods of Peltophorum pterocarpum (PpMGDA) can be efficiently used as green adsorbent for the removal of Cd(II) from aqueous solutions and can therefore be employed as an substitute method for the cost-effective treatment of wastewater.

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