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Evaluation of Biosorption Capacity of Methylglycinediacetic Acid Modified Pericarp of *Gossypium herbaceum* L. for Cadmium (II) Removal from Aqueous Solution

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Abstract: Increased usage of heavy metals for industrial activities has resulted in an increased concentration of these metals in waste water. Presence of heavy metals in wastewater is of great interest because of their known toxic effects on the nearby environment. In this study, the removal of cadmium (II) ions from an aqueous solution using Methylglycinediacetic acid (MGDA) modified pericarp of *Gossypium herbaceum* L. as a green adsorbent, in batch condition was investigated. The equilibrium studies were systematically carried out in a batch process which covered a various process parameter inclusive of pH, contact time, temperature, adsorbent dose, agitation rate and initial ion concentration. The adsorption equilibrium data were adequately characterized by Langmuir, Freundlich, Temkin and DKR isotherm models. Best fitting isotherm models were in the following order, Langmuir ($R^2 = 0.9996$) > Freundlich ($R^2 = 0.9974$) > Temkin ($R^2 = 0.9637$) > DKR ($R^2 = 0.899$). The adsorption kinetics was found to follow pseudo-second-order rate kinetic model. Thermodynamic study confirmed that the biosorption process was endothermic, spontaneous and proceeded with increased randomness. All results showed that the MGDA modified pericarp of *Gossypium herbaceum* L. is an alternative low-cost green adsorbent for removal of cadmium (II) ions from an aqueous solution.

Keywords: Methylglycinediacetic acid, *Gossypium herbaceum* L., cadmium (II), isotherm\

1. INTRODUCTION

Water contaminated with several heavy metals is discharged annually by a number of industries. Heavy metals like lead, cadmium, chromium, zinc and copper contamination in wastewater is primarily come from manmade sources like battery, electronics, paper and pulp industries, metal fabrication and mining activities, smelting, electrolysing, drug manufacturing, paint preparation, alloy manufacturing, galvanizing, printing, dyeing, paper making, ceramics manufacturing and inorganic dyestuff preparation etc. [1]. Untreated and uncontrolled discharge of metal containing wastewater into the environment could be toxic to humans, animals, plants and to urban ecosystems [2].

Removal of heavy metals from the effluent is very significant part of the research carried out in the field of environmental science. Over the last few periods, numerous treatment and management methodologies have been used for the elimination of heavy metals from water and waste water. The conventional methods such as chemical precipitation, ultra-filtration, ion exchange, reverse osmosis, electrodialysis, cementation, coagulation & flocculation and solvent extraction seems to be ineffective or quite expensive or require long duration for heavy metal ion removal from waste water. Hence, efforts are currently being made to develop novel technologies that are cost effective, eco-friendly and highly efficient to remove the metal ions. In this endeavour, biosorption has emerged as an alternative and sustainable strategy for clean-up water. Biosorption is a physico-chemical process, simply defined as the removal of contaminants from solution by biological materials. It uses inexpensive biomaterials to sequester environmental pollutants from aqueous solutions by a wide range of physicochemical mechanisms including ion exchange, chelation, coordination, complexation, physical adsorption, and surface microprecipitation [3]. The search for innovative green ways for removal of heavy metals has forced attention on the use of new natural materials for removal of metal ions.

The research will emphasis on the removal of Cd(II) from its aqueous solution by Methylglycinediacetic acid modified pericarp (fruit wall) of *Gossypium herbaceum* L.(GhMGDA) as green adsorbent. The study was conducted with the objective for optimization of various process parameters affecting the biosorption of metals such as solution pH, contact time, temperature, adsorbent dose, agitation rate and initial Cd(II)) metal ion concentration. Adsorption isotherms, kinetics and thermodynamic studies were employed to understand the probable biosorption mechanism.

2. EXPERIMENTAL METHODS OR METHODOLOGY

2.1 Preparation of Chemicals and Reagents

All the chemicals and reagents utilized for experimental work were of analytical reagent (AR) grade. The desired pH of the metal ion solution was adjusted with the help of 0.1 N HCl and 0.1 N NaOH solutions. 1000 ppm of Cd(II) was prepared by dissolving 2.032 g of cadmium chloride (CdCl2) in Millipore water and the volume was made to the mark in a 1000 cm3 volumetric flask using Millipore water. Further desired working solutions of cadmium (II) were prepared using appropriate subsequent dilutions of the stock solution.

2.2 Preparation of green adsorbent

Pericarp (fruit wall) of *Gossypium herbaceum* L. (Family: Malvaceae) was collected from Ahmednagar District. Initially, it was washed with tap water and then after with distilled water to remove the dust and other impurities. The washed green adsorbent was initially dried 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 green adsorbent powder was sieved through 250 µm size sieve. Methylglycinediacetic acid modification of green adsorbent was carried out according to a similar method described by Zhu et. al., (2008) [4]. For the modification of green adsorbent by Methylglycinediacetic acid, 50 gm *Gossypium herbaceum* pericarp 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 treated powder 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 subsequently rinsed with double distilled water to eliminate 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 pericarp of *Gossypium herbaceum* (GhMGDA) green adsorbent powder was stored in air tight container to protect it from moisture.

2.3 Batch biosorption studies

The batch adsorption method was employed at temperature (30 °C) to study the biosorption of Cd(II) by GhMGDA. Different experimental conditions such as solution pH, contact time, temperature, adsorbent dose, agitation rate and initial Cd(II) ion concentration were optimized. 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). The following equation was used to compute the percent adsorption of Cd(II) by the GhMGDA adsorbent,

$$\% \textbf{ Adsorption} = \frac{(C_i - C_e)}{C_i} \times 100 \qquad (1)$$

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

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

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

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 green adsorbent used.

Adsorption isotherm studies were systematically carried out by considering Langmuir, Freundlich, Dubinin–Radushkevich (DKR) and Temkin adsorption isotherm models. Determination of adsorption kinetics was studied with the help of Pseudo-first-order, Pseudo-second-order, Elovich and Weber and Morris intraparticle diffusion kinetics model. Thermodynamic parameters such as Gibbs free energy (ΔG°), change in enthalpy (ΔH°) and change in entropy (ΔS°) have also been estimated.

3. RESULTS AND DISCUSSION

3.1 Batch biosorption study

3.1.1 Effect of pH

The solution pH can have a significant effect on the adsorption of Cd(II). The effect of pH onto Cd(II) metal ions by GhMGDA as adsorbents were analysed over the pH range from 2 to 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 slight decrease in the % adsorption of Cd(II) by GhMGDA. Hence, optimum pH was found to be pH 6 with 90.987% Cd(II) removal by GhMGDA. The lesser adsorption at lower pH was due to lesser surface sites are available for sorption. This is due to the fact that proton (H+) vies with cadmium ions in lower pH, the sorbent surface takes up more H+, consequently, reducing cadmium ions bind on the sorbent surface. In higher pH, the sorbent surface takes more negative changes, thus attracting greater cadmium ions. However, with a further increase in pH, the formation of anionic hydroxide complexes decreases the concentration of free cadmium ion, and thereby, the biosorption capacity of cadmium ion decreased [5].

3.1.2. Effect of adsorbent dose

The green adsorbent dosage is an important parameter because this determines the capacity of a green adsorbent for a given initial concentration. The biosorption efficiency for Cd(II) ions as a function of green adsorbent dosage was investigated at 30 °C temperature by varying the amount of sorbents from 0.1 to 0.6 g/50 ml, 120 rpm for 90 min using initial Cd(II) concentration of 100 mg/L and at pH value of 6.0. The percentage of adsorbed cadmium by GhMGDA increases with increasing dosage of green adsorbent. It can be observed from Fig. 2 that the adsorption of Cd(II) increased from 47.667% to 90.901% by varying GhMGDA green adsorbent dosage from 0.1 g to 0.5 g. Increase in adsorption by increase in green adsorbent dose is because of increase of ion exchange site ability, surface areas and the number of available adsorption sites [6].

3.1.3 Effect of initial metal ion concentration

The extent of removal of heavy metals from aqueous solution depends on the initial metal ion concentration. Adsorption capacity of GhMGDA for Cd(II) adsorption at various initial concentrations of Cd(II) ranging from 20 mg/L to 100 mg/L is presented in Fig. 3. The experiment was conducted by maintaining the contact time at 90 minutes, pH 6, 0.5 g of adsorbent dose (0.5 g/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 GhMGDA adsorbent, which shows a significant relationship between the removal efficiency and initial metal concentration. In case of low metal ion concentrations, a greater number of vacant sites are available for adsorption which results rise in the concentration slope and rate of cadmium ions spread to adsorbent. In the case of high concentration of metal, the obtainable sites of green adsorbents are decreases and therefore the removal percentage of Cd(II) ions decreases [7].

3.1.4. Effect of contact time

The contact time is one of the important parameters affecting the biosorption process. It is very useful to design a successful biosorption procedure. The effect of contact time on biosorption of Cd(II) ions by GhMGDA are shown in Fig. 4. There is a significant increase in the biosorption efficiency with time by GhMGDA. The maximum removal of Cd(II) was found to be 90.995% by GhMGDA after 90 minutes of contact time. This is a relatively fast adsorption process. The fast adsorption in the initial stage of adsorption was attributed to the large number of active sites available [8].

3.1.5. Effect of temperature

Fig. 5 illustrates Cd(II) sorption on GhMGDA at different temperatures. It can be inferred from the graph that sorption of Cd(II) was significantly increased from 10 °C to 50 °C by GhMGDA. This observation could be attributed to the fact that more chemical sites were present as temperature rises. This also suggests that the adsorption mechanism of Cd(II) ion on green adsorbents could be chemical sorption in addition to physical sorption in which sorption increases with an increase in temperature [9].

3.1.6. Effect of agitation rate

Experiment was carried out by taking Cd(II) ion concentration 100 mg/L, adsorbent dose 0.5 g/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 GhMGDA for removal of Cd(II) also increased from 32.954% to 90.492%. Further increase in agitation speed resulted in significant decrease in removal efficiency of Cd(II) by GhMGDA.

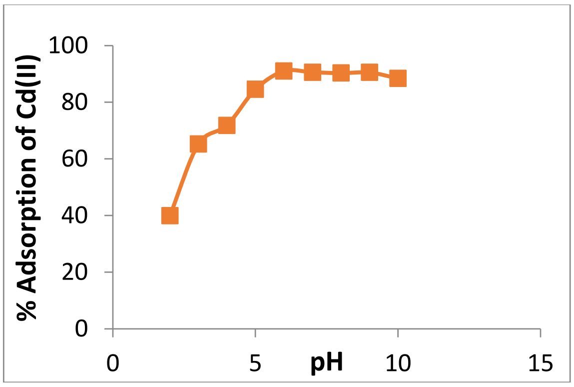

Fig. 1: Effect of pH on Cd(II) biosorption by GhMGDA (Adsorbent dose : 0.5 g/50 ml, Cd(II) concentration: 100 mg/L, Contact time: 90 minutes, Temperature: 30 °C, Agitation rate: 120 rpm)

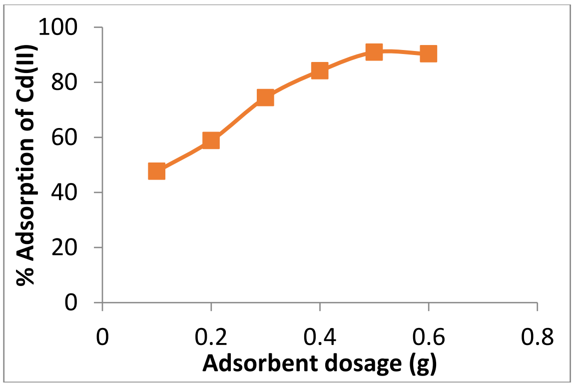

Fig. 2: Effect of adsorbent dose on Cd(II) biosorption by GhMGDA (pH: 6, Cd(II) concentration: 100 mg/L, Contact time: 90 minutes, Temperature: 30 °C, Agitation rate: 120 rpm)

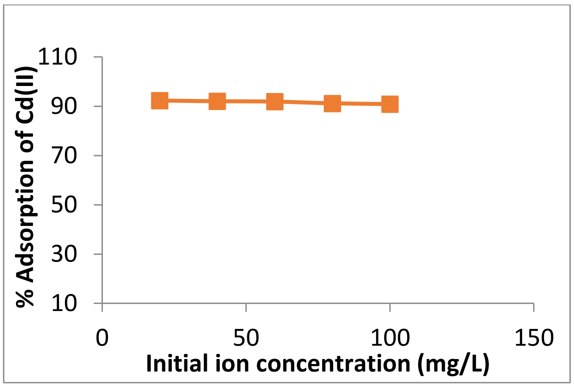

Fig. 3: Effect of initial Cd(II) ion concentration on biosorption by GhMGDA (pH: 6, Adsorbent dose: 0.5 g/50 ml, Contact time: 90 minutes, Temperature: 30 °C, Agitation rate: 120 rpm)

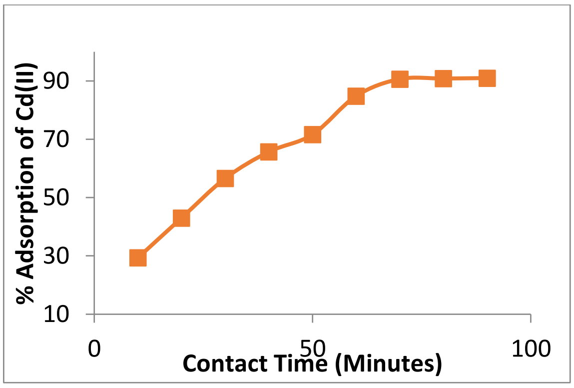

Fig. 4: Effect of contact time on Cd(II) biosorption by GhMGDA (pH: 6, Adsorbent dose: 0.5 g/50 ml, Cd(II) concentration: 100 mg/L, Temperature: 30 °C, Agitation rate: 120 rpm)

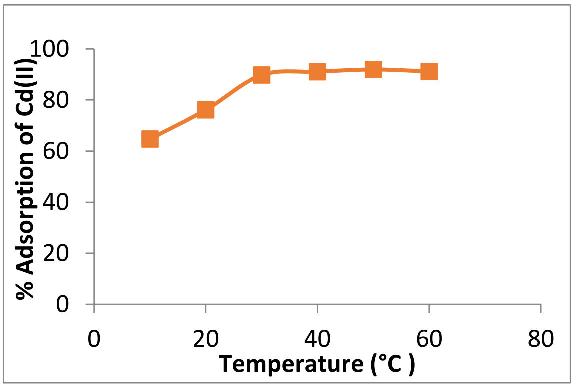

Fig. 5: Effect of temperature on Cd(II) biosorption by GhMGDA (pH: 6, Adsorbent dose: 0.5 g/50 ml, Cd(II) concentration: 100 mg/L, Contact time: 90 minutes, Agitation rate: 120 rpm)

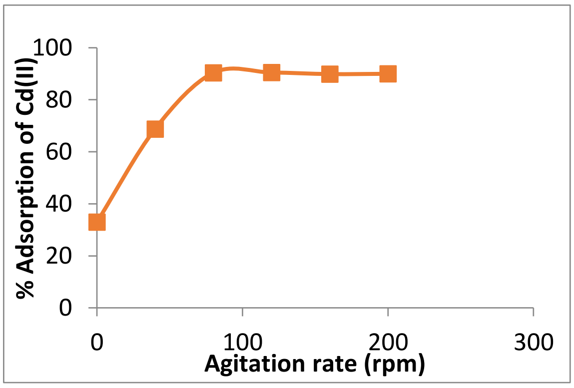

Fig. 6: Effect of agitation rate on Cd(II) biosorption by GhMGDA (pH: 6, Adsorbent dose: 0.5 g/50 ml, Cd(II) concentration: 100 mg/L, Contact time: 90 minutes, Temperature: 30 °C

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3.2 Adsorption isotherm study

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

3.2.1. Langmuir isotherm

The Langmuir equation is valid for monolayer sorption onto a surface of finite number of identical sites [10], which is given by;

$$q = \frac{q_m b C_e}{1+bC_e} \qquad (3)$$

Where q_m is the maximum biosorption capacity of biosorbent (mg g^{-1}), b is the Langmuir biosorption constant (L mg^{-1}) related to the affinity between the biosorbent and biosorbate.

The linearized Langmuir isotherm allows the calculation of biosorption capacities and Langmuir constants and is represented as follows:

$$\frac{1}{qe} = \frac{1}{q_m b C_e} + \frac{1}{q_m} \qquad (4)$$

The linear plots of $1/q_e$ vs $1/c_e$ is shown in Fig. 7 (a). Constants b and q_m are computed from the slope ($1/q_m \cdot b$) and intercept ($1/q_m$) of the line and the values are listed in Table 1.

3.2.2. Freundlich adsorption isotherm

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

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

Where K and n are empirical constants which incorporating all parameters affecting the process of biosorption such as, biosorption capacity and biosorption intensity respectively [11]. Linearized Freundlich adsorption isotherm was used to determine the sorption data and is represented as:

$$\log qe = \log K + \frac{1}{n}\log C_e \qquad (6)$$

Equilibrium data for the biosorption process is plotted as log q_e vs log C_e, as shown in Fig. 7 (b). Constants n and K are calculated from the slope ($1/n$) and intercept (log K) of the line, respectively and the values are listed in Table 1.

3.2.3. Dubinin-Kaganer-Radushkevich (DKR) adsorption isotherm

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

$$lnq_e = \ln q_m - \beta\, \varepsilon^2 \qquad (7)$$

Where q_m is the maximum biosorption capacity, β is the activity coefficient related to mean biosorption energy and ε is the polanyi potential [12], which is calculated from the following relation;

$$\varepsilon = RTln\,(1 + \frac{1}{C_e}) \qquad (8)$$

Equilibrium data for the adsorption is plotted as lnq_e vs ε^2, as shown in Fig. 7 (c). Constants β and q_m are calculated from the slope (β) and intercept (lnq_m) of the line, respectively and the values of adsorption energy E was obtained by the following relationship,

$$E = \frac{1}{\sqrt{-2\beta}} \qquad (9)$$

The E value was found to be 0.7454 KJ mol^{-1}. The mean free energy gives an idea about biosorption mechanism; whether it is physical or chemical biosorption. If the value of E is less than 8 KJ mol^{-1}, then the biosorption process can be explained by physisorption mechanism, if E is between 8 and 16 KJ mol^{-1}, the process is dominated by ion exchange mechanism, and if E is > 16 KJ mol^{-1}, the biosorption process is dominated by chemisorption [13]. In the present work, E value (0.7454 KJ mol^{-1}) which is less than 8 KJ mol^{-1}, the biosorption of Cd(II) ions onto GhMGDA is of physical in nature.

3.2.4. Temkin adsorption isotherm

The linearized Temkin adsorption isotherm is given by the equation;

$$q_e = \frac{RT}{b_T} \ln A_T + \frac{RT}{b_T} \ln C_e \qquad (10)$$

Where b_T is the Temkin constant related to heat of biosorption (J/mol) and A_T is the Temkin isotherm constant (L/g) [14]. Equilibrium data for the adsorption is plotted as q_e vs lnC_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 ($RT/b_T \cdot \ln A_T$) of the line and the values are listed in Table 1.

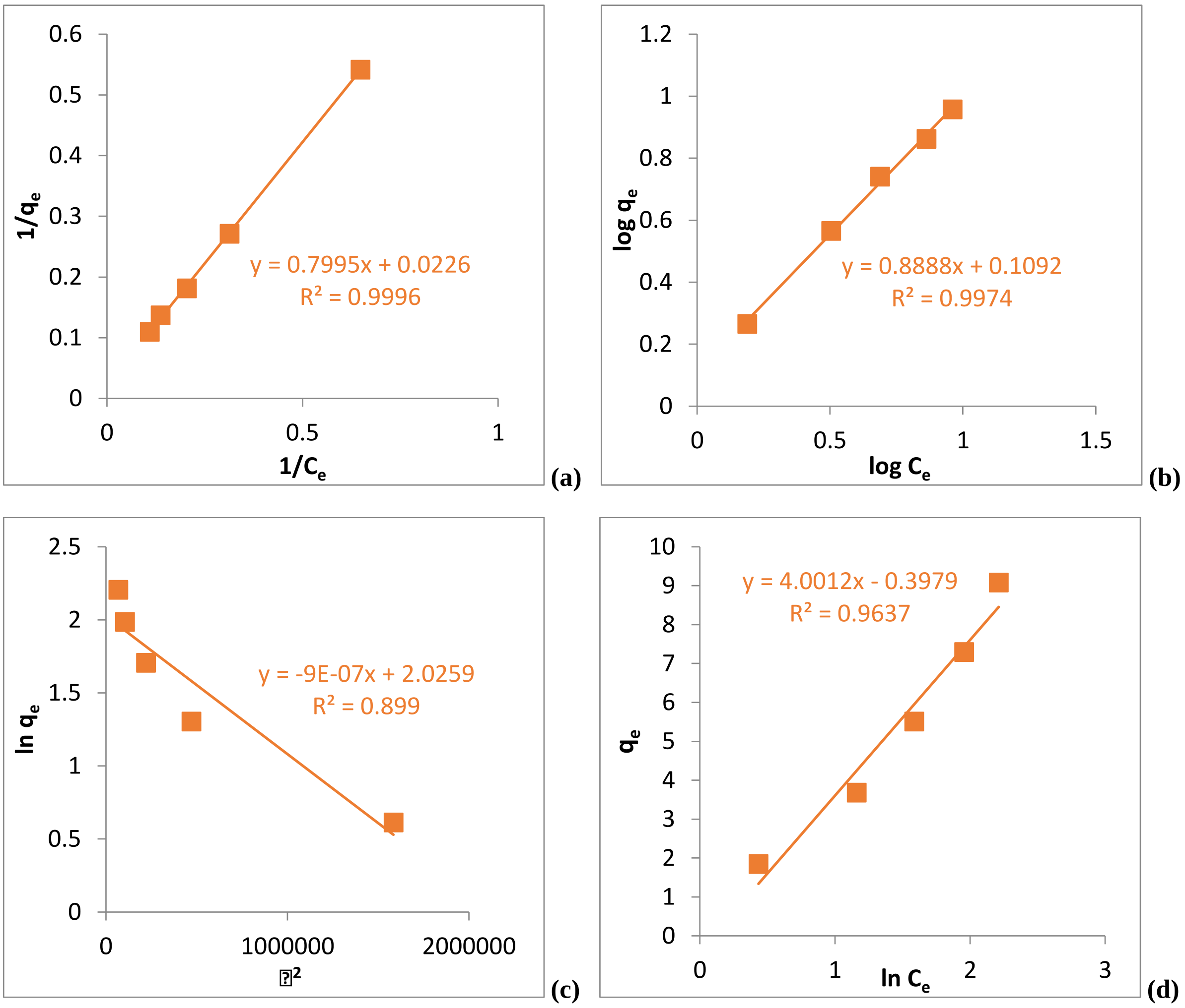

Fig. 7: Adsorption isotherms (a) Langmuir, (b) Freundlich (c) DKR and (d) Temkin for Cd(II) biosorption by GhMGDA (pH: 6.0, Adsorbent dose: 0.5 gm/50 ml, Contact time: 90 minutes, Temperature: 30 °C, Agitation rate: 120 rpm)

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

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	b_T	R^2
44.25	0.028	0.9996	1.2859	1.1251	0.9974	-9×10^{-7}	7.58	0.7454	0.899	0.9054	0.6296	0.9637

3.3. 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 on these active sites via sorption, complexation or intra-particle precipitation phenomena [15]. To determine the controlling mechanism of the biosorption process, experimental data were scrutinized for pseudo-first-order equation [16], pseudo-second-order equation [17], Elovich equation [18] and Weber & Morris intra-particle diffusion equation [19] which is presented below;

$$\ln(q_e - q_t) = \ln q_e - k_1 t \qquad (11)$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \qquad (12)$$

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

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

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

If the biosorption process follows the pseudo-first-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 biosorption process obeys the pseudo-second order model. If the biosorption process obeys Elovich model, a plot of q_t against ln t should be a straight line. Also, a plot of q_t against $t^{0.5}$ changes lineally the biosorption process obeys the Weber and Morris intra-particle diffusion model [20].

Biosorption of Cd(II) onto GhMGDA was monitored at different specific time interval. The Cd(II) uptake 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_1 and q_e were estimated from the slope (k_1) and intercept ($ln\ q_e$) of the plot and shown in Table 2. Pseudo-first-order model exhibited the correlation value (R^2 = 0.8312) being lower than the correlation coefficient for the pseudo-second-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 [21].

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= 0.9809). 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 [21].

The Elovich model was plotted for q_t against $ln\ t$ as shown in the Fig. 8 (c). The values of β and α are calculated from the slope ($1/\beta$) 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 [22]. The Elovich model showed a correlation coefficient (R^2= 0.9742).

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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 intra-particle diffusion model showed a ($R^2 = 0.9343$) 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 rate-limiting step [19, 24].

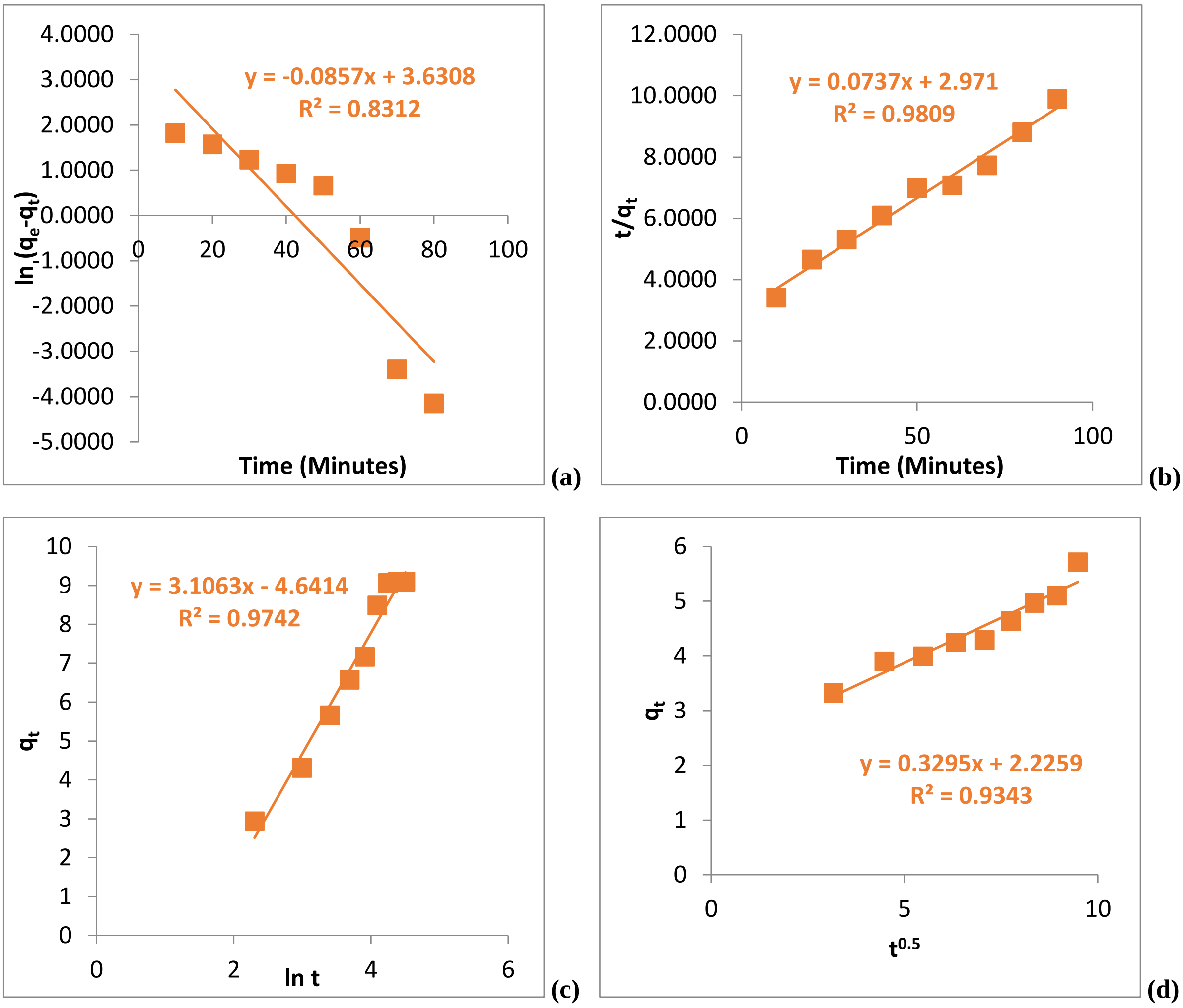

Fig. 8: Adsorption kinetic models (a) pseudo-first-order, (b) pseudo-second-order (c) Elovich and (d) Weber and Morris intra-particle diffusion for Cd(II) biosorption by GhMGDA (pH: 6.0, Adsorbent dose: 0.5 gm/50 ml, Initial Cd(II) concentration: 100 mg/L, Temperature: 30 °C, Agitation rate: 120 rpm)

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

Pseudo-first-order model			Pseudo-second-order model			Elovich model			Intra-particle diffusion model		
q_e	k_1	R^2	q_e	k_2	R^2	α	β	R^2	K_i	C	R^2
37.74	0.1974	0.8312	13.57	0.0018	0. 9809	0.6972	0.3219	0.9742	0.3295	2.2259	0.9343

3.4. 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;

$$K_c = \frac{C_{Ae}}{C_e} \qquad (15)$$

DOI: 10.17148/IARJSET.2021.8909

$$\Delta G^0 = -RT \ln K_c \qquad (16)$$

$$\Delta G^0 = \Delta H^0 - T\Delta S^0 \qquad (17)$$

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

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). $\Delta G°$, ΔH °and $\Delta S°$ 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) [24].

The values of ΔH °and $\Delta S°$ were determined from the slope and the intercept from the plot of *ln Kc* versus *1/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 (ΔH °) were represented in Table 3. It was revealed that 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 GhMGDA. The positive value of $\Delta S°$ shows an affinity of biosorbent and the increasing randomness at the solid-solution interface during the biosorption process [25].

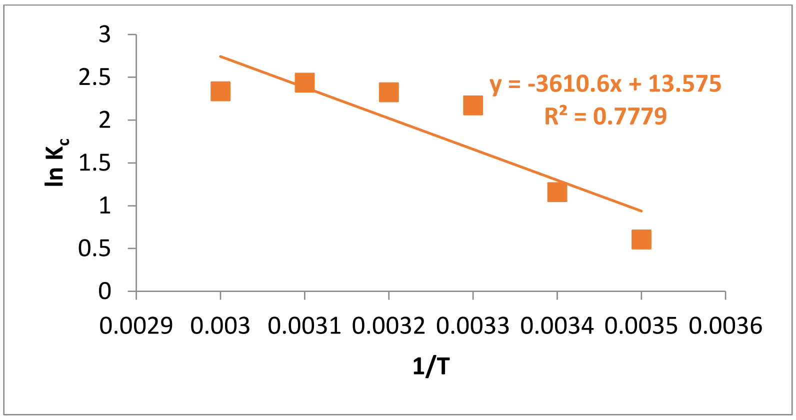

Fig. 9: Plot of *lnKc* against *1/T* for determination of thermodynamic parameters for Cd(II) biosorption by GhMGDA (pH: 6.0, Adsorbent dose: 0.5 g/50 mL, Cd(II) concentration: 100 mg/L, Contact time: 90 minutes, Agitation rate: 120 rpm)

Table 3: Thermodynamic parameters of Cd(II) biosorption by GhMGDA

Sr. No.	Temperature (^{0}C)	Temperature (K)	*Kc*	-ΔG^0 (KJ/mol)	ΔH^0 (KJ/mol)	ΔS^0 (J/mol)
1	10 °C	283	1.8353	1.4286	30.0185	112.86
2	20 °C	293	3.1906	2.8263		
3	30 °C	303	8.7876	5.4750		
4	40 °C	313	10.2196	6.0485		
5	50 °C	323	11.4471	6.5464		
6	60 °C	333	10.3598	6.4727		

CONCLUSION

Environmental pollution particularly from heavy metals and minerals in the waste water has turned out as a very serious problem in the Indian subcontinent. Biosorption is one amongst such evolving technologies, which utilizes naturally occurring biological materials to sequester heavy metals from wastewater. Methylglycinediacetic acid modified pericarp of Gossypium herbaceum L. (GhMGDA) as low-cost green adsorbent investigated in this study showed good potential for the removal of cadmium from aqueous solutions. The removal efficiency of GhMGDA was found to be dependent on the pH, adsorbent dose, initial Cd(II) ions concentration, temperature, contact time and agitation rate. The adsorption isotherm study revealed that the adsorption equilibrium data best fitted to the Langmuir ($R^2 = 0.9996$) model in comparison to other isotherm models at the studied temperature. The maximum monolayer coverage adsorption capacity from the Langmuir isotherm model was obtained as 44.25 mg/g. The sorption process was best described by a pseudo-second-order kinetic model. Thermodynamic study confirmed that the biosorption process was endothermic, spontaneous and proceeded with increased randomness. The study results signify that Methylglycinediacetic acid modified pericarp of Gossypium herbaceum L. can be efficiently used as a green adsorbent for the removal of Cd (II). Hence, the approach is sustainable in nature, owing to the fact that the green adsorbents as well as the chelating agents i.e. Methylglycinediacetic acid used for the modification of green adsorbents are biodegradable.

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