CADMIUM (II) SEQUESTRATION FROM AQUEOUS SOLUTION USING METHYLGLYCINEDIACETIC ACID MODIFIED LEAVES OF FICUS BENGHALENSIS

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Abstract : As a result of different anthropogenic activities, the world is facing serious threats of air, land and water pollutions. Water pollution in particular, has elevated severe environmental impacts. The released heavy metals in water streams represent a risk of ecotoxicity and a potential danger of bioaccumulation. Therefore, removal of heavy metal is one of the most important and severe environmental issues worldwidely. In the present study the potential of Methylglycinediacetic acid modified leaves of *Ficus benghalensis* (FbMGDA) as a green adsorbent for removal of cadmium [Cd(II)] from aqueous solution was investigated. The modified green adsorbent; before and after biosorption process was characterized by FTIR, SEM-EDX and XRD analysis. The equilibrium studies were systematically carried out in a batch process which covered various process parameters such as effect of pH, contact time, temperature, adsorbent dose, agitation rate and initial ion concentration of Cd(II). The adsorption isotherm study showed that Langmuir model ($R^2 = 0.9985$) provides an appropriate description of metal ion sorption process. The adsorption kinetics was found to follow pseudo-second-order rate kinetic model ($R^2 = 0.9896$). Thermodynamic study revealed that the biosorption process for removal of Cd(II) by using FbMGDA was endothermic, spontaneous and proceeded with increased randomness. Maximum desorption of the Cd(II) metal ions (77.019%) was acquired in 0.1 M HCl eluent. The results from this study revealed that Methylglycinediacetic acid modified leaves of *Ficus benghalensis* (FbMGDA) is an excellent green adsorbent, economically feasible and sustainable solution for the removal of Cd(II) from water.

Key words- Ecotoxicity, Methylglycinediacetic acid, cadmium, green adsorbent, biosorption

I. INTRODUCTION

Advances in science and technology have brought progress and developments in many spheres of the society but in the process also contributed to the degradation of environment. Man in his interest towards the development got addicted to various luxuries and comforts which have resulted in continuously increasing adverse impact on the environment adding to the already existing complexities of the nature. The pollution due to heavy metals and metalloids is a widespread problem and causes a major degradation in each segment of the environment. It is indeed a matter of great concern to everyone as it has direct indirect effects on human health and environment.

Heavy metals like lead, cadmium, chromium, zinc and copper contamination in wastewater is mainly arises 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 (Liu et. al., 2008; Sari et. al., 2007). Cumulative anthropogenic release of heavy metals into the environment has disrupted the natural biogeochemical cycles. On the other hand, discharge of these toxic metals from industrial waste streams in to the environment without proper management has become of a great global environmental concern today. Heavy metals persist in the environment and through a process of bioaccumulation; they can further enter into the food chains and affects ecosystem (Bhattacharya, 2007).

Poor and developing countries are at high risk due to lack of waste water treatment technologies. Several techniques such as solvent extraction, ion exchange, membrane process, electrodialysis, precipitation, phytoextraction, ultra filtration and reverse osmosis and adsorption have been tested for removal of heavy metals and treatment of effluents laden with heavy metals (Chong and Volesky, 1995; Elouear et. al., 2009). These methods are non-economical with disadvantages such as incomplete metal removal, high reagent cost, energy requirements and generation of toxic sludge or other waste products that require further disposal or treatment. Therefore, the importance of applying inexpensive metal remedial technologies will be increased. This requires a compendious research in this field to find economically viable solution to metal pollution. In this endeavor, 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 substances 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 (Nouri et. al., 2001). 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 leaves of *Ficus benghalensis* (FbMGDA) as green adsorbent. The objective of this study was to characterize green adsorbent before and after biosorption of Cd(II) by using FTIR, SEM-EDX and XRD analysis. The study was extended 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. In addition desorption studies were also performed.

II. MATERIALS AND METHODS

1. 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. 1000 mg/L of Cd(II) solution was prepared by dissolving 2.032 gm of cadmium chloride ($CdCl_2$) in millipore water and the volume was made to the mark in a 1000 cm^3 volumetric flask using millipore water. Further desired working solutions of Cd(II) were prepared using appropriate subsequent dilutions of the stock solution**.**

2. Preparation of green adsorbent

Leaves of *Ficus benghalensis* L. (Family: Moraceae) 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. For the modification of green adsorbent by Methylglycinediacetic acid, 50 gm *Ficus benghalensis* leaf 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 leaves of *Ficus benghalensis* (FbMGDA) green adsorbent powder was stored in air tight container to protect it from moisture (Zhu et. al., 2008).

3. 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). Characterization study of FbMGDA before and after adsorption of Cd(II) was studied by Fourier Transform Infrared (JASCO; Model: FT/IR-4100), Scanning Electron Microscope and Energy-dispersive X-ray (ESEM; Model; FEI Quanta 200) and X-ray diffraction (PANalytical; Model; X' Pert Pro) analysis.

4. Batch biosorption studies

The batch biosorption method was employed to study the biosorption of Cd(II) by FbMGDA. 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 adsorption of Cd(II) by the FbMGDA green adsorbent,

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

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 determined by the following equation,

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

Where, q_e (mg metal per g dry green adsorbent) 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-Kaganer-Radushkevich (DKR) and Temkin adsorption isotherm models. 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.

III. **RESULTS AND DISCUSSION**

1.   Characterization of green adsorbent

A.   Fourier Transform Infrared (FTIR) analysis

The Fourier Transform Infrared (FTIR) spectroscopy was used to recognize the functional groups exist in the green adsorbent and the spectra before and after Cd(II) adsorption are shown in Fig.1. The spectrum was recorded by using Fourier Transform Infrared (JASCO; Model: FT/IR-4100) spectrophotometer in a spectral range of 400-4000 cm^{-1}. All the FTIR analysis was executed using KBr as back ground material. As seen in the figure; green adsorbent FbMGDA before Cd(II) adsorption displays the prominent peaks at 3694.94 cm^{-1} and 3408.57 cm^{-1} are the indicators of amide N-H stretch and alcohol (O-H) group respectively. The peak located at 2918.73 cm^{-1} is strongly associated with the presence of carboxylic acid group. The peaks at 2850.27 and 1727.91 cm^{-1} represents the characteristic peaks of alkyl C-H stretch and carboxylic acid C≡O stretching respectively. The peak at 1620.88 cm^{-1}and 773.315 cm^{-1} was attributed to aromatic C=C bending and aromatic C-H bending respectively. FTIR spectra of Cd(II) adsorbed FbMGDA showed that the peaks at 1727.91, 1620.88 and 773.315 cm^{-1} were shifted, respectively, to 1731.76, 1619.91 and 775.244 cm^{-1} due to Cd(II) interaction with these functional groups.
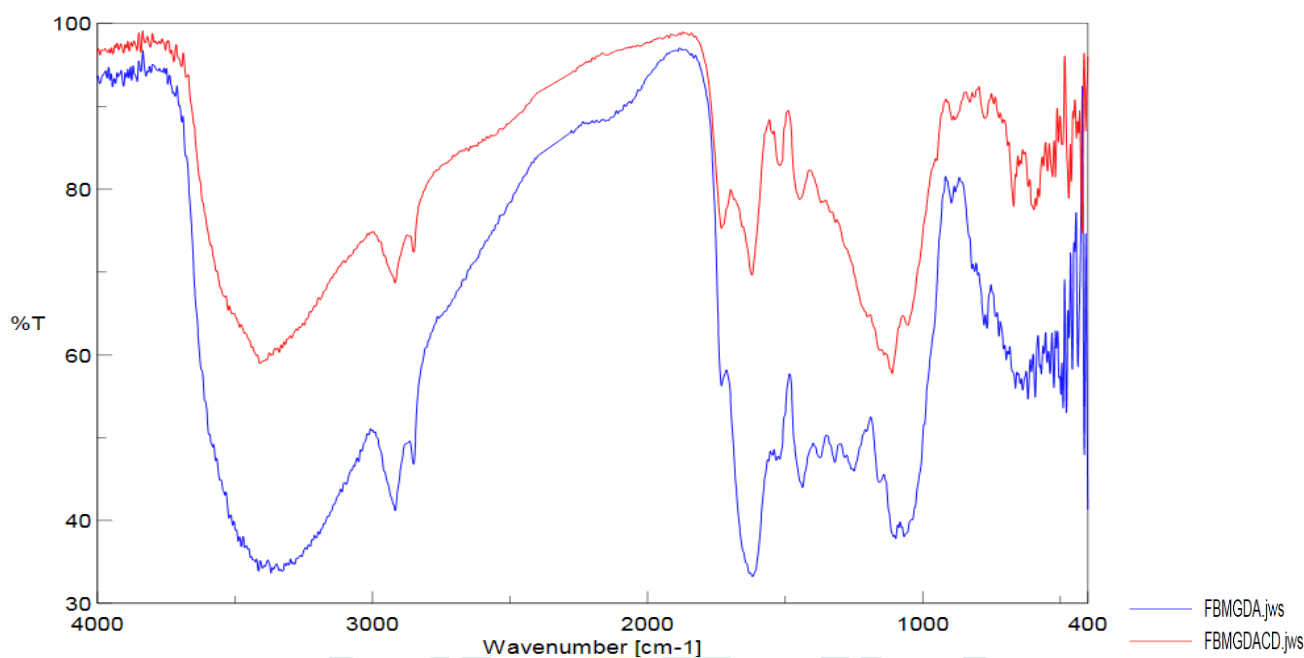

Fig. 1: Fourier Transform Infrared (FTIR) spectra of FbMGDA before and after Cd(II) adsorption

B.   Scanning Electron Microscope (SEM) and Energy-dispersive X-ray (EDX) analysis

Environmental Scanning Electron Microscope was used to characterize the surface morphology of the green adsorbent. The SEM images of green adsorbent before and after Cd(II) metal uptake at 2500 × magnification are shown in Fig. 2. As presented in Fig. 2 (a), FbMGDA exhibited a dense and porous surface texture with large surface area for ion-surface interaction. Interaction of FbMGDA with Cd(II) has resulted in the formation of discrete aggregates on its surface and surface become highly irregular and rough as presented in Fig. 2 (b). From this analysis, it is clear that there was significant alteration in the surface morphology of the green adsorbent before and after cadmium adsorption.
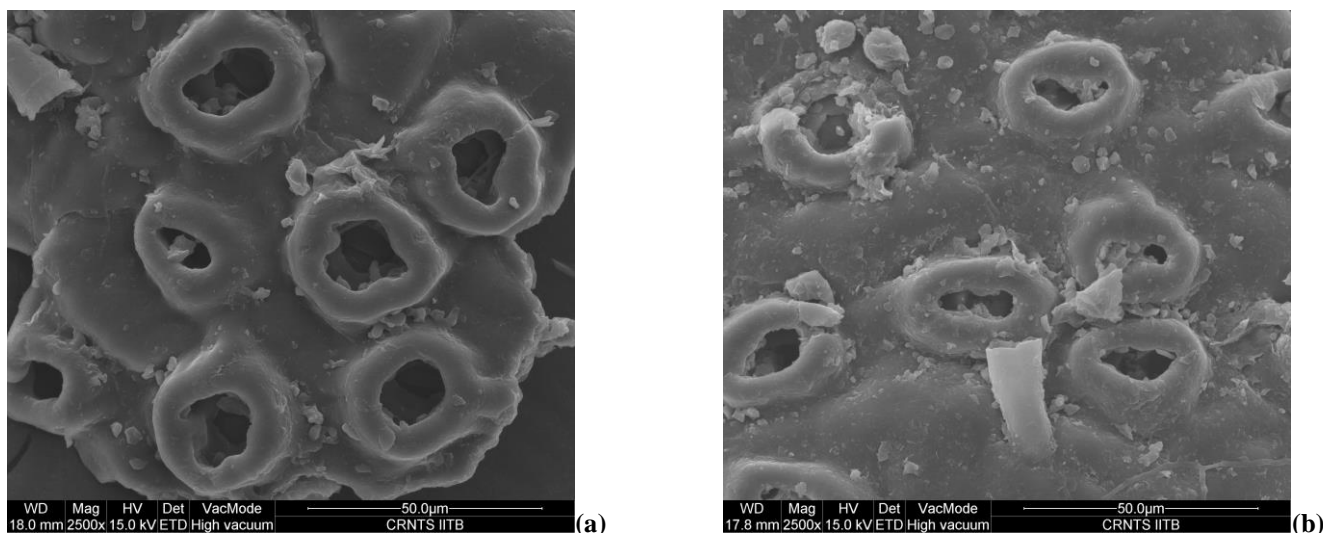
Fig. 2: Scanning Electron Microscope (SEM) images of FbMGDA before Cd(II) adsorption (a) and after Cd(II) adsorption (b)

EDX is a technique which is used to recognize the elemental presence on the material surface based on its characteristic X-ray energy. Fig. 3 displays the typical EDX patterns for FbMGDA before and after Cd(II) adsorption. The EDX pattern for the FbMGDA before adsorption did not display the characteristic indication of Cd(II) as shown in Fig. 3 (a), whereas the FbMGDA following cadmium biosorption exhibited distinct peak for cadmium as shown in Fig. 3 (b), thus providing a direct confirmation for cadmium biosorption onto the green adsorbent FbMGDA.
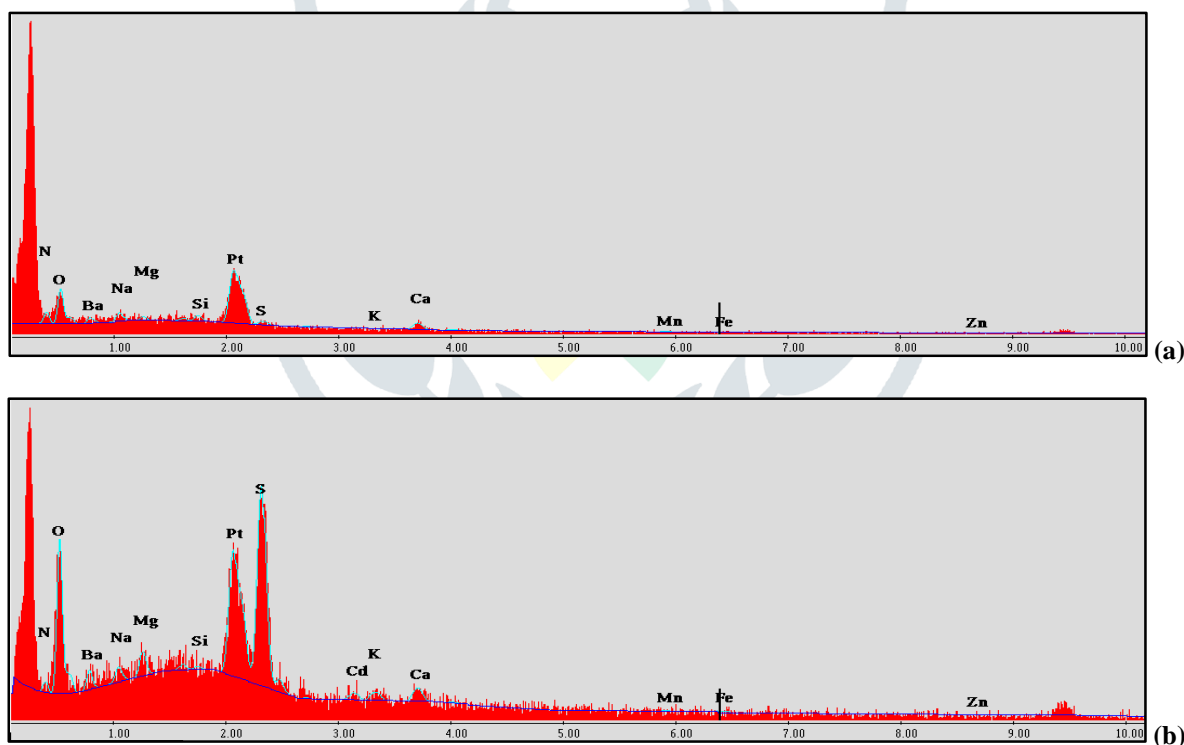

Fig. 3: Energy Dispersive X-Ray (EDX) analysis of FbMGDA before Cd(II) adsorption (a) and after Cd(II) adsorption (b)

C. X-ray diffraction (XR-D) analysis

XRD patterns for FbMGDA before and after Cd(II) adsorption is shown in Fig. 4. This provides evidence about the changes in the crystalline and amorphous nature of the green adsorbent. The sharp peaks present in the figures specified the crystalline nature of the biosorbent. In addition, the occurrence of other weak intensity peaks in the spectra directs the amorphous nature of the biosorbent. The amorphous nature of the adsorbent suggests that metal ions can easily penetrate the surface which is desirable for an effective removal. It can be seen from the XRD patterns that there is significant difference in the intensity of the peaks and it is also interesting to note that there is shift in the diffraction pattern after adsorption. The shift in peak is attributed to the adsorption of the Cd(II) metal on to the surface of the green adsorbent FbMGDA (Kugbe et. al., 2009).
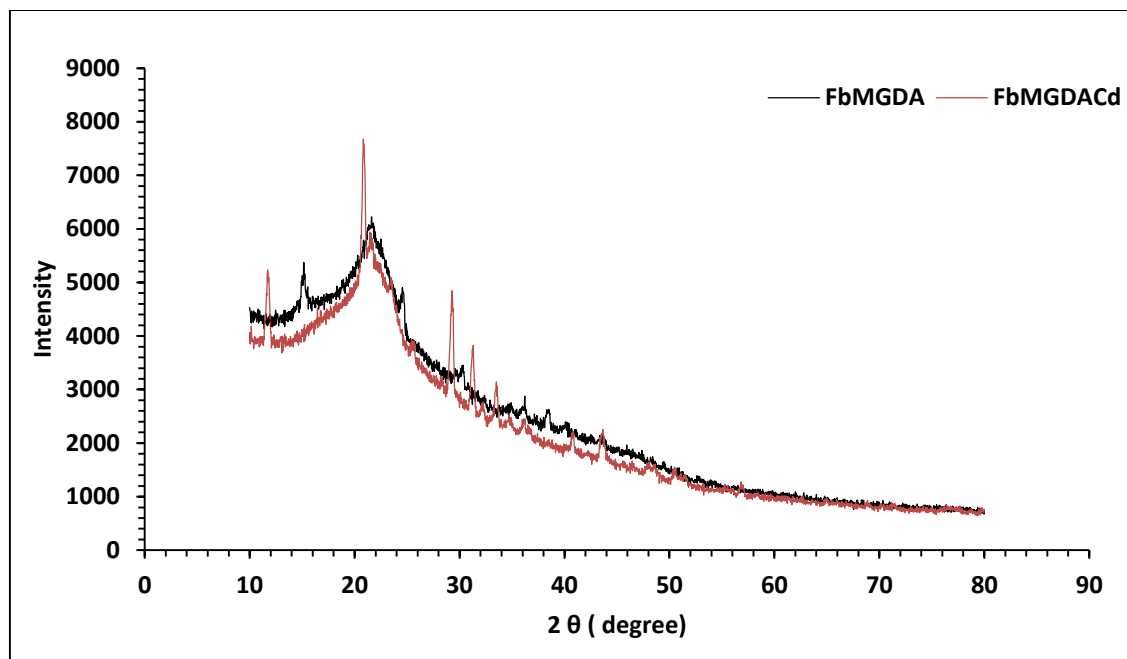
Fig. 4: X-ray diffraction (XRD) analysis of FbMGDA before and after Cd(II) adsorption

2.   Batch biosorption study

A.   Study of Experimental Parameters
1.   Effect of pH

pH controls the process of biosorption by influencing the surface change of the green adsorbent, the degree of ionization and the species of adsorbate. The effect of pH of aqueous solution on % removal of Cd(II) is shown in Fig. 5. The % removal of metal was increased from 52.596% to 77.499% for FbMGDA green adsorbent as pH was increased from 1 to 6 and decreased beyond pH value of 6. Low pH depresses biosorption of cadmium, due to competition with H^+ ions for appropriate sites on the green adsorbent surface. However, with increasing pH, this competition weakens and Cd ions replace H^+ ions bound to the green adsorbent (Stephen and Sulochana, 2004).

2.   Effect of green adsorbent dose

Fig. 6 shows the effect of green adsorbent dose on the percentage removal of Cd(II). The percentage of Cd(II) ions adsorbed by FbMGDA increased from 35.911% to 77.983% 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).

3.   Effect of initial cadmium (II) ion concentration

The experiment was conducted by varying the initial Cd(II) ions concentration (20 mg/L to 100 mg/L) and 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. 7 percentage removal of Cd(II) ions to some extent decreased with the increase in initial Cd(II) ions concentration by FbMGDA green adsorbent.

4.   Effect of contact time

The effect of contact time on biosorption of Cd(II) ions by FbMGDA are shown in Fig. 8. There is a significant increase in the biosorption efficiency with time by FbMGDA. The maximum removal of Cd(II) was found to be 78.987 % after 90 minutes of contact time. This fast metal sorption specifies that binding might have resulted from interaction with functional groups of the biosorbent rather than diffusion (Sanusi et. al., 2018; Teli and Bhalerao, 2019).

5.   Effect of temperature

Biosorption of Cd(II) by FbMGDA was studied at different temperatures 10 °C to 60 °C, at fixed pH 6, cadmium concentration (100 mg/L), adsorbent dosage (0.5 gm/50 ml), agitation rate (120 rpm) and contact time (90 minutes). Fig. 9 illustrates Cd(II) sorption on FbMGDA at different temperatures. It can be inferred from the graph that rise in temperature brings about a sharp increase in Cd (II) sorption from 10 °C to 60 °C. The optimum removal of Cd(II) was observed at 60 °C temperature with

87.387% removal by FbMGDA green adsorbent. 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 FbMGDA could be chemical sorption in addition to physical sorption in which sorption increases with an increase in temperature (Singh et. al., 2005; Singh and Hasan, 2005).

6. 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 rpm to 200 rpm). The effect of agitation speed on the adsorption of Cd(II) ions by FbMGDA green adsorbent is shown in Fig. 10. As agitation speed increased up to 120 rpm, adsorption capacity of FbMGDA for removal of Cd(II) also increased from 49.700 % to 77.984% %. Further increase in agitation speed resulted in significant decrease in removal efficiency of Cd(II) by FbMGDA.
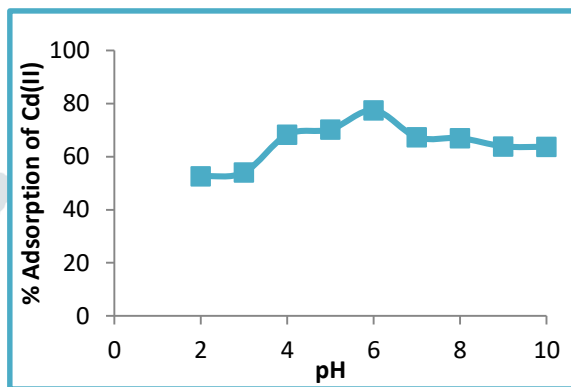

Fig. 5: Effect of pH on Cd(II) biosorption by FbMGDA (Adsorbent dose: 0.5 gm/50 ml, Cd(II) concentration: 100 mg/L, Contact time: 90 minutes, Temperature: 30 °C, Agitation rate: 120 rpm)
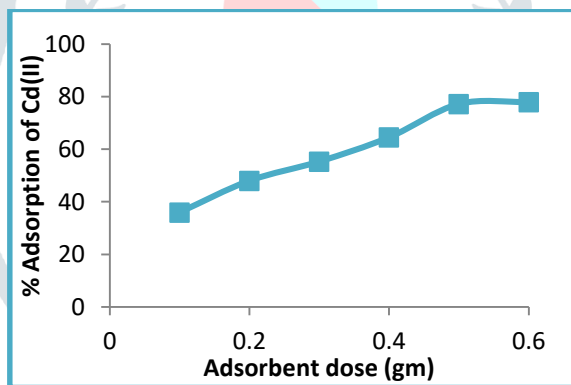

Fig. 6: Effect of adsorbent dose on Cd(II) biosorption by FbMGDA (pH: 6, Cd(II) concentration: 100 mg/L, Contact time: 90 minutes, Temperature: 30 °C, Agitation rate: 120 rpm)
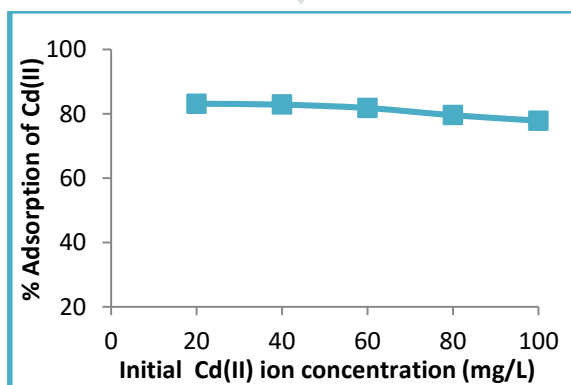

Fig. 7: Effect of initial Cd(II) ion concentration on biosorption by FbMGDA (pH: 6, Adsorbent dose: 0.5 gm/50 ml, Contact time: 90 minutes, Temperature: 30 °C, Agitation rate: 120 rpm)
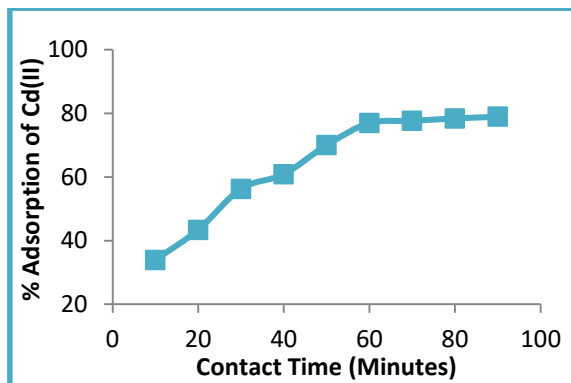
Fig. 8: Effect of contact time on Cd(II) biosorption by FbMGDA (pH: 6, Adsorbent dose: 0.5 gm/50 ml, Cd(II) concentration: 100 mg/L, Temperature: 30 °C, Agitation rate: 120 rpm)
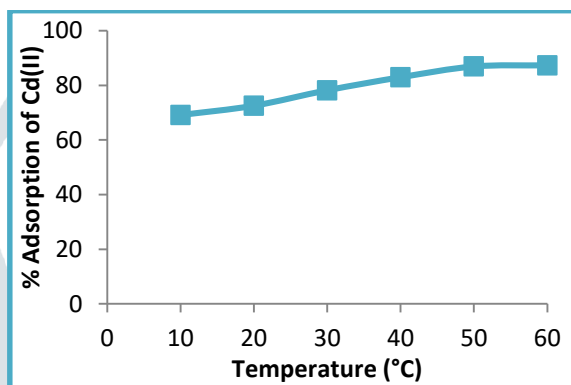

Fig. 9: Effect of temperature on Cd(II) biosorption by FbMGDA (pH: 6, Adsorbent dose: 0.5 gm/50 ml, Cd(II) concentration: 100 mg/L, Contact time: 90 minutes, Agitation rate: 120 rpm)
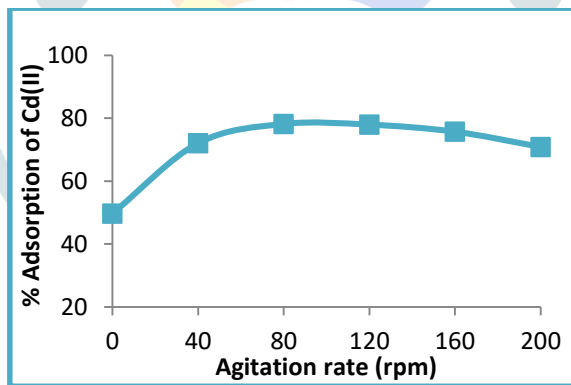

Fig. 10: Effect of agitation rate on Cd(II) biosorption by FbMGDA (pH: 6, Adsorbent dose: 0.5 gm/50 ml, Cd(II) concentration: 100 mg/L, Contact time: 90 minutes, Temperature: 30 °C)

B. Adsorption isotherm study

The results obtained from the biosorption of Cd(II) ions on FbMGDA 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 the Table 1.

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;

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

Where q_m is the maximum biosorption capacity of adsorbent (mg g^{-1}). b is the Langmuir biosorption constant (L mg^{-1}) 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:

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

The linear plots of $1/q_e$ vs $1/c_e$ is shown in Fig. 11 (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.

The essential characteristics of the Langmuir isotherm parameters can be used to predict the affinity between the biosorbate and biosorbent which is calculated using following equation;

$$R_L = \frac{1}{1 + bC_i} \qquad (5)$$

Where, b is the Langmuir constant and C_i is the maximum initial concentration of metal. The value of separation parameters (R_L) provides imperative evidence about the nature of adsorption. The value of R_L indicated the type of Langmuir isotherm to be irreversible ($R_L = 0$), favorable ($0 < R_L < 1$), linear ($R_L = 1$) or unfavorable ($R_L > 1$). The value of separation factor (RL) was found to be 0.3378-0.7184 for FbMGDA with Cd(II) concentration range of 20 mg/L to 100 mg/L. Since the values of RL lies in the range of 0 to 1 ($0 < RL < 1$), the present data satisfies Langmuir isotherm condition (Malkoc and Nuhoglu, 2005).

Biosorption can also be interpreted in terms of surface area coverage against initial metal ion concentration. Langmuir model for surface area of green adsorbents surface has been represented in the following equation:

$$bC_i = \frac{\theta}{1 - \theta} \qquad (6)$$

Where, θ is the surface area coverage.

The θ was found to be 0.2816-0.6622 for FbMGDA with Cd(II) concentration range of 20 mg/L to 100 mg/L. It was revealed that increase in initial metal ion concentration for green adsorbent biomass increases the surface coverage on the biomass until the surface is nearly fully covered with a monomolecular layer. Surface coverage values indicated that FbMGDA green adsorbent is the most effective in biosorption of Cd(II).

2. 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;

$$q = KC_e^{1/n} \qquad (7)$$

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:

$$\log qe = \log K + \frac{1}{n} \log C_e \qquad (8)$$

Equilibrium data for the adsorption is plotted as log q_e vs log C_e, as shown in Fig. 11 (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.

The n value indicates the degree of non-linearity between solution concentration and adsorption as follows: if $n = 1$, then adsorption is linear; if $n < 1$, then adsorption is chemical process; if $n > 1$, then adsorption is a physical process. The n value in Freundlich equation was found to be 1.2210 for FbMGDA. Since $n > 1$, this indicates that biosorption is a physical process.

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

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

$$ln q_e = \ln q_m - \beta \, \varepsilon^2 \qquad (9)$$

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

$$\varepsilon = RTln\left(1 + \frac{1}{C_e}\right) \qquad (10)$$

Equilibrium data for the adsorption is plotted as lnq_e vs ε^2, as shown in Fig. 11 (c). The two constants β and q_m are calculated from the slope (β) and intercept (lnq_m) of the line, respectively. The values of adsorption energy E was obtained by the following relationship,

$$E = \frac{1}{\sqrt{-2\beta}} \qquad (11)$$

The E value was found to be 0.4082 KJ mol^{-1}. 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^{-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 (Olivieri and Brittenham, 1997). In the present work, E value (0.4082 KJ mol^{-1}) which is less than 8 KJ mol^{-1}, the biosorption of Cd(II) ions onto FbMGDA is of physical in nature.
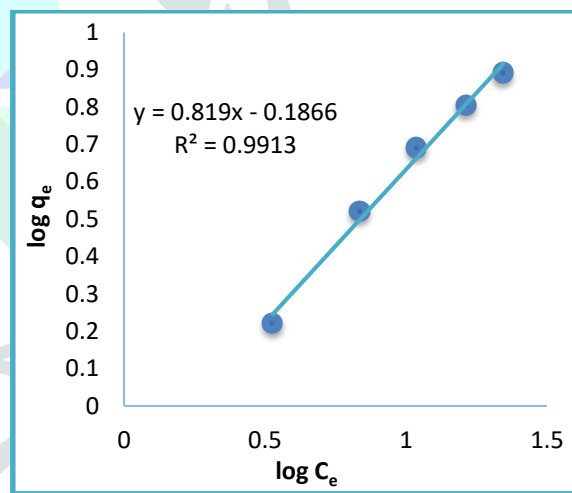
4. Temkin adsorption isotherm

Linearized Temkin adsorption isotherm is given by the equation;

$$q_e = \frac{RT}{b_T}\, ln\, A_T + \frac{RT}{b_T}\, ln\, C_e \qquad (12)$$

Where b_T is the Temkin constant related to heat of biosorption (KJ/mol) and A_T is the Temkin isotherm constant (L/g) (Temkin, 1940). Equilibrium data for the adsorption is plotted as q_e vs lnC_e, as shown in Fig. 11 (d). The two constants b_T and A_T are calculated from the slope (RT/b_T) and intercept (RT/b_T. $ln\, A_T$) of the line. The values of A_T, b_T and regression coefficient (R^2) are listed in Table 1.
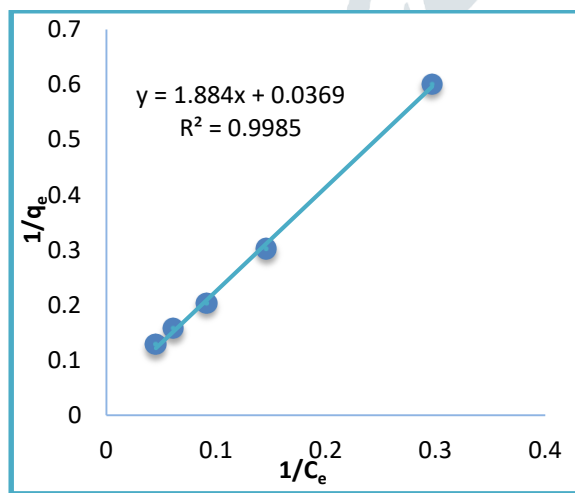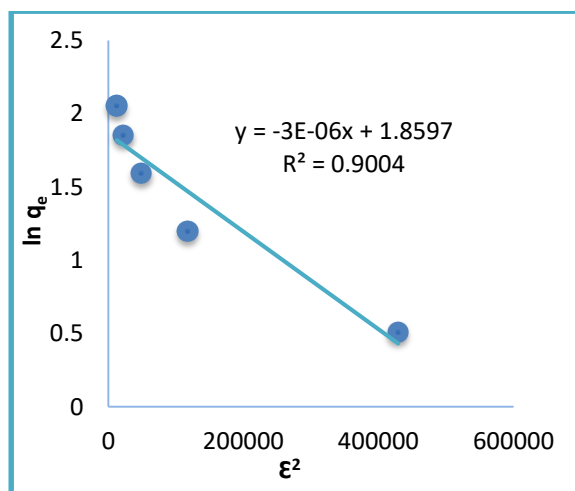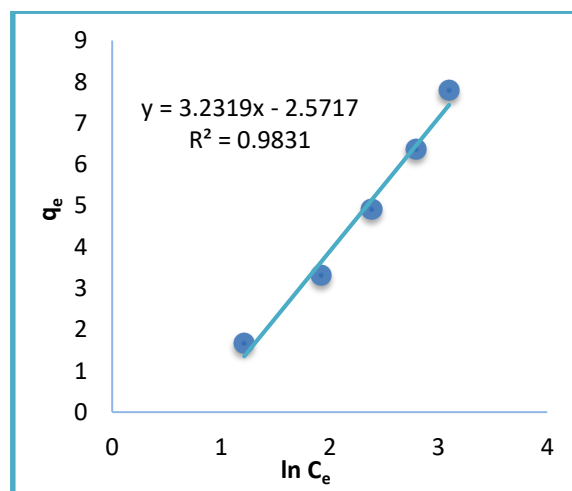
Fig. 11: Adsorption isotherms (a) Langmuir, (b) Freundlich (c) DKR and (d) Temkin for Cd(II) biosorption by FbMGDA

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

Langmuir parameters			Freundlich parameters			DKR parameters				Temkin parameters		
q_m (mg/g)	b (L/mg)	R^2 (L/mg)	K	$1/n$	R^2	β (mol^2/J^2)	q_m (mg/g)	E (KJ/mol)	R^2	A_T (L/mg)	b_T (KJ/mol)	R^2
27.10	0.02	0.9985	0.65	0.82	0.9913	-3 x 10^{-6}	6.43	0.408	0.9004	0.45	0.78	0.9831

C. Adsorption kinetics studies

To determine the controlling mechanism of the biosorption process, experimental data were scrutinized for pseudo-first-order equation (Lagergren, 1898), pseudo-second-order 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;

$$\ln(q_e - q_t) = \ln q_e - k_1 t \qquad (13)$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \qquad (14)$$

$$q_t = \frac{1}{\beta} \ln(\alpha\beta) + \frac{1}{\beta} \ln t \qquad (15)$$

$$q_t = k_i t^{0.5} + c \qquad (16)$$

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 symbols of α (mg g^{-1} min^{-1}) and β (g mg^{-1}) are Elovich coefficients representing 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 adsorption 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 adsorption process obeys the pseudo-second order model. If the adsorption 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 adsorption process obeys the Weber and Morris intra-particle diffusion model (Septhum et. al., 2007).

Biosorption of Cd(II) onto FbMGDA 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.12 (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 coefficient value $(R^2 = 0.9451)$ 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 (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.12 (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 $(R^2= 0.9896)$. 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 green adsorbent (Jadav et. al., 2015).

The Elovich model was plotted for q_t against ln t as shown in the Fig. 12 (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 (Thomas and Thomas, 1947; Poojari and Bhalerao, 2018). The Elovich model showed a correlation coefficient $(R^2= 0.9725)$.

The Weber & Morris intra-particle diffusion model was plotted for q_t against $t^{0.5}$ as shown in the Fig. 12 (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 $(R^2 = 0.9529)$ 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 (Weber and Morris, 1963; Poojari and Bhalerao, 2018).
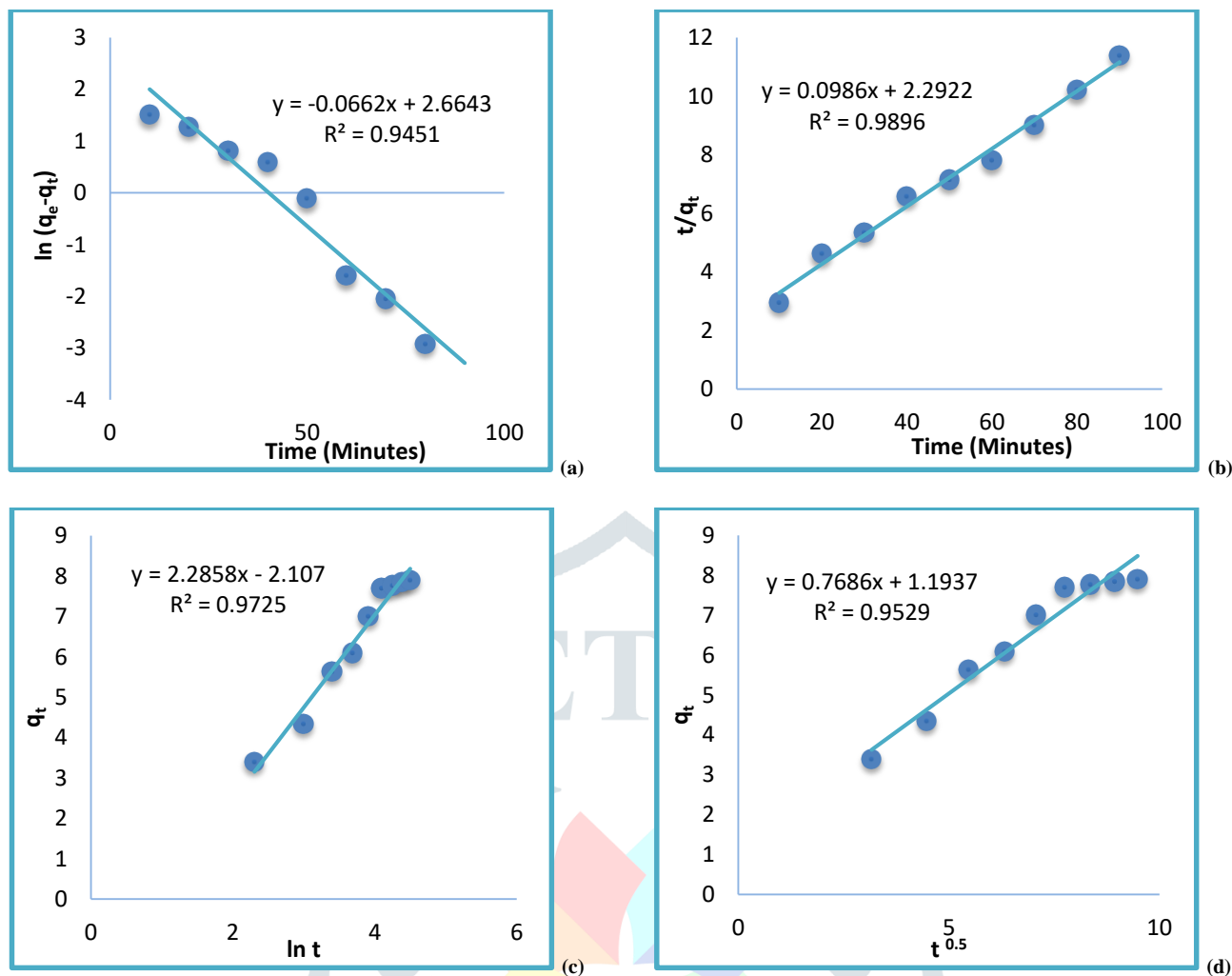
Fig.12: Adsorption kinetic models (a) pseudo-first-order, (b) pseudo-second-order (c) Elovich and (d) Weber and Morris intra-particle diffusion, for Cd(II) biosorption by FbMGDA

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

Pseudo-first-order model			Pseudo-second-order model			Elovich model			Intra-particle diffusion model		
q_e (mg gm^{-1})	k_1 (min^{-1})	R^2	q_e (mg gm^{-1})	k_2 (gm mg^{-1} min^{-1})	R^2	α (mg gm^{-1} min^{-1})	β (gm mg^{-1})	R^2	K_i (mg gm^{-1} min$^{-1/2}$)	C (mg gm^{-1})	R^2
14.36	0.15	0.9421	10.14	0.0042	0. 9896	0.91	0.44	0.9725	0.77	0.19	0.9529

D. 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;

$$K_c = \frac{C_{Ae}}{C_e} \tag{15}$$

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

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

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

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 green adsorbent per liter of solution at equilibrium (mg/L). $\Delta G°$, $\Delta H°$ 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) (Catena and Bright, 1989).

The values of $\Delta H °$and $\Delta S°$ were determined from the slope and the intercept from the plot of *ln Kc* versus *1/T* (Fig. 13). 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 FbMGDA. The positive value of $\Delta S°$ shows an affinity of green adsorbent and the increasing randomness at the solid-solution interface during the biosorption process (Sharma and Bhalerao, 2018).
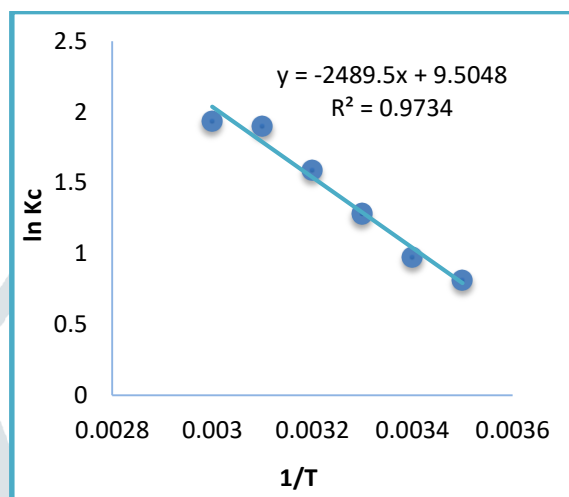

Fig. 13: Plot of *lnKc* against *1/T* for determination of thermodynamic parameters for Cd(II) biosorption by FbMGDA

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

Sr. No.	Temperature (^{0}C)	Temperature (K)	Kc	$-\Delta G^0$ (KJ/mol)	ΔH^0 (KJ/mol)	ΔS^0 (J/mol)
1	10 °C	283	2.2454	1.9032		
2	20 °C	293	2.6495	2.3736		
3	30 °C	303	3.5969	3.2247		
4	40 °C	313	4.8872	4.1288	20.6977	79.0229
5	50 °C	323	6.6770	5.0987		
6	60 °C	333	6.9283	5.3589		

E. Desorption study

Desorption of Cd(II) metal ions from Cd(II) loaded FbMGDA was carried out using 0.1M NaOH, 0.1M HCl, 0.1M HNO$_3$ and 0.1M H$_2$SO$_4$. It was observed from Fig.14 that the maximum desorption obtained in 0.1 M HCL. FbMGDA found to be the most effective biosorbent with desorption efficiency 77.019% (0.1 M HCl), 72.517% (0.1 M NaOH), 71.825% (0.1M HNO$_3$) and 66.234% (0.1 M H$_2$SO$_4$). The maximum desorption demonstrated high reusability of the adsorbent, making removal and recovery of Cd(II) from waste water containing Cd(II) a more sustainable and economical alternative.
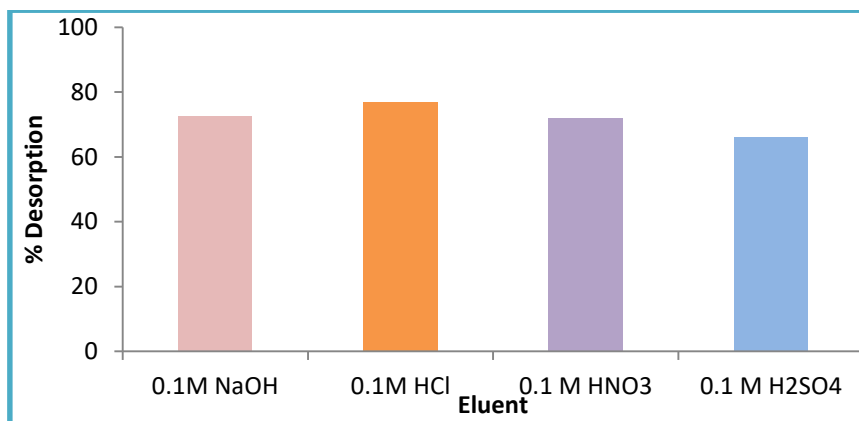
Fig. 14: Desorption study using 0.1M NaOH, 0.1M HCl, 0.1M HNO$_3$ and 0.1M H$_2$SO$_4$

CONCLUSION

Methylglycinediacetic acid modified leaves of *Ficus benghalensis* (FbMGDA) as low-cost green adsorbent investigated in this study appears to be a promising green adsorbent for the removal of cadmium from aqueous solution. Biosorption characteristics of Cd(II) onto FbMGDA were found to be influenced by pH, adsorbent dose, initial Cd(II) ions concentration, temperature, contact time and agitation rate. The optimum removal of the Cd(II) ions was observed at pH 6. FTIR, SEM-EDX and XRD characterization of the FbMGDA green adsorbent before and after the adsorption of Cd(II) ions have shown marked differences in morphology and chemical constitution of the native and Cd(II) ions loaded FbMGDA. These morphological and compositional changes provided evidence of the adsorption of Cd(II) ions onto the available binding sites in the green adsorbent. Langmuir, Freundlich, DKR and Temkin isotherm models were applied to the experimental adsorption data and the data fitted Langmuir (R^2 = 0.9985) model better than the other adsorption isotherm models. The maximum monolayer coverage adsorption capacity from the Langmuir isotherm model was obtained as 27.10 mg/g. The kinetic data followed the pseudo-second-order kinetic model (R^2 = 0.9896). Maximum desorption of the metal was observed in 0.1 M HCl eluent. Thermodynamic study revealed that the biosorption process was endothermic, spontaneous and proceeded with increased randomness. In the view of these results, it can be concluded that the leaves of *Ficus benghalensis* (FbMGDA) can be effectively used as a green adsorbent for the removal of Cd(II) from wastewater and industrial effluents.

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