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Role of MGDA Modified Pods of Peltophorum Pterocarpum (DC.) K. Heyne for the Removal of Hexavalent Chromium from Aqueous Solution: A Sustainable and Economical Approach

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Abstract: ***Occurrence of heavy metals in wastewater is of great anxiety because of their known toxic effects on the environment as well as on human beings. Progressively severer discharge regulations on heavy metals have accelerated the search for highly competent but economically viable or alternative treatment approaches for its removal. Biosorption process has been proposed as an efficient, potential, cost effective way of eliminating toxic metals from industrial effluents at low concentrations. In this study the removal of chromium [Cr(VI)] ions from aqueous solution using Methylglycinediacetic acid modified pods of Peltophorum pterocarpum (PpMGDA) as a adsorbent, in batch condition was investigated. The modified biosorbent; before and after biosorption process was characterized by FTIR, SEM-EDX and XRD analysis. The equilibrium studies were carried out covering a various process parameters which includes pH, contact time, temperature, adsorbent dose, agitation rate and initial Cr(VI) ion concentration. The equilibrium adsorption data was scrutinised with four isotherm models. Best fitting isotherm model was positioned in the following order, Langmuir (R^2 = 0.9996) > Freundlich (R^2 = 0.9991) > Temkin (R^2 = 0.9555) > DKR (R^2 = 0.9176). The adsorption kinetics was found to follow pseudo-second-order rate kinetic model (R^2 = 0.9986). Maximum desorption of the metal was acquired in 0.1 M HNO_3 eluent. Thermodynamics study showed that the biosorption process was endothermic, spontaneous and proceeded with increased randomness. The results from this study revealed that Methylglycinediacetic acid modified pods of Peltophorum pterocarpum (PpMGDA) are excellent adsorbent, widely available, economically feasible and sustainable solution for the removal of Cr(VI) from water.***

Keywords: Biosorption, chromium, Peltophorum pterocarpum, isotherm, kinetics, thermodynamics.

I. INTRODUCTION

Environmental pollution predominantly from heavy metals and minerals in the wastewater is the most severe problem in India. The quality of our environment is deteriorating day by day with the excessive and accumulative release of toxic metals from industrial effluents due to rapid industrialization. For instance, effluent discharges from textile, electroplating and battery industries are commonly contaminated with heavy metals [1].

Poor and developing countries are at great risk due to lack of waste water treatment technologies [2]. Heavy metal contamination may cause serious health problems such as cancer and brain damage due to the accumulation in living tissues and organs [3]. The numerous metals which are considerably toxic to human beings and environment include chromium (Cr), arsenic (As), copper (Cu), lead (Pb), cadmium (Cd), mercury (Hg), zinc (Zn) etc. [4]. Chromium (VI) is often found in effluents discharged from industries involved in acid mine drainage, galvanizing plants, natural ores and municipal waste water treatment plants and is not biodegradable and travels through the food chain via bioaccumulation. When chromium enters the gastric system; epigastric pain, nausea, vomiting, severe diarrhoea, corrosion of skin, respiratory tract and lung carcinoma are detected. The discharge limit of chromium from industry is less than 1 mg/L. Chromium is hazardous to health when its limit in potable water exceeds 0.5 mg/L [5]. Therefore, there is substantial interest regarding chromium removal from waste waters.

The scantiness and high cost of traditional metal treatment technologies coupled with the imposition of stricter environmental regulations and guidelines for industrial point source discharges have increased the demand for economically feasible alternative methods. Different treatment techniques such as ion exchange, membrane filtration, oxidation-reduction, chemical precipitation, adsorption, reverse osmosis and evaporative recovery are cost exhaustive for separation of heavy metals, have been developed for

effluents laden with heavy metals [6], [7]. Each process has its own merits and limitations in application, so these traditional metal removal methods have certain drawbacks (incomplete metal removal, high reagent and energy requirements, generation of toxic sludge or other waste products). The treatment of metal bearing effluents requires more effective techniques with lower costs than the conventional ones. In this endeavour, biosorption has emerged as an alternative and sustainable strategy for clean-up water. Biosorption can be defined as the ability of biological materials to accumulate heavy metals from wastewater through metabolically mediated or physico-chemical pathways of uptake [8]. Biosorption, which is the ability of various certain natural materials of biological origin, including plants, bacteria, fungi, yeast, algae, etc. to bind and concentrate heavy metals from even the most dilute aqueous solutions, offers a technically feasible and economically attractive alternative [9].

The research will emphasis on the removal of Cr(VI) from its aqueous solution by Methylglycinediacetic acid modified pods of *Peltophorum pterocarpum* (PpMGDA) as a adsorbent.

The objective of this study was to characterize biosorbent before and after biosorption 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 Cr(VI) 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

A. *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 solutions.

B. *Preparation Of Chromium (Vi) Synthetic Waste Water*

1000 ppm of Chromium (VI) was prepared by dissolving 2.8289 gm of potassium dichromate ($K_2Cr_2O_7$) 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 Cr(VI) were prepared using appropriate subsequent dilutions of the stock solution**.**

C. *Preparation Of Green Adsorbent*

Pods of *Peltophorum pterocarpum* (DC.) K. Heyne (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 to protect it from moisture.

D. *Preparation Of Methylglycinediacetic Acid Modified Pods Of Peltophorum Pterocarpum (Ppmgda)*

Methylglycinediacetic acid modification of Pods of *Peltophorum pterocarpum* was carried out according to a similar method described by Zhu *et. al.*, (2008) [10]. 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.

E. *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 Cr(VI) in the solutions before and after equilibrium was determined by measuring absorbance using Atomic Absorption Spectrophotometer (Agilent; Model: AA 240 FS). Characterization study of MGDA modified and unmodified pods of *Peltophorum pterocarpum* before and after adsorption of Cr(VI) was studied by Fourier Transform Infrared (FTIR), Scanning Electron Microscope (SEM), Energy-dispersive X-ray (EDX) and X-ray diffraction (XRD) analysis.

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F. Batch Biosorption Studies

The batch adsorption method was employed at temperature (30 °C) to examine the biosorption of Cr(VI) 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 Cr(VI) ion concentration were optimized.

The parameters were studied by combining PpMGDA with Cr(VI) solution in 250 ml conical flask. The conical flasks were placed in an incubator shaker with a constant speed and left to equilibrate. The samples were collected at predefined time intervals and the solution was separated from the adsorbent by filtration, using Whatman filter paper No. 1 and the concentration of Cr(VI) in the filtrate solutions was determined by AAS. The following equation was used to compute the percent removal (% Adsorption) of Cr(VI) by the 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 chromium (VI) 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 biosorbent) is the amount of Cr(VI) 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–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 and Morris intraparticle diffusion kinetics model.

G. Metal Desorption Studies

To evaluate desorption efficacy, Cr(VI) loaded biosorbent was dried after equilibrium sorption experiment. The dried biosorbent was contacted with 0.1M NaOH, 0.1M HCl, 0.1M HNO_3 and 0.1M H_2SO_4 separately for 90 minutes to allow Cr(VI) to be released from biosorbent. After 90 minutes of contact time the biosorbent were separated from the eluent by filtration, using Whatman filter paper No. 1 and concentration of Cr(VI) in the filtrate solution was determined by AAS to find out desorption efficiency.

$$\textit{Desorption efficiency}\ (\%) = \frac{\text{released metal ions in mg/L}}{\text{initially adsorbed metal ions in mg/L}} \times 100 \qquad (3)$$

III.RESULTS AND DISCUSSION

A. Fourier Transform Infrared (FTIR) Analysis

The Fourier Transform Infrared (FTIR) spectroscopy was used to recognize the functional groups exist in the biosorbent and the spectra before and after Cr(VI) 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; unloaded biosorbent exhibits a number of absorption peaks, reflecting the complex nature of biosorbent. The broad peak at 3410.49 cm^{-1} is the indicator of -OH group. The peaks located at 1633.41 cm^{-1} are characteristics of carbonyl group. The presence of -OH group along with carbonyl group confirms the existence of carboxyl acid groups in the biosorbent. The peaks observed at 1224.58 cm^{-1} are due to C-O bonds.

The –OH, –NH, carbonyl and carboxyl groups are essential sorption sites. The spectra for the before and after adsorption of Cr(VI) on PpMGDA samples were compared and it was revealed that there were minor shifts in most of the functional groups. From FTIR study, the formation of new absorption bands, the change in absorption intensity and the shift in wavenumber of functional groups could be due to interaction of Cr(VI) metal ions with active sites of biosorbent. T

he Cr(VI) metal ions bound to the active sites of the biosorbent through either electrostatic attraction or complexation mechanism [11].

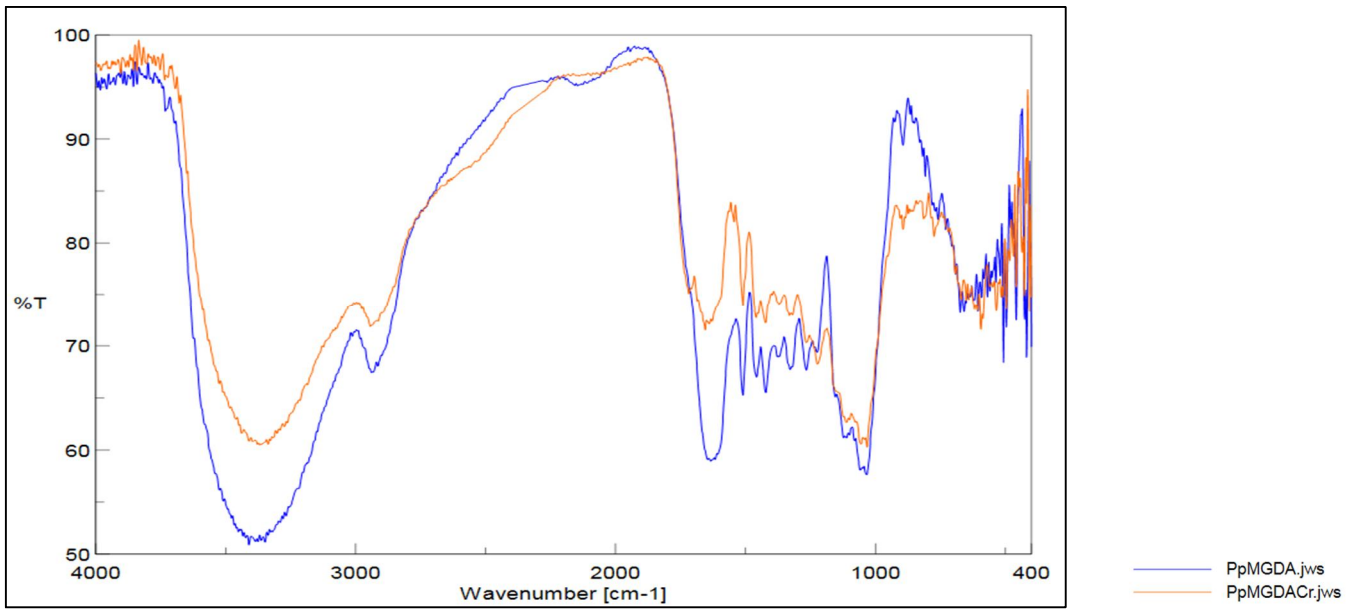


Fig. 1: FTIR spectra of PpMGDA before and after Cr(VI) adsorption

B. Scanning Electron Microscope (SEM) Analysis

Environmental Scanning Electron Microscope (ESEM; Model; FEI Quanta 200) was used to characterize the surface morphology of the biosorbent. The biosorbent samples were covered with a thin layer of platinum and an electron acceleration voltage of 20 KV was applied and then Scanning Electron Micrograph was documented. The SEM images of before and after Cr(VI) metal uptake at 1500 × magnification are shown in Fig. 2. As presented in Fig. 2 (a), PpMGDA exhibited a dense and porous surface texture with large surface area for ion-surface interaction. Interaction of PpMGDA with Cr(VI) has resulted in the formation of discrete aggregates on its surface and surface become highly irregular and rough Fig. 2 (b). From this analysis, it is clear that there was significant transformation in the surface morphology of the biosorbent before and after chromium adsorption.

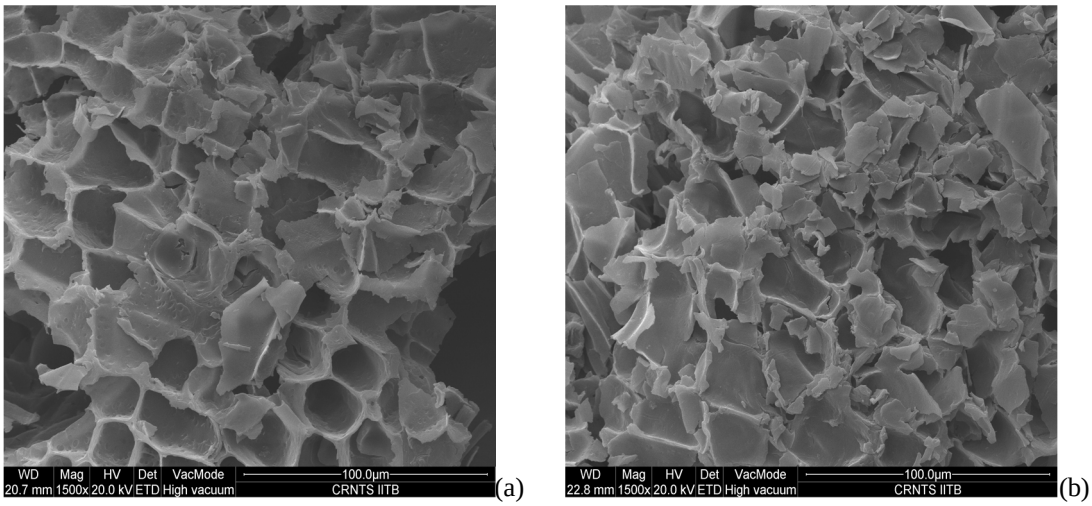


Fig. 2: Scanning Electron Microscope (SEM) images of PpMGDA before Cr(VI) adsorption (a) and after Cr(VI) adsorption (b)

C. Energy-Dispersive X-Ray (EDX) Analysis

EDX is an analytical technique which is used to recognize the element presence on the material surface based on its characteristic X-ray energy. Fig. 3 displays the typical EDX patterns for PpMGDA before and after Cr(VI) adsorption. The EDX pattern for the PpMGDA before adsorption did not display the characteristic indication of Cr(VI) as shown in Fig. 3 (a), whereas the PpMGDA following chromium biosorption exhibited distinct peak for chromium Fig. 3 (b), thus providing a direct confirmation for chromium biosorption onto the biosorbent.

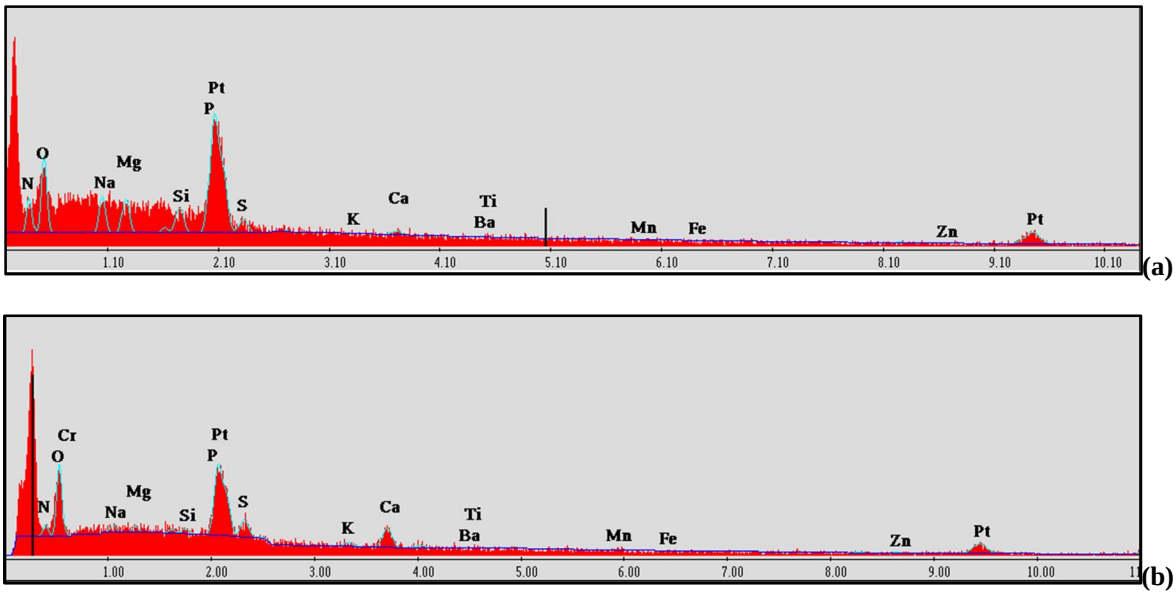
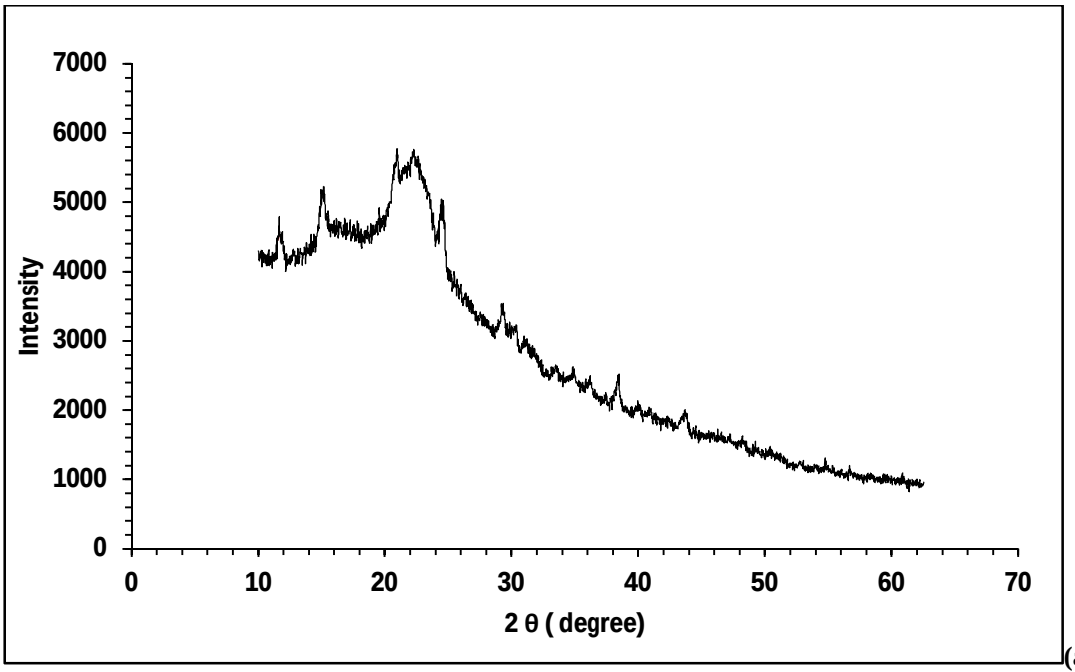
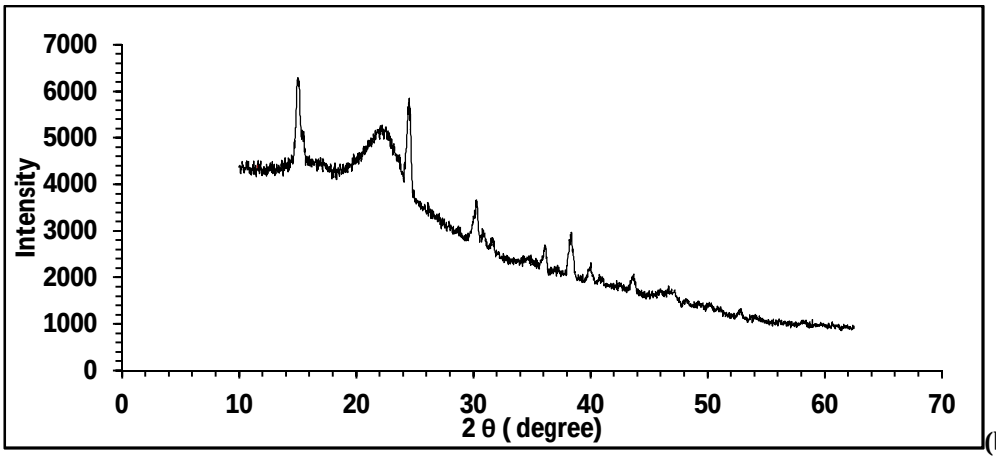


Fig. 3: Energy Dispersive X-Ray (EDX) analysis of PpMGDA before Cr(VI) adsorption (a) and after Cr(VI) adsorption (b)

D. X-ray Diffraction (XR-D) Analysis

X-ray diffraction (XRD) analysis was carried out by using X-ray diffractometer (Rigaku, Model: Miniflex II) using CuKα X-ray radiation. XRD patterns for PpMGDA before and after Cr(VI) adsorption is shown in Fig. 4. This provides evidence about the alterations in the crystalline and amorphous nature of the 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. These results are in good agreement with those reported by Kugbe *et al.* (2009) [12]. 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 Cr(VI) metal on to the surface of the adsorbent.





(b)

Fig. 4: X-ray diffraction (XRD) analysis of PpMGDA before Cr(VI) adsorption (a) and after Cr(VI) adsorption (b)

E. Effect of pH

pH is a vital parameter in the biosorption process due to its influence on the surface properties of the biosorbent and the ionic form of the metal ion in solution [13]. The effect of pH on the adsorption process was examined by undertaking the batch adsorption technique at different hydrogen ion concentrations (pH range 2-10) while keeping the other experimental parameters constant. The results of effect of different pH on adsorption of Cr(VI) ions are shown in Fig. 5, which showed that biosorption of Cr(VI) decreases with increase in pH. The optimum removal was found to be at pH 2 (96.349 %). From this observation, it is clear that the efficiency of adsorption is very high at low pH. At lower pH values, the surface of the biosorbent is surrounded by hydronium ions, which enhance the Cr(VI) interaction with binding sites of the biosorbent by greater attractive forces. However, at higher pH, the overall surface charge on the biosorbent became negative and sorption of Cr(VI) decreased. In aqueous phase, Cr(VI) may exist in different anionic forms, such as chromate CrO_4^{2-}, dichromate $Cr_2O_7^{2-}$ or hydrogen chromate $HCrO_4^-$ [14]. Acid chromate ion species $HCrO_4^-$ is mainly present at lower pH, which gets converted to other forms as the pH increases. At lower pH due to protonation, the surface of the biosorbent becomes positively charged. Protons can easily coordinate with the functional groups present on the surface of the biosorbent. Binding of anionic Cr(VI) species increases with the increase in positive surface charge of the biosorbent, resulting in higher biosorption at lower pH values. As the pH increases, the hydrogen ion concentration decreases and the surface charge of the biosorbent becomes negative which prevents the sorption of negatively charged chromium ion species [15], [16].

F. Effect Of Adsorbent Dose

Experiment was conducted by keeping other parameters constant except amount of biosorbent which was varied from 0.1 - 0.6 gm/50 ml. It can be observed from Fig. 6 that the adsorption of Cr(VI) increased from 38.667 % to 97.015 % on to PpMGDA by varying its dosage from 0.1 gm to 0.6 gm. This is attributed to increased adsorbent surface area and availability for more adsorption sites [17], [18].

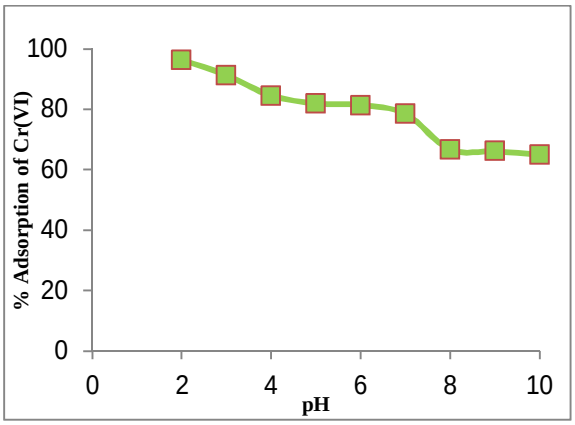


Fig. 5: Effect of pH on Cr(VI) biosorption by PpMGDA (Adsorbent dose : 0.5 gm/50 ml, Cr(VI) concentration: 100 mg/L, Contact time: 90 minutes, Temperature: 30 °C, Agitation rate: 120 rpm)

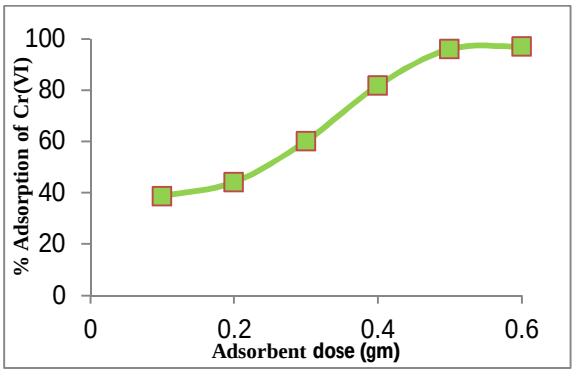


Fig. 6: Effect of adsorbent dose on Cr(VI) biosorption by PpMGDA (pH: 2, Cr(VI) concentration: 100 mg/L, Contact time: 90 minutes, Temperature: 30 °C, Agitation rate: 120 rpm)

G. Effect Of Initial Chromium (Vi) Ion Concentration

The experiment was conducted by maintaining the contact time at 90 minutes, pH 2, 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 Cr(VI) ions to some extent decreased with the increase in initial Cr(VI) ions concentration by PpMGDA adsorbent.

H. Effect of Contact time

In this experiment, all of the parameters except contact time were kept constant. The effect of contact time on Cr(VI) adsorption efficiency is shown in Fig.8. There is a significant increase in the biosorption efficiency with time by PpMGDA. The maximum removal of Cr(VI) was found to be 96.841 % 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 biosorbent rather than diffusion [19].

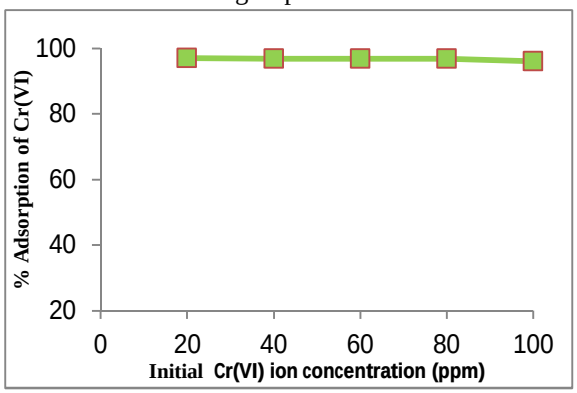


Fig. 7: Effect of initial Cr(VI) ion concentration on biosorption by PpMGDA (pH: 2, Adsorbent dose: 0.5 gm/50 ml, Contact time: 90 minutes, Temperature: 30 °C, Agitation rate: 120 rpm)

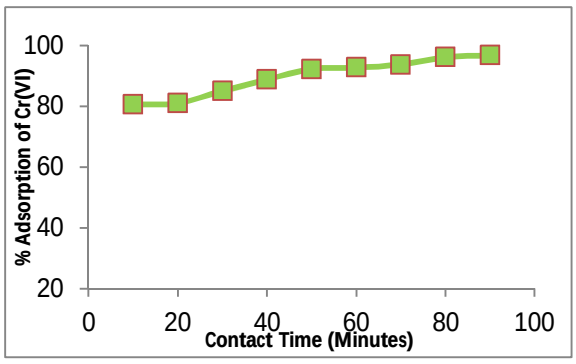


Fig. 8: Effect of contact time on Cr(VI) biosorption by PpMGDA (pH: 2, Adsorbent dose: 0.5 gm/50 ml, Cr(VI) concentration: 100 mg/L, Temperature: 30 °C, Agitation rate: 120 rpm)

I. Effect of Temperature

Experiment was performed at different temperatures 10 °C - 60 °C. The biosorption of Cr(VI) increases with increase in temperature i.e. from 75.793 % to 96.667 % in the temperature range of 10 °C - 60 °C by PpMGDA as shown in the Fig. 9. Results also specify that biosorption was endothermic in nature. Increase in temperature favours the chromium ions transport within the pores of biosorbent [20]. This trend might also be due to the increased number of biosorption sites generated because of breaking of some internal bonds near the edge of active surface sites of biosorbent [21], [22]. Some authors do explain that temperature affects the kinetic energies of chromium ions. At lower temperature, the kinetic energy remains low and increase in temperature increases the mobility of the ions [23], [24].

J. Effect Of Agitation Rate

Experiment was carried out by taking Cr(VI) ion concentration 100 mg/L, adsorbent dose 0.5 gm/50 ml, pH 2, contact time of 90 minutes and temperature at 30 °C with varying agitation speed (40 – 200 rpm). The effect of agitation speed on the adsorption of Cr(VI) ions is shown in Fig. 10. As agitation speed increased up to 120 rpm, adsorption capacity of PpMGDA for removal of Cr(VI) also increased from 83.745 % to 96.119 %. Further increase in agitation speed resulted in slight decrease in removal efficiency of Cr(VI) by PpMGDA.

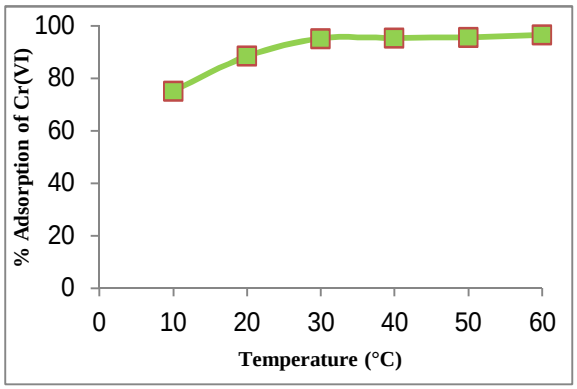


Fig. 9: Effect of temperature on Cr(VI) biosorption by PpMGDA (pH: 2, Adsorbent dose: 0.5 gm/50 ml, Cr(VI) concentration: 100 mg/L, Contact time: 90 minutes, Agitation rate: 120 rpm)

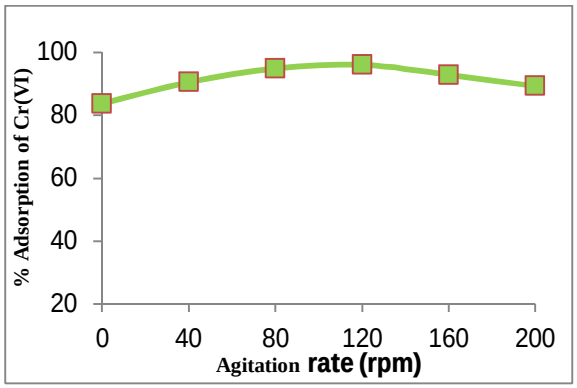


Fig. 10: Effect of agitation rate on Cr(VI) biosorption by PpMGDA (pH: 2, Adsorbent dose: 0.5 gm/50 ml, Cr(VI) concentration: 100 mg/L, Contact time: 90 minutes, Temperature: 30 °C)

K. Adsorption Isotherm Study

The adsorption isotherm specifies distribution of metal ions between the liquid phase and the solid phase at equilibrium. The results obtained from the biosorption of Cr(VI) ions on PpMGDA was verified 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.

1) *Langmuir Adsorption Isotherm:* The Langmuir equation, which is valid for monolayer sorption onto a surface of finite number of identical sites [25], is given by;

$$q = \frac{q_m b C_e}{1+bC_e} \quad (4)$$

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:

$$\frac{1}{qe} = \frac{1}{q_m b C_e} + \frac{1}{q_m} \quad (5)$$

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;

$$R_L = \frac{1}{1+bC_i} \quad (6)$$

Where b is the Langmuir constant and C_i is the maximum initial concentration of Cr(VI). The value of separation parameters R_L provides imperative evidence about the nature of adsorption. If 0 < RL < 1 then adsorption is favorable. Since the R_L value was found in the range of 0.1200 to 0.4050 for concentration range 20 mg/L to 100 mg/L which is in the range of 0 to 1 that indicates favorable biosorption [26], [27].

2) *Freundlich Adsorption Isotherm:* Freundlich equation is represented by;

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

Where K and n are empirical constants which incorporating all parameters affecting the biosorption process such as, biosorption capacity and biosorption intensity respectively [28].

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

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

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 1.1024. Since n > 1, this indicates that biosorption is a physical process. The higher value of K (3.2129) indicates the higher adsorption capacity of the PpMGDA for Cr(VI) [29].

3) *Dubinin-Kaganer-Radushkevich (DKR) Adsorption Isotherm:* Linearized Dubinin-Kaganer-Radushkevich (DKR) adsorption isotherm equation is represented as;

$$lnq_e = \ln q_m - \beta \varepsilon^2 \quad (9)$$

Where q_m is the maximum biosorption capacity, β is the activity coefficient related to mean biosorption energy and ε is the polanyi potential [30], which is calculated from the following relation;

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

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,

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

The E value was found to be 1.5873 KJ mol^{-1}. The magnitude of the mean adsorption energy is useful for assessing the nature of the biosorption process. 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 $kJmol^{-1}$, the biosorption process can be explained by physisorption mechanism, if E is between 8 and 16 $kJmol^{-1}$, the process is dominated by ion exchange mechanism, and if E is > 16 $kJmol^{-1}$, the biosorption process is dominated by chemisorption [31]. In the present work, E value (1.5873 KJ mol^{-1}) which is less than 8 KJ mol^{-1}, the biosorption of Cr(VI) ions onto PpMGDA 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 (J/mol) and A_T is the Temkin isotherm constant (L/g) [32]. Equilibrium data for the adsorption is plotted as q_e vs $\ln C_e$, as shown in Fig. 11 (d). The two constants b_T and A_T are calculated from the slope (RT/b_T) and intercept ($RT/b_T \cdot ln\, A_T$) of the line. The values of A_T, b_T and regression coefficient (R^2) are listed in Table 1.

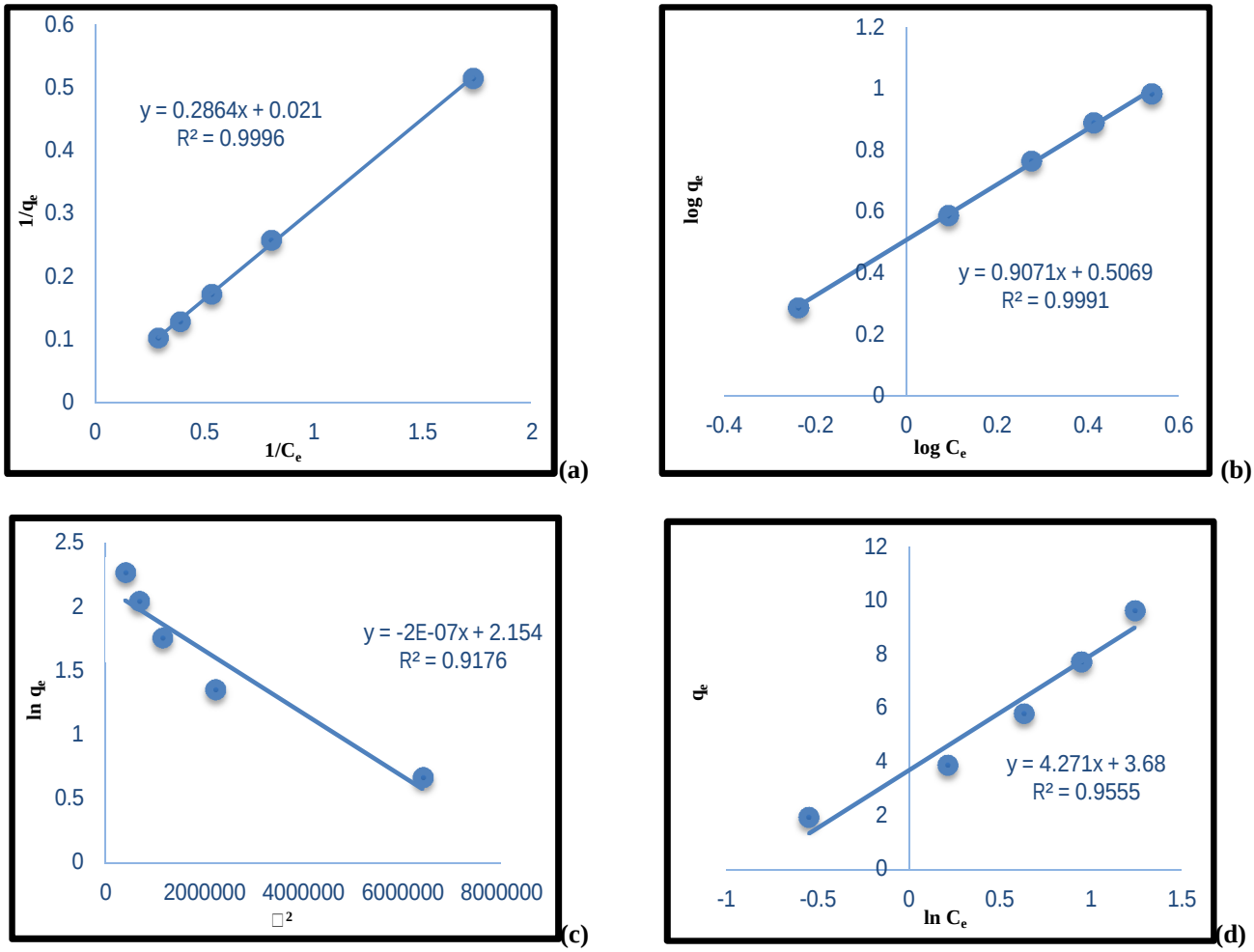


Fig. 11: Adsorption isotherms (a) Langmuir, (b) Freundlich (c) DKR and (d) Temkin for Cr(VI) biosorption by PpMGDA (pH: 2.0, Adsorbent dose: 0.5 gm/50 ml, Contact time: 90 minutes, Temperature: 30 °C, Agitation rate: 120 rpm)

Table 1: Adsorption isotherm constants for Cr(VI) 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	b_T	R^2
47.62	0.0733	0.9996	3.2129	0.9071	0.9991	-2 x 10^{-7}	8.62	1.5873	0.9176	2.3670	0.5898	0.9555

L. 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 [33]. To determine the controlling mechanism of the biosorption process, experimental data were scrutinized for pseudo-first-order equation [34], pseudo-second-order equation [35], Elovich equation [36] and Weber & Morris intra-particle diffusion equation [37] which is presented below;

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

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

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

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

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 [38].

Biosorption of Cr(VI) onto PpMGDA was monitored at different specific time interval. The Cr(VI) uptake was calculated from the data obtained.

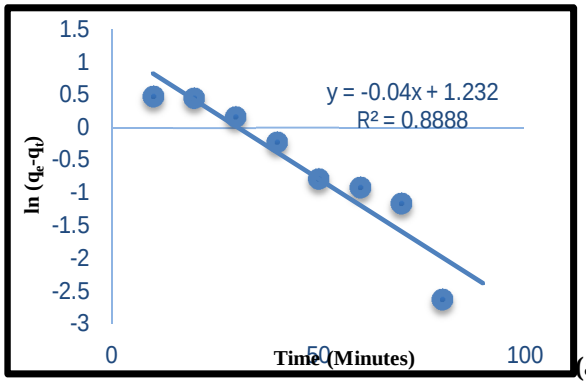
The pseudo-first-order model was plotted for ln (q_e-q_t) against t as shown in the Fig.12 (a). The values of k_1 and q_e were estimated from the slope (k_1) and intercept (ln q_e) of the plot and shown in Table 2. Pseudo-first-order model exhibited the correlation value (R^2 = 0.8888) being lower than 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 [16], [38].

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= 0.9986). This finding indicates that Cr(VI) biosorption follows in a monolayer fashion and which relies on the assumption that chemisorption or chemical adsorption is the rate-limiting step. Cr(VI) reacts chemically with the specific binding sites on the surface of biosorbent [16].

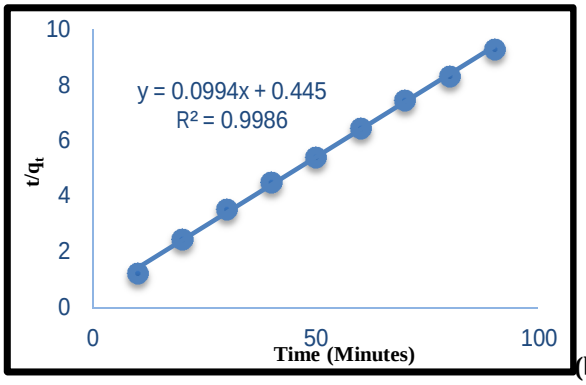
The Elovich model was plotted for q_t against ln t as shown in the Fig. 12 (c). The values of β and α are calculated from the slope ($1/\beta$) and the intercept (ln $(\alpha\beta)/\beta$) of the plot and values are shown in Table 2. The Elovich model has been used with the assumption that the actual adsorption surface is energetically heterogeneous [39], [40]. The Elovich model showed a correlation coefficient (R^2= 0.9314).

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 = 0.9654) 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 [37], [40].

The plot of intra-particle diffusion model showed multilinearity, indicating that three steps take place. The first, sharper portion is attributed to the diffusion of adsorbate through the solution to the external surface of biosorbent or the boundary layer diffusion of solute molecules. The second portion describes ion stage, where intra-particle diffusion is a rate limiting. The third portion is attributed to the final equilibrium stage. However the intercept of the line fails to pass through the origin which may attribute to the difference in the rate of mass transfer in the initial and final stages of biosorption [41].



(a)



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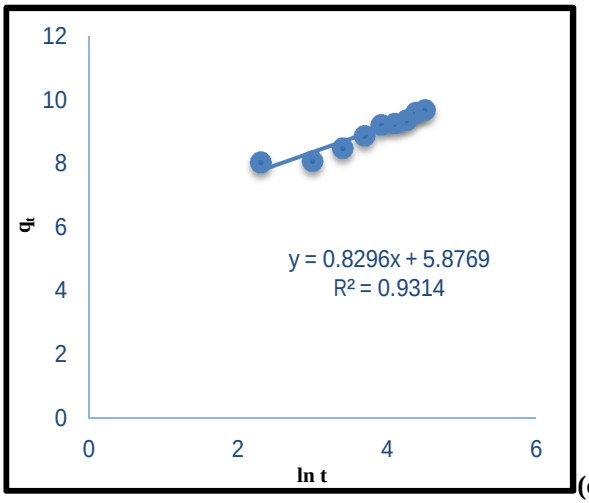

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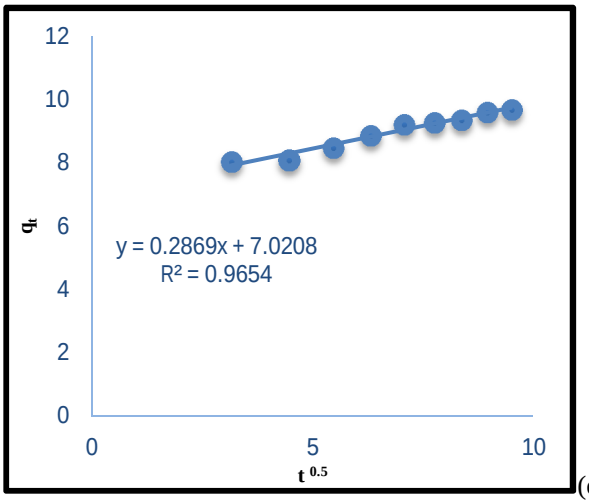

(d)

Figure 12: Adsorption kinetic models (a) pseudo-first-order, (b) pseudo-second-order (c) Elovich and (d) Weber and Morris intra-particle diffusion, for Cr(VI) biosorption by PpMGDA (pH: 2.0, Adsorbent dose: 0.5 gm/50 ml, Initial Cr(VI) concentration: 100 mg/L, Temperature: 30 ℃, Agitation rate: 120 rpm)

Table 2: Adsorption kinetics data for Cr(VI) biosorption by PpMGDA

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
3.4281	0.0921	0.8888	10.060	0.0222	0. 9986	989.51	1.2054	0.9314	0.2869	7.0208	0.9654

M. Thermodynamic Studies

Thermodynamic parameters are imperative factors that determine the feasibility and spontaneity of an adsorption process. These parameters were determined by carrying out equilibrium studies at different temperatures. The equilibrium constant at various temperatures and thermodynamic parameters of adsorption can be estimated from the following equations;

$$K_c = \frac{C_{Ae}}{C_e} \quad (17)$$

$$\Delta G^0 = -RT \ln K_c \quad (18)$$

$$\Delta G^0 = \Delta H^0 - T\Delta S^0 \quad (19)$$

$$\ln K_c = \frac{\Delta S^0}{R} - \frac{\Delta H^0}{RT} \quad (20)$$

Where K_c is the equilibrium constant, C_e is the equilibrium concentration in solution (mg/L) and C_{Ae} is the amount of Cr(VI) 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) [42].

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. 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 (ΔH °) were represented in Table 3. The equilibrium constant (*Kc*) increases with increase in temperature, which may be attributed to the increase in the pore size and enhanced rate of intra-particle diffusion. 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 Cr(VI) 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 [29].

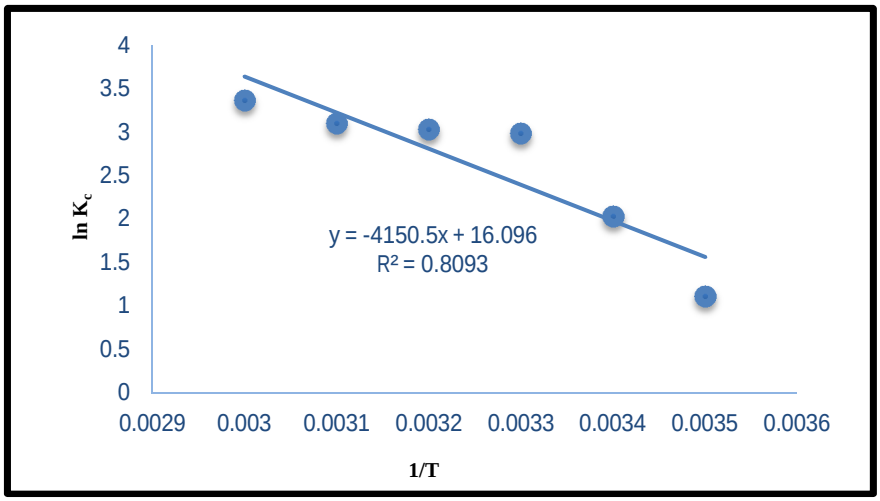

Fig. 13: Plot of lnKc against 1/T for determination of thermodynamic parameters for Cr(VI) biosorption by PpMGDA (pH: 2.0, Adsorbent dose: 0.5 g/50 mL, Cr(VI) concentration: 100 mg/L, Contact time: 90 minutes, Agitation rate: 120 rpm)

Table 3: Thermodynamic parameters of Cr(VI) biosorption by PpMGDA

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	3.0311	2.6092	34.5073	133.8220
2	20 °C	293	7.6505	4.9567		
3	30 °C	303	19.9776	7.5438		
4	40 °C	313	20.7723	7.8943		
5	50 °C	323	22.1965	8.3246		
6	60 °C	333	29.0030	9.3229		

N. Desorption Study

Desorption of Cr(VI) metal ions from Cr(VI) loaded PpMGDA was carried out using 0.1M NaOH, 0.1M HCl, 0.1M HNO_3 and 0.1M H_2SO_4. It was observed from Fig.14 that the maximum desorption obtained in 0.1 M HNO_3. PpMGDA found to be the most effective biosorbent with desorption efficiency 81.957 % (0.1 M HNO_3), 76.681 % (0.1 M H_2SO_4), 66.032 % (0.1M HCl) and 55.114 % (0.1 M NaOH). The maximum desorption demonstrated high reusability of the adsorbent, making removal and recovery of Cr(VI) from waste water containing Cr(VI) a more sustainable and economical alternative.

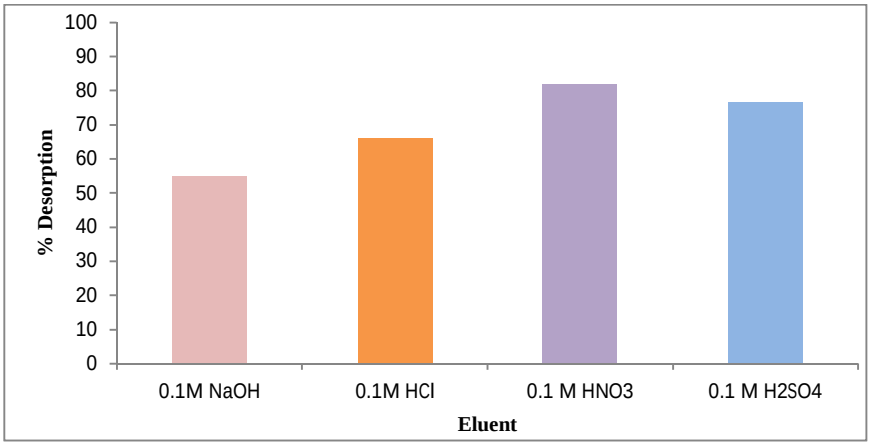

Fig. 14: Desorption study using 0.1M NaOH, 0.1M HCl, 0.1M HNO_3 and 0.1M H_2SO_4

IV. CONCLUSION

The present study evaluates the efficiency of Methylglycinediacetic acid modified pods of *Peltophorum pterocarpum* (PpMGDA) as low-cost adsorbent for effective removal of Cr(VI) ions from aqueous solution. The removal efficiency of PpMGDA was found to be dependent on the pH, adsorbent dose, initial Cr(VI) ions concentration, temperature, contact time and agitation rate. Langmuir, Freundlich, DKR and Temkin isotherm models were applied to the experimental adsorption data and the data fitted Langmuir (R^2 = 0.9996) model better than the other models. The maximum monolayer coverage adsorption capacity from the Langmuir isotherm model was obtained as 47.62 mg/g. The kinetic data followed the pseudo-second-order kinetic model. Maximum desorption of the metal was observed in 0.1 M HNO_3 eluent. Thermodynamic study revealed that the biosorption process was endothermic, spontaneous and proceeded with increased randomness. The obtained results are indication that the Methylglycinediacetic acid modified pods of *Peltophorum pterocarpum* (PpMGDA) can be effectively used as biosorbent for the removal of Cr(VI) from aqueous solutions and can therefore be employed as an effective alternative method for the economic treatment of wastewater. Since green adsorbent used for this research i.e. pods of *Peltophorum pterocarpum* are naturally occurring and chelating agent used for modification of green adsorbent i.e. Methylglycinediacetic acid (MGDA) to increase the sorption capacity of green adsorbent is biodegradable [43] in nature therefore making the approach economically viable and sustainable. Further investigation is needed to check the adsorption capacity of the PpMGDA for other metal species from water.

V. ACKNOWLEDGMENT

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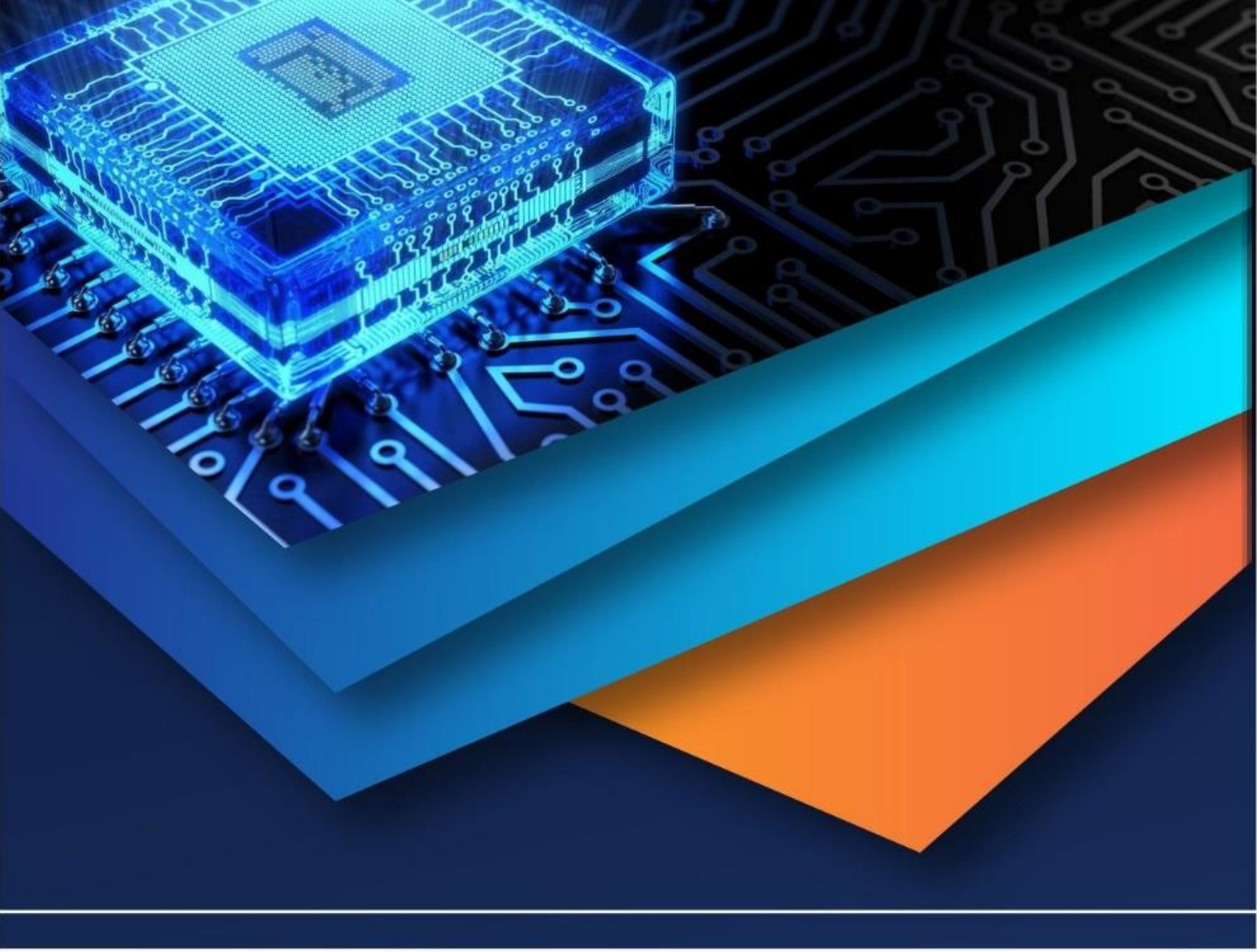

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