EQUILIBRIUM ISOTHERM, KINETIC MODELING, AND CHARACTERIZATION STUDIES OF CADMIUM ADSORPTION IN AN AQUEOUS SOLUTION BY ACTIVATED CARBON PREPARED FROM *BAUHINIA PURPUREA* LEAVES

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ABSTRACT

Cadmium is the toxic metal selected for adsorption in this study and adsorbent of interest was activated carbons prepared from *Bauhinia Purpurea* leaves as a plant biomass. Batch experimental studies conducted for the given adsorbent imparted that the experimental data were fitted very well with the Freundlich isotherm for the Cadmium adsorption process. The sorption kinetic studies for a given adsorbent indicated that the adsorption tends to follow the pseudo-second order. The suitability of kinetic models followed in the order by Second - order kinetic model > First - order model > Elovich model > Intra-particle diffusion model. The mean adsorption energy E value of Cadmium adsorption was decreased with increasing isothermal temperature (303–323K) from 1.936 to 1.79 kJ/mole. It was observed that the scope of an ordinary free energy credited to physical adsorption and the force of attraction between the adsorbate and adsorbent is very weak, therefore this type of adsorption can be easily reversed by heating or by decreasing the pressure. The characterization of metal-adsorbent interactions before and after adsorption was studied using SEM, FTIR and XRD techniques. FTIR spectrum of raw activated carbon of *Bauhinia Purpurea* leaves reveals that there were a large number of hydroxyl and carboxyl groups present on the surface of the adsorbent, which possibly reacted with metal ions in aqueous solution.

Keywords: *Bauhinia Purpurea* leaves, Equilibrium Isotherm, Kinetic Modeling, Characterization.

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INTRODUCTION

The liquid pollutants discharged from industrial sources to the ecosystem, the usable water has decreased drastically and the cost of purifying the water has increased dramatically. The rapid pace of population growth, industrialization and improper planning of urban development activities have been severely contributing to the contamination of water and soil systems. Industries produce much wastewater and sludge containing heavy metal (Zinc, Copper, Nickel, Lead, Chromium, Cadmium, Mercury, etc.) ions with various concentrations, which are very toxic and carcinogenic to the human and other living organisms^{1,2}. Cadmium, an element which is spread widely and found naturally, but a rare element. The leachates from hazardous waste sites and industrial wastewaters seldom contaminate the groundwater with high levels of cadmium. 0.005 mg/L is set as the maximum cadmium concentration in the domestic water supplies by the World Health Organization and the EUD directive³. Indian standard code IS: 10500 has set the maximum permissible limit of Cd in effluents while discharging them into the municipal sewers and surface waters as 2 and 1 mg/L respectively. Moreover, IS: 10500 has set the maximum permissible limit of Cd in drinking water as 0.003 mg/L⁴. From this study, it is evident that adsorption has

been used by most of the researchers during the last few decades and it has proved to be a very efficient and economic process. Several methods which were used for the treatment of wastewater include precipitation, ion exchange, coagulation, and reverse osmosis^{5,6}. However, these methods are either less effective or more expensive in treating high volumes; require the use of expensive chemicals and low metal concentration in aqueous form. Most of these processes suffer from high operating cost and recurring expenses such as chemicals, which are not suitable for the small-scale industries.

Adsorption is one of the most versatile and widely used techniques for the removal of metal ions. There are numerous materials used as adsorbents like fullers-earth, zeolite, activated alumina, biomass, resins, activated carbons, etc. Activated carbon is the most effective and widely used adsorbent because it has the large specific surface area, micro-porous structure, and excellent adsorption ability. Activated carbon has been the water industry's standard adsorbent for the reclamation of municipal and industrial wastewater for potable use for more than three decades. Despite its prolific use of the water and wastewater treatment plants, activated carbon remains an expensive material. In recent years, research interest in the production of low cost⁷⁻⁹ activated carbon produced from unused materials has grown. Low cost activated carbons are prepared by thermo-chemical methods of various unused materials and plant biomass used to remove heavy metals from effluents^{10,11}. With this brief introduction about the heavy metal pollution and importance of the cadmium removal in particular from wastewater streams, an attempt has been made to study the use of low cost activated carbon from *Bauhinia Purpurea* leaves as an adsorbent to treat the simulated metal solutions¹². Linear isotherm models, Langmuir, Freundlich, Temkin and Dubinin-Radushkevich (D-R) were tested in the equilibrium studies of Cadmium metal ion using the adsorbent. The fitness of equilibrium data from the pseudo first order, pseudo-second order, Elovich, and Intra-particle diffusion models were investigated and compared for the two adsorbents. Scanning Electron Microscopy (SEM), Fourier Transform Infrared Spectroscopy (FTIR) and X-ray diffraction (XRD) is used for the characterization of the adsorbents.

EXPERIMENTAL

Material and Chemicals

The following material and chemicals are used for the preparation and activation of adsorbent: *Bauhinia Purpurea* leaves, Cadmium Nitrate $\text{Cd}(\text{NO}_3)_2$, Hydrochloric Acid (HCl), and Zinc Chloride (ZnCl_2).

Preparation of Adsorbent

The adsorbents, waste tires and *Bauhinia Purpurea* leaves used in the present study were collected in Rajam and Srikakulam, Andhra Pradesh, INDIA. The *Bauhinia Purpurea* leaves were washed several times with deionized water until the wash water contains no dirt. These washed leaves were completely dried under sunlight for 30 days and were cut into small pieces and powdered using a domestic mixer. The powder, dried in an oven at 100°C for 120 min. The dried material was now placed in the cooker for carbonization and it was heated continuously for 10 min. The dried material was activated to 650°C for 120 min in a covered silica crucible by heating in a muffle – furnace^{13,14}. After that, taken 100 g of carbon powder from a muffle furnace and mixed with 100 g ZnCl_2 dissolved in 500 ml of distilled water containing 22 g of HCl. The chemically treated material was left overnight and carbonized. The carbonized material was refluxed with 10% HCl solution for 180 min and filtered. This was followed by drying of the material at 100°C for 24 hrs. The dried product was sieved to the desired particle size range of 74 - 177 μm .

Batch Adsorption Experimental Studies

The adsorption studies were conducted in the exploratory conditions of various effective process parameters of pH 2–10 for cadmium, contact time of 2-120 min, metal ion concentration ranges from 2-10 mg/L, the dosage of the adsorbent 0.025-0.15 g, and the particle size of the adsorbent varies from 74 (200 mesh) -177 (80 mesh) μm . The agitation speed of 250 rpm was kept constant in the orbital shaker with the suitable time interims from 2 -120 min. The mixed adsorbent solutions were taken out and filtered by Watmann filter paper and analyzed for metal ion concentration in an Atomic Absorption Spectrophotometer (Perkin Elmer model-3100). Batch experiments were conducted at various

temperatures of the metal solution utilizing orbital shaker from 303K - 323K with an optimum contact time of 50 min at pH values of 6.5.

Metal Adsorption Capacity

After experimentation, the amount of metal deposited on the adsorbent surface was calculated by using the following equation:

$$q_t = \frac{V(C_i - C_f)}{1000w} \quad (1)$$

Where q_t is the amount of metal deposited on the adsorbent surface (mg/g), C_i is the initial solute concentration in the solution before adsorption (mg/L), C_f is the final concentration of solute in the solution after adsorption (mg/L), V is the volume of metal solution (L) and w is the dosage of the adsorbent (g).

Freundlich and Langmuir Isotherms

The adsorption isotherms indicate the distribution of adsorbed molecules between the liquid phase and solid phase when the adsorption process reaches an equilibrium state. The application of the isotherm equation is compared by judging the correlation coefficients R^2 . Isotherms are calculated under existing equilibrium conditions. Freundlich isotherm model describes the ratio of the amount of metal adsorbed onto a given mass of adsorbent to the concentration of the metal in the solution. This model can be applied to multi-layer adsorption, with non-uniform distribution of adsorption heat and affinities over the heterogeneous surface and can be represented by the equation in linear form as:^{15,16}

$$\ln q_{eq} = \ln K_f + \frac{1}{n_f} \ln C_{eq} \quad (2)$$

Where q_{eq} is the amount of metal deposited on the adsorbent surface per unit mass of adsorbent (mg/g), C_{eq} is the equilibrium concentration (mg/L), and $k_f((\text{mg/g})/(\text{L/g})^n)$ is the Freundlich adsorption constant related to adsorption capacity and $1/n_f$, a dimensionless constant, which can be used to explain the extent of adsorption and the adsorption intensity between the solute concentration and adsorbent respectively. A plot of $\ln q_e$ versus $\ln C_{eq}$ based on experimental data gives a straight line, from the slope of which $1/n_f$ may be calculated and k_f may be evaluated from the intercept. Freundlich isotherm is widely applied in heterogeneous systems, particularly for organic compounds or highly interactive species on activated carbon and molecular sieves.

The Langmuir mathematical statement was used for the estimation of maximum adsorption capacity corresponding to the complete monolayer scope on the adsorbent surface, and after that no further adsorption happens. Thereby, the Langmuir represents the equilibrium distribution of metal ions between the solid and liquid phases^{17,18}. The Langmuir isothermal model is presented by the following equation

$$\frac{1}{q_{eq}} = \frac{1}{q_{max}K_L C_{eq}} + \frac{1}{q_{max}} \quad (3)$$

Where q_{max} is the adsorption binding capacity, that is, the maximum adsorption upon complete saturation of the adsorbent surface, and K_L (L/g) is an affinity of adsorbent towards adsorbate. A linear plot of $1/q_{eq}$ versus C_{eq} was drawn to determine q_{max} and K_L . From the shape of the isotherm, one can predict whether an adsorption process is favorable or unfavorable. The essential feature of the Langmuir isotherm can be expressed by means of R_L , a dimensionless constant referred to a separation factor or equilibrium parameter. R_L is calculated using the following equation:

$$R_L = \frac{1}{1 + K_L C_i} \quad (4)$$

The value of the separation factor R_L describes the nature of adsorption of the isotherm.

Temkin and Dubinin–Radushkevich Isotherms

The Temkin isotherm model assumes that the heat of adsorption of all the molecules in layer decreases linearly with coverage due to adsorbent–adsorbate interactions, and that the adsorption is characterized by a uniform distribution of the bonding energies, up to some maximum binding energy. The linear form of Temkin equation is:¹⁹

$$q_{eq} = \frac{RT}{b_T} \ln A_T + \frac{RT}{b_T} \ln C_{eq} \quad (5)$$

Where A_T (L/mg) and b_T (J/mole) are Temkin isotherm constants. A plot of q_{eq} versus $\ln C_{eq}$ enables the determination of the isotherm constants A_T and b_T .

Dubinin–Radushkevich isotherm is an empirical model, applied to examine the adsorption mechanism with a Gaussian energy distribution onto a heterogeneous surface. The model has frequently effectively fitted high solute affinity and the intermediate range of concentrations. The methodology was usually applied to differentiate between the physical and chemical adsorption of metal ions, with its mean free energy (E). The linear form of the D-R isotherm model is given by:^{20,21}

$$\ln q_{eq} = \ln q_o - K_d \varepsilon^2 \quad (6)$$

The parameter ε is Polanyi potential computed by an empirical equation:

$$\varepsilon = RT \ln \left(1 + \frac{1}{C_e} \right) \quad (7)$$

Where, K_d (Mol^2/J^2) is related to the free energy of adsorption per mole of the adsorbate, and q_o (mg/g) is the Dubinin–Radushkevich isotherm constant related to the degree of adsorbate adsorption by the adsorbent surface. The values of q_o and K_d can be obtained by plotting $\ln q_e$ versus ε^2 . The mean free energy of adsorption process was evaluated by the following equation:

$$E = \frac{1}{\sqrt{2K_d}} \quad (8)$$

The magnitude of E can be utilized for assessing the kind of adsorption. The adsorption behavior can be depicted as the physical adsorption when the mean adsorption energy (E) is somewhere around 1 to 8 kJ/mol. However, the value of mean adsorption energy (E) is more than 8 KJ/mol indicates that the adsorption process is chemisorption^{22, 23}.

Pseudo-First and Second Order Kinetic Models

A number of models with varying degrees of complexity have been developed to describe the kinetics of metal adsorption in batch systems²⁴. Due to the presence of a greater number of metal ions in industrial wastewater, the adsorption equilibrium was reached much faster due to faster occupancy of adsorption sites by metal ions. The pseudo-first order kinetic model presented by Lagergren²⁵ is mostly suited for solutes of lower concentrations. The pseudo-first order kinetic model can be expressed as:

$$\ln(q_{eq} - q_t) = \ln q_{eq} - k_f t \quad (9)$$

Where, q_t (mg/g) is the adsorption intensity at time t ; q_{eq} (mg/g) is the adsorption intensity at equilibrium; k_f ($1/\text{min}$) is the rate constant of the first-order adsorption. Thus, a plot of $\ln(q_{eq} - q_t)$ vs t will be a straight line with k_f as slope and $\ln q_{eq}$ as an intercept.

The pseudo-second order model proposed by Ho and McKay⁸ can be used to explain the sorption kinetics, if the rate of sorption is found to be a second-order mechanism. The pseudo-second order model can be written as:

$$\frac{t}{q_t} = \frac{1}{k_s q_{eq}^2} + \frac{1}{q_{eq}} (t) \quad (10)$$

The parameters, slope and intercept can be estimated by plotting t/q_t against t of the equation (10).

Intra - Particle Diffusion and Elovich Kinetic Models

Weber and Morris^{8,16} presented the intra-particle diffusion kinetic model as:

$$q_t = k_p t^{0.5} + C \quad (11)$$

Where k_p represents intra-particle diffusion rate constant and C is a parameter, that symbolizes the external convective mass transfer from the bulk liquid to the surface of the solid as it delivers the same unit as q_t . It gives an estimate of the thickness of the boundary layer, i.e., the greater the C value, the higher the boundary layer effect. The values are obtained by fitting q_t vs $\sqrt{t}$. If the plot passes through the origin, $C = 0$, the intra-particle diffusion is the rate-limiting step, according to Weber and Morris²⁶. But, if the plot generates multi linear proportions, there may be considerable rate-limiting steps in the adsorption²⁷. The Elovich equation is given as follows,

$$q_t = \frac{1}{\gamma} \ln(\alpha\gamma) + \frac{1}{\gamma} \ln t \quad (12)$$

Where γ is desorption constant (g/mg) and α is the initial adsorption rate (mg/g min). q_t is the amount of metal removed at time t . The constants are obtained from the slope and intercept of a straight line plot of q_t versus $\ln t$. The initial adsorption rate is determined using this Elovich equation.

Characterization of the Adsorbents

Scanning Electron Microscopy (SEM) uses a focused beam of high-energy electrons to generate a variety of signals at the surface of solid specimens. In most SEM microscopy applications, data are collected over a selected area of the surface of the sample and a two-dimensional image is generated that displays spatial variation in properties including chemical characterization, texture and orientation of materials²⁸. The SEM is also capable of performing analyses of selected point locations on the sample. This approach is especially useful in qualitatively or semi-quantitatively determining chemical compositions, crystalline structure and crystal orientations.

X-ray diffraction (XRD) is an analytical technique primarily used for a quick identification of phases in a crystalline material and the unit cell dimensions. The sample is scanned through a range of 2θ angles, so that all possible diffraction directions of the lattice may be attained. The diffraction peaks are converted to d-spacings to simplify the identification of the mineral since each mineral has distinctive d-spacings. This can be achieved by comparing the d-spacings with standard reference patterns. To understand the adsorption process, it is very important to know the chemical structure of the adsorbents. FTIR plays an important role in identifying the characteristic functional groups responsible for the adsorption of heavy metals. FTIR spectra of the adsorbents were obtained using an FTIR spectrometer^{29, 30}. The plot, IR transmission vs frequency helps to identify the material when compared to reference spectra.

RESULTS AND DISCUSSION

The experimental data were obtained for the adsorption of cadmium from aqueous solutions using activated carbons prepared from *Bauhinia Purpurea* leaves as an adsorbent.

Freundlich and Langmuir Adsorption Isotherms

The experimental data were tested for the fitness of the Freundlich isotherm model by using the linear graphical method. The adsorption data were analyzed by plotting $\ln q_e$ versus $\ln C_e$ and shown in Fig.-1. The values of Freundlich constants and correlation coefficients (R^2) obtained from the linear Freundlich plots for Cadmium was given in Table 1. The value of the coefficient of determination was close to unity ($R^2=0.982$). The values of $\frac{1}{n_f} < 1$ (0.261), indicate that the intensity of adsorption of Cadmium onto activated carbon of *Bauhinia Purpurea* leaves as an adsorbent surface was high. The high value of adsorption capacity constant K_f (0.65) obtained indicated the fast uptake capacity of the adsorbent.

Similar trends were obtained for other isothermal temperatures for the Cadmium. The K_f value of Cadmium adsorption was increased from 0.65 to 1.104 (mg/g)/(L/g)ⁿ with an increase in temperature (303K-323K), reflect that deposition rate is more at higher effluent isothermal temperatures. The magnitudes of K_f and $\frac{1}{n_f}$ show easy separation of metal ions from effluents with a high adsorptive capacity of the activated carbons prepared from *Bauhinia Purpurea* leaves, especially at 303±1 K and pH = 6.5 (t : 50 min and C_i : 2 mg/L). Fig.2 shows that $1/q_e$ was plotted against $1/C_{eq}$ yielding a straight line with $R^2 = 0.951$, indicating that adsorption data fitted well with the Langmuir model. The value of q_{max} is 0.923 mg/g at 2 mg/L was calculated from the slope of the linear plot, whereas the value of K_L was derived from the intercept and compiled in Table-1. The separation factor (R_L) was estimated for the Cadmium at different initial metal concentrations by using equation (4) shown in Fig.-3. The values of R_L for cadmium were found to be in the range of 0.02 to 0.1, respectively. These results revealed that the adsorption of cadmium onto activated carbon from *Bauhinia Purpurea* leaves adsorbent was favorable and has an R_L value between 0 and 1.

Fig-1: Freundlich Isotherm Model for Adsorption of Cadmium.

Fig-2: Langmuir Isotherm Model for Adsorption of Cadmium

Fig-3: Separation Factor for Adsorption of Cadmium.

Fig-4: Temkin Isotherm Model for Adsorption of Cadmium.

Temkin and Dubinin–Radushkevich Adsorption Isotherms

The adsorption data were analyzed according to the linear form of Temkin model and is shown in Fig.-4. The linear Temkin isotherm constants A_T and b_T , were determined from the slope and intercept of the plots of q_e versus $\ln C_e$, respectively, and are tabulated along with corresponding correlation coefficients in Table-1. The R^2 value for Cadmium was found to 0.956. These high correlation coefficients suggested that a uniform binding energy was increased due to the interaction of the metal ions. These values also indicated that the adsorption process may be due to the heterogeneous surface coverage and the possible involvement of chemisorption. The linear plot of D–R isotherm is shown in Fig.-5. The values of D–R isotherm parameters were calculated by using equations (6,7 and 8) and shown in Table-1. The mean adsorption energy E value of Cadmium adsorption was decreased with increasing isothermal temperature (303–323K) from 1.936 to 1.79 kJ/mole. It was observed that the scope of an ordinary free energy credited to physical adsorption and the force of attraction between the adsorbate and adsorbent is very weak, therefore this type of adsorption can be easily reversed by heating or by decreasing the pressure. From the Table-1. For the given initial metal concentration of the solution, it was observed that

the adsorption data were very well represented by Freundlich isotherm with an average higher correlation coefficient of 0.983; followed by Langmuir, Temkin and D-R with a correlation coefficient of 0.951, 0.956 and 0.825, respectively.

Fig.-5: Dubinin - Radushkevich Isotherms for Adsorption of Cadmium.

Fig.-6: First- Order Kinetic Model for Adsorption of Cadmium.

Pseudo-First and Second Order Kinetic Models

The experimental results were analyzed to test the kinetic model and the linear plots of $\ln(q_e - q_i)$ versus t for Cadmium adsorption was shown in Fig.-6. The calculated first-order rate constants (k_f) and their corresponding linear regression, correlation coefficient values are compiled in Table-2. The linear regression correlation coefficient value R^2 found in the range of 0.959 to 0.996, which shows that the correlation coefficients were very high, the experimental q_e values did not match with the calculated q_e values. This implies that the adsorption of Cadmium onto activated carbon prepared from *Bauhinia Purpurea* leaves adsorbent did not follow the first-order kinetics. Figure-7 shows the plot of second order kinetic model for the Cadmium, The pseudo-second order rate constant k_s , the calculated q_{eq} value and

the corresponding linear regression correlation coefficient values R^2 are given in Table-3. The results indicate that the experimental q_e , and calculated q_e values are very close to each other and also R^2 value is closer to unity. The high R^2 value indicates that the experimental data were well correlated to the second-order kinetic equation.

Table -1: Isotherm Constants for Cadmium Adsorption at C_i : 2-10 mg/L, w: 0.1g, d: 149 μ m, T:303-323K, pH: 6.5 and t: 50 min.

Isotherm model	Parameter	Solution temperature (K)				
		303	308	313	318	323
Freundlich	$K_f(\text{mg/g})/(\text{L/g})^n$	0.65	0.74	0.846	0.975	1.104
	n_f	3.82	3.75	3.732	3.66	3.73
	R^2	0.982	0.996	0.994	0.997	0.997
	$q_{\max}(\text{mg/g})$	0.923	1.00	1.090	1.178	1.237
Langmuir	$K_L(\text{L/g})$	4.344	5.45	7.060	9.700	14.59
	R^2	0.951	0.954	0.959	0.953	0.942
	$R_L=1/(1+K_L C_i)$	0.103	0.084	0.066	0.049	0.033
	$A_T(\text{L/g})$	53.63	63.26	82.22	105.0	154.9
Temkin	$b_T(\text{L/mg})$	14502	13520	12762	11909	11685
	R^2	0.956	0.978	0.981	0.987	0.986
	K_d ($\text{Mol}^2 \text{kJ}^{-2}$)	7.5×10^{-10}	1.6×10^{-5}	1.8×10^{-35}	9×10^{-14}	4×10^{-5}
Dubinin - Radushkevich	$q_o(\text{mg/g})$	0.133	0.056	0.0216	0.098	10^{-5}
	$E(\text{kJ/Mole})$	1.936	2.94	4.81	2.249	1.790
	R^2	0.825	0.824	0.823	0.808	0.795

Table- 2: First- Order Kinetic Constants for Cadmium Adsorption.

$C_i(\text{mg/L})$	$q_{e,\text{exp}}(\text{mg/g})$	Cadmium (pH 6.5)		
		$K_f(\text{min}^{-1})$	$q_{eq, \text{cal}}(\text{mg/g})$	R^2
2	0.419	0.074	0.43	0.959
4	0.694	0.666	0.678	0.992
6	1.033	0.771	2.08	0.911
8	1.299	0.912	2.16	0.899
10	1.507	1.032	2.25	0.891

Table-3: Second- Order Kinetic Constants for Cadmium Adsorption.

$C_i(\text{mg/L})$	$q_{e,\text{exp}}(\text{mg/g})$	Cadmium (pH 6.5)		
		$k_s \left(\frac{\text{g}}{\text{mg} \cdot \text{min}} \right)$	$q_{eq, \text{cal}}(\text{mg/g})$	R^2
2	0.419	0.180	0.489	0.996
4	0.694	0.055	0.870	0.990
6	1.033	0.052	0.990	0.991
8	1.299	0.050	1.142	0.992
10	1.507	0.041	1.306	0.991

Intra particle diffusion and Elovich Models

The k_p values were obtained from the slope of the straight-line portions of the plot of q_{eq} versus $\left(t^{1/2}\right)$ for various temperatures. From the Table-4, it was observed that intra-particle rate constant values (k_p) increased with solution temperature. The Fig.-8 shows that the straight line did not pass through the origin and this indicates that the intra-particle diffusion is not the only rate-controlling step. The values of initial

adsorption rate (α) and desorption constant (γ) were obtained from the slope and intercept of q_{eq} vs $\ln(t)$ and are tabulated in Table-5, along with R^2 coefficients for the cadmium adsorption process.

Fig.-7: Second-Order Kinetic Model for Adsorption of Cadmium.

The values were found to be quite acceptable based on the observed R^2 value. The theoretical q_e values from the first order kinetic, Elovich and intra – particle diffusion models gave significantly different values compared to experimental values, and the correlation coefficients were also found to be lower. These results showed that the first- order kinetic, Intra-particle diffusion and Elovich models did not describe the sorption system. The results indicated that the calculated q_e values were very close to the experimental q_e values and the correlation coefficients were close to unity in the case of second – order kinetics for the adsorption of Cadmium ions. The applicability of second - order kinetic model confirm that the rate limiting step involved in the present process is chemisorption. The suitability of kinetic models followed in the order by second - order kinetic model > First - order model > Elovich model > Intra-particle diffusion model. The experimental results obtained with activated carbon of *Bauhinia Purpurea* leaves as adsorbents was well fitted with the pseudo second – order kinetic model.

Table-4: Intra-Particle Diffusion Kinetic Constants for Cadmium Adsorption.

C_i (mg/L)	Cadmium (pH 6.5)		
	k_p	C	R^2
2	0.060	0.0127	0.981
4	0.104	0.064	0.998
6	0.118	0.0583	0.999
8	0.1355	0.0436	0.998
10	0.1532	0.0578	0.998

Table-5: Elovich Kinetic Constants of Cadmium Adsorption Using Activated Carbons Prepared from *Bauhinia Purpurea* Leaves.

C_i (mg/L)	Cadmium (pH 6.5)		
	γ (g/mg)	α (mg/g.min)	R^2
2	9.082	0.0923	0.988
4	5.411	0.1036	0.957
6	4.766	0.125	0.960
8	4.15	0.158	0.963
10	3.690	0.173	0.957

Fig.-8: Intra-Particle Diffusion Kinetic Model for Adsorption of Cadmium.

Fig.-9: Elovich Kinetic Model for Adsorption of Cadmium.

The following Isothermal and Kinetic model equations were correlated for *Bauhinia Purpurea* leaves for the adsorption of cadmium:

Table-6: Isothermal modeling of Cadmium adsorption.

Isotherm	Cadmium(C_i : 2 mg/L)	
	Modeling	R^2
Langmuir	$q_e = \frac{4C_e}{1 + 4.344C_e}$	0.951
Freundlich	$q_e = 0.65C_e^{0.26}$	0.982
Temkin	$q_e = \frac{RT}{14502} \ln(53.63C_e)$	0.956
R - D	$q_e = 0.133e^{(-7.5 \times 10^{-7})\epsilon^2}$	0.825

Table-7: Kinetic modeling of Cadmium adsorption.

Model	Cadmium (C_i : 2 mg/L)	
	Kinetic model	R^2
Pseudo – First order	$q_t = 0.419 (1 - e^{-0.074t})$	0.959

<i>Pseudo – Second order</i>	$\frac{dq_t}{dt} = 0.180 (0.419 - q_t)^2$	0.996
<i>Elovich</i>	$\frac{dq_t}{dt} = 0.0923e^{(9.082q_t)}$	0.988
<i>Intra-particle diffusion</i>	$q_t = 0.045t^{0.5} + 0.026$	0.964

Characterization of Adsorbent

Figures-10(a) and 10(b) shows the SEM micrographs of activated carbon of *Bauhinia Purpurea* leaves after adsorption of cadmium. It is evident from the figure that the adsorbent is highly heterogeneous and the surface morphology of the adsorbent is rough. It is clear that the adsorbent has a considerable number of heterogeneous layer pores where there is a good possibility of heavy metal to be adsorbed. The surface texture of activated carbon of *Bauhinia Purpurea* leaves was completely changed before and after adsorption of heavy metals. The surface of the metal-loaded adsorbent clearly shows that the surface of the adsorbent dosage was covered with metal ions. The pores were completely filled with the metal ions after the adsorption of cadmium and the pores appear to be smooth. This observation indicates that the metal is adsorbed to the functional groups present in the pores. The surface of the adsorbent became smooth after the adsorption of cadmium ions. Smoothing of the surface is due to the adsorption of metal ions onto the pores of the adsorbent. It may also occur due to the decrease in the surface heterogeneity of the adsorbent.

The functional groups present in the activated carbon of *Bauhinia Purpurea* leaves were investigated by FTIR spectra within the range of 400-4000 cm^{-1} wave number. Figures-11(a) and 11(b) show the band positions in the FTIR spectra of the activated carbon of *Bauhinia Purpurea* leaves before and after adsorption cadmium and presented in Table-6. The adsorption spectra displayed a number of adsorption peaks indicating the complex nature of the activated carbon of *Bauhinia Purpurea* leaves and it was composed of various functional groups which are responsible for the binding of cadmium ions. The broad peak at 3000 cm^{-1} corresponds to the C-H, O-H and =C-H stretching vibrations of alkanes, aromatic and carbonyl acids, thus showing the presence of free hydroxyl groups on the adsorbent surface. The peaks at range from 3850 to 3740 cm^{-1} are due to stretching vibration of O-H. The peak at 2850 cm^{-1} represents the symmetric C-H, =C-H, O-H and (C=O)/C-C stretching of Alkanes/ Aldehydes/Carbonyl acids functional groups present on the adsorbent surface. The sharp peak at 1650 cm^{-1} could be due to the C=C, C=O stretching of alkene, carbonyl and amide stretch. The carboxylic acid groups take part in the adsorption of metal ions from the aqueous solution in addition to the other active sites on the carbon surface. The peak at 1680 cm^{-1} is attributed to the graphite's characteristic sp^2 hybridized C=C aromatic skeletal stretching. The peak present at 1500 cm^{-1} represents the NH (bending) and NO (stretch) stretching vibration of amide and nitro functional groups on the adsorbent surface. While the band at 1350 cm^{-1} corresponds to the C-F, C-N, and N-Stretching vibrations of alkyl halide, amine and nitro functional groups on the adsorbent surface. It is concluded that the prepared activated carbon material includes oxygen-containing functional groups that provide additional active sites for the adsorption process. After adsorption of cadmium, the asymmetrical stretching, and vibration at 3850 cm^{-1} were shifted to 3890 cm^{-1} . This shift in peak indicates the interaction between cadmium and –OH groups of adsorbent due to the presence of alcohols, phenols and carboxylic acid. A new peak at 2800 cm^{-1} was observed due to the chemical reaction involved in the adsorption process. The peak C=O stretch at 1650 cm^{-1} and 1350 cm^{-1} were shifted to 1625 cm^{-1} , and 1300 cm^{-1} due to the presence of carboxyl groups. After cadmium deposition on the adsorbent surface, the peak of 1500 cm^{-1} was disappeared. The shift in peak values could be due to the formation of a chemical bond between the functional groups present on activated carbon of *Bauhinia Purpurea* leaves and cadmium. FTIR spectrum of raw activated carbon of *Bauhinia Purpurea* leaves reveals that there were a large number of hydroxyl and carboxyl groups present on the surface of the adsorbent, which possibly reacted with metal ions in aqueous solution. These groups may largely contribute to the active adsorption sites required for the adsorption of cadmium metal ions. These results also indicate that chemisorption could also be involved in the adsorption of cadmium.

(a)

(b)

Fig.-10: SEM Micrographs of Activated Carbon of *Bauhinia Purpurea* Leaves Before(a) and After adsorption(b) of Cadmium.

(a)

Fig.-11: FTIR Spectra of Activated Carbon of *Bauhinia Purpurea* Leaves Before(a) and After Adsorption (b) of Cadmium.

Table-6: FTIR Spectra of Activated Carbon Prepared from *Bauhinia Purpurea* Leaves

IR frequency range, (cm ⁻¹)			Activated carbon prepared from <i>Bauhinia Purpurea</i> leaves	
ACBPL	Cd loaded	Diff.	Type of vibration	Functional groups
3850	3890	40	OH, Stretch, free	Alcohols
3740	3750	10	OH, Stretch, free	Alcohols
3000	3075	75	C-H, Stretch =C-H, Stretch C-H, Stretch	Alkane/Alkene/ Aromatics
2890	2850	40	C-H, Stretch =C-H, Stretch O-H, Stretch (C=O)	Alkanes/ Aldehydes/ Carbonyl acids
2850	2800	50	C-H, Stretch =C-H, Stretch O-H, Stretch (C=O)	Alkanes/ Aldehydes/ Carbonyl acids
2390	2390	0	-	-
1650	1625	25	C=C, stretch NH, Bending C=C, stretch C=O, stretch NH, Bending	Alkene/Amine/ Aromatics /Amide
1500	-	-	C-H, Stretch O-H, Stretch =C-H, Stretch NO, Stretch	Alkane/Carbonyl acid/Aldehydes/ Nitro
1350	1380	30	C-F, Stretch C-N, Stretch N-O, Stretch	Alkyl Halide/Amine/ Nitro
450	450	0	-	-

Table-7: XRD Details of Activated Carbon of *Bauhinia Purpurea* Leaves Before, and After Adsorption of Cadmium.

Count /Sec	Peak Position (2 θ) Before Adsorption	Peak Position (2 θ) by Cadmium Loaded
31.74	9.4230	18.5928
521.63	18.7038	18.8552
162.55	22.4870	22.5708
110.91	24.8137	24.7547
198.81	30.0364	30.1972
30.02	31.2790	33.6767
79.33	33.5363	34.9539
81.28	34.9501	40.4934
17.50	38.1884	43.2529
61.19	40.3130	48.2378
40.69	43.2591	51.5447
26.68	44.2534	57.9088
34.03	46.7713	18.5928
46.69	48.2610	18.8552
41.90	51.4902	22.5708
31.74	9.4230	24.7547
521.63	18.7038	30.1972
162.55	22.4870	33.6767

(a)

(b)

Fig.-12: XRD of Activated Carbon of *Bauhinia Purpurea* Leaves Before (a) and After Adsorption (b) of Cadmium.

The adsorbent can be crystallographically characterized by means of X-ray diffraction (XRD). Figures-12(a) and 12(b) shows the XRD diagram of the activated carbon of *Bauhinia Purpurea* leaves before and after adsorption of cadmium metal ions. The XRD pattern of raw adsorbent showed a typical spectrum of cellulosic material, with main and secondary peaks at 2θ of 18.60° and 22.45° respectively. The height of the peak and corresponding position angles are shown in Table-7. The main peak at 18.60° corresponds to the (002) crystallographic planes and it is taken as indicative of the presence of highly organized crystalline cellulose²⁹. The secondary peak at 22.45° corresponding to the (101) crystal plane and it is a measure of a less organized polysaccharide structure. The planes at (002) and (101) indicate the presence of a negative form of cellulose found in the natural source that is cellulose-I polymorphic form. The presence of cellulose indicates the irreversible adsorption of metals through coulombic attraction since the negative surface charge is acquired by cellulose on contact with water³¹. The cellulose present in the natural materials contains some crystalline oriented zones, which give a certain degree of crystallinity in fiber materials. The XRD pattern of raw the activated carbon of *Bauhinia Purpurea* leaves showed a characteristic peak at a 2θ value of 18.60° . The peaks at 22.72° , 29.47° , 33.59° , 34.92° , 40.3° , 43.13° and 48.21° corresponding to the peak height (count/Sec) was slightly changed to 24.72° , 30.07° , 33.58° , 34.93° , 40.35° , 43.23° and 48.15° for cadmium adsorption. The shift in peaks, disappearance of peak and formation of new peaks after adsorption of cadmium samples was due to the chemical reaction involved during the process. Thus, XRD results confirmed that the significant interactions were occurring between metal ions and the adsorbent surface. These variations in adsorption capacity could be due to the difference in the properties of the adsorbents such as active surface area, porosity, functional groups, etc. The abundant availability, cost effectiveness, better adsorption capacity rates suggested that the activated carbons prepared from *Bauhinia Purpurea* leaves can be an efficient and effective adsorbent for the removal of cadmium from the effluents.

CONCLUSION

The following conclusions could be drawn from the present study on the removal of cadmium from aqueous solutions using adsorption technique:

- It was found that for activated carbon *Bauhinia Purpurea* leaves, the experimental data were very well represented by Freundlich isotherm for the removal of cadmium from the solution.
- The adsorption activation energy (E) values for the given adsorbent under study was decreased with an increase in solution temperature. It was observed that the scope of an ordinary free energy credited to physical adsorption and the force of attraction between the adsorbate and adsorbent is very weak, therefore this type of adsorption can be easily reversed by heating or by decreasing the pressure.
- Kinetic studies indicated that the adsorption process followed well with the pseudo second-order kinetic model for the adsorption of cadmium using activated carbons of *Bauhinia Purpurea* leaves for the range of initial metal concentrations studied for the entire adsorption period.
- SEM micrographs showed the binding of metal ions on the surface the adsorbents. FTIR analysis indicated the presence of various functional groups such as hydroxyl, carboxyl, amino, etc., on the surface of the adsorbent which was responsible for the adsorption of metals. XRD studies confirmed the crystalline and amorphous nature of the adsorbents.

REFERENCES

1. M. A.Momodu, and C.A. Anyakora, *Res. J. Environ. Earth Sci.*, **2** (1), 39(2010).
2. O. S. Amuda, A. A. Giwa and I. A. Bello, *Biochem. Eng. J.*, **36**, 174(2007).
3. A .Doyurum and Celik, *J. Hazard. Mater.*, **138**,22 (2006).
4. Deswati, Hamzar Suyani, Rahmiana Zein, Admin Alif and Hilfi Pardi, *Rasayan J. Chem.*, **10**(2), 549 (2017), DOI: [10.7324/RJC.2017.1021591](https://doi.org/10.7324/RJC.2017.1021591).
5. F.Boudrahem, B. F.Aissani and A. H.Amar, *J. Environ. Manage.*, **90**,3031(2009).
6. N.Kannan and G. Rengasamy, *Water Air Soil Pollut.*, **163**,185(2005).
7. K. A. Krishnan and T.S. Anirudhan, *Ind. Eng. Chem. Res.*, **41**, 5085 (2002).
8. J.Febrianto, A.N.Kosasih, J.Sunarso, Y.H.Ju, N.Indraswati and S.Ismadji, *J. Hazard. Mater.*, **162**, 616 (2009).
9. F.Fu and Q. Wang, *J. Environ. Manage.*, **92**,407(2011).

10. C. Sumithra, and K.Sakthikeyan, *Rasayan J.Chem*, **7**, 149 (2014).
11. T. Fan, Y. Liu, B. Feng, G. Zeng, C. Yang, M. Zhou, H. Zhou, Z. Tan and X. Wang, *J. Hazard.Mater.*, **160**, 655(2008).
12. K. Mona, K.Ahmad and H.Hanafy,*Energy Procedia*, **50**, 113(2014).
13. G.Venkatesan and U. Senthilnathan, *Research Journal of Chemistry and Environment*, **17**, 5(2013).
14. Lakshmi Adathodi, Raja Murugadoss J. and Kalyani Gaddam, *Rasayan J. Chem.*, **11** (3), 1204 (2018), [DOI: 10.31788/RJC.2018.1134009](https://doi.org/10.31788/RJC.2018.1134009).
15. O. Gercel, H. F. Gercel, *Chemical Engineering Journal*, **132**, 289(2007).
16. H. BehzadSusana, C. Rodriguez, A. Mohammad, A. Ghouti, M. Asif, T. Inderjeet, A. Shilpi and G. Vinod Kumar, *Journal of Molecular Liquids* **208**, 99(2015).
17. M. Momcilovic, M. Purenovic, A.Bojic, A. Zarubica and M. Randelovid, *Desalination*, **276**, 53 (2011).
18. G. Kalyani, Y. Prasanna Kumar and P. King, *Rasayan J. Chem.*, **9** (3), 510 (2016).
19. H. L. Yadav and A.Jamal, *Rasayan J. Chem.*, **10**(3), 1062 (2017), [DOI:10.7324/RJC.2017.1031775](https://doi.org/10.7324/RJC.2017.1031775).
20. N.K .Akunwa, M.N. Muhammad and J. C. Akunna, *J. Environ. Manage*, **146**, 517 (2014).
21. P.Deba sree, M. Umesh and B.Swarup, *Journal of Water Process Engineering*, **2**, 105 (2014).
22. A. M.Awwad and M. Salem, *Journal of Saudi Chemical Society*, **18**, 486 (2014).
23. I. G. Umar, O. Emmanuel and H.A. Abdul, *Springer plus*, **4**, 458 (2015).
24. K. Y.Foo and B.H.Hameed, *Rev. Chem. Eng.*, **156**, 2 (2010).
25. H. Joga Rao, P.King and Y.Prasanna Kumar, *Rasayan J.Chem.*, **9**(2), 254(2016).
26. M.M.Olga,Freitas, J.E.Ramiro, Martins and M.Cristina, Delerue-Matos, A.R.Rui and Boaventura,*J. Hazard. Mater.*, **153** ,493 (2008).
27. A.K. Wanjari and U. E. Chaudhari, *Rasayan J. Chem.*, **10**(1), 82 (2017), [DOI: 10.7324/RJC.2017.1011556](https://doi.org/10.7324/RJC.2017.1011556).
28. M. Mohamed, Ghoneim, S. Hanaa, E. Desoky, M. Khalid, E. Moselhy, A.Adel, H. Emad, E. N. Abou, I. Lamiaa and A.E.Prol, *Egyptian Journal of Aquatic Research*, **40**, 235(2014).
29. W. Sadia, D. M.Imran, N. Saira and A. Rasool, *Arab. J. Chem.*, **7**, 1091 (2014).
30. J. S. Leandro, R. P. Fernanda, A. A. Luiz, H. Crispin and C. Garcia, *Water. Treat.*, **52**, 7878 (2014).
31. P. Girods, A. Dufour, V. Fierro, Y. Regime, C. Rogaumea and A. Zoulaliana, *J. Hazard.Mater.*, **188**, 917 (2011).

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