Eugenia Jambolana Lam. Seed as an Adsorbent: Evaluation of Adsorptive Characteristics for Cr (VI) from Aqueous Solution

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Abstract: *Biosorption is one of the most useful techniques for environmental remediation especially for heavy metal pollution. Kinetics of the biosorption is of great significance to evaluate the performance of a given adsorbent and gain insight into the underlying mechanisms. Presently, the removal of chromium (VI) from aqueous solutions using Eugenia jambolana Lam. (commonly known as Jamun) seed investigated. Adsorption study were performed in batch adsorption techniques to evaluate various parameters like pH of the solution, time of contact between adsorbent and adsorbate, dose of adsorbent, chromium ion concentration and solution temperature. The adsorption of Cr(VI) increased with dose of adsorbent and reached maximum at 1.0g/ 100mL at pH 6. Kinetic models like pseudo first and second-order were used to correlate the adsorption data. For both kinetic models, kinetic constants were computed and the second-order rate expression fitted well with high correlation coefficient. Two isotherm models, namely; Freundlich and Langmuir isotherm were used to know adsorption mechanism and Langmuir correlated the data well inferring a monolayer adsorption at the binding sites on the surface of the adsorbent. It may be concluded that Eugenia jambolana Lam. seed can be used as an efficient adsorbent for removing Cr (VI) from aqueous solutions.*

Keywords: *Adsorption kinetics, Eugenia jambolana Lam. Seed, Freundlich, Langmuir*

I. INTRODUCTION

Environmental pollution by heavy metals has received wide spread attention in the recent years. One of the most important problems is wastewater containing heavy metals like chromium. Chromium is a familiar toxic heavy metal and exists in the aqueous environment mainly in the Cr(VI) and Cr(III) oxidation states and Cr(VI) is five hundred times more toxic than the trivalent one [1]. Industries including like manufacturing of paint and pigment, production stainless steel, corrosion retardation plants, leather tanning plants and processing plating of chromium, wood preservation plants, fertilizers industries, photography and textile, etc., releases Cr (VI) to surface water [2]. Cr (VI) adversely affects humans and causes skin disease, respiratory and other biological problems. However, Cr (III) is considered as a source element which influences the metabolic activities in living organisms in a desired amount but increased amount of chromium may also results in skin allergies and cancer, therefore chromium should be regained from the industrial wastewater before its discharge in natural water system[3]. Conventional methods for removing Cr(VI) include chemical precipitation using alkali, oxidation or reduction via use of chemicals, filtration process, ion exchange using natural and synthetic exchangers , electrochemical method, and membrane technology process. However, above method have noteworthy disadvantages like imperfect metal removal, requirements for expensive chemicals and equipment, high reagent and energy requirements/ generation of toxic sludge and waste products that require disposal which is costlier [4,5]. In recent years, researchers explore the use of natural adsorbents as an alternative to replace the conventional adsorbents. These natural adsorbents found abundantly in nature as well as industrial or agricultural waste having potential for the removal of heavy metals. People used number of low-cost adsorbents for Cr removal. These include rice husk [6], wheat straw and barley straw sawdust [7] water lilies [8], tyres[9], Eugenia jambolana Lam. seed [10], olive oil industry waste [11], tamarind hull [12], orange waste [13] red algae [14]. The plant fibers contains various organic compounds mainly lignin, cellulose, hemi-cellulose and some pectin and extractives. These contents have functional groups or sites like carboxylic acid, phenolic and to some extent hydroxylic and carbonyl group which are responsible for metal sorption. [15]. The aim of this studies was to recite the adsorption of chromium (VI) to *Eugenia jambolana Lam.* seed at relatively low concentration with adsorption dependency on - adsorption isotherms, adsorption kinetics and pH specifically effects of various batch adsorption parameters.

II. MATERIAL AND METHOD

1. *Preparation of biosorbent*

Plant wastes i.e. *Eugenia jambolana Lam.* seed used as an adsorbent for the removal of Cr (VI) ions. To remove the impurities like the mud, debris and other soluble impurities *Eugenia jambolana Lam.*

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washed several times with deionised water and its peel is removed to obtain seed and were oven grind. After crushing and grinding it was sieved to obtain average particles of 100 mesh size and were stored in sealed polythene bags and use for further experiment.

2. Preparation of synthetic stock solution

All the chemicals used were of analytical reagent grade. Deionised water was used throughout the experimental studies. Stock solution of Cr(VI) were prepared by dissolving Sodium dichromate dihydrate (Merck India make) in 1000 ml of deionised water and 0.1 M HNO_3 and 0.1 M NaOH (as appropriate) used to adjust pH to value 6. The pH of solution was adjusted with accuracy $\pm$ 0.1 using a digital pH meter (Elico Model LI-612) with a combination glass electrode.

3. *Batch equilibrium study*

Adsorption experiments employed at room temperature (25 $\pm$ 2 ^{0}C) with pH 5.5 $\pm$ 0.5. In 100ml of solution of chromium salt, 0.8gm of adsorbent (*Eugenia jambolana Lam.* seed) was agitated at 250 resolution/minute on a mechanical shaker for a experimental require time in 250 ml Erlenmeyer flask and kept 2, 4, 6, 12, 18, 36 and 48 hours. Metal ion concentration was used in the range of 10 to 1000mg/L. pilot experiments revealed that process of adsorption is fast and it become negligible after 18h of contact time. Therefore, 18 h is fixed as a contact time for rest of the batch experiments. The mixture was filtered at the end of contact time and the Cr(VI) ions of the filtrate was analyzed using Atomic Absorption Spectrophotometer (Shimadzu Model Analyst- 6300).

4. Sorption kinetics

Adsorption kinetics provides the mechanistic insights of the reaction and describes the uptake rate of the solute which in turn controls the residence time of metal ions at the solid-liquid interface [16]. The metal uptake q_t (mg/g) was determined as follows

$$q_t = (C_o - C_f) V/m \tag{1}$$

Where, C_o and C_f are the original and final Cr(VI) ion concentration in mg/L, respectively; V is the volume of solution in litre and m is the weight of *Eugenia jambolana Lam.* seed in dry form in grams. Two kinetic models; pseudo-first order and pseudo-second order kinetic model were applied to analyze the adsorption data. These models are expressed as follows.

Table- I: Kinetic models used in the present study.

Pseudo-first-order	*Pseudo-second-order*
$Log(q_e-q_t) = lnq_e - k_1/2.303. t$	$t/qt = 1/k_2 q_e^2 + 1/q_e . t$
The pseudo-first order rate constant k_1 can be calculated by plotting log (q_e-q_t) Vs.T	The pseudo-second order rate constant k_2 and qe can be calculated by plotting t/qt versus time, t.
Where, q_e and q_t are the sorption capacities at equilibrium and at time t, respectively (mgg^{-1}), k_1 (min^{-1}), k_2 ($gmg^{-1}min^{-1}$) is pseudo-first-order, pseudo-second-order rate constant respectively.	

5. Sorption Isotherms

The relationship between the amounts adsorbed per weight of solid adsorbent and the amount of solute left behind in the solution at equilibrium is computed by isotherm studies. Two isotherm model namely Langmuir [17] and Freundlich models were applied in the present study.

Freundlich isotherms:

Freundlich model is based on the mono-molecular layer coverage of metal ions by the adsorbent assuming that the adsorbent has a different affinity for adsorption due to distribution of a heterogeneous valence. This model is represented by the following equation [18].

$$q_e = kC_e^{1/n} \tag{2}$$

This equation is conveniently used in the linear from by taking the logarithm of both side as:

$$lnq_e = 1/n\, lnC_e + lnk \tag{3}$$

Where, q_e is the amount of Cr(VI) ions adsorbed/unit volume of adsorbent (mg/g) and C_e is the equilibrium aqueous Cr(VI) ions concentration (mg/l). Isotherm parameter K denotes adsorption capacity and 1/n denotes adsorption intensity, and obtained by the intercept and the slope of plot lnqe vs. lnC$_e$, and showing the applicability of this model on *Eugenia jambolana Lam.* seed.

Langmuir isotherms:

The Langmuir isotherm is based on monolayer adsorption on to a surface with finite number of identical sites and is represented as

$$q_e = \theta^0 bC_e/1 + bC_e \tag{4}$$

This may be linearized as follows [19]

$$C_e/q_e = 1/\theta^0 b + C_e/\theta^0 \tag{5}$$

$$Or,\ 1/q_e = 1/\theta^0 b.1/C_e + 1/\theta^0 \tag{6}$$

θ^o and b (Langmuir constant) are related to the adsorption capacity and binding energy of adsorption, respectively (mg/g) and (L/mg). The linear plot of $1/q_e$ Vs. $1/C_e$ (regression analysis) at different temperatures for Cr(VI) ions proof the applicability of this model. The value of Langmuir constants b and θ^o reported in table-2 can be calculated from intercept and slope of plot $1/q_e$ vs. $1/C_e$.

III. RESULTS AND DISCUSSION

A. Effect of contact time on removal efficiency

The removal of Cr (VI) with contact time is shown in Fig. 1. It is apparent that removal efficiency increased with an increase in contact time before equilibrium is reached due to presence of the surface active sites on the adsorbent however after equilibrium it become almost constant because of saturation of active sites thus another metal adsorption was not possible. Other parameters such as quantity of adsorbent, pH of solution and agitation speed was kept constant. It can be seen from the figure that removal efficiency of Cr(VI) reached to maximum value 84%, 78% and 71% for 10, 50 and 100mg/l metal ion concentration respectively,

after 18 h and then no further considerable increase was observed for contact time up to 48 h. Thus an optimum contact time of 18h was selected for the rest of the batch experiments.
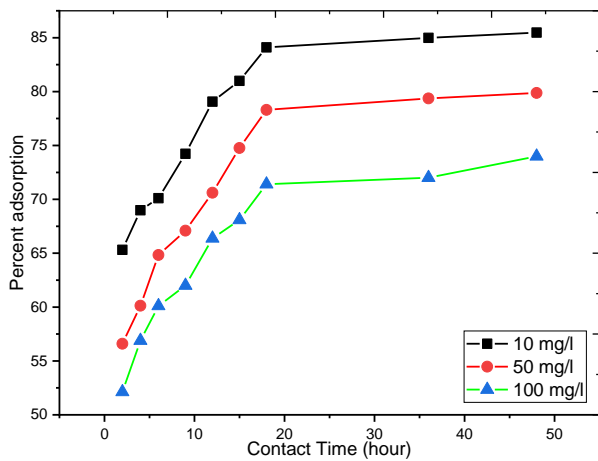
Fig. 1.Effect of contact time on adsorption of Cr(VI) ions from aqueous solution using Eugenia jambolana Lam. Seed.

B. Dose of adsorbent

The removal of Cr(VI) with dose of adsorbent for all different concentrations is shown in Fig. 2. At initial stage the removal of Cr(VI) ions increased rapidly giving rising trends with increase in adsorbent doses but later stage it become steady, because surface area increases with the weight of adsorbent and hence, results in a higher percent of Cr(VI) ions removal at initial phase. However at higher dosages desorption of slackly bound Cr(VI) from the surface of the is caused Eugenia jambolana Lam. Seed powder by particle-particle interaction. These counteracting process leads to the steady trends at later stage of the adsorption process as evident from the graph. As seen in fig.2, optimum Eugenia jambolana Lam. Seed dosages can be used in Cr(VI) removal are 1.0 gm for chromium ion and further experiments were carried on using these selected value.
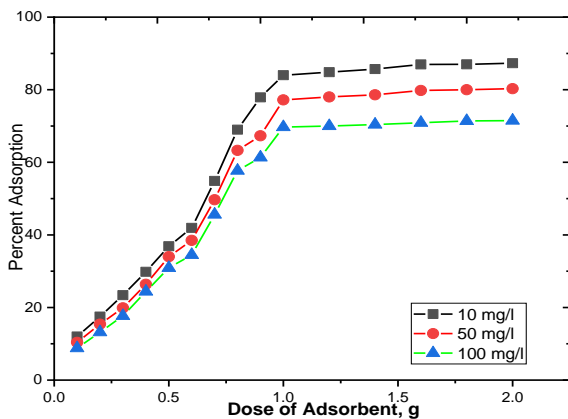

Fig. 2. Effect of dose of Eugenia jambolana Lam. Seed on adsorption of Cr(VI) ions from aqueous solution.

C. Effect of initial metal ion concentration

The adsorption studies were carried out with varying initial Cr(VI) ion concentrations of chromium, ranging from 10 to 1000 mg/l using 1.0 gm of Eugenia jambolana Lam. seed dose at pH 6.0; the results are shown in fig. 3. With the rise in initial metal ion concentration the equilibrium sorption capacity or loading capacity of the biomass increased while the percentage adsorption of Cr(VI) ions decreased (Fig.3). This increase in loading capacity is probably due to a high driving force for mass transfer [20]. However the percentage adsorption of Cr(VI) ions on Eugenia jambolana Lam. seed were decreased from 91% to 39%. This may be attributed to lack of sufficient surface area to accommodate much more metal ion available in the solution.
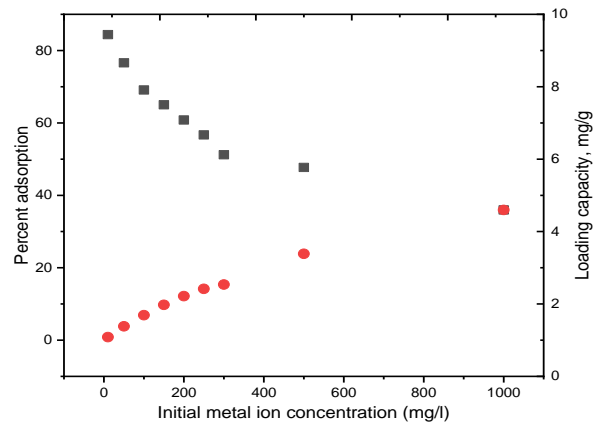

Fig 3: Effect of initial Cr(VI) ions concentration on adsorption by Eugenia jambolana Lam seed.

D. Effect of temperature

Temperature of the reaction mixture markedly influences the removal capacity of adsorbent. The removal of Cr(VI) ions from 100ml solution containing 10, 50, 80 and 100mg/L metal ions was carried out with 1.0 gm Eugenia jambolana Lam. seed at 30, 35, 40, 45, 50, 55 and 60 ^{o}C (fig. 4). Removal of chromium is monitored to increase with increase in temperature for entire range of concentration of metal ions, representing exothermic reaction which is taking place during the adsorption of Cr(VI) ions on Eugenia jambolana Lam. seed. These trends might be caused by various factors like; activation of adsorbent surface and some function, segregation of adsorbent particles and sorption of metal ions with thermal energy.
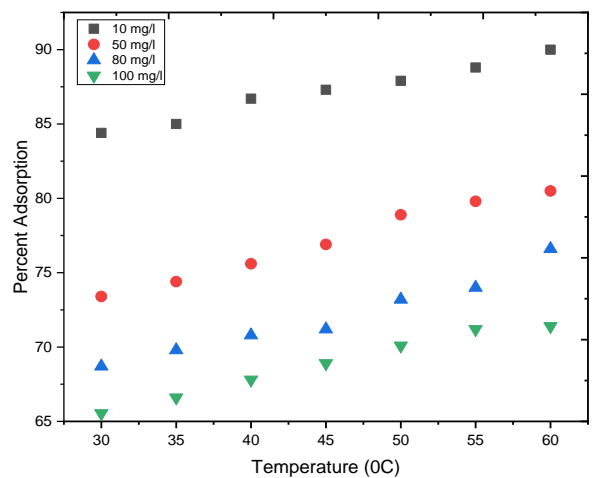

Fig. 3. Effect of solution temperature on adsorption of Cr(VI) ions from aqueous solution.
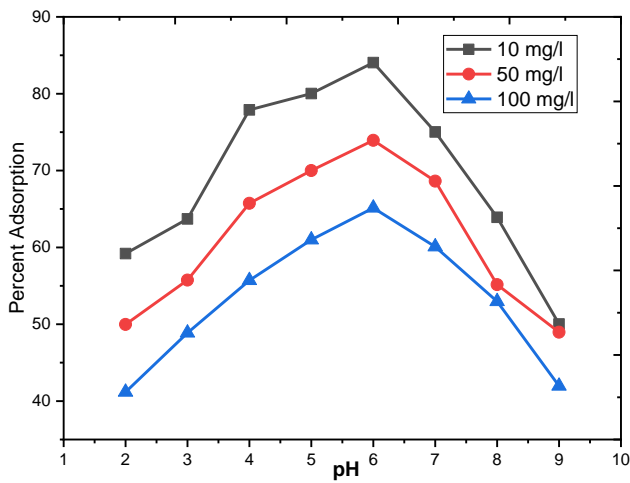
Fig. 4. Effect of solution pH on adsorption of Cr(VI) ions from aqueous solution.

E. Effect of solution pH

The binding of Cr(VI) ions by surface functional groups of Eugenia jambolana Lam. Seed is pH dependant [21]. The effect of solution pH on Cr(VI) removal efficiency is shown in fig. 5. It is clear from the figures that as pH of the solution increases the Cr(VI) uptake increased. These trends can be explained as the solution pH increased, the overall surface of Eugenia jambolana Lam. became negative and thus more and more Cr(VI) ions attract towards surface and sorption increased. In the range of pH 5.3 to 7.1, dissolved Cr(VI) start precipitating in the form of insoluble chromium hydroxide, making exact sorption studies impossible. Therefore, at higher pH values both precipitation and sorption occurred and making true adsorption studies difficult.

F. Adsorption kinetics

The adsorption kinetics informed the solute uptake rate which controls the residence time of sorbate at solid liquid interface [22]. The pseudo first order rate constant k_1 (min^{-1}) was calculated by plotting $log (q_e – q)$ vs. t (Fig.6) pseudo second order rate constant k_2 (g $mg^{-1}min^{-1}$) values was calculated by plotting t/q_t vs. t (Fig. 8) and linear regression correlation coefficient (R^2) values are reported in table 2. The linear regression correlation coefficient values R^2_1 found in the range of 0.934, similarly linear regression correlation coefficient values (R^2_2) for pseudo second order was found in range 0.999. At all initial chromium ion concentrations, the linear regression correlation coefficient R^2_2 values were higher for pseudo second-order model. The higher R^2_2 values signify pseudo-second order kinetics represents the kinetic data well and support the assumption behind the model that the adsorption is due to chemisorptions.
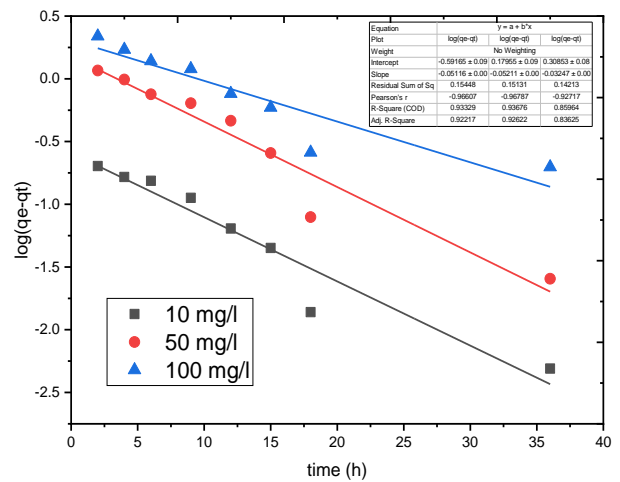

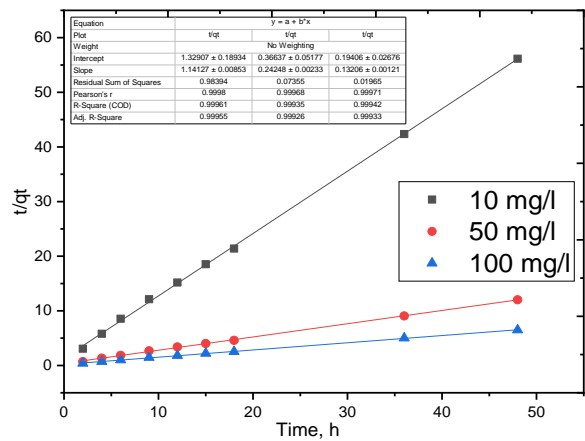**Fig. 5. Pseudo First-order graph for adsorption of Cr(VI) ions from aqueous solution.**

Fig. 7. Pseudo Second-order graph for adsorption of Cr(VI) ions from aqueous solution.

Table- II: Pseudo first order (K_1) and pseudo second order (K_2) rate constants and correlation coefficient (R^2_1) and (R^2_2).

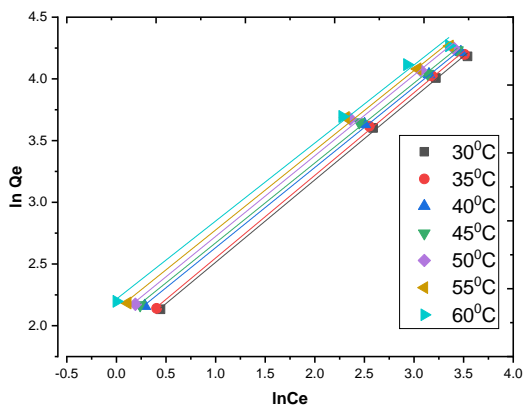| Initial metal ions cons. (mg/l)	Pseudo first-order		pseudo-Second-order	
	$K_1 x 10^{-2}$	R^2_1	$K_2 x 10^{-2}$	R^2_2
10	0.118	0.933	0.980	0.999
50	0.120	0.936	0.160	0.999
100	0.075	0.859	0.089	0.999

Fig. 8 Freundlich Adsorption curve for adsorption of Cr(VI) ions from aqueous solution.
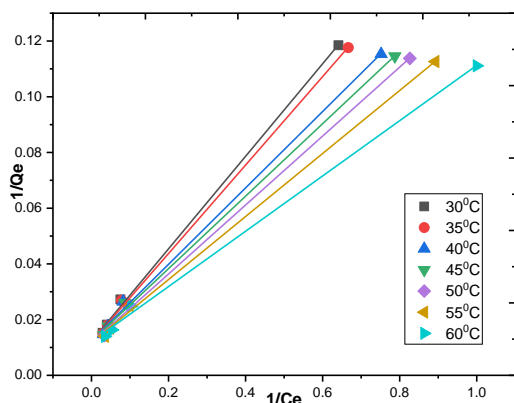

Fig. 9. Langmuir Adsorption curve for adsorption of Cr(VI) ions from aqueous solution.

Table-III: Freundlich isotherm parameters and Langmuir isotherm parameters and correlation coefficient (R^2_F) and (R^2_L).

Temp.	Freundlich isotherm parameters			Langmuir isotherm parameters		
	n	K_F	R^2_F	qe	b	R^2_L
30^0C	1.468	0.266	0.999	82.03	0.073	0.998
35^0C	1.493	0.274	0.999	83.61	0.075	0.998
40^0C	1.539	0.297	0.999	80.39	0.091	0.997
45^0C	1.544	0.306	0.999	81.50	0.094	0.998
50^0C	1.530	0.316	0.996	85.98	0.094	0.999
55^0C	1.549	0.328	0.997	85.03	0.104	0.998
60^0C	1.581	0.346	0.995	83.19	0.121	0.998

G. Adsorption isotherm

The Freundlich adsorption isotherm plot log Qe Vs. log Ce is shown in Fig. 8. K_f and n are the Freundlich constants and reported in Table 3. The value of Freundlich constant *n* for Eugenia jambolana Lam. Seed lies in between 1 and 10 which shows the applicability of Freundlich adsorption isotherm for the removal of Cr (VI) [23]. Similarly Fig. 9 shows the Langmuir adsorption isotherm plot of log 1/Qe versus 1/Ce. The values of b obtained from slope of the plot and Qe from

intercept are given in Table 3. The Langmuir monolayer adsorption capacity is found to be 85.98 mg/g. Since, the correlation coefficient for Langmuir equation is higher than Freundlich equation, thus fitted well. This indicated that the adsorption process of Cr (VI) ion adsorption by surface of Eugenia jambolana Lam. Seed was a monolayer adsorption.

IV. CONCLUSIONS

In this study, the removal of Cr(VI) from aqueous solutions have been carried out using Eugenia jambolana Lam. seed as an adsorbent in batch system. The adsorption characteristics have been examined at different pH values, contact time, initial metal ion concentrations, adsorbent concentrations and temperature. The pH experiments showed that the governing factors affecting the adsorption characteristics of chromium on Eugenia jambolana Lam. Seed. As the number of adsorption sites increase with the dose of adsorbent, percent of Cr(VI) adsorption also increases. In the study of sorption kinetics, the pseudo second order rate model provides better correlation of sorption data with high correlation coefficient, thus suggesting that the rate-limiting step may be chemical sorption rather than diffusion. Equilibrium data agreed well with Langmuir isotherm than Freundlich and monolayer sorption capacity was found to be 85.98 *mg/g* for Eugenia jambolana Lam. Seed.

ACKNOWLEDGMENT

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