

SORPTION KINETICS AND INTRA PARTICULATE DIFFUSIVITY OF HEAVY METALS BIOSORPTION BY *CASSIA ANGUSTIFOLIA* FROM AQUEOUS SOLUTION

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ABSTRACT:

Industrialization and urbanization has led to increased utilization of heavy metals, as a consequence polluting the waters by discharging their waste. Biosorption is an effective process which sequesters metal ions from dilute complex solutions with high efficiency as a removal strategy. The present study was carried out to investigate the efficiency of removal of heavy metals Cd^{+2} , Pb^{+2} and Cu^{+2} using *Cassia angustifolia* bark. The objective was to evaluate the biosorbent for its metal uptake, batch equilibrium, kinetic studies and intra particle diffusivity. The batch mode was carried out at varying initial pH (5 to 9), temperature ($30^{\circ}C$ to $45^{\circ}C$), biosorbent dosage (0.25 g to 1.0 g/50 ml), biosorbent particle size (1.18 mm to below $425\mu m$), metal ion concentration (20 mg to 140 mg/L) and contact time (5 min to 240 min). The equilibrium data obtained fit well in Langmuir and Freundlich isotherms. Biosorption kinetics was tested for pseudo first order with Lagergreen, Venkobacharya and Bhattacharya, Natarajan and Khalaf and Ho's pseudo second order models. The biosorption was pseudo second order indicating that biosorption is controlled by rate diffusion and low binding energy indicates physical adsorption.

Keywords – *Biosorption, metal uptake, isotherms, kinetic equations, intra particle diffusion.*

[I] INTRODUCTION

Heavy metals are important environmental pollutants and many of them are toxic even at very low concentrations. Pollution of the biosphere with toxic metals has accelerated dramatically since the beginning of the industrial revolution [1]. The need for concern has risen because it has now been proven that these metal ions are non biodegradable resulting into bioaccumulation. This bioaccumulation more than the normal values are toxic to fauna and flora and humans, thus removal is a necessity. Higher concentration of copper causes neurotoxicity, commonly known as "Wilson's disease" due to the deposition of copper in the lenticular nucleus of the brain and liver [2]. Cadmium is carcinogenic in nature. Lead has been the most dreaded toxic heavy metal with long term negative impact on health causing anemia, encephalopathy, hepatitis and nephritic syndrome.

The conventional methods of metal removal are chemical precipitation, oxidation, reduction, ion exchange, filtration, reverse osmosis, adsorption, etc. These methods have disadvantages as they leave behind sludge, making filtration process less efficient and are also uneconomical for industrial scale implementation. Biosorption is an alternative cost effective sustainable technology. Large amounts of bark residues are generated annually by timber processing mills and are one of the most abundant renewable resources that can be converted into high value, low cost environment sustainable biomaterials, for treatment of water streams contaminated with organic pollutants [3]; [4], toxic oil wastes,[5] and reactive dyes. Various low cost biosorbents have been used like neem [6], bamboo [7], bagasse [8], marine algal mass [9], and coconut fiber [10]. The present investigation carries out the efficacy of *Cassia angustifolia* bark as biosorbent by optimizing batch mode, studying

equilibrium, kinetic study and intra particle diffusivity.

[II] MATERIALS AND METHODS:

2.1 Preparation of biosorbent:

Cassia angustifolia is a perennial tree growing in tropical countries. Locally available *Cassia angustifolia* tree barks were collected and washed thoroughly with distilled water to remove dust and dirt adhering to it, sun dried for a week and later oven dried for two days at 80°C. The dried biomass was ground into fine particles in a blender and sieved to different sizes. The biomass sieved below 425µm was kept stored in an air tight bottle for further experimental use [10].

2.2 Preparation of synthetic aqueous solution:

A synthetic aqueous solution was prepared by dissolving 20 mg/L each of lead nitrate (Loba Chemie), Cadmium chloride (Himedia), Cupric sulphate pentahydrate (Merk) in 1000ml distilled water. All chemicals were AR grade [10].

2.3 Characterization of the biosorbent:

To study the nature and mechanism of sorption the surface of biosorbent was studied by FTIR (Perkin- Elmer spectrum 100), in the range of 450cm⁻¹ to 4000cm⁻¹[11] and SEM (JOEL) microscope.

2.4 Batch studies:

To optimize the biosorption batch experiments were conducted at fixed metal ion Pb⁺², Cu⁺², Cd⁺² concentration of 20 mg/L and effect of pH (5,7,9) ; temperature (30°C to 45°C) ; biosorbent dosage (0.25g to 1.0g/50 ml), biosorbent particle size (1.18mm to below 425µm), kinetics studies by contact time from 5 to 240 minutes; initial metal ion concentration 20-140 mg/L for equilibrium study; desorption studies of pH (1 to 11) were studied. Batch experiments were agitated in a Remi orbital shaker at 180 rpm usually for 1 hr. After 1 hr the biosorbent was separated from metal ion solution using Whatman filter paper No: 42. The filtrate was analyzed for residual metal ion concentration using AAS (Perkin-Elmer).

Percentage removal and metal uptake were evaluated from the following equation:

$$\% \text{ removal of metal} = [(C_i - C_e)/C_i] * 100 \quad (1)$$

Where, C_i is the initial metal ion concentration before biosorption process in mg/L, C_e is the equilibrium metal ion concentration after biosorption process in mg/L.

$$\text{Metal uptake } q = [(C_i - C_e)/M] * V \quad (2)$$

Where, V is the volume of metal ion solution in ml and M is the mass of biosorbent taken in gm.

[III] RESULTS AND DISCUSSIONS:

3.1 Characterization of biosorbent surface:

FTIR analysis in range of 450cm⁻¹ to 4000cm⁻¹ shows the presence of characteristic polymeric –OH as in cases of celluloses and hemicelluloses (Xylan), phenolic –OH as in case of tannins and lignins, O=C-O, carboxylate ion as in glucouronates of hemicellulosics present in bark. FTIR spectrum is shown in Fig.1. SEM of *Cassia angustifolia* was examined at 200x, 500x, 2000x. Rough surface texture and porosity could be distinctly noticed. This increases the surface area of biosorption and show that intra particle diffusion could also be the mechanism of biosorption. SEM analysis is shown in Fig.2 [12].

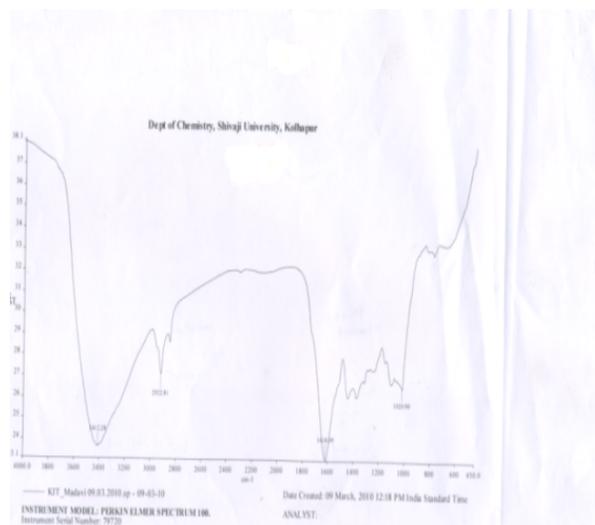
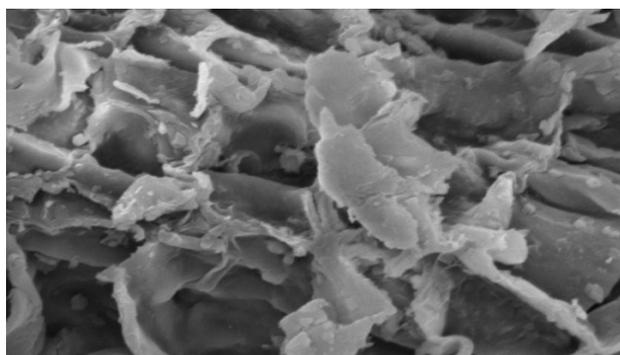


Fig.1. FTIR spectrum of *Cassia bark*



100µm
Fig.2. *Cassia bark* at 2000x

3.2 Batch optimization:

Batch mode experimentations indicated an optimization of pH 7, temperature 35°C, 1 gm/100ml biosorbent dosage, biosorbent particle size 425 µm, contact time of 1hour and desorption at pH 1. This indicates that sorption is pH dependent ion exchange phenomenon, exothermic and reversible process.

3.3 Equilibrium biosorption isotherm studies:

The biosorption isotherm is important from practical point of view in order to design the biosorption system. Both models of Langmuir and Freundlich were tested for the best fit to describe the equilibrium achieved.

A) Langmuir Isotherm model: In order to account for the surface phenomenon Langmuir isotherm plots were analyzed. It is given as:

$$1/q_e = 1/(q_0b)C_e + 1/q_0 \quad (3)$$

where, C_e is the metal ion concentration at equilibrium (mg/ml), q_e is the amount of metal ions adsorbed per unit mass of biosorbent (mg/g), q_0 is the Langmuir monolayer sorption capacity (mg/g), b is the Langmuir constant related to intensity of biosorption i.e. energy of biosorption. The separation factor R_L is given as:

$$R_L = 1/(1+bi) \quad (4)$$

Where, b is the energy of biosorption and i is the highest metal ion concentration in mg/g. If R_L is less than 1, biosorption is favorable.

B) Freundlich isotherm model: The Freundlich isotherm model is an empirical equation and

indicator of extent of heterogeneity of the biosorbent. It is given as:

$$\log q_e = \log K_f + (1/n) \log C_e \quad (5)$$

where, C_e and q_e have the same meaning as in

	Langmuir $1/q_e$ vs $1/C_e$			Freundlich $\log q_e$ vs $\log C_e$		
	q_0 mg/g	b	R^2	K_f mg/g	n	R^2
Cd^{+2}	32.5	0.13	0.995	0.499	0.81	0.965
Cu^{+2}	11.6	1.19	0.958	2.218	1.52	0.894
Pb^{+2}	15.8	2.62	0.990	10.52	2.44	0.946

Langmuir isotherm, K_f is biosorption capacity (mg/g), n is biosorption intensity i.e. energy of biosorption (binding energy). The equilibrium studies carried out in the metal ion concentration range of 20mg to 140mg/L were tested. The separation factor R_L , biosorption capacity q_0 and K_f , intensity of biosorption b and n were evaluated using eqn. 3, 4 and 5. The experimental data is summarized in table no.1. Langmuir and Freundlich isotherm fit well for Cd^{+2} , Cu^{+2} and Pb^{+2} . The R_L is less than 1 indicating the biosorption to be favorable.

Table No.1 Isotherm Equilibrium Summarization

3.4 Kinetics of biosorption:

A study of biosorption kinetics models correlates the metal uptake rate with the bulk concentration of the metal; these models are important in wastewater treatment process for the design and optimization of a system. In order to examine and understand the mechanism of biosorption onto *Cassia angustifolia* bark and the rate controlling steps the kinetic data were modeled using pseudo first order and pseudo second order and intra particle diffusion. The data obtained was fitted into pseudo first and pseudo second order kinetics model and studied.

The rate equation for **pseudo first order** given by Lagergreen is –

$$\log (q_e - qt) = \log q_e - (k/2.303) t \quad (6)$$

Where, q_e is the equilibrium metal ion adsorbed in mg/gram, qt is the biosorption of metal ion per unit biomass at time t , k is the pseudo first order rate constant.

The rate equation for **pseudo first order** given by **Venkobacharya and Bhattacharya** is-

$$\text{Log}(1 - U(T)) = - (k/2.303) t \quad (7)$$

Where, $U(T) = [(C_i - C_t)/(C_i - C_e)]$, C_i is the initial metal ion concentration, C_t is the metal ion concentration at time t , C_e is the equilibrium time metal ion concentration, k is the pseudo first order rate constant.

The rate equation for **pseudo first order** given by **Natarajan and Khalaf** is-

$$\text{Log}(C_i/C_t) = (k/2.303) t \quad (8)$$

Where, C_i is the initial metal ion concentration, C_t is the metal ion concentration at time t , k is the pseudo first order rate constant.

The rate equation for **pseudo second order** is given by **Ho et al.** is given as -

$$t/qt = 1/h_0 + (1/q_e) t \quad (9)$$

where, t is the time in minutes, qt is biosorption of metal ion per unit biomass biosorption at time t , q_e is the equilibrium concentration of metal ions at optimum time, k_2 is the pseudo second order rate constant,

$$h_0 = k_2 q_e^2.$$

The kinetics of biosorption for Cd^{+2} , Cu^{+2} , Pb^{+2} is as in figures 3 to 5 showing well fit into Ho's pseudo second order model. It confirms that the biosorption has two phase reactions; a very rapid biosorption for shorter duration in initial stage followed by a very slow one for longer duration. The fast reaction is due to chemisorptions involving valence forces present as high affinity ligands on the surface of the biomass providing fast metal ion binding surface active sites thus sharing or exchange of electrons or electrostatic (coulombic) sorption between biosorbent and adsorbate metal ions [9] The low binding energies suggest the probability of physical biosorption. The second slower reaction is due to diffusion of ions [13]. Hence the rate limiting step is the diffusion controlled. This clearly indicates the mechanism to be physisorption, chemisorptions and intra particle diffusion controlled.

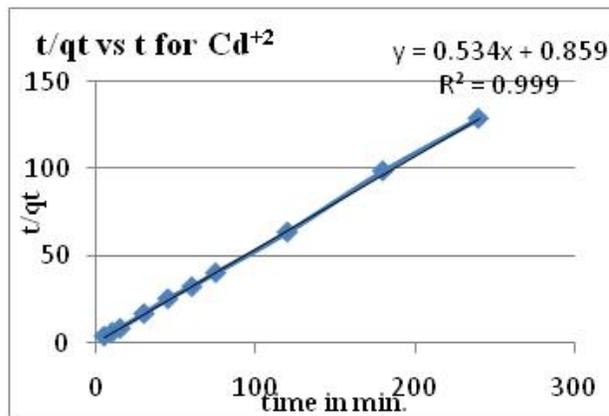


Fig.3. Ho's pseudo second order for Cd^{+2}

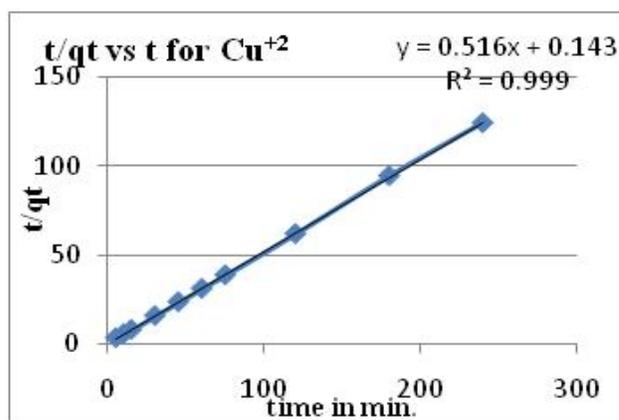


Fig.4. Ho's pseudo second order for Cu^{+2}

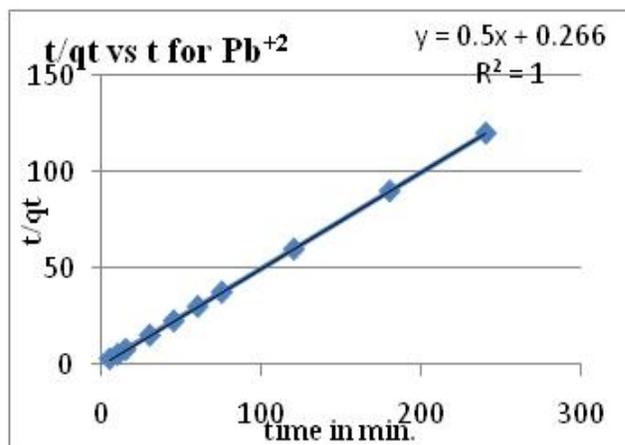


Fig.5. Ho's pseudo second order for Pb^{+2}

The kinetics of biosorption for Cd²⁺, Cu²⁺, Pb²⁺ is summarized in table no.2 shows well fit into Ho’s pseudo second order model.

Table no.2. Biosorption Kinetics Summarization

	Cd ²⁺	Pb ²⁺	Cu ²⁺
Lagergreen pseudo first order			
k in /min	3.9*10 ⁻²	5.527*10 ⁻²	5.52*10 ⁻²
qe in mg/g	2.2	4.405	4.055
R ²	0.870	0.940	0.932
Venkobacharya & Bhattacharya pseudo first order			
k in /min	3.9*10 ⁻²	5.29*10 ⁻²	5.527*10 ⁻²
R ²	0.875	0.936	0.896
Natarajan & Khalaf pseudo first order			
k in /min	1.8*10 ⁻¹	3.45*10 ⁻²	2.072*10 ⁻²
R ²	0.764	0.609	0.658
Ho pseudo second order			
k ₂ in g/mg min	3.32*10 ⁻¹	9.39*10 ⁻¹	1.879
h ₀ in g/mg min	1.16	3.759	6.99
qe in mg/g	1.87	2.0	1.93
R ²	0.999	1.0	0.999

The intra particle diffusion Weber Morris studies were carried out to check for intra particle diffusivity for Cd²⁺, Cu²⁺ and Pb²⁺. Mass transfer is driven by both – 1) film diffusion controlled (external mass transfer resistance), 2) intra particle diffusion controlled (internal mass transfer resistance) [10]. This can be experimentally confirmed by Weber Morris model for intra particle diffusion by plotting qt vs √t. The Weber Morris equation is given as:

$$qt = K_{id} \sqrt{t} + c. \tag{10}$$

Where, qt is the amount of biosorption of metal ion at time t, K_{id} is the intra particle diffusion rate constant, t is the time interval at which the biosorption is evaluated.

Higher values of K_{id} indicate that the intra particle diffusion mechanism predominates. The intercept values c is considered as boundary layer thickness which gives an insight into the tendency of the metal ions to get adsorbed or remain in solution. The boundary layer is considered to be a viscous drag between biosorbent surface and metal ion diffusing across its surface. Higher values of c represent depict higher biosorption capacities. It

has been reported that as temperature increases the thickness of the boundary layer decreases due to increased tendency of the metal ion to remain in solution phase, resulting in decreased biosorption with increased temperature [10]. The sorption decreases with higher temperature affirming this theory.

Figures 6 to 8 show the Weber Morris plots for intra particle diffusivity for Cd²⁺, Cu²⁺, Pb²⁺.

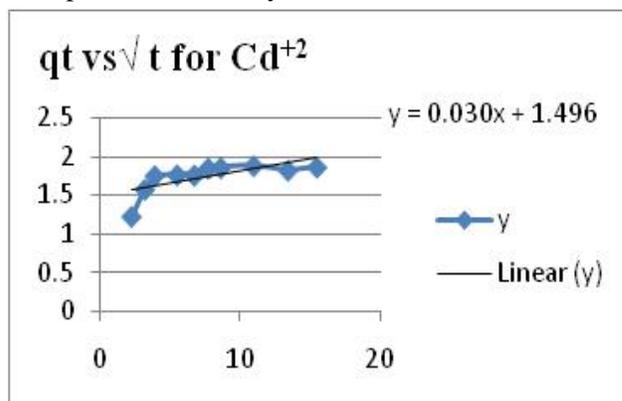


Fig.6. Weber Morris’s plot qt vs √t for Cd²⁺

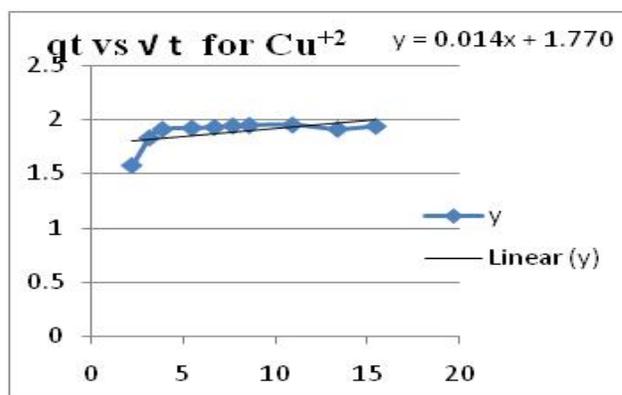


Fig.7. Weber Morris’s plot qt vs √t for Cu²⁺

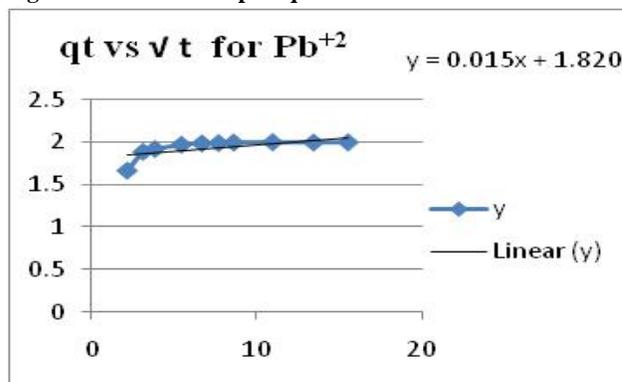


Fig.8. Weber Morris’s plot qt vs √t for Pb²⁺

Table no.3 summarizes intra particle diffusivity.

Table no. 3. Intra Particle Diffusion Summarization

	Cd ⁺²	Cu ⁺²	Pb ⁺²
K _{ad} in mg/g min	0.030	0.014	0.015
c	1.496	1.770	1.820

[IV] CONCLUSION:

Cassia angustifolia bark can be a promising low cost biosorbent for large scale industrial heavy metal sorption with 32.5, 11.62 and 15.87 mg/g metal uptake capacity for Cd⁺², Cu⁺² and Pb⁺² respectively with good R² values. Kinetic study shows pseudo second order predicting the sorption to be both physiosorption as well as diffusion controlled.

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