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Equilibrium sorption studies for Cu^{2+} and Pb^{2+} metal ions on three different biomasses

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ABSTRACT

Presence of heavy metals in the aquatic system is posing serious problems. The aim of this study was to utilize the locally available agricultural waste materials for scavenging these heavy metals. In the present study, the biomass generated from the dried leaves of *Terminalia Catappa, Dalbergia latifolia and Ficus benghalensis* was used for evaluating the biosorption characteristics of Pb and Cu ions in aqueous solutions. Batch adsorption experiments were performed on these leaves and it was found that the amount of metal ions adsorbed increased with the increase in the initial metal ion concentration. The equilibrium sorption capacity for 800 mg l^{-1} metal solution was 77.55, 59.35 and 19.35 mg g^{-1} respectively for these three leaves. Out of the two isotherms tried Langmuir gave the best fit with r^2 values ranging from 0.96 to 0.98. *Terminalia Catappa* leaves were found to be best sorbent than *Dalbergia latifolia followed* by *Ficus benghalensis* leaves which showed least sorption. From the leaf composition from XRF, Ion exchange also could be one of the options for studying the mechanism of adsorption of these cations on these leaves. Comparing with other similar studies these were found to be the excellent adsorbents and can be successfully used by Industries for heavy metal removal.

Key words: Biosorption, heavy metals, Langmuir Isotherm.

INTRODUCTION

Water gets polluted from leaching of ore deposits and from anthropogenic sources which include mainly industrial effluents and solid waste disposal. Industrial development in the recent past has substantially increased the level of heavy metals.

Removal of heavy metals from aqueous solution by using inactive and dead biomass is an alternative technology for removing toxic heavy metals which cause life-threatening illnesses and pose environmental disposal problem due to their non degradable and persistence nature (Ahluwalia & Goyal, 2006). There is a need to treat the industrial wastewaters before being released into the environment.

Different treatment techniques such as ion-exchange, membrane filtration, oxidation-reduction, chemical precipitation, adsorption, reverse osmosis and evaporative recovery are cost intensive, for separation of heavy metals, have been developed for effluents laden with heavy metals (Chong and Volesky, 1995; Elouear et al., 2009). The treatment of metal-bearing effluents requires more effective techniques with lower costs than the conventional ones.

Low-cost adsorbents have been evaluated for the removal of heavy metals from aqueous solutions [Chaiyasith *et al.,* 2006, Patterson J W, 1985; Aksu *et al.,* 1991] because of the following:

1. Plants have a natural tendency to sequester heavy metals because of the presence of of an elaborate network of capillary tubes which have an excellent sorptive matrix
2. Also the cell walls of these biomasses have varied composition of proteins, carboxylic acids and phenolic compounds (M.Friedman, 1972) which allow ion exchange.

3. Leaf litter creates significant disposal problem and if it can be used for cleaning polluted water than there can be double benefit where the disposal problem is solved and waste becomes a useful and inexpensive sorbent for water cleaning.

4. No nutrients are required to keep them alive and 5.There is a possibility of metal recovery.

Forest residues are low cost, renewable, and widely available making them a logical choice to remove metal ions from contaminated waters like rubber leaf powder (Hanafiah et al., 2006), Lalang leaf (Hanafiah et al., 2007) etc many low –cost adsorbents have been used to study their adsorption capacities. *Saraca indica* leaf powder could remove 95.37% of Pb at the pH 6.5 (Goyal et al., 2008), Mahvi et al. (2008) reported that cadmium uptake was 85% and 92% for both *Ulmus* leaves and their ash, respectively. The leaf biomass of *Cercis siliquastrum* L. eliminated Pb(II), Cu(II) and Ni(II) from waste water (Salehi*et al.,2008), *ficus religiosa* leaves were used for treatment of lead and chromium waste (Qaiser* *et al*., 2007) , *S. cumini* L. was chosen as a biosorbent for Lead (King et al., 2007).

From the eco-toxicological point of view Pb, Cd, Cu etc. are the dangerous metals, therefore; removal of these heavy metals from wastewaters is of prime importance.

Since Lead and Copper are widely used in Industries Pb can cause chronic toxicity and can damage the nervous system, kidneys, and reproductive system, liver and brain (Hepple, 1972). It is used in industries like storage-battery manufacture, pigments, leaded glass, photographic materials, matches and explosives, printing, pigment manufacturing, petrochemicals, fuel combustion and photographic materials (Carson et al., 1986; Raji and Anirudhan, 1997) and Cu which is relatively less toxic, however, higher concentrations are equally toxic and is mainly employed in electric goods industry, hydrometallurgy, tire manufacturing, *etc*

In the present study, the biomass generated from the dried leaves of *Terminalia Catappa**,** Dalbergia latifolia and Ficus benghalensis,* which are locally available plants, is used for evaluating the biosorption characteristics of Pb and Cu ions in aqueous solutions. Sorption isotherms are used to model the adsorption equilibrium.

Terminalia Catappa also called Badam has obovate leaves with smooth grey bark. Now days it is used as an ornamental tree also apart from its usage as almond fruit bearing tree. Its leaves are big in size and were collected from around the Uttam Nagar area, near NDA, Pune.

Dalbergia latifolia is a large genus of small to medium-size trees and shrubs. It is a tall,deciduous tree. It gives premium quality timber which is rich in aromatic oils. Its leaves were collected from Pune University campus area.

Banyan is found throughout the year and is very common. The leaves of banyan tree have a beautiful heart shape which taper to a needle point. When the leaves first appear their color is red-pinkish but then turn deep green and grows to about 12 to 18 cm long. The banyan tree *(Ficus benghalensis),* also called Indian fig,is evergreen and is supported with copious aerial roots. The bark surface is smooth and grey. Its leaves were collected from NDA area.

To know if these three biomasses are good adsorbents of Pb and Cu heavy metals, they were tested for variation with time, pH, biomass concentration and initial metal ion concentration. Composition of leaves was found with the help of ED XRF.

MATERIAL AND METHODS

The leaves of *Terminalia Catappa, Dalbergia latifolia* and *Ficus benghalensis* were kept in oven at 333–343 K for 24 h in an air oven. The dried leaves were then converted into fine powder by grinding in a mechanical grinder. The powder was than sieved through 10 mesh sieve and preserved as adsorbents in glass bottles for further experiments. For all experiments, the stock solutions (1000 ppm) of Cu (II) and Pb (II) were prepared in distilled water.

The three biomasses were analyzed by XRF for their chemical composition using model

AMETEK (Material Analysis Division). The 4 g. of the ground and dried samples were taken in cups for XRF determination by powder method.

To study the variation with contact time, the metal removal was tested in batches at different time intervals and the residual metal ion concentration of supernatant was determined using Varian Spectrophotometer, Model Spectra AA220.

To study the effect of pH, the pH of the metal solution was varied between 2 to 6, keeping the concentration of the biomass and contact time constant.

0.5g to 2.0g of the biomass was treated with 400 mg l^{-1} metal ions keeping all other variables constant. All the three biomasses were treated with varying initial metal ion concentration ranging between 50 to 800 ppm.

Adsorption isotherms:

The biosorption capacities (q_{eq}) at equilibrium were calculated as follows:

$$q_{eq} = \frac{(C_o - C_{eq})}{X} XV$$

where C_0 was the initial metal ion concentration (mg 1^{-1}); C_{eq} the metal ion concentration at equilibrium (mg 1^{-1}); V the volume of solution used in litres ; *X* was dry leaves powder weight(g).

The Langmuir isotherm model in linearized form is given as

$$\frac{1}{q_{eq}} = \frac{1}{b_m}\frac{1}{C_{eq}} + \frac{1}{q_m}$$

where b_m is a coefficient related to the affinity between the sorbent and sorbate, and q_m is the maximum sorbate uptake under the given condition.

The Freundlich isotherm in linearized form was applied as follows

$$\text{In } q_{eq} = \text{In } K_F + \frac{1}{n} \text{In } C_{eq}$$

where q_{eq} and *C*eq are the biosorption capacity of the biosorbent at equilibrium and the equilibrium metal ion concentration, respectively. K_F and n are adsorption isotherm parameters.

RESULTS AND DISCUSSION

Effect of contact time, pH and initial biomass concentration on biosorption

It was found that the Cu and Pb metal uptake was very fast and it reached equilibrium in the first 15 minutes only which is in agreement with results of (Ajmal et al., 2006) for Cd (II) adsorption on parthenium and the weed adsorbed it in 20 min. It is in conformation with (Bhattacharyya and Gupta, 2006) who inferred that this initial high uptake is

Table 1: Comparison of biosorption of metal ions on three types of biomass

	Metal ion concentration		Biosorption Efficiency		Metal adsorbed
	Initial(ppm)	Final(ppm)	Int.- final	(%)	q (mg/g)
Pb					
Ficus benghalensis	800	26.16	773.84	96.73	19.346
Dalbergia latifolia	800	206.51	593.49	74.18625	59.349
Terminalia Catappa	800	24.49	775.51	96.93875	77.551
Cu					
Ficus benghalensis	800	28.42	771.58	96.4475	19.29
Dalbergia latifolia	800	40.78	759.22	94.9025	75.922
Terminalia Catappa	800	21.05	778.96	97.37	77.896

Table 2: Results of isotherm models

Biomass	Element	Isotherm	R2	b	q_{max}	n	1/n
Ficus benghalensis	Pb	Langmuir	r2=0.9749	0.357	19.64		
		Freundlich	r2=0.9877	-	-	0.898	1.113
Dalbergia latifolia	Pb	Langmuir	r2= 0.9694	7.024	61.36		
		Freundlich	r2=0.8578			1.056	0.947
Terminalia Catappa	Pb	Langmuir	r2= 0.9731	0.0896	77.78		
		Freundlich	r2=0.8223			0.269	3.714
Ficus benghalensis	Cu	Langmuir	r2=0.96	1.142	20.289		
		Freundlich	r2=0.9399			0.255	3.928
Dalbergia latifolia	Cu	Langmuir	r2=0.9842	0.671	40.45		
		Freundlich	r2= 0.9774			0.319	3.131
Terminalia Catappa	Cu	Langmuir	r2=0.9859	1.319	82.85		
		Freundlich	r2=0.9544			0.563	1.777

Table 3: Ion-exchange

S.No.	Source of plant biomass	SiO2%	K2O%	CaO%	MgO%	S ppm
1	*Terminalia Catappa*	8.017	1.817	5.251	0.904	1711
2	*Dalbergia latifolia*	2.214	1.985	4.963	2.003	2936
3	Ficus benghalensis	2.854	3.45	2.043	0.526	1185

Table 4: Gibbs free energy of the biosorption process

Type of Biomass	ΔG°	
	Pb	Cu
Ficus benghalensis	-5893.44	-9850.76
Dalbergia latifolia	-10555.8	-6932.35
Terminalia Catappa	-11728.3	-7324.47

due to the bare surface after which the adsorption is gradual as the available sites decrease.

From (Fig. 1 & 2) it was observed that adsorption maxima reached at pH 3 only and the adsorption values remain stable after pH 3. For further experiments the pH value was maintained at 4 throughout because at lower pH the sites on the cell wall remain protonated and don't allow the approach of cations whereas at higher pH

Table 5: Type of isotherm for various R_L

R_L Values	NDG		UFL		UTH	
Initial Metal concentration	Pb	Cu	Pb	Cu	Pb	Cu
50ppm	0.558691	0.275866	0.794872	0.65945	0.497416	0.277344
100 ppm	0.387628	0.160003	0.659574	0.491925	0.331041	0.160998
200 ppm	0.240408	0.086958	0.492063	0.326194	0.198352	0.087546
400ppm	0.136627	0.045455	0.326316	0.194882	0.110094	0.045777
500 ppm	0.112373	0.036698	0.279279	0.162228	0.090059	0.03696
800ppm	0.073323	0.023256	0.194969	0.107961	0.058254	0.023425

deprotonation takes place and the sites become negatively charged attracting the cations with different concentrations of the biomasses, it was found that lower the initial concentration of the biomass, higher was the sorption (Fig.3 & 4) because of the simple reason that the mass transfer is rapid at lower biomass concentrations Similar trends were observed in the sorption of cations on the waste beer yeast by (Hana *et al*., 2006).

Effect of initial metal ion concentration on biosorption

The initial Pb and Cu metal ion concentration was in the range of 50 to 800 mg/l and there is a constant increase in the uptake of the heavy metal ions as seen in the Fig. 5 & 6. Biosorption values (mg/g) were highest for Terminalia Catappa (77.896 for Cu and 77.551 for Pb) followed by Dalbergia *latifolia (75.922 for Cu*

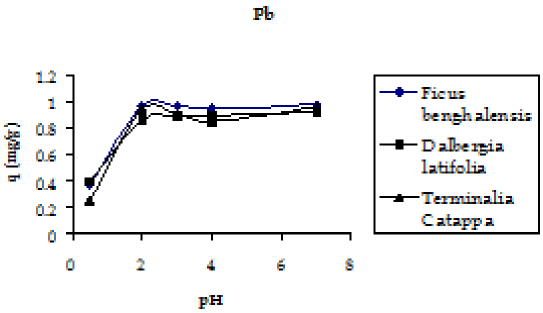

Fig. 1: Biomass in equilibrium with 50 ml. of 400 mg/l metal solution for 3 hours

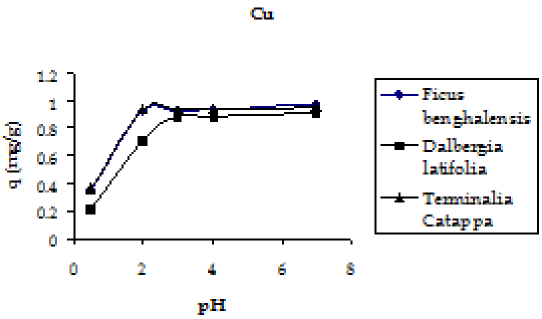

Fig. 2: Biomass in equilibrium with 50 ml. of 400mg/l metal solution for 3 hrours

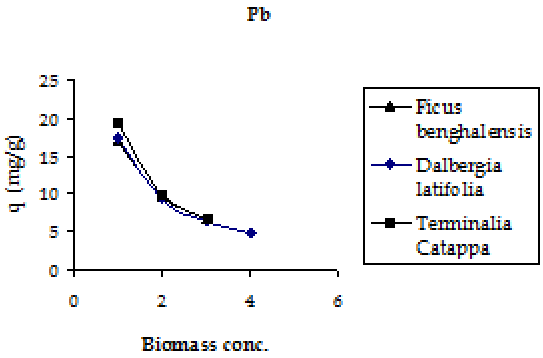

Fig. 3: Biomass in equilibrium with 50 ml. of 400 mg/l metal solution at pH 4 for 3 hours

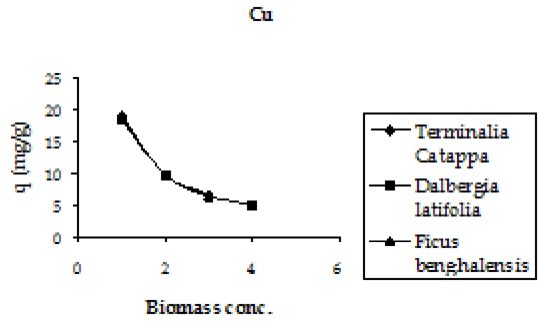

Fig. 4: Biomass in equilibrium with 50 ml of 400 mg/l metal solution at pH 4 for 3 hours.

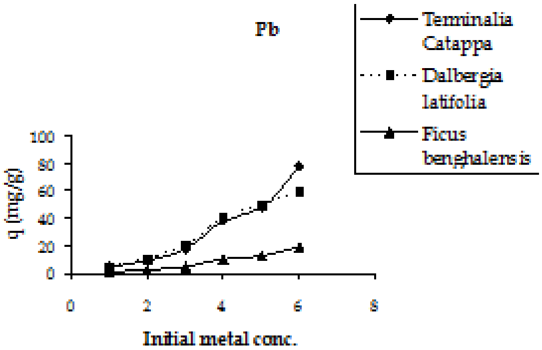

Fig. 5: 0.5 g biomass in equilibrium with 50 ml. metal solution at pH 4 for 3 hours

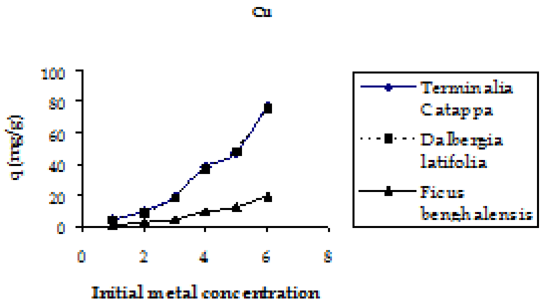

Fig. 6: 0.5 g biomass in equilibrium with 50 ml. metal solution at pH 4 for 3 hours.

*and 59.349 for Pb) (Table 1).*The reason for this preference is that the size of the Cu metal ion which is smaller than Pb ion. Ficus benghalensis showed the lowest biosorption values (19.29 for Cu and 19.346 for Pb).

Percent sorption for both the elements was between 95 to 97 % for all the three biomasses except for Pb on *Dalbergia latifolia* which was 74% (Table 1).

Data fitted both Langmuir and Freundlich equation but more so with Langmuir as is evident from r^2 values. Also, calculated r^2 values match the

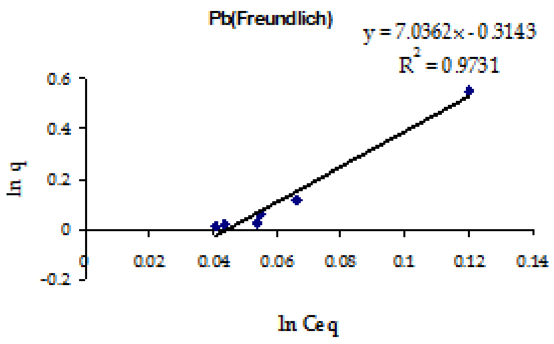

Fig. 7: Terminalia Catappa

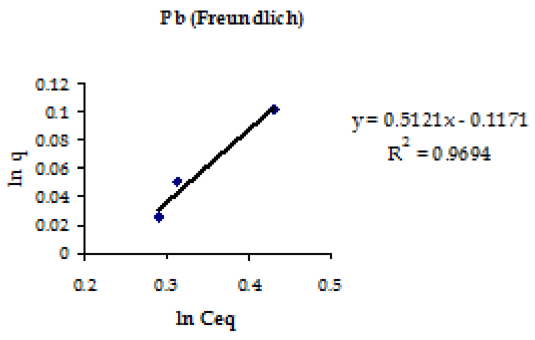

Fig. 8: Dalbergia Latifolia

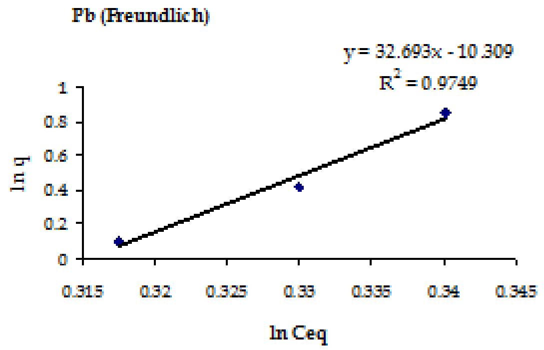

Fig. 9: Ficus benghalensis

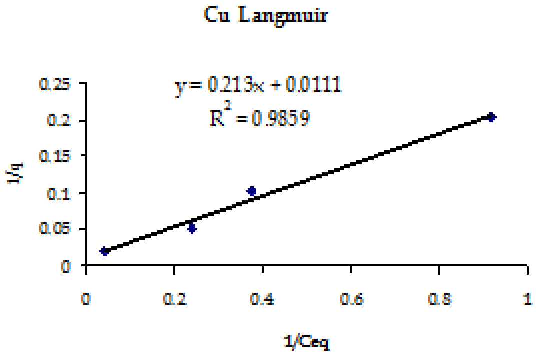

Fig. 10: Terminalia Catappa

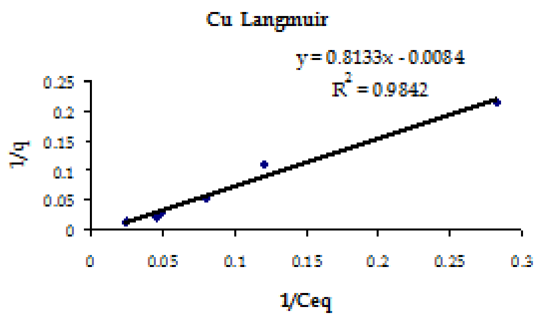

Fig. 11: Dalbergia Latifolia

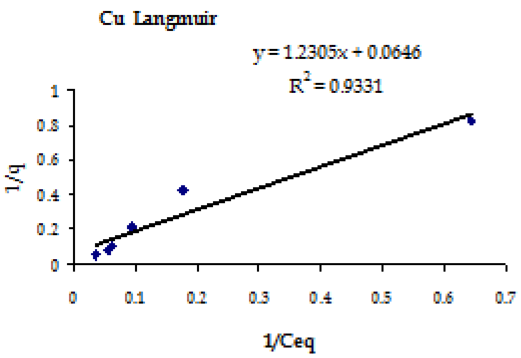

Fig. 12: Ficus Benghalensis

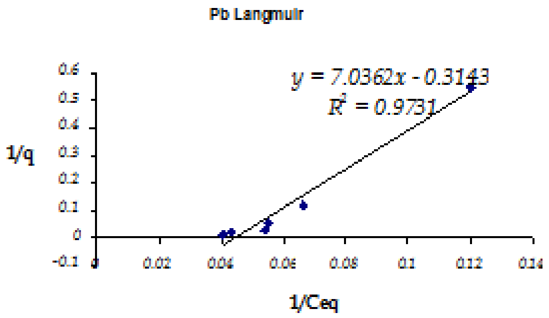

Fig. 13: Terminalia Catappa

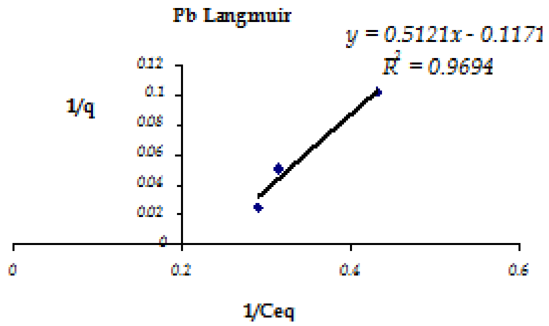

Fig. 14: Dalbergia Latifolia

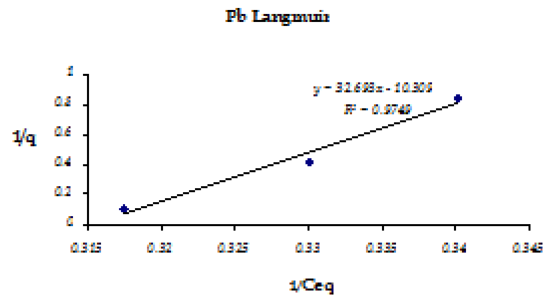

Fig. 15: Ficus Benghalensis

experimental values (Table 2). This shows that there is monolayer sorption. Cu and Pb show almost similar sorption capacities on the three biomasses. The reason for this preference is that the size of the Cu metal ion which is smaller than Pb ion and thus it can get attached to the powder easily. Sorption was low on Ficus benghalensis but both the cations were equally adsorbed by this biomass without any preference (Fig. 7 to 12). The 'n' values should fall in 1-10 range for beneficial adsorption (Kalin et al., 2005). Values are in the range 0.25 to 1.056 suggesting the presence of heterogenous surface and bonding sites with different energies as is seen in (Salamatinia et al., 2007) where the similar results were observed.

Ion-exchange also is playing a significant role as is evident from their leaf composition values determined by XRF (Table 3). Ion-exchange is feasible more in *Terminalia Catappa* than in *Dalbergia latifolia and* which in turn can be more than in Ficus benghalensis.

Negative values of Gibbs free energy indicate the spontaneity of the adsorption process between metals and the leaf powders. The standard Gibbs free energy of the biosorption process corresponding to Pb and Cu on the biomass was evaluated using equation described by Babarinde et al. (2008) (Table 4). The negative values of ÄGº indicate the spontaneous sorption by the biomass. As the values are more than -40 kJ/ml (Jnr and Spiff, 2005) chemisorption is implied from the Langmuir graph monolayer coverage can be used to calculate surface area with the following equation:

The dimensionless constant separation factor R_L is given by:

$$R_L = 1/ (1+bC_o)$$

It is an essential feature of Langmuir Model where b is the Langmuir constant and C_o is the initial metal concentration (mg $l^{-1)}$. For favourable adsorption its values should be between 0 and 1 (Poots et al., 1978). It can be seen that all the values are between 0.02 and 0.7 (Table5) which indicates favourable adsorption.

CONCLUSION

These three biomasses can be obtained without excessive cost.

Terminalia Catappa leaves show highest adsorption capacity compared to *Dalbergia latifolia* and Ficus benghalensis. The results show that in very less time, a good amount of the metal can be taken up by the biomass. The present results demonstrate that the Langmuir model fits better than the Freundlich model for the adsorption equilibrium data in the examined concentration range. Langmuir Model suggests monolayer adsorption whereas ÄG° values favour chemisorption. R_L values also show favourable adsorption. It is important to note that the biomass works efficiently without any pre treatment.

Terminalia Catappa & Dalbergia latifolia seem to be the promising biosorbents for heavy metals from aqueous solutions.

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