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Kinetic and Isothermal Biosorption Studies of Co(II), Cu(II) and Ni(II) Using *Polyalthia longifolia* Leaf Powder

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Kinetic and isothermal biosorption studies of cobalt, copper and nickel ions using *Polyalthia longifolia* leaf powder has been carried out in this study on batch scale. Various factors like adsorbent dose, pH, initial concentration of metal ion and agitation time were optimized. Maximum biosorption of Cu(II), Co(II) and Ni(II) occurred at pH 6, 6 and 5, respectively. Isothermal models like Langmuir, Freundlich and Temkin were studied and observed to fit well. The maximum removing capacity of *Polyalthia longifolia* leaves was found to be 1.74, 3.99 and 4.08 mg/g for copper, cobalt and nickel ions, respectively following pseudo-second-order model. So, *Polyalthia longifolia* leaves found to besuitable for amputation of cobalt, copper and nickel ions in an environmentally benign way.

Key Words: Biosorption, *Polyalthia longifolia*, Heavy metals, Isotherms, Kinetics.

INTRODUCTION

With increasing population and industrial growth environmental pollution problems increasing rapidly and lead to ecological disequilibrium along with health hazards. Industries like mining, electroplating, tanneries, fertilizer, plastic, ceramic, textile, pigments and metallurgical processes are the chief contributors in discharging heavy metals into the fresh water and marine environment[1,2]. Several heavy metals like copper, cobalt and nickel are the frequently found pollutants in the industrial water streams. These kinds of metals are essential component of human nutrition in trace quantities but in larger amount, they are deposited in various internal organs and severely damage them[3]. Various processes are used to minimize the metals' concentration to their acceptable limits, but due to their water-soluble tendencies, these processes are not much effective.

Some conventional methodologies are precipitation, electrodialysis, phytoremediation, ion-exchange, reverse osmosis, phyto-chemical reactions and oxidation/reduction. These processes have several inherent disadvantages, some are less effective removal, high reagent requirements, high costs, generation of toxic sludge and its safe disposal[4]. In recent years, adsorption on activated charcoal is being evolved as an alternate of these processes for water purification, but activated charcoal is very expensive. For this reason, researchers are investigating the adsorption capacities of various materials found indigenously and abundantly as an alternate of activated carbon. Agricultural products such as rice husk ash, wheat straw, orange peel, maize leaf, tea waste, sugar cane leaves, rubber leaf powder, canola meal and almond husk, *etc.*, have been studied[5-8].

Here the potential of *Polyalthia longifolia* leaves to remove Cu(II), Co(II) and Ni(II) ions is investigated in terms of various factors, such as adsorbent dose, pH and contact time. Its ability to biosorb Cr(III) and Cr(VI) had been investigated and reported already by authors, where its high biosorption potential was confirmed[9]. Langmuir, Freundlich and Temkin isothermal models are applied for mechanistic evaluation of data and sorption behaviour is investigated by applying kinetic models.

EXPERIMENTAL

Processing of *Polyalthia longifolia* leaves: The leaves of *Polyalthia longifolia* were taken from home institute lawns, washed and dried in sunlight for a week. Then dried in oven at 80 ºC for 2 h. After wards, they were crushed to powder by grinding and sieved to 60 mesh (ASTM) particle size, then stored in plastic containers. Their surface was characterized by recording FT-IR spectrum by Perkin Elmer Spectrum RXI[10].

Working solutions: Stock solutions of metal ions were prepared by dissolving 2.683 g of $CuCl_2·2H_2O$, 4.037 g of $CoCl_2·6H_2O$ and 4.967 g of $NiCl_2·6H_2O$ (Merck)/L double distilled water separately. Sequential dilutions of respective stock solution of metal ion were done, for preparing further standard and working solutions, with double distilled water.

Biosorption studies: Adsorbent dose, pH of solution, contact time of agitation of waste-water solution along with biosorbent and initial metal concentration conditions were optimized on batch scale for stripping of Cu(II), Co(II) and Ni(II) ions from water on dried leaf powder of *Polyalthia longifolia* in a similar fashion as reported earlier. 50 mL of metal ion solutions with 50 mg/L metal ion concentration were employed separately, varying adsorbent dosage 0.25-2.5 g, pH from 1-7 and contact time from 5-50 min[10]. For isothermal studies, concentration was varied from 30-80 ppm. Metal uptake by adsorbent was quantified using eqn. 1:

$$q = \frac{(C_o - C_e)V}{m} \quad (1)$$

RESULTS AND DISCUSSION

Surface characterization of *Polyalthia longifolia* leaves: Plant based adsorbents have cellulosic nature. Several characteristic functional groups of cellulosic materials, which are capable of adsorbing metal ions, can be identified by using FT-IR technique. The FT-IR spectrum of *Polyalthia longifolia* leaves (Fig. 1) shows the presence of various functional groups as indicated from various absorption peaks values, presented in Table-1. Especially hydroxyl (-OH) and carbonyl groups, due to hemicellulose and pectin and arenes (C=C of aromatic ring stretching), because of the presence of limonene, plays an important role in adsorption of metal ions[11].

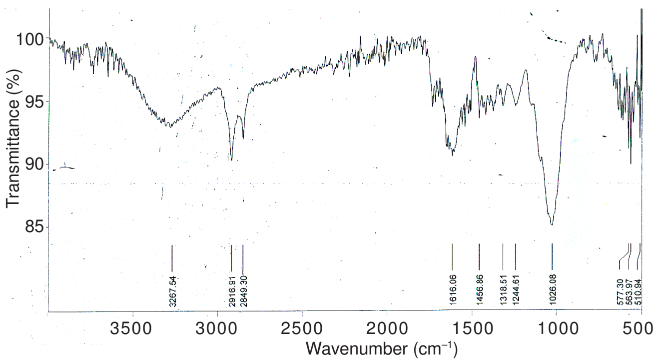

Fig. 1. FT-IR spectrum of *Polyalthia longifolia* leaf powder

TABLE-1
CHARACTERISTIC FT-IR BAND ABSORPTION FREQUENCIES OF *Polyalthia longifolia* LEAF POWDER

Vibrational assignments	Bond frequencies (cm^{-1})
ν(O-H) stretching	3267.54
ν(C-H) stretching	2916.91, 2849.30
ν(N-H) bending (primary amines)	1616.06
ν(C=C) stretching (aromatic ring)	1456.86
ν(C=O) stretching (alcohols, carboxylic acids, esters, ethers)	1318.51
ν(C-N) stretching (aliphatic amines)	1244.61, 1028.08
ν(C-Br) stretching (alkyl halides)	577.30, 563.97, 510.94

Influence of biosorbent dosage: It was studied by varying *Polyalthia longifolia* leaf powder quantity from 5 to 50 g/L at constant temperature and agitation speed. The effect of leaf powder quantity on copper, cobalt and nickel ion removal is indicated in Fig. 2. Metal sorption capacity, at equilibrium, decreases with an increase in adsorbent dosage. This decrease can be due to the concentration gradient between the biosorbent and metal ions[2]. Biosorbent dosage increase enhances surface area and number of available active sites due to which the biosorption of metal ions increases[12].

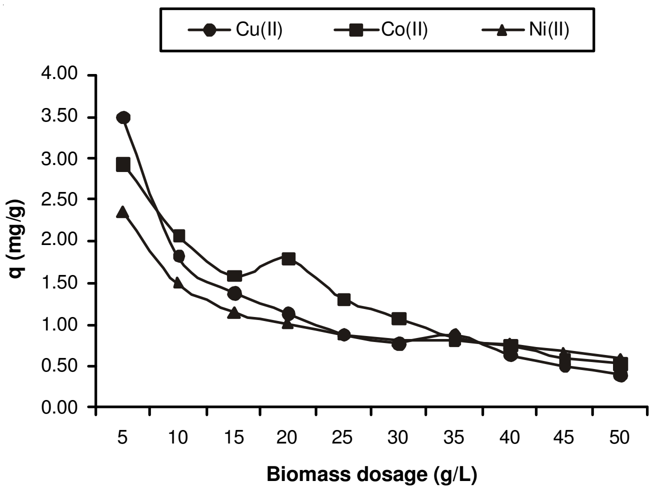

Fig. 2. Effect of biomass dosage on Cu(II), Co(II) and Ni(II) biosorptive removal by *Polyalthia longifolia* leaf powder

Solution pH effect: The influence of metal ion solution pH on amputation of cobalt, copper and nickel ions by biosorption on *Polyalthia longifolia* leaf powder was studied pH range of 1-7. Experiments were not conducted above pH 7, in order to avoid metal precipitation in basic conditions[7-10]. Fig. 3 showed that the stripping of these metals from water by adsorption is highly pH dependent because it affect the protonation of the functional groups of biosorbent and metal chemistry. The removing capacity of *Polyalthia longifolia* leaf powder for copper and cobalt ions increase by the increase of pH from 1-6 and that of nickel increase from 1-5. But low biosorption capacity at lower pH, like at 1, is ascribed to higher concentration and greater mobility of H^+ ions, which results in preferential biosorption of hydrogen ions rather than these metal ions[13]. At higher pH, greater number of functional groups with negative charges and lower concentration of H^+ ions results in better metal ions biosorption. Maximum biosorption capacity for copper, cobalt and nickel by *Polyalthia longifolia* leaves was achieved at pH 6, 6 and 5, respectively.

Influence of agitation time: The influence of agitation time was investigated in 5-50 min range. Results are presented in Fig. 4. It is indicated from this figure that biosorption capacity of *Polyalthia longifolia* leaves for removing copper, cobalt and nickel increase significantly with the time initially and equilibrium was established in 35, 40 and 40 min, respectively. More biosorptive removal of Co(II) ions as compared to Cu(II) and Ni(II) is attributed to its lower ionic weight. After maximum removal of metal ions by *Polyalthia longifolia* leaves, the curves become parallel to x-axis, indicating that no further binding sites were available for chelating metal ions.

Biosorption kinetics: For kinetic study, adsorption equilibrium data of copper, cobalt and nickel ions is analyzed by Lagergren pseudo-first order rate eqn. 2[14].

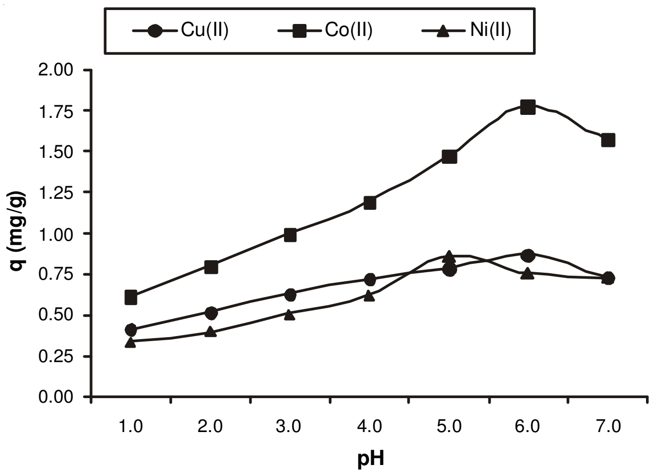

Fig. 3. Effect of pH on Cu(II), Co(II) and Ni(II) biosorptive removal by *Polyalthia longifolia* leaf powder

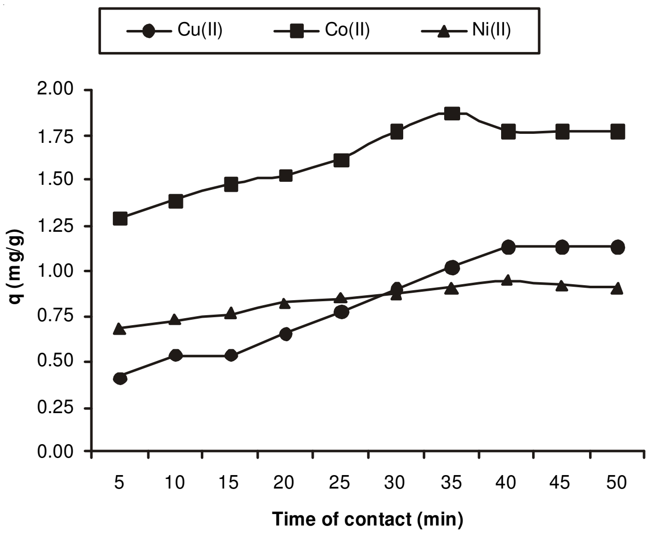

Fig. 4. Effect of agitation time on Cu(II), Co(II) and Ni(II) biosorptive removal by *Polyalthia longifolia* leaf powder

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303}t \qquad (2)$$

Here 'q_e' and 'q_t' are the amounts of metal ions adsorbed (mg/g) at equilibrium and at any time t, respectively and 'k_1' (min^{-1}) is pseudo-first order rate constant. The 'k_1' and 'q_e' values were calculated from slope and intercept of 'log ($q_e - q_t$)' against 't' graph. These q_e(cal.) values compared with experimental q_e(exp.) values and should be in accordance if this model is applicable[15].

Pseudo-second order model is investigated by using eqn. 3:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \qquad (3)$$

Here 'k_2' (g/mg min) is pseudo-second order rate constant. A plot of 't/q_t' against 't' gives ($1/q_e$) as slope and ($1/k_2q_e^2$) as intercept, from which k_2 can be found. The results of kinetic studies are presented in Table-2. It indicated that pseudo-second order 'q_e' values agree well to experimental 'q_e' values with 0.998 and 0.997 regression coefficient (R^2) for cobalt and nickel, respectively, whereas copper followed the pseudo-first order kinetics, as clear from correlation coefficient, *i.e.*, 0.981.

Initial metal ion concentration effect: It was investigated by employing optimized pH, biosorbent dose and equilibrium time conditions for copper, cobalt and nickel ions at 25 ºC. Initial concentrations of these metal ions varied from 30 to 80 mg/L. As shown in Fig. 5, the increase of initial concentrations of these metal ions enhances biosorption capacity of *Polyalthia longifolia* leaf power. These results point toward the fact that the surface saturation of adsorbent was reliant on initial concentration of metal ions. At low concentrations, adsorption sites chelate metal ions quicker than at higher concentrations, because in that case metal ions penetrates into inner binding sites of *Polyalthia longifolia* leaf power by intra-particle diffusion at slower rate[9].

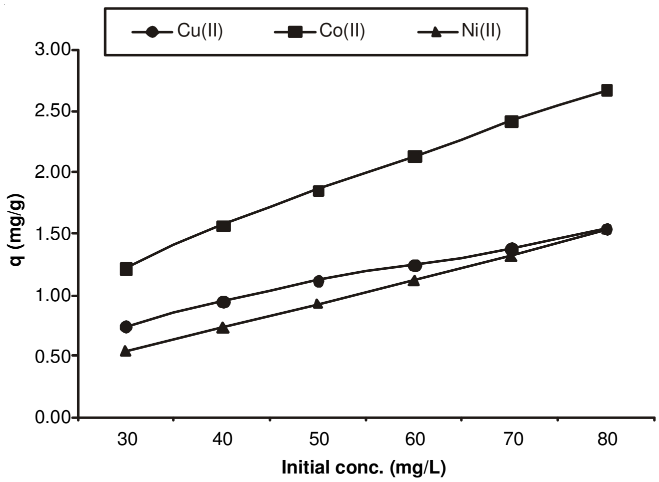

Fig. 5. Effect of initial concentration of adsorbate on Cu(II), Co(II) and Ni(II) biosorptive removal by *Polyalthia longifolia* leaf powder

Biosorption isotherms: The biosorption capacity and surface properties are normally evaluated by applying the isotherms analysis obtained from the equilibrium study of metal ions sorption. The Langmuir (eqn. 4), Freundlich (eqn. 5) and Temkin (eqn. 6) isotherms were plotted (Figs. 6-8, respectively) and corresponding parameters were quantified and given in Table-3.

$$\frac{1}{q_e} = \frac{1}{b.q_m.C_e} + \frac{1}{q_m} \qquad (4)$$

TABLE-2
KINETIC PARAMETERS FOR BIOSORPTION OF Cu(II), Co(II) AND Ni(II) IONS ON *Polyalthia longifolia* LEAF POWDER

Metal ions	q_e (exp.) (mg/g)	Pseudo-first order			Pseudo-second order		
		q_e (cal.) (mg/g)	k_1 (min^{-1})	R^2	q_e (cal.) (mg/g)	k_2 (g/mg min)	R^2
Cu(II)	1.138	1.141	0.054	0.981	1.358	0.045	0.942
Co(II)	1.872	0.932	0.060	0.910	1.856	0.161	0.998
Ni(II)	0.923	0.474	0.082	0.940	0.963	0.332	0.997

TABLE-3
ADSORPTION ISOTHERM PARAMETERS FOR BIOSORPTION OF Cu(II), Co(II) AND Ni(II) ON *Polyalthia longifolia* LEAF POWDER

Metal ions	Langmuir model			Freundlich model			Temkin model		
	q_m	b	R^2	K_F	n	R^2	K_T	B_T	R^2
Cu(II)	1.741	0.182	0.993	0.453	2.689	0.994	1.503	5.996	0.990
Co(II)	3.996	0.098	0.994	0.549	2.073	0.998	0.685	2.721	0.991
Ni(II)	4.081	0.014	0.999	0.039	0.806	0.996	0.181	2.093	0.974

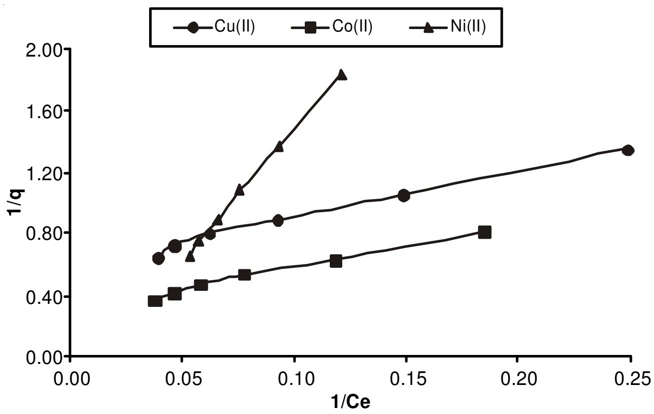

Fig. 6. Langmuir isotherm for Cu(II), Co(II) and Ni(II) biosorptive removal by *Polyalthia longifolia* leaf powder

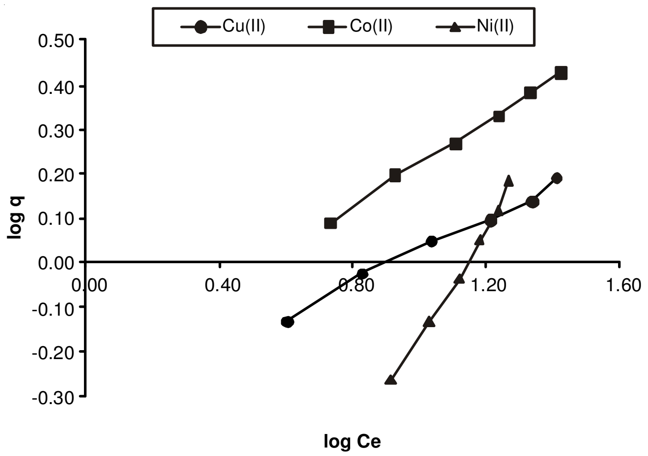

Fig. 7. Freundlich isotherm for Cu(II), Co(II) and Ni(II) biosorptive removal by *Polyalthia longifolia* leaf powder

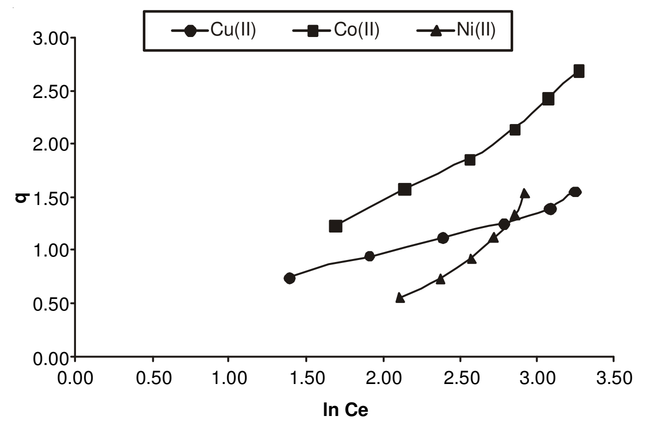

Fig. 8. Temkin isotherm for Cu(II), Co(II) and Ni(II) biosorptive removal by *Polyalthia longifolia* leaf powder

$$\log q_e = \log K_F + \frac{1}{n}\log C_e \quad (5)$$

$$q_e = \frac{RT}{B_T}\ln K_T + \frac{RT}{B_T}\ln C_e \quad (6)$$

Maximum adsorption capacity 'q_m' correspond to complete monolayer coverage is 1.741, 3.996 and 4.081 mg/g for copper, cobalt and nickel ions, respectively. The values of adsorption intensity, 'n', obtained from Freundlich plot are in the range 1-10, showing favorable adsorption[9]. The heat of adsorption, 'B_T', from Temkin model, is 5.996, 2.721 and 2.093 for copper, cobalt and nickel correspondingly. A value less than 8 corresponds to weak interaction of metal ions with biosorbent[16]. High values of correlation coefficient of Langmuir model over Freundlich and Temkin models suggested that chemisorptive removal of these metal ions occurred more as compared to physiosorption. It is also in accordance with kinetic investigations.

Conclusion

This study showed that *Polyalthia longifolia* leaves efficiently remove copper, cobalt and nickel ions from water. Kinetics study indicated that pseudo-second order model was suitable more for these metal ions. The equilibrium data of the sorption was in good agreement with the Langmuir, Freundlich and Temkin models. It can be concluded that leaf powder of *Polyalthia longifolia* is an effective biosorbent for stripping of copper, cobalt and nickel ions from wastewater.

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