Biosorption of Ni(II), Cu(II), Fe(III) and Cr(VI) from dilute aqueous solutions using *Tamarindus indica* fruit shells

A. EDWIN VASU

Post Graduate and Research Department of Chemistry,
St. Joseph's College (Autonomous), Tiruchirappalli - 620 002 (India).

ABSTRACT

Biosorption of four metal ions, namely, Ni(II), Cu(II), Fe(III) and Cr(VI), has been studied by *tamaridus indica* fruit shells in batch mode. The sorption processes were found to obey the Redlich-Peterson adsorption isotherm. Kinetic studies performed indicate that the sorptions are better represented by the pseudo-second order kinetic model. It is also observed that the overall rates of the sorptions were governed by particle diffusion constraints at the concentrations of metal ions studied. Thermodynamic studies reveal that the processes are endothermic and the thermodynamic parameters like, ΔG, ΔH and ΔS were evaluated.

Key words: Biosorption, metal ions removal, adsorption isotherm, tamarind fruit shell.

INTRODUCTION

As the human population is increasing by leaps and bounds, there is need for more production in all spheres. Many industries are coming up polluting more and more while leaving the biosphere foul and unpleasant. Wastewater containing heavy metal pollutants cause direct toxicity, both to human and other living organisms due to their presence beyond specified limits. The main goal today is to adopt appropriate methods and to develop suitable techniques either to prevent metal pollution or to reduce it to very low levels.

Exposure to nickel and nickel compounds lead to allergic dermatitis and increased incidence of cancers of the lungs and nasal mucosa[1-4]. Copper, used both in industrial and agricultural processes, is toxic as well.[5] Cellular uptake of Cr(VI), followed by its reduction to Cr(III) with the formation of reactive Cr(V/IV) intermediates, leads to genotoxicity and carcinogenicity.[3, 6] Chromium is also highly toxic non-essential metal for microorganisms and plants.[7] Fe (III) is also toxic at higher concentrations. Among various methods available for metal ions removal from aqueous solutions, namely, chemical precipitation, membrane filtration, electrolytic reduction, chemical coagulation, ion and adsorption, the last process appears to be most suitable appears to have the least adverse effects. It includes a broad range of carbonaceous materials at a high degree of porosity and large surface area[8] and finds use for the removal of toxic, biodegradable and non- biodegradable substances from wastewaters. It is attractive as it can treat wastewater to acceptable quality suitable for reuse. To reduce the cost of the wastewater treatments containing metal ions by the adsorption method, many low-cost materials like agricultural wastes, activated carbons prepared from easily available agricultural wastes and naturally available materials like chitosan, zeolites, soils, etc.[9, 10] have been used

as adsorbents. In this context, it is aimed in the present work to study the suitability of *Tamarindus Indica* fruit shells (TFS) in removing the following metal species from aqueous solutions: Ni(II), Cu(II), Fe(III) and Cr(VI). *Tamarindus Indica* (tamarind tree) is one of the common and most important trees of India. On the average the pod is composed of 55% pulp, 34% seed and 11% shell and fibre.[11] Tamarind fruit shells are of moderate density, high volume and highly porous agricultural waste, which have no commercial value.

EXPERIMENTAL

All the chemicals used were of analytical grade. Ni(II), Cu (II) and Fe (III) solutions were prepared by dissolving their nitrates in double distilled water. Nitric acid was used to make pH adjustments in order to avoid precipitation. Cr(VI) solutions were prepared from potassium dichromate.

Adsorbent preparation and characterization

The adsorbent particles were prepared from shells of a single tree. The shells were washed with water to remove any adhered pulp and dust, air dried and powdered to particles of size 150-250 µm. Physico-chemical parameters of the adsorbent like, moisture, ash and volatile matter contents, apparent density, water soluble and acid extractable and liquid phase adsorption parameters like iodine number and methylene blue number were determined following ASTM procedures.[12] Surface area was measured by adsorption of nitrogen using BET method.

Analysis of metal ions

All the ions were analyzed spectrophotometrically. Ni(II) by the DMG method[13] Fe(III) and Cu(II) by thiocyanate methods[14] and Cr(VI) by the diphenyl carbazide method.[15]

Equilibrium adsorption experiments

Prior to isotherm studies, minimum contact times for adsorption equilibria to become established were estimated for each adsorbent. Each experiment comprised three replicate 100mL glass-stoppered bottles containing appropriate amount of adsorbent and 50mL of adsorbate solutions of selected concentrations. Control flasks

without the adsorbents also prepared simultaneously. Mixtures were maintained in a rotary shaker (Orbitek, Chnnai, India) at constant temperature (30, 45 or 60°C). After the attainment of equilibrium the contents of each flask were filtered through a Whatmann No. 41 filter paper, with the first 10mL discarded. The filtered samples were then analysed for unadsorbed solutes.

Kinetic studies

Each experiment comprised triplicate glass bottles containing selected adsorbent (0.1-0.25g) and adsorbate doses (50mL) at a fixed pH. The bottles were kept in the mechanical shaker at a constant temperature of 30 ± 2°C. At time intervals (in minutes) of 0, 10, 20, 30, 40, 50, 60, 90, 120, ¼etc, one triplicate was sacrificed for measurement of the non-adsorbed solutes. The slurries were filtered through a Whatmann No. 41 filter paper, with the first 5mL discarded. The filtered samples were then analyzed.

pH variation studies

In order to find out the optimum pH for maximum removal of adsorbates, experiments were carried out with solutions of same concentration but adjusted to different pH values (with 0.1M HCl or 0.1M NaOH). Measurements were carried out below which chemical precipitation of metal hydroxides do not occur. These values have been estimated as pH - 7.8 for $Ni(OH)_2$; pH - 2.5 for $Fe(OH)_3$; pH - 7.5 for $Cu(OH)_2$. For chromium (VI) the selected pH range was 1 to 9.

RESULTS AND DISCUSSION

Characteristics of the adsorbent

The physico-chemical parameters evaluated are presented in table 1.

Adsorption isotherms

The equilibrium sorption data are mathematically represented by the following isotherms: Freundlich, Langmuir and Redlich-Peterson. The Langmuir model assumes monolayer surface coverage on equivalent sites,[16] the Freundlich model, on the other hand, assumes a heterogeneous adsorption surface with sites that have different energies of adsorption and which are not equally available. The Freundlich equation[17] is

more widely used but provides no information on the monolayer adsorption capacity in contrast to the Langmuir model. The Redlich-Peterson model[18] is described as a combination of both the other models and is often used to describe equilibrium over a wide range of concentration.

Freundlich $q_e = x/m = K_F C_e^{(1/n)}$ ...(1)

Langmuir $q_e = K_L C_e / (1+ b C_e) = q_m b C_e / (1+ b C_e)$ ...(2)

Redlich-Peterson $q_e = K_R C_e / (1+ b_R C_e^{\beta})$ ...(3)

The individual isotherm shapes have been found from these plots and were labeled under Giles's classification.[19] All the isotherms are of L2 type. These L curves are characteristic of systems in which monofunctional ionic substances are adsorbed from water by ion-ion attraction. The isotherm constants are useful parameters for predicting adsorption capacities. These have been calculated and their values are presented in table 1 along with their correlation coefficient values.
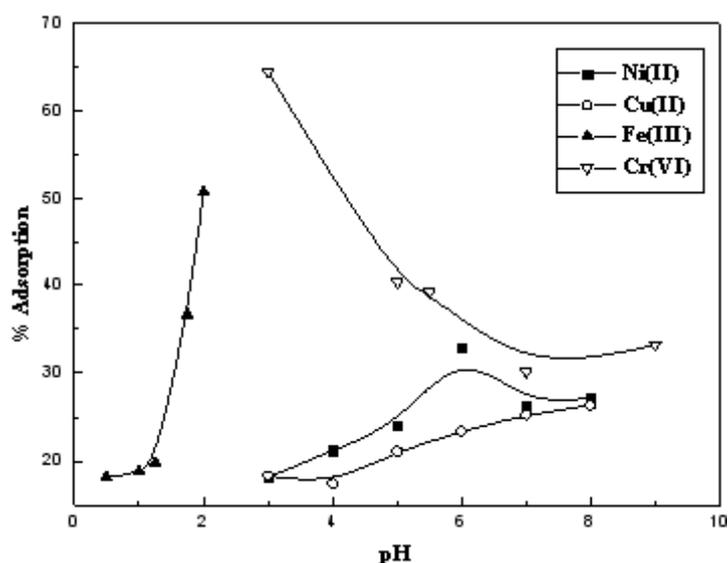
Fig. 1: Effect of pH on the sorption of metal ions on TFS
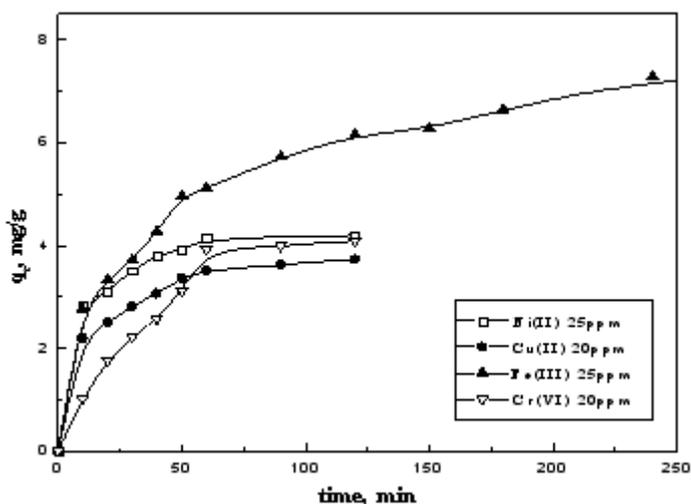
Fig. 2: Kinetic curves for the sorption of metal ions on TFS

The correlation coefficient values in table 2 indicate that of the three isotherm models used to describe the sorptions, it is the three-parameter Redlich-Peterson model that fits the data well with highest correlation coefficient values. This is expected as the Redlich-Peterson equation has three fitting parameters, especially with β being a more direct parameter for adsorbate–adsorbent interaction strength.

pH variation studies

pH of the metal ion solutions had significant effect in the extent of retention of metal ions studied over TFS (Fig. 1). It is seen that increase in solution pH increased the sorption of metal ions that exist as cations in aqueous solutions, namely, Ni(II), Cu(II) and Fe(III) while for the anionic Cr(VI) the opposite trend is observed. These behaviours can be explained by the fact that increasing solution pH increases the negative charge density on the adsorbent's surface leading to a greater affinity for the positively charged species like hydrated Ni^{2+} and decreased affinity towards such species as CrO_4^- and $Cr_2O_7^{2-}$ of Cr(VI).

Table 1: Characteristics of TFS

Characteristics	Result
Proximate Analysis (%)	
Moisture	0.6268
Ash	2.4139
Volatile matter	70.3863
Particle size, mm	150- 250
Surface area (N_2- BET), m²/g	16.0732
Apparent density, g/mL	0.6381
Water solubles, %	5.6273
Acid- extractable content, %	10.2316
IN, mg/g	137.074
MBN, mg/g	6.051

Table 2: Isotherm parameters for the sorption of metal ions on TFS at 30°C

Metal ion	Model	Model parameters				
			K_F		1/n	n	r²
		mmol/g		mg/g			
Ni (II)	Freundlich	0.3049	1.5621	0.3702	2.7012	0.9553
Cu(II)		0.2665	1.6093	0.3538	2.8265	0.9821
Fe(III)		0.2178	3.3177	0.3233	3.0931	0.9509
Cr(VI)		0.1957	1.4309	0.3659	3.1547	0.8998

Metal ion	Model	Model parameters			
		K_L	b	q_m	r²
Ni (II)	Langmuir	0.4898	0.6897	0.7102	0.9910
Cu(II)		0.4737	0.8291	0.5713	0.9932
Fe(III)		1.6737	7.1632	0.2337	0.9928
Cr(VI)		0.8858	61.1707	0.0145	0.9568

Metal ion	Model	Model parameters			
		K_R	b_R	β	r²
Ni (II)	Redlich-	0.3508	0.2644	1.3185	0.9990
Cu(II)	Peterson	0.5059	0.9469	0.9659	0.9933
Fe(III)		1.4422	6.1637	1.0854	0.9942
Cr(VI)		0.6602	68.7560	1.2012	0.9973

Kinetics

      Adsorption isotherms are useful quantitative tools when representing the adsorption capacity of an adsorbent for a given solute. However, isotherms are obtained under equilibrium conditions, whereas in most adsorption treatment applications the retention time is too short for equilibrium to be attained. For this reason, we must obtain information on the time dependence of adsorption processes by carrying out process oriented kinetic studies. The kinetic curves obtained for the sorption of metal ions on TFS are shown in figure 2.

      To describe the adsorption kinetics, the pseudo-fist order model proposed by Lagergren[20] and the pseudo-second order model proposed by Ho and McKay[21] were used n the following forms:

First order rate equation
$$\log(q_e\text{-}q_t) = \log q_{e(1)} - k_1 t \qquad ...(4)$$
Second order rate equation
$$t/q_t = (1/h) + (1/q_{e(2)})t \qquad ...(5)$$

      where, q_t (mg/g) is the amount adsorbed at time t (min); q_e, amount adsorbed at equilibrium (mg/g); $q_{e(1)}$, adsorption capacity predicted by the I order model (mg/g); k_1, first order rate constant (min^{-1}); h (=$k_2/q_{e(2)}^2$), initial sorption rate (mgg^{-1}min^{-1}); and

Table 3: Pseudo-second order parameters for TFS–metal ion systems

Metal ion	C_i mg/L	Equilibrium uptake, mg/g		k_2 gmg^{-1}min^{-1}	h mgg^{-1}min^{-1}	r^2
		$q_{e(2)}$	$q_{e(exp)}$			
Ni(II)	25	4.6189	4.14	2.614×10^{-2}	0.5577	0.9972
Cu(II)	20	4.0850	3.73	2.143×10^{-2}	0.3576	0.9989
Fe(III)	25	8.0386	7.46	3.812×10^{-3}	0.2463	0.9981
Cr(VI)	20	8.0386	3.93	1.675×10^{-3}	1.0820	0.9174

Table 4: Pseudo-first order parameters for TFS–metal ion systems

Metal ion	C_i mg/L	Equilibrium uptake, mg/g		k_1 min^{-1}	r^2
		$q_{e(1)}$	$q_{e(exp)}$		
Ni(II)	25	2.3578	4.14	0.0474	0.9900
Cu(II)	20	2.3179	3.73	0.0357	0.9851
Fe(III)	25	5.3976	7.46	0.0124	0.9740
Cr(VI)	20	4.0560	3.93	0.0302	0.9856

Table 5: Effective pore diffusion coefficients controlling the rate of adsorption of metal ions on TFS

Adsorbate	C_i, mg/L	B min^{-1}	Effective pore diffusion coefficient $D_i\times10^{-7}$(cm^2 min^{-1})	r^2
Ni(II)	25	0.0472	4.7872	0.9885
Cu(II)	20	0.0021	0.2130	0.9984
Fe(III)	25	0.0122	1.2374	0.9595
Cr(VI)	20	0.0237	2.4037	0.9687

$q_{e(2)}$, adsorption capacity predicted by the II order model (mg/g).

The results of kinetic fittings and the parameters associated with each model along with the correlation coefficients are shown in tables 3 and 4.

The high correlation coefficients and the good agreement between the theoretical q_e and experimental q_e values for the II order model suggest that the sorptions are better described by this model. Such a betterment of the II order model over I order model has been observed for many adsorption processes[21].

Assuming that the process of binding of an adsorbate species on adsorbent's is very rapid for sorptions from solutions we are left with film and particle diffusion steps and Boyd *et al.*[22] have outlined a graphical procedure to assist in deciding the relative contributions of film and pore diffusion to limiting the overall rate of adsorption. Film diffusion will be rate- determining if a graph of time versus ln(*1-F*) yields a straight line. Alternatively, particle diffusion control the overall adsorption rate if a plot of $t^{0.5}$ against F (= q/q_e) produces a straight line. Such linear relationships do exist for all the systems under study (figures not shown) and an additional quantitative treatment proposed by Boyd[22] and Reichenberg[23] as adapted by Kelleher *et al.*[24]

and others[25] was followed. The sorption dynamics can be represented by the following expressions:

$$F = q_t / q_e \qquad ...(6)$$
$$F = 1 - 6/\pi^2 \sum_{n=1}^{\infty} 1/n^2 \exp (D_i t \pi^2 n^2 / r^2) \qquad ...(7)$$
$$F = 1 - 6/\pi^2 \sum_{n=1}^{\infty} 1/n^2 \exp (-n^2 Bt) \qquad ...(8)$$

where,

$$B = D_i p^2 r^2 = \text{time constant} \qquad ...(9)$$

F = fractional attainment of equilibrium at time t
D_i = effective diffusion coefficient of the ions in the adsorbent phase
r = adsorbent particle radius
n = 1,2,3,¼ are the integers defining the infinite series solution obtained by a Fourier type of analysis.

Bt values were derived for each F value by the use of Reichenberg's table.[23]. A plot of t versus Bt was employed to assess the contributions of film and particle diffusion on rates of adsorption. All the t versus Bt plots were linear (presented in figure 3). Examination over figure 3 reveals that metal ion adsorptions under study pass near the origin indicating that the rate-limiting step for these processes are predominately governed by particle diffusion constraints.

The effective particle diffusion coefficient values (D_i's) are calculated by equation (9) where B is the slope of the t versus Bt plots. The B and D_i values calculated are listed in table 5.
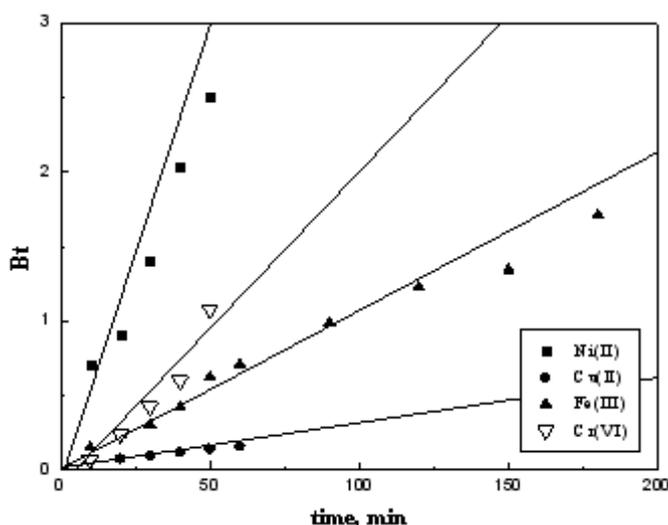
Fig. 3: t versus Bt plots for the sorption of metal ions on TFS

Table 6: Isotherm constants for metal ion adsorptions on TFS at 45°C

Metal ion	Model	Model parameters			
		$K_F, mg/g$	$1/n$	n	r^2
Ni (II)	Freundlich	0.3876	0.3431	2.9146	0.9859
Cu(II)		0.2803	0.3939	2.5387	0.9821
Fe(III)		0.2365	0.3336	2.9976	0.9544
Cr(VI)		-	-	-	-

Metal ion	Model	Model parameters			
		K_L	b	q_m	r^2
Ni (II)	Langmuir	0.7334	0.9147	0.8018	0.9687
Cu(II)		0.4621	0.6981	0.6619	0.9991
Fe(III)		1.7640	6.9754	0.2529	0.9949
Cr(VI)		0.9003	30.8842	0.0292	0.9827

Metal ion	Model	Model parameters			
		K_R	b_R	β	r^2
Ni (II)	Redlich-	0.7334	0.9700	0.9542	0.9709
Cu(II)	Peterson	0.4621	0.7053	0.9922	0.9991
Fe(III)		1.7640	7.0467	1.0187	0.9952
Cr(VI)		-	-	-	-

Table 7: Isotherm constants for metal ion adsorptions on TFS at 60°C

Metal ion	Model	Model parameters			
		$K_F, mg/g$	$1/n$	n	r^2
Ni (II)	Freundlich	0.5245	0.2811	2.9146	0.9937
Cu(II)		0.3089	0.4545	2.5387	0.9910
Fe(III)		0.2365	0.3476	2.9976	0.9676
Cr(VI)		-	-	-	-

Metal ion	Model	Model parameters			
		K_L	b	q_m	r^2
Ni (II)	Langmuir	1.4066	1.5788	0.8909	0.9711
Cu(II)		0.4570	0.5340	0.8558	0.9950
Fe(III)		1.8595	6.9159	0.2689	0.9937
Cr(VI)		1.5544	39.4480	0.0394	0.9683

Metal ion	Model	Model parameters			
		K_R	b_R	β	r^2
Ni (II)	Redlich-	1.4066	1.6626	0.9550	0.9750
Cu(II)	Peterson	0.4570	0.5289	1.0073	0.9950
Fe(III)		1.8595	6.9026	0.9967	0.9938
Cr(VI)		-	-	-	-

Effect of temperature and thermodynamics

The equilibrium studies for all the systems were conducted at two more temperatures in addition to room temperature (30°C), namely 45 and 60°C. For all the systems increase in temperature resulted in greater adsorption. This is also seen in the trends of Langmuir q_m and K_L values, the former increases but the latter decreases with increase in temperature. The isotherm parameters evaluated at the higher temperatures are furnished in tables 6 and 7.

The increased adsorption at higher temperatures can be due to acceleration of some originally slow step(s),[26] creation of some new activation sites on the adsorbent surface[27] or to decrease in the size of the adsorbing species.[28] This could well occur due to progressive desolvation of the adsorbing ion as the solution temperature increases.

Thermodynamic parameters such as Gibbs's free energy change (ΔG), enthalpy change (ΔH) and entropy change (ΔS) were calculated using the following expressions:

$$K_C = C_{ae} / C_e \qquad ...(10)$$
$$\Delta G = RT \ln K_C \qquad ...(11)$$

Table 8: Thermodynamic parameters for TFS-metal ion systems

Dye	C_i mg/L	$-\Delta G$ kJ mol^{-1} 30°C	45°C	60°C	ΔH kJ mol^{-1}	ΔS JK^{-1}mol^{-1}
Ni(II)	15	1.1870	-0.5871	-2.0274	35.7182	114.0595
	25	1.7704	0.9774	-0.1835	21.6112	65.2400
	35	2.1003	1.6934	0.7071	15.3547	43.4047
	45	2.4759	2.0946	1.1193	14.1418	38.1947
	50	2.6638	2.3518	1.3927	13.9882	37.0019
	60	3.1060	2.4780	1.8748	13.6626	34.8210
	70	3.4822	2.8255	2.2643	13.5267	33.1686
	80	3.8306	3.1884	2.5796	13.8839	33.1629
	100	4.4760	3.7859	3.2046	14.1177	31.8264
Cu(II)	20	1.3084	1.2256	1.0004	-	-
	40	2.5796	2.2628	1.9833	6.6208	13.3379
	60	3.1494	2.9292	2.3834	8.4412	17.2726
	80	3.8135	3.5597	2.9698	9.3009	17.9102
	100	4.3975	4.0249	3.5318	9.5822	17.0237
Fe(III)	10	1.8671	-2.0748	-2.3668	5.5294	24.3513
	20	1.4290	-1.5872	-1.8126	-	-
	30	0.7169	-1.0319	-1.2940	6.4118	23.5414
	40	0.3229	0.0021	-0.1588	5.3648	16.6925
	50	0.7460	0.5300	0.4222	3.6115	9.5046
	60	1.5511	1.2226	1.0407	5.6884	13.7189
	80	2.2940	2.0466	1.7188	6.2973	13.1713
Cr(VI)	5	1.0635	0.6895	0.0862	10.8626	32.1921
	10	-0.0403	0.7615	-1.9366	20.9575	69.0159
	15	-0.0739	0.8545	-2.2601	24.1501	79.5660
	20	1.1004	0.1310	-1.3759	-	-
	30	1.9434	0.4645	-1.1180	33.9411	105.4816
	40	2.8831	0.8364	-0.6051	39.4577	36.7903
	50	3.4205	1.6463	0.1078	36.7903	110.1707
	75	4.5730	2.7568	1.7734	31.0879	88.2511

log K_C=[ΔS/2.303R]-[ΔH/ 2.303 RT]   ...(12)

where, K_C is the equilibrium constant for the distribution of metal ions between the two phases; C_{ae} is the solid phase metal ion concentration, mg/L; C_e is the liquid phase metal ion concentration, mg/L; T is the absolute temperature, °K and R, the gas constant.

Equation (12) was used to construct Van't Hoff plots and ΔH and ΔS were calculated from the slope and intercept of the Van't Hoff plot respectively. Thermodynamic parameters evaluated for varied metal ion concentrations are listed in table 8.

CONCLUSIONS

The present work has shown that tamarind fruits shells can be successfully used for the removal of Ni(II), Cu(II), Fe(III) and Cr(VI) from dilute aqueous solutions. Of the three isotherm models used in this study, the three-parameter Redlich-Peterson model was the best in describing the equilibrium adsorption data. Increase of solution pH resulted in greater retentivity of Ni(II), Cu(II) and Fe(III) while that of Cr(VI) lowered. The sorptions of all the metal ions studied were more accurately represented by the pseudo-second order rate model. As the tamarind fruit shells are of no commercial value, the work described opens the pathway to increase its economic value and also opened up a new economic treatment method for wastewaters containing metal ions.

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