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Equilibrium, Kinetics and Thermodynamic Studies for Adsorption of Hg (II) on Palm Shell Powder

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***Abstract*—**Palm shell obtained from coastal part of southern India was studied for the removal for the adsorption of Hg (II) ions. Batch adsorption experiments were carried out as a function of pH, concentration of Hg (II) ions, time, temperature and adsorbent dose. Maximum removal was seen in the range pH 4.0- pH 7.0. The palm shell powder used as adsorbent was characterized for its surface area, SEM, PXRD, FTIR, ion exchange capacity, moisture content, and bulk density, soluble content in water and acid and pH. The experimental results were analyzed using Langmuir I, II, III, IV and Freundlich adsorption isotherms. The batch sorption kinetics was studied for the first order reversible reaction, pseudo first order; pseudo second order reaction and the intra-particle diffusion reaction. The biomass was successfully used for removal Hg (II) from synthetic and industrial effluents and the technique appears industrially applicable and viable.

***Keywords*—**Biosorbent, mercury removal, borassus flabellifer, isotherms, kinetics, palm shell.

I. INTRODUCTION

THE discharge of heavy metals into environment has become a matter of concern over the last few decades. The heavy metals like lead, mercury, zinc, aluminum, arsenic, nickel, chromium, cobalt etc. are the common pollutants present in the environment from various natural and industrial sources. The main sources of mercury emissions to land, water and air are the processes of ore mining and smelting (in particular Cu and Zn smelting), burning of fossil fuels (mainly coal), industrial production processes (Hg cell chlor-alkali processes for the production of Cl_2 and caustic soda) and consumption related discharges (including waste incineration) [1]. The conventional technologies for the removal of heavy metals from wastewater mainly include: chemical precipitation, ion exchange, adsorption, membrane processes and evaporation that require high capital investment and running costs [2, 3]. These techniques apart from being economically expensive have disadvantages like incomplete metal removal, high reagent and energy requirements, and generation of toxic sludge or other waste products that require disposal. Efficient and environment friendly methods are thus needed to be developed to reduce heavy metal content. Therefore considerable attention has been focused in recent years upon the field of bio-sorption for the removal of heavy metal ions from aqueous effluents. In general, a sorbent can be assumed as "low cost" if it requires little processing, is abundant in nature, or is byproduct or waste material from another industry [4]. The search for new treatment technologies has focused on bio sorption [5-7]. Bio sorption is a term that describes the removal of heavy metals by the passive binding to nonliving microorganisms (bacteria, fungi and algae) and other biomass (such as peat, rice hull, fruit peel, leave and bark of tree etc.) from an aqueous solution [8-10]. Agrowastes are currently receiving attention as raw materials for water pollution control because of their low cost and availability. A range of adsorbents has been examined clay [11], sago waste [12], cassava waste [13], banana pith [14], peanut skin [15], Alfalfa [16] and sphagnum moss peat [17] just to mention a few have been used mostly for divalent metal ions. A literature search reveals that no work has been reported on the thermodynamic and kinetic study of use of palm shell as adsorbent for mercury removal from aqueous systems. So an attempt was made to study the feasibility of palm shell powder (Borassus Flabellifer), a cheap, easily available bio sorbent for the adsorption of mercury. An additional goal was to establish the ability of five equations - (the Langmuir I, II, III, IV, and Freundlich isotherms) to model the equilibrium sorption data.

The effect of pH, temperature, duration of contact, concentration of metal ion and concentration of sorbent on the adsorption kinetics was studied. The batch sorption kinetics was studied for the first order reversible reaction, pseudo first order; all the 4 types for second order reaction and the intraparticle diffusion reaction.

II. MATERIALS AND METHODS

A. Preparation of Biosorbent Material (PSP) and Characterization

The shell of palm fruit (*Borassus Flabellifer)* was collected from coastal Andhra Pradesh, India. The biomass was extensively washed with running tap water for 30 to 40 minutes to remove dirt and other particulate matter followed by washing in double distilled water. The palm shell was then cut into the small pieces. The biomass was dried in an oven at 70°C.

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The dried biomass was ground in a laboratory blender and sorted using standard test sieves. The sample used was of particle size passing 40µm sieve. This sample was then stored in desiccators and used for bio-sorption studies**.** The general characterization of the adsorbent used: Moisture content 0.4186%, Bulk density 2.82 x10^{-4} gm/cm^3, matter soluble in water 0.0344 %, matter soluble in acid 0.095 %, pH 6, ion exchange capacity 0.0041meq/gm. The powder X-ray diffraction (PXRD) pattern suggested amorphous nature of the adsorbent. The PXRD of the ingredients were taken and held in place on quartz plate for exposure to CuKα radiation of wavelength 1.5406 Å [18]. The sample was analyzed at room temperature over a range of 5-70^0 2θ with sampling intervals of 0.02^0 2θ and scanning rate of 6^0 /min. Surface area measurements from BET studies showed the surface area to be 2.2295 m²/g and the pore volume to be 0.003149 cm³/g. FTIR of the raw powder has also been carried out to check the functionality present in the powder, given in Table 1. The surface morphology of the adsorbent was observed using scanning electron microscopy (JSM-5610LV) The SEM image (Fig. 1) shows well defined porous nature of the biosorbent.

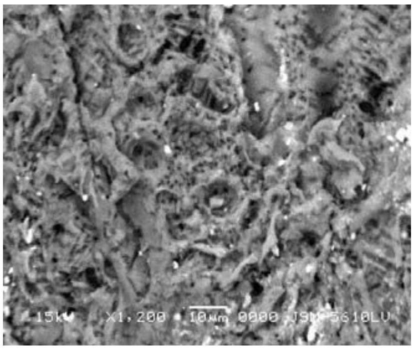

Fig. 1 SEM Image of Borassus Flablifferr

TABLE I
FTIR DATA OF PALM SHELL POWDER

	Frequency (Observed)	Possible functional group
C=O (Stretching)	1870.56, 1739.43	5-membered ring, Saturated acyclic ester or lactone, Saturated acyclic aldehydes
NO_2 (stretching)	1510, 1460	Aromatic C-Nitro compound
C—H (deformation)	1460.53, 1379.06	-CH_2-, CH_3-O, CH3-C-
C═C (Stretching Arom.)	1622.64	Conjugated aromatic
NH3 (deformation)	1622.64, 1510	Often appears as CO_2 band,
C-O (stretching) & O-H(deformation)	1379.06, 1252.32, 1163.12	Tertiary alcohols or phenols, Unsaturated acetates, 1^0alcohols
S=O (stretching)	1379.06, 1044.99	Sulphonates, Sulphoxides
C—H (Stretching)	2924.27	2^0 asymmetric carbon
N—H (Stretching)	3422.37	Sec. amide without H-Bond
N—H (deformation)	1622.64, 1510.19	1^0 or 2^0 amine, Non cyclic 2^0 amide
C=S (stretching)	1250	Thioketones, dithioesters

B. Batch Adsorption Measurements

Batch adsorption experiment was carried out at room temperature (28-30°C). In each experiment 25 mL of Hg (II) solution of known initial concentration (0.004mg/L– 0.032 mg/L) was treated with a specified known amount (by wt) of biomass (4g/L), and known pH for a specified period of time. The pH was adjusted either with 0.1N HNO_3 or 0.1N NaOH as required. Batch kinetic studies were first conducted using fresh biomass to determine the time needed for Hg (II) binding process to reach the equilibrium state. Based on kinetic experiment results all experiments were conducted for a period of 30 minutes. After the equilibrium was reached the adsorbent was separated from the metal solution by using Whatmann filter paper no 42. The equilibrium concentrations of Hg (II) remaining in solution were measured by MA 5840 mercury analyzer (ECIL model). The mercury uptake by the biomass was calculated as follows:

$q_e = C_i - C_e / m$;

Where, C_i-initial concentration of metal ion mg/L;
C_e – Equilibrium concentration of metal ion mg/L;
m – Mass of adsorbent g/L;
q_e – Amount of metal ion adsorbed per gram of adsorbent.

Elution of bound Hg (II) from biomass was carried out using aqueous 0.1N NaCl solution. The eluted biomass was washed with distilled water for regeneration.

III. RESULT AND DISCUSSION

A. Adsorption Dynamics

The kinetics of adsorption of mercury was studied using six kinetic models, i.e., the pseudo-first-order model, the pseudo-second-order (I, II, III, IV) models, and the intraparticle diffusion model at low initial mercury concentrations.

1) Pseudo-first-order model

In order to examine the controlling mechanism of adsorption process such as mass transfer and chemical reaction, several kinetic models are used to test experimental data. The sorption kinetics can be defined by a pseudo-first-order according to Ho, Mc Kay, Namasivayam and Kardivelu [19-21].

$$dq/dt = K_1'(q_e - q) \tag{1}$$

Where q_e is the amount of solute adsorbed at equilibrium per unit weight of adsorbent (mg/ g), q is the amount of solute adsorbed at any time (mg/ g) and K_1' is the adsorption constant. Eq. (1) can be linearized as function of time.

$$\log(q_e - q) = \log(q_e) - K_1' t/2.303 \tag{2}$$

Eq^n (2) was used to construct pseudo first order plots for different pH values as shown in Fig. II. Approximately linear fits were observed for all the pH values. The correlation coefficients and rate constants were calculated and are given in Table II. The correlation coefficients were quite high suggesting pseudo first order kinetics.

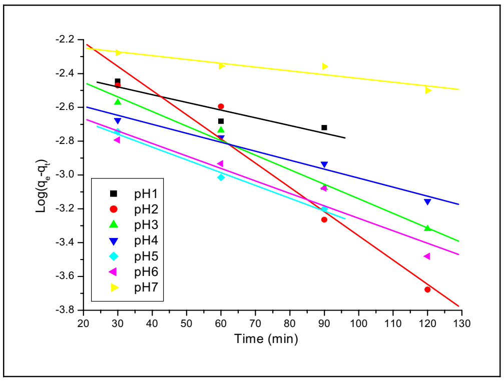

Fig. 2 Lagergren's plot

2) First-order reversible reaction model

The sorption of metal ion from liquid phase to solid may be considered as reversible reaction with an equilibrium state between two phases [22]. A simple first-order reaction model can be used to correlate the rates of the reaction, which can be expressed as

$$A \overset{K_1}{\underset{K_2}{\longleftrightarrow}} B \tag{3}$$

If this model holds true, the rate eq^n for the reaction is expressed as

$$C_B/dt = -dC_A/dt = K_1C_A - K_2C_BC_{A0}dX_A/dt$$
$$= K_1(C_{A0} - C_{A0}X_A) - K_2(C_{B0} - C_{A0}X_A) \tag{4}$$

Where C_B (mg/g) is the concentration of Hg (II) on the sorbent and C_A (mg/L) is the concentration of Hg (II) in the solution at any time, C_{B0} and C_{A0} is the initial concentrations of Hg (II) ions on sorbent and solution respectively, X_A is the fractional conversion of Hg (II) ions and K_1 and K_2 are the first order rate constants. At equilibrium conditions,

$$dC_B/dt = -dC_A/dt \tag{5}$$

And

$$X_{Ae} = K_c - (C_{B0}/C_{A0})/K_c + 1 \tag{6}$$

Where X_{Ae} is the fractional conversion of mercury at equilibrium and K_c is the equilibrium constant defined as follows.

$$K_c = C_{Be}/C_{Ae} = K_1/K_2 \tag{7}$$

Where C_{Be} and C_{Ae} are the equilibrium concentrations for the mercury on sorbent and solution respectively. The rate equation in terms of equilibrium conversion can be obtained from Eq^{ns} (4), (6), (7).

$$dX_A/dt = (K_1 + K_2)(X_{Ae} - X_A) \tag{8}$$

Integrating Eqn (8) and substituting for K_2 from Eqn (7) gives

$$-\ln[1 - X_A/X_{Ae}] = K_1[1 + 1/K_c]t \tag{9}$$

This Eqn can be rewritten as

$$\ln[1 - U(t)] = K_r' t \tag{10}$$

Where K_r' is the overall rate constant,

$$U(t) = (C_{A0} - C_A)/(C_{A0} - C_{Ae}) \tag{11}$$

Where U(t) is called the fractional attainment of equilibrium. At t=0, Eq^{n}10 yields U(t) = 0, connecting this point to the next data point resulted in initial drop, which may cause error and to avoid this error in the evaluations for the rate constants, the segments after the, 'initial drop' were adopted [23-25]. Plot for Eq^n (10) for 1st order reversible reaction model was made for palm shell powder at different pH is shown in Fig. III. Approximate linear fits was generally observed for all pH indicating that sorption reaction can be approximated to be of the first order reversible kinetics. Correlation coefficients were found to be between 0.855 and 0.998, which means there is a good agreement but not the perfect one. Constants k_c and K_r' were calculated and are summarized in the Table II.

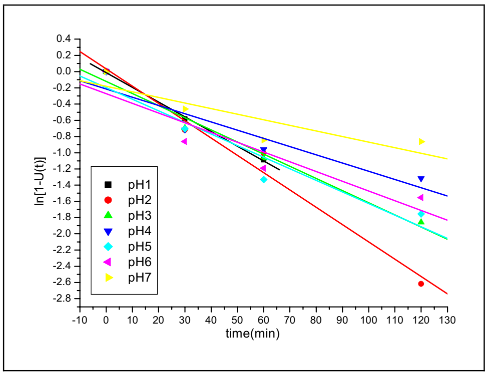

Fig. 3 1st order reversible reaction

3) Pseudo-second-order model

This model is based on the solid capacity has been presented for the kinetics of sorption of divalent metal ions onto palm shell powder [25-27].

$$q_t = q_e^2 K_2' t/(1 + q_e K t) \tag{12}$$

Where K_2' is the pseudo second order rate constant (g/ mg min), q_e is the amount of mercury ion adsorbed at equilibrium (mg/ g), and q_t is the amount of mercury ion adsorbed onto the surface of palm shell powder at any time, t, (mg/ g). The Eqn (12) can be rearranged to obtain the linearised form which is shown as follows:

$$t/q_t = 1/K_2' q_e^2 + t/q_e \tag{13}$$

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If the initial sorption rate, as h= q_t/ t when t approaches 0, h (mg/ g min), is

$$h = Kq_e^2 \tag{14}$$

Eq^n (13) can be rearranged to obtain

$$t/q_t = 1/h + t/q_e \tag{15}$$

In these eq^{ns} h is the initial sorption rate (mg/ g min). The pseudo second order constants can be determined experimentally by plotting t/ q_t vs t. The plot for pseudo second order was made for different pH values as shown in Fig. 4.

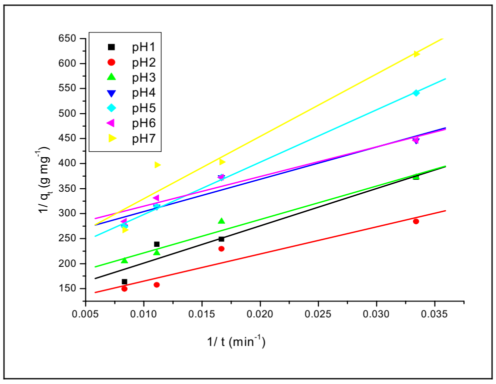

Fig. 4 Pseudo second order Type 1

TABLE II
KINETICS STUDIES

Type		Parameters	pH4	pH5	pH6
Pseudo 1st order		q_e	0.00325	0.00488	0.00303
		K'_1	0.01223	0.175	0.01697
		r^2	0.973	0.988	0.923
Pseudo2nd order	Type1	q_e	0.00466	0.00545	0.00431
		H	0.00012	0.00009	0.00013
		K'_2	5.6573	2.9586	7.143
		r^2	0.9769	0.9625	0.977
	Type2	q_e	0.00417	0.00517	0.00391
		H	0.00016	0.0001	0.00017
		K'_2	8.888	3.576	11.03
		r^2	0.9341	0.9978	0.9351
	Type3	q_e	0.00425	0.00512	0.00397
		H	0.00015	0.00009	0.00016
		K'_2	8.318	3.64	10.366
		r^2	0.843	0.9044	0.846
	Type4	q_e	0.00449	0.00537	0.00418
		H	0.00013	0.00009	0.00015
		K'_2	6.632	3.135	8.335
		r^2	0.843	0.9031	0.846
Intraparticle		k_i	0.00033	0.000334	0.000277
		r^2	0.9846	0.9955	0.83
1st order reversible reaction		K_c	0.2982	0.20967	0.23204
		K_r'	0.010140	0.0143	0.01199
		r^2	0.8743	0.9168	0.855

Rate constants for all the four types of linearised forms of pseudo second order model are presented in Table II. From the above discussion, it can be concluded that the process of Hg (II) is fitted to pseudo second order kinetics since the R^2 values are greater than 0.9.

4) *Intra-particle diffusion model*

Because the above two equations cannot give definite mechanism, another simplified model is tested. Intra-particle diffusion model used here refers to the theory proposed by Weber and Morris. The initial rate of intra-particle diffusion can be obtained by linearization of the curve according to equation [24, 28].

$$q_t = K_i t^{0.5} \tag{16}$$

Where k_i is the intra-particle diffusion rate constant (mg/ g min$^{0.5}$). Fig. V depicts that intraparticle diffusion is slow and the slope of the linear portion of the curve gives the value of K_i. The K_i values were found to be 0.000328, 0.0003340 and 0.000277 (mg g^{-1}) at initial pH values of 4, 5 and 6 respectively. The linear portions of the curves do not pass through the origin (Fig. 5) indicating that mechanism of mercury removal on palm shell powder is complex and both the surface adsorption as well as intraparticle diffusion contribute to the rate determining step.

The high values of R^2 coefficients (>0.900) and the negligible deviation between the various models, make it difficult to distinguish which kinetic model fits better. The only clear conclusion is that both the physical and chemical adsorption equally participate in the overall process of mercury adsorption on palm shell powder in which one major mechanism is intraparticle diffusion. The applicability of pseudo second order model shows that the rate limiting step is chemisorption involving valency forces caused by sharing or exchange of electrons between sorbent and sorbate and applicability of pseudo first order shows that adsorption rate depends on the Hg (II) concentration.

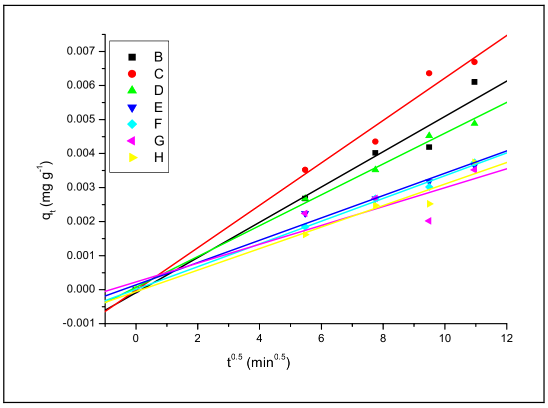

Fig. 5 Intraparticle diffusion studies

B. *Adsorption Isotherms*

The equilibrium adsorption isotherms data are important to develop an equation which accurately represents the results and will be useful for designing the bio sorption reactors. Equations for the isotherm models are given in Table III.

Equilibrium isotherms were determined by shaking a fixed mass of palm shell powder (0.1 g) with 25 mL of Hg (II) solutions in conical flasks. A range of Hg (II) concentrations (0.1 ppm to 0.8 ppm) was tested at different temperatures. Stock solutions of Hg (II) chloride were prepared in 2% nitric acid. All solutions used in this study were diluted with 2% nitric acid as required. The plots of specific sorption (C_e/ q_e) against the equilibrium concentration (C_e) for Hg^{+2} are shown in Fig. 6.

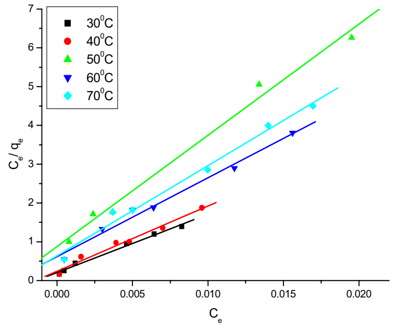

Fig. 6 Langmuir-I Isotherm

The linear plot between $1/C_e$ and $1/q_e$ for Hg^{+2} indicates the validity of Langmuir adsorption isotherm, consequently suggesting the formation of monolayer coverage of the adsorbate on the surface of the adsorbent in the concentration range studied. The values of q_m and K_a were determined from the slopes and intercepts of the plots and are reported in Table III. The Langmuir-I, II, III & IV plots had good correlation coefficients. The Freundlich model as observed in Fig. 7 was also found to be linear. The coefficient of correlation value (r^2) was also high.

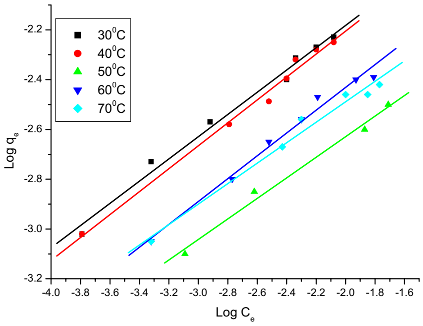

Fig. 7 Freundlich Isotherm

Values of Freundlich constants are depicted in Table III. Since the value of 1/n is less than 1, it indicates favourable adsorption. A smaller value of 1/n indicates better adsorption mechanism and formation of relatively stronger bond between adsorbate and adsorbent [29].

TABLE III
ISOTHERM PARAMETERS

Isotherm	T (^0K)	303	313	333	343
Langmuir-I	q_m	0.0058	0.00567	0.00421	0.0037
	K_a	1501.1	990.09	393.665	242.3
	r^2	0.986	0.99	0.989	0.98
	ΔG	-18438	-17963	-16556	-15668
Langmuir-II	q_m	0.0059	0.00984	0.00382	0.0033
	K_a	1221.7	113.93	621.81	307.75
	r^2	0.993	0.971	0.996	0.935
Langmuir-III	q_m	7.134	7.2186	2.276	0.1197
	K_a	-0.0084	-0.00078	-0.0017	0.046
	r^2	0.989	0.998	0.979	0.962
Langmuir-IV	q_m	-23.18	-7.22	-2.312	-1.7
	K_a	-0.0003	-0.00078	-0.00173	-0.0013
	r^2	0.989	0.998	0.9799	0.999
Freundlich	K_f	0.12616	0.07875	0.0209	0.00421
	1/n	0.56999	0.60581	0.4095	0.1717
	n	1.754	1.01456	2.442	0.421
	r^2	0.977	0.98565	0.994	0.988

Isotherm data reveals that the adsorption process follows both Freundlich and Langmuir isotherm and that the adsorption is favorable. The Langmuir equation and Freundlich model described the isotherm Hg (II) sorption with high correlation coefficient (R^2>0.98). According to Langmuir equation the maximum capacity of Hg (II) sorption (q_m) was obtained as 0.0058 mg/g. The applicability of the Langmuir isotherm indicates good monolayer coverage of mercury on the surface of the palm shell powder. The decrease in k (Langmuir constant) values for Langmuir I and II with the rise in temperature indicates weakening of adsorbate - adsorbent interactions at high temperature. It reveals that the adsorption affinity of mercury decreases with the rise in temperature. So adsorption is less favorable at high temperature. Langmuir III and IV isotherms have good correlation coefficients but do not show any particular trend with temperature.

C. *Thermodynamic Parameters*

The thermodynamic parameters standard free energy (ΔG°), enthalpy change *(ΔH°),* and entropy change *(ΔS°)* were estimated to evaluate the feasibility and exothermic nature of the adsorption process. The thermodynamic parameters like ΔG°, enthalpy change ΔH° and entropy change ΔS°, for the adsorption processes are calculated using the following equations:

$$\Delta G^{0} = -RT \ln K_{a}$$

and

$$\Delta G^{0} = \Delta H^{0} - T\Delta S$$

Where R is universal gas constant (8.314 J/mol K) and T is the absolute temperature in K.

A plot of $\Delta G°$ obtained using Ka of Langmuir-1 versus temperature, T, was found to be linear. The values of $\Delta H°$ and $\Delta S°$ were respectively determined from the slope and intercept of the plots. The thermodynamic parameter, $\Delta G°$, is shown in Table 2. $\Delta H°$ for the sorption is 48.502, 29.269 and 47.816 whereas $\Delta S°$ is 153.54, 104.686 and 161.86 at pH 4, 5 and 6 respectively. The high negative value of $\Delta G°$ confirms the feasibility of the process and the spontaneous nature of sorption with a high preference for Hg (II) to adsorb onto palm shell powder. The value of $\Delta H°$ was positive, indicating that the sorption reaction is endothermic. The positive value of $\Delta S°$ shows the increasing randomness at the solid/liquid interface during the sorption of mercury ions onto palm shell powder.

D. *Breakthrough*

The breakthrough capacity, defined as the volume of column effluent where the ratio of the effluent-to-influent concentration of a metal ion is equal to 1.0, was estimated .In order to study the efficiency of the adsorbent, effluent from CETP, Nandesari GIDC was spiked with standard 0.8ppm $HgCl_2$ and effluent prepared of known conc.[Hg(II)-4x10^{-6}M, $NaNO_3$-5x10^{-4} M, $Cu(NO_3)_2$-1x10^{-5} M, $Cd(NO_3)_2$-1x10^{-5} M, $Ni(NO_3)_2$-1x10^{-5} M, $Bi(NO_3)_2$-1x10^{-5} M, $Pb(NO_3)_2$-1x10^{-5} M were used. Breakthrough capacities for the palm shell powder was found out by column studies and were found to be 0.04425mg/ g, 0.2547mg/g and 1.1204mg/ g.

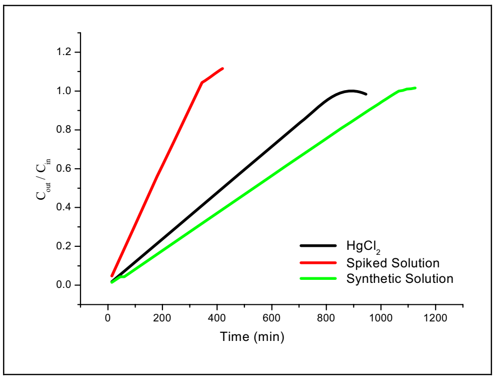

Fig. 8. Breakthrough curve

IV. CONCLUSION

The studies reveal that palm shell powder is a promising adsorbent for the removal of mercury. It is comparable to other conventional adsorbents and economical. The increase in percentage reduction may be attributed to higher degree of ionization of metal ion at higher pH and the reduced competition of H^+ ions with the metal ions for adsorption sites. The physicochemical characteristics of the adsorbent may also play an important role. It was reported that free metal ions are adsorbed better than hydroxides of the metal ions [30]. On variation of contact time, initially faster rate may be due to the availability of the uncovered surface area of the adsorbents, since the adsorption kinetics depends on the surface area of the adsorbents. The Hg^{2+} adsorption takes place at the more reactive sites. As these sites are progressively filled the more difficult the sorption becomes, as the sorption process tends to be more unfavorable. These changes and differences in metal ion uptake rate could be attributed to 2 different adsorption processes, namely a fast ion exchange followed by chemisorptions [31]. The removal of Hg (II) ions was found to increase from 29.39% to 100%, with an adsorbent dose varying from 1.6 g/L to 9.6 g/L. However, with the further increase in adsorbent dose, there was no appreciable increase in mercury removal.

In the present study, the pseudo first-order, pseudo second-order and saturation rate equations describe the bio-sorption of Hg (II) with good correlation coefficient (>0.90). Kinetic analysis of Hg (II) bio-sorption represented that the pseudo first-order rate equation described bio-sorption better than rest [32]. The free energy ΔG^0 of the process at all temperatures is negative indicating that that the adsorption is spontaneous process. The value of ΔH^0 is positive indicating that the endothermic nature of adsorption. The positive ΔS^0 shows increased randomness at the solid solution interface during adsorption. Mercury sorption with palm shell powder was found to be rapid and reversible. Equilibrium was reached after 120 min. Sorption isotherm was modeled with Langmuir and Freundlich equations based on sorption experiments carried out on dilute solutions. The adsorption was found to be strongly dependent on pH, adsorbent dose and contact time. Maximum ($\geq$98%) Hg (II) removal could be achieved at pH 6.0. The results suggest that adsorption of Hg (II) removal by palm shell powder is complex mechanism where both surface adsorption and intraparticle diffusion contribute to the rate determining step. The adsorption process was spontaneous and decreased with increase in temperature showing endothermic nature of the adsorption. Laboratory tests on mercury removal from the effluent showed the potential applicability of this method in the industrial waste water treatment.

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