Kinetic, equilibrium isotherm and thermodynamic study for removal of cadmium from wastewater by using modified pomegranate peel

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ABSTRACT

The ability of formaldehyde modified pomegranate peel (FMPGP) to adsorb Cd (II) from wastewater has been investigated through batch experiments. The adsorption process was relatively fast and equilibrium was achieved at agitation rate of 120 rpm and after about 120 min of contact. The highest Cd(II) adsorption (98.9%) was observed at pH range 6-8. The kinetic of the adsorption were analyzed using pseudo-first order, pseudo-second order and intraparticle diffusion rate equation. It was shown that the adsorption of cadmium could be described by the pseudo-second order equation suggesting that the ladsorption process is presumably chemisorptions. The equilibrium data fitted Freundlich and Langmuir isotherm model. The maximum adsorption capacity determined from the Langmuir isotherm was found to be 18.52 mg/g at 30^0 C. Thermodynamic parameters such as ΔG^0; ΔH^0 and ΔS^0 have been evaluated. The ΔG^o value for the adsorption processes of Cd (II) was obtained as –2.645, -4.453 and -11.36 kJ/mole at 15^0, 22^0 and 30^0 C, The negative value, ΔG^0 indicates the degree of spontaneity of the adsorption process and the higher negative value confirms a more energetically favorable adsorption. The values of ΔH^0 and ΔS^0 for Cd(II) were obtained as 19.77 kJ/mol and 69.15 J/mol K^1 respectively. The positive value of ΔH^0 indicates endothermic nature of adsorption, while positive ΔS^0 value confirms the increased randomness at the solid-liquid interface during adsorption. The activation energy for the adsorption of Cd(II), was found as 11.37 kJ/mol also indicating chemisorptions. Therefore FMPGP investigated in this study showed good potential for the removal of cadmium from wastewater

Key words: Adsorption, pomegranate peel, Cd (II), Kinetic, Isotherm, Thermodynamics.
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INTRODUCTION

The increase in environmental pollution caused by toxic metals is of great concern because of their carcinogenic properties, their non-biodegradability and bio-accumulation. Cadmium is a toxic heavy metal of significant environmental and occupational concern. It is introduced into water from smelting, metal plating, cadmium nickel batteries, phosphate fertilizers, mining, pigments, stabilizers, alloy industries and sewage sludge. It is non-biodegadable and travels through the food chain. In humans, nausea and vomiting has been recorded at levels of 15 mg Cd^{2+}/L. Severe toxic but non fatal, symptoms are reported at concentrations of 10-326 mg Cd^{2+}/L of cadmium. The kidneys are the critical target organ after ingestion (renal dysfunction, hypertension and anemia) [1, 2].

Therefore, it is urgent to remove cadmium from wastewater streams. Although heavy metal removal from aqueous solutions can be achieved by conventional methods, including chemical precipitation, reverse-osmosis, oxidation/reduction, electro-chemical treatment, evaporative recovery, filtration, ion exchange and membrane technologies, they may be ineffective or cost-expensive, especially when the metal ion concentrations in solution are in the range of 1–100 mg/L [3-5].

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Recently, adsorption technology has become one of the alternative treatments[6,7] especially the widespread industrial use of low-cost adsorbents for wastewater treatment is strongly recommended due to their local availability, technical feasibility, engineering applicability and cost effectiveness.

Different types of biosorption have been investigated for the adsorption of Cd ions, including algae [8,9]; bacteria [10]; clay mineral [11]; polymer [12]; fly ash [13] and agricultural by-product like peanut shell [14]; rice husk [15,16]; *Sesamum Idicum* [17]; Tamrix articullata wastes [18]; Sugarcane Bagasse [19] and wheat bran [20].

In our continued study on the use of low-cost material for the removal of organic and inorganic pollutants from water and wastewater, we investigated pomegranate peel as a sorbent for the removal of Cd(II). Pomegranate peel is rich in ellagitannins (ETs) such as punicalagin and its isomers, as well as lesser amounts of punicalin (4, 6-gallagylglucose), gallagic acid, ellagic acid (EA) and EA-glycosides [21]. Moghadam *et al.* [22] have used pomegranate peel carbon for removal of Fe (II). The same material for removal of lead and cadmium from aqueous solutions was reported by Deosarkar [23]. El-Ashtoukhy *et al.* [24] also used raw and activated carbon prepared from pomegranate peel for removal of lead (II) and copper (II) from aqueous solutions. Similar trend was observed for removal of heavy metal ions from industrial wastewater by using raw pomegranate peel by Shartooh *et al.* [25]. Ahmad *et al.* [26] also used pomegranate peel activated carbon for removal of synthetic dye.

The application of biological adsorbents directly may suffer from lack of specificity and poor adsorption capacity. It is observed that chemical modification on solid biomasses has been used as a remedy to improve their physical, chemical and biosorption capacity [27, 28].

Therefore, we thought pomegranate peel as modified form can be used as adsorbent for Cd (II) ions as it is a material composed of several constituents, including polyphenols, ellagic tannis and gallic and ellagic acids [29], flvonol [30], flavones, flavonoes [31] and anthocyanidins [32]. The objective of this work was to remove Cd (II) ions from wastewater by using formaldehyde modified pomegranate peel (FMPGP) as new adsorbent and to investigate the physicochemical parameters involved during the adsorption process. This research focuses on adsorption kinetics, isotherm studies and evaluation of thermodynamic parameters for the adsorption process of Cd (II) ion onto FMPGP from wastewater .

EXPERIMENTAL SECTION

2.1 Preparation of Cd (II) stock solution
All chemical used were of analytical grade (E. Merek. India). Stock solution (1000 mg/L) of Cd (II) was prepared by dissolving 1.37g cadmium nitrate [Cd $(NO_3)_2$ $4H_2O$] in 100 mL beaker and transferred the solution into a 500 mL volumetric flask. The flask was filled up to 500 mL with distilled water to reach 1000 mg/L. The solution was diluted as required to obtain the working solution. The initial pH of the working solution was adjusted using 0.1 N HNO_3 or 0.1 N NaOH solutions. Fresh dilutions were used for each study.

2.2 Biosorbent preparation
Pomegranate peels were collected from different local markets, washed thoroughly by de-ionised distilled water and dried in dark at atmospheric temperature. It was reacted with 8% formaldehyde solution in a ratio of pomegranate peel to formaldehyde 1:5 w/v at 60^0 C for 4 hours [33]. The yield was filtered out, washed with deionized water to remove free formaldehyde and then activated at 80^0 C for 24 hours in an air oven. The product was dried and then milled to 150 μm; this was named as formaldehyde modified pomegranate peel (FMPGP).

2.3 Adsorption studies
2.3.1 Batch equilibrium and kinetic studies
Batch mode adsorption experiments were executed by mixing known weight of adsorbent and 100 mL of Cd(II) ion solution of known concentration adjusted to a known pH. The mixture was taken in a polythene bottle of 300 mL capacity and shaken in a mechanical shaker (120 rpm) for a predetermined period at 30 ± 0.5^0C. Then the equilibrated solutions were centrifuged and the concentration of Cd(II) ions in the supernatant solution was measured by Atomic Absorption Spectrophotometer. Adsorption isotherm and kinetic studies were carried out with different initial concentrations of Cd(II) ions by maintaining the adsorbent dosage at constant level. Adsorption capacities were calculated using following equations:

$$q_e = \frac{Co-Ce}{m} \text{x v} \qquad\qquad\qquad (1)$$

$$q_t = \frac{Co-Ct}{m} \text{x v} \qquad\qquad\qquad (2)$$

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The removal efficiency of the metal ion was calculated by using Eq. (3):

$$\% \; removal = \frac{Co - Ce}{Co} \times 100 \tag{3}$$

Where q_e and q_t are the adsorption capacity per unit mass of adsorbent (mg/g) at equilibrium and time t respectively; C_0, C_e and C_t (mg/L) are liquid-phase concentration of Cd(II) at initial, equilibrium and time t respectively; m, mass of adsorbent (g); and v, volume of sample (L). To minimize error, the mean value was used for calculation.

2.4 Effect of variable parameters
2.4.1 Dosage of adsorbent
The adsorption capacities for different doses of adsorbent (50 to 300 mg/l00 mL) were determined at definite time intervals by keeping all other factors constant.

2.4.2 Initial concentration of solution
In order to determine the rate of adsorption, experiments were conducted with different initial concentrations of Cd (II) solutions ranging from 10 to 80 mg/L. All other factors have kept constant.

2.4.3 Contact time
The effect of period of contact (20 -200 min) on the removal of the Cd (II) on adsorbent in a single cycle was determined by keeping particle size, initial concentration, dosage, pH and concentration of other ions constant.

2.4.4 pH
pH adjustment was made (2-10) with digital pH meter by adding the required amounts of dilute nitric acid and sodium hydroxide solutions by keeping all other factors constant.

2.4.5 Temperature
The adsorption experiments were performed at three different temperatures viz., 15°C, 22°C and 30°C in a thermostat attached with a shaker. The constancy of the temperature was maintained with an accuracy of ± 0.5 °C.

2.5 Kinetic modeling
In order to investigate the controlling mechanism of the adsorption processes such as mass transfer and chemical reaction, the pseudo-first-order, pseudo-second-order and intraparticle diffusion rate equations are applied to model the kinetics of cadmium adsorption onto FMPGP.

2.5.1 Pseudo-first-order model
The integral form of pseudo-first-order equation is given as (Lagergren, 1898) [34].

$$log_{10} \, (q_e - q_t) = log_{10} \, q_e - \frac{k1}{2.303} \, t \tag{4}$$

Where q_t and q_{e} (mg/g) are the amount of adsorbate adsorbed at time *t* and at equilibrium respectively, k_1 (min^{-1}) is the pseudo-first-order rate constant and *t* is the time (min).

2.5.2 Pseudo-second-order model
The linearized-integral form of pseudo-second-order model is given as (McKay & Ho, 1999) [35].

$$t/q_t \; = \; 1/ k_2 \, q^2_e + \; \; t/q_e \tag{5}$$
$$t/q_t \; = \; 1/h + \; \; t/q_e$$

The initial biosorption rate, *h* (mg/g min) is defined as:
$$h \; = k_2 q^2_e$$

Where k_2 (g/mg min) is the rate constant of pseudo-second order.

2.5.3 Adsorption mechanism
The adsorption mechanisms of Cd (II) ions on the FMPGP were investigated using intraparticle diffusion model [36] represented by Eq. (6).

$$q_t \; = k_{id} \, t^{1/2} \tag{6}$$

Where k_{id} (mg/g min$^{1/2}$) is the intraparticle diffusion rate constant and t½ is the half adsorption time.

2.6 Equilibrium modeling
The equilibrium sorption isotherm is fundamentally important in the design of biosorption system. This was carried out by fitting equilibrium data to the Frendlich and Langmuir isotherms.

2.6.1 Frendlich isotherm
The logarithmic form of Frendlich isotherm [37] model is expressed as follows

$$log_{10}\, q_e = log_{10}\, K_F + \frac{1}{n}\, log_{10}\, C_e \qquad (7)$$

Where K_F (mg/g) (L/mg)$^{1/n}$ and 1/n are Freundlich constant related to adsorption capacity and adsorption intensity of the adsorption, respectively; q_e (mg/g) is the amount of adsorbate adsorbed at equilibrium and C_e (mg/L) is the concentration of adsorbate at equilibrium.

2.6.2 Langmuir isotherm
The linearized form of Langmuir isotherm [38] can be written as:

$$C_e/q_e = 1/K_L\, q_{max} + C_e/q_{max} \qquad (8)$$

q_{max} is a Langmuir constant that expresses the maximum sorption capacity corresponding to complete monolayer coverage (mg/g) and K_L (L/mg) is also Langmuir constant related to the energy of adsorption and the affinity of the sorbent.

2.6.3 Separation factor
The favorable nature of adsorption can be expressed in terms of constant referred as a separation factor or equilibrium parameter, R_L, which is defined as [39].

$$R_L = 1/1 + K_L C_0 \qquad (9)$$

Where K_L (L/mg) is the Langmuir constant and *Co* is the initial Cd (II) concentration (mg/L) of the adsorbate in solution and R_L indicates the shape of isotherm.

2.7 Estimation of Thermodynamic parameters
The adsorption process of metal ions can be summarized by the following reversible process, which represents a heterogeneous equilibrium.

Csolid ⇌ C_{liquid}

The adsorption distribution coefficient constant (K_D) of the adsorption is defined

$$K_D = C_{solid}/\ C_{liquid} \qquad (10)$$

$$\Delta G = -2.303RT\, log_{10}\, K_D \qquad (11)$$

$$log_{10}\, K_D = \Delta S^0 / 2.303R - \Delta H^0 / 2.303RT \qquad (12)$$

Where, C_{solid} and C_{liquid} are solid phase and liquid phase concentration (mg/L) of metal ion at equilibrium, ΔG^0 is standard Gibb's energy change, ΔS^0 is standard entropy change, ΔH^0 is standard enthalpy change; T is temperature (K); R is the gas constant (8.314 J/mol K) .

2.7.1 Activation Energy (Ea)
Arrhenius equation which is used to calculate the activation energy for the metal ion sorption [40-42] as given below:

$$log_{10}\, k_2 = log_{10}\, A_0 - \frac{Ea}{2.303\, RT} \qquad (13)$$

Where k_2 is the rate constant of pseudo-second order sorption (g/mg min); A_0 is the temperature-independent factor (g/mg min); Ea is the activation energy of sorption (kJ/mol).

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RESULTS AND DISCUSSION

3.1 Effect of contact time
It has been observed that maximum Cd (II) removal was achieved **(98.9%)** within 120 min after which Cd(II) concentration in the test solution became constant as shown in figure-1. It may be explained by the fact that initially for adsorption large number of vacant sites was available, which slowed down later due to exhaustion of remaining surface sites and repulsive force between solute molecule and bulk phase [43]. Lower adsorption rate in the later stage (after 120 min) was also supported by Ucun *et al.* [44]. This may also be due to intraparticle diffusion process dominating over adsorption [45]

Plot of% Removal versus Time
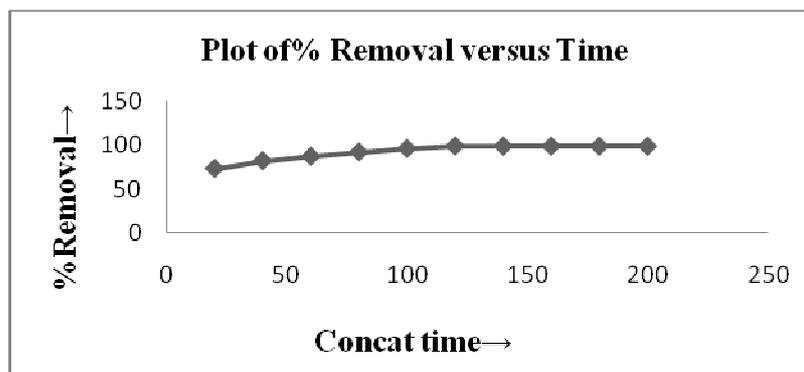
Fig. 1 [Cd (II) conc = 10 mg /L; pH = 6.0; adsorbent dose = 200 mg/100 mL; temp = 30⁰C]

3.2 Effect of pH
The pH is one of the most important controlling parameters in the heavy metal ions adsorption process [46]. Moreover, due to the different functional groups on the adsorbent surface, this became active sites for the metal binding at a specific pH. The effect of pH on percentage removal of Cd(II) for pH ranging between 2 to 10 is shown in figure-2. It could be seen that 98.9 % removal of Cd(II) was achieved by the adsorbent over the pH range of 6.0-8.0. According to Ajmal *et al.* [47] and Namasivayam *et al.* [48] precipitation of cadmium starts at pH 8.3. Therefore, in this study the effect of pH on cadmium adsorption was performed at pH 2-6. At low pH H_3O^+ ions compete with Cd^{2+} ions for exchange sites in the adsorbent surface. Cd^{2+} uptake was decreased because the surface area of the adsorbent was more prorogated. When the pH value increased (6-8), adsorbent surfaces were more negatively charged and functional groups of the adsorbent more deprotonated which results higher attraction of Cd(II) ions. Similar trends of dependency of Cd (II) on pH have been reported in literature [16, 49, and 50].

Plot of% Removal verrsus pH
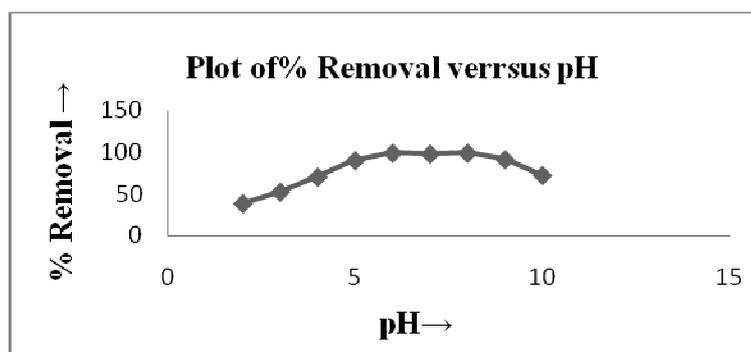
Fig. 2 [Cd (II) conc = 10 mg/L; adsorbent dose 200 mg /100 mL; time = 120 min; temp = 30º C]

3.3 Effect of adsorbent dose
Effect of biosorbents dosage on percentage removal of Cd(II) was investigated by varying adsorbents dosage in the range of 50 to 300 mg/100 mL. It was observed that the percentage removal of Cd (II) increases from 70% to 98.9 % with the increase in the adsorbent dosage from 50-200 mg/100 mL as shown in figure-3.The phenomenon of increase in percentage removal of Cd(II) with increase in adsorbent dose may be explained as with increase in adsorbent dose, more and more surface becomes available for metal ion to adsorb and this increase the rate of adsorption [51].

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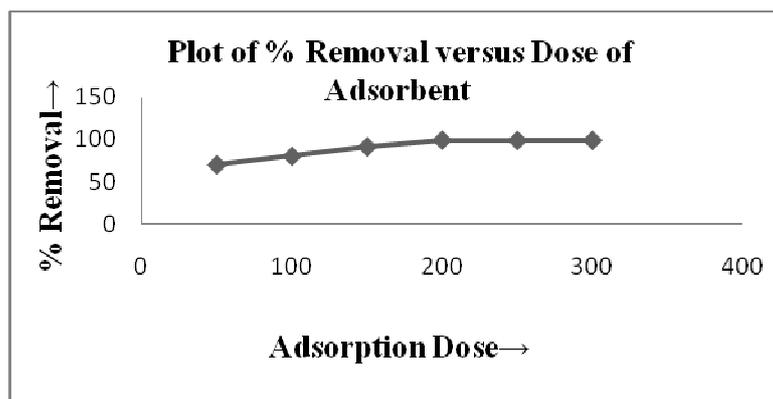
Fig. 3 [Cd (II) conc = 10 mg /L; pH = 6.0; stirring speed = 120 rpm; temp = 30^{0}C]

3.4 Effect of initial Cd(II) concentration
The effect of initial concentration of Cd (II) for adsorption was investigated with the initial concentration of Cd (II) range from 10 to 80 mg/L. The results are presented in figure-4. It has been found Cd(II) removal percentage increases when the initial Cd(II) ion concentration decreases. At low Cd(II) concentration the surface active sites to the total metal ions in the solution is high and hence all the Cd(II) ions may interact with the binding sites of the adsorbent and may be removed from the solution. At higher concentration, most of the Cd (II) is left unabsorbed due to saturation of adsorption sites.
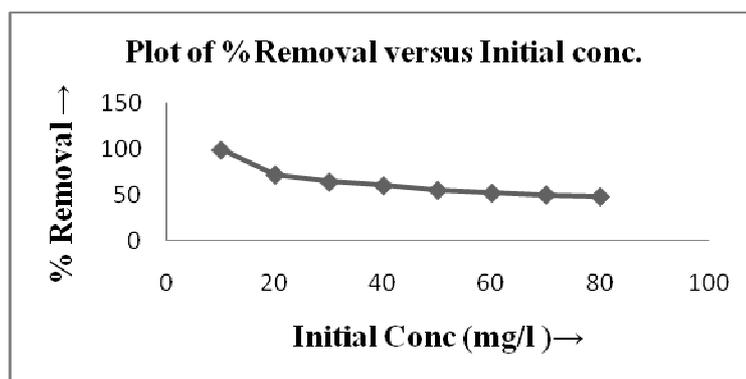
Fig. 4 [adsorbent dose = 200 mg /100 mL; pH = 6.0; time = 200 min; temp = 30°C]
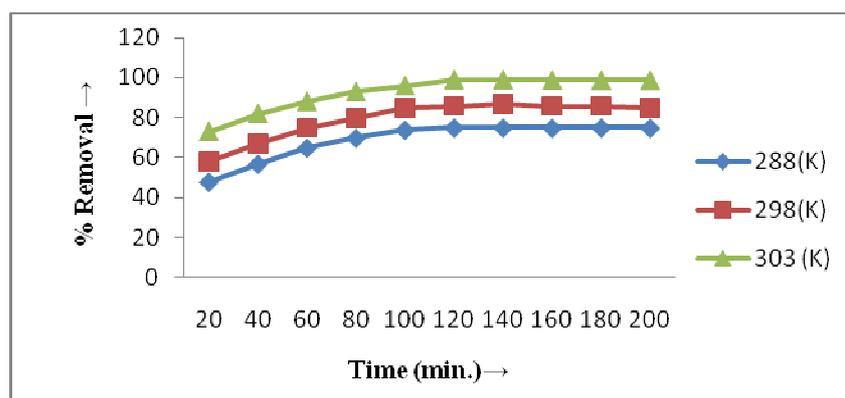
Fig.5 [Cd (II) conc. = 10 mg/L; adsorbent dose 200 mg /100 mL; stirring speed = 120 rpm; pH=6

3.5 Effect of Temperature
The removal kinetics of Cd(II) by FMPEP were obtained at 15°, 22° and 30°C. At an equilibrium time of 120 min for initial Cd(II) concentration of 10 mg/L, the percentage removal increases from 75.1 to 98.9 % with the increase in temperature from 15° to 30^{0}C (figure-5). The sorption capacity increases with increase in temperature indicating that the sorption process was endothermic and the sorption of Cd (II) ions by FMPEP may involve not only physical but also chemical sorption [40]. The increase in sorption capacity of FMPEP at high temperature may be attributed

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to enlargement of pore size or increase in the active surface for sorption. This could also be due to the enhanced mobility of the metal ions from the bulk solution towards the adsorbent surface and extent of penetration within FMPEP structure overcoming the rate of intraparticle diffusion [40, 41].

Table-1 Effect of temperature on Cd(II) removal rate

T(K)	Time (min)	20	40	60	80	100	120	140	160	180	200
288	C_e(mg/L)	5.2	4.3	3.5	3.0	2.6	2.49	2.49	2.5	2.49	2.5
	%removal	48	57	65	70	74	75.1	75.1	75	75.1	75
295	C_e(mg/L)	4.2	3.3	2.5	2.0	1.5	1.4	1.3	1.4	1.4	1.5
	%removal	58	67	75	80	85	86	87	86	86	85
303	C_e(mg/L)	2.7	1.8	1.2	0.7	0.4	0.11	0.11	0.13	0.14	0.14
	%removal	73	82	88	93	96	98.9	98.9	98.7	98.6	98.6

3.6 Kinetic Model
3.6.1 Pseudo-First-order model
Lagergren proposed a pseudo-first order kinetic model. The integral form of the model is shown in Eq. (4). The rate constant k_1 and the correlation coefficients for cadmium adsorption at different concentrations were calculated from the linear plots of $\log_{10} (q_e - q_t)$ versus t (figure-6.) and are listed in table-2. The correlation coefficients for the pseudo-first-order kinetic model are low. Moreover, a large difference of equilibrium adsorption capacity (q_e) between the experiment and calculation was observed, indicating a poor pseudo first-order fit to the experiment data.
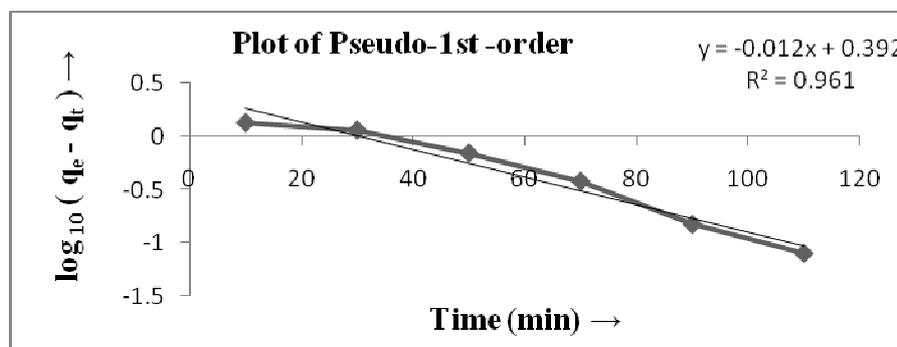
Fig. 6 [Temperature: 30 ± 0.5^0 C, pH: 6.0, adsorbent dose: 200 mg/100 mL]

Table -2 Pseudo-first-order kinetic constant for the adsorption of Cd(II) onto FMPGP

Conc. (mg/L)	Expt. q_e(mg/g)	Pseudo-first-order kinetic			
		k_1(min^{-1})	Theo.q_e(mg/g)	R^2	P
10	4.95	0.0276	2.4660	0.961	7.169

3.6.2 Pseudo-second-order model
The adsorption kinetics can also be described by a pseudo-second order reaction. The linearized-integral form of the model is shown in Eq. (5). The plot of (t/q_t) versus t produces straight line with slope of $1/q_e$ and intercept of $1/k_2q^2_e$. It indicated the applicability of pseudo-second-order model (figure -7). The values of rate constant (k_2) for 15°, 22° and 30° C was obtained as 0.0140, 0.0176 and 0.0212 g/mg min. The overall rate constants (k_2) and other constants of pseudo-second-order kinetics at different are given in table-3. The correlation coefficients value (R^2) was also calculated and presented in table-3.

The values of q_e (theo) calculated from these models are compared with experimental values q_e (exp) and shown in table-3. It is found that values of q_e (theo) calculated from the pseudo-first-order kinetic model differed appreciably from the experimental values q_e (exp). On the other hand, values of q_e (theo) are found to be very close to q_e (exp) when pseudo-second-order rate equation was applied. The value of correlation coefficients (R^2= 0.996. 0.992 and 0.985) is very high for pseudo-second-order when compared with pseudo-first-order kinetics (R^2= 0.961).These suggest that the adsorption data are well represented by pseudo-second-order kinetics and supports the assumption that the rate-limiting step of cadmium adsorption on FMPGP may be chemical sorption or chemisorptions. In chemisorptions, the metal ions stick to the adsorbent surface by forming a chemical (usually covalent) bond and tend to find sites that maximize their coordination number with the surface [52].

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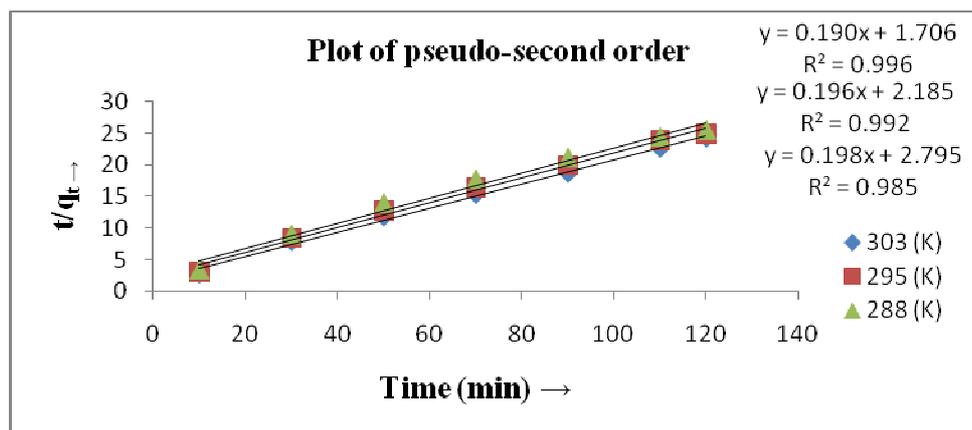
Fig. 7 [Temp. range 15. 22, 30^0 C; pH: 6.0; adsorbent dose: 200 mg/100 mL]

Table -3 Pseudo-second-order kinetic constant for the adsorption of Cd(II) onto FMPGP

Conc. (mg/L)	Temp .(K)	Expt. q_e(mg/g)	Pseudo-second-order kinetic				
			K_2(g/mg min)	Theo.q_e (mg/g)	R^2	h (mg/g min)	P
10	288	4.7	0.0140	5.05	0.985	0.3578	-1.06
10	295	4.8	0.0176	5.10	0.992	0.4577	-0.89
10	303	4.95	0.0212	5.26	0.996	0.5861	-0.89

3.6.3 Percent relative deviation (P)
In order to evaluate the applicability of kinetic models in fitting to data, the percent relative deviation (P) was calculated using the experimental data as given by the following equation [53].

$$P = \frac{100}{N} \left\{ \Sigma \; \frac{q_e(exp) - q_e(theo)}{q_e(exp)} \right\} \qquad (14)$$

Where q_e (exp) is the experimental value of q_e at any value of C_e, q_e (theo) the corresponding theoretical value of q_e and N is the number of observations. It is identified that lower the value of percentage deviation (P), better is the fit. It is generally accepted that when P value is less than 5, the fit is considered to be excellent [53]. .The percent deviation (P) is also very high in case pseudo-first-order and well within the range for pseudo-second-order as shown in table 3.

3.6.4 Intraparticle diffusion rate equation
According to Poots et al [54], during mode operation, there was a possibility of intraparticle pore diffusion of cadmium, which is often the rate –limiting step. The intraparticle diffusion varies with square root of time and is introduced by Waber and Morris [36] is shown in Eq. (6). The value of k_{id} determined from the slope of plot of q_t versus $t^{1/2}$ is 1.91 x10^{-2} mg /g min$^{1/2}$. The intercept (2.906) does not pass through the origin, which indicates that pore diffusion is not the only rate- limiting step [55]
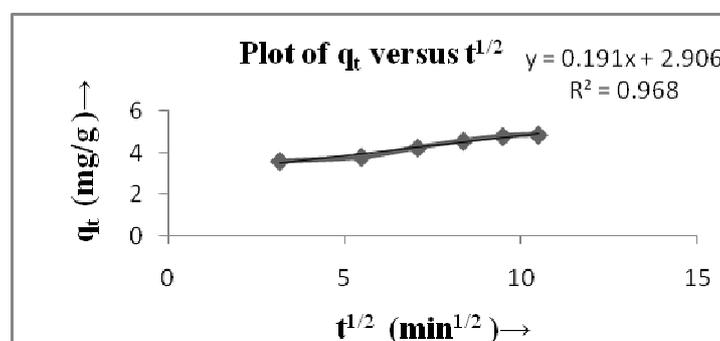
Fig. 8 [Intraparticle diffusion effect for cadmium adsorption by FMPGP]

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3.7 Adsorption isotherm
3.7.1 Freundlich isotherm

It is an experimental expression that takes into account the heterogeneity of the surface and multilayer adsorption to the binding sites located on the surface of the sorbent [56]. The logarithmic form of Freundlich model is expressed as Eq. (7). The linear plot of $\log_{10} q_e$ versus $\log_{10} Ce$ (figure-9) exhibits that the adsorption obeys the Freundlich isotherm and value of Freundlich constants, K_F=7.03 (mg/l) (L/mg) $^{1/n}$ and 1/n=0.198 calculated from the intercept and slope of the plot respectively are presented in table-4. The adsorption intensity 1/n value was found to be between zero and one which indicate the favorable adsorption of Cd(II) ions onto surface of adsorbent.
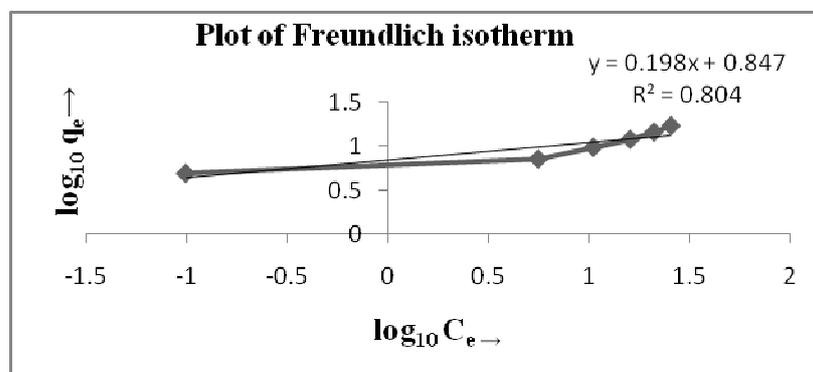
Fig.9 [Temp: 30⁰C, Cd (II) conc:(10-60 mg/L), time:24h, pH: 6, adsorbent dose:200 mg/100 mL]

Table-4 Freundlich and Langmuir constants for Cd(II) removal

Metal ion	Freundlich Model			Langmuir Model		
	K_F(mg/l)(L/mg)$^{1/n}$	1/n	R^2	q_{mix} (mg/g)	K_L(L/mg)	R^2
Cd(II)	7.031	0.198	0.804	18.52	0.1725	0.862

3.7.2 Langmuir isotherm

Langmuir Isotherm model is given by equation (8). A linear plot of Ce/qe versus Ce exhibits that the adsorption obeys the Langmuir isotherm and values of Langmuir constants (q_{max} =18.52 mg/g and K_L=0.1725 L/mg) calculated from the slope and the intercept (figure-10) are presented in table-4. The correlation coefficient (R^2) value of Langmuir model is found to be higher (0.862) than Freundlich model (0.804). These results indicated that the Freundlich model is not proficient to describe effectively the relationship between the amounts of Cd(II) ions adsorbed and their equilibrium concentration in the solution. Hence, it could be concluded that the Langmuir isotherm model was found to be a best fit with the equilibrium data since R^2 values were closer to unity as shown in table-4.
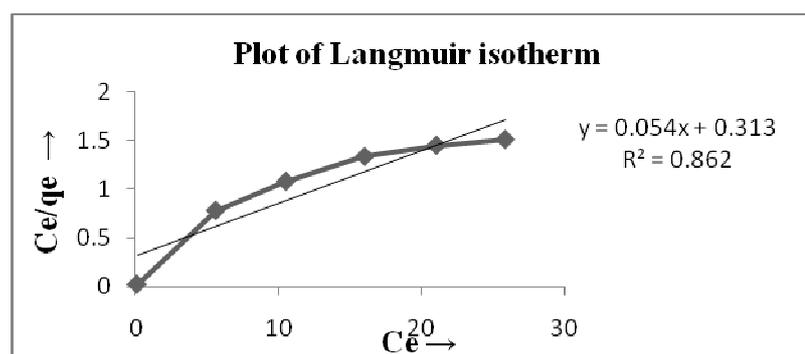
Fig.10 [Temp: 30⁰C; Cd (II) conc: (10-60mg/L); time: 24h; pH: 6; adsorbent dose: 200 mg/100mL]

The correlation coefficient (R^2) value of Langmuir model is found to be higher (0.862) than Freundlich model (0.804). These results indicated that the Freundlich model is not proficient to describe effectively the relationship between the amounts of Cd(II) ions adsorbed and their equilibrium concentration in the solution. Hence, it could be concluded that the Langmuir isotherm model was found to be a best fit with the equilibrium data since R^2 values were closer to unity as shown in table-4.

3.7.3 Separation factor
The essential characteristics of the Langmuir equation can be expressed in terms of a dimensionless factor, R_L which is given in Eq. (9). Separation factor demonstrate the nature of adsorption process and its value indicates the sorption process could be favorable, linear and unfavourable when $0 < R_L < 1$, $R_L = 1$, $R_L > 1$, respectively. The R_L values at different concentrations were found to be in the range of 0 to 1 indicated a highly favorable adsorption of Cd(II) ions onto adsorbent.(figure- 11) [57].
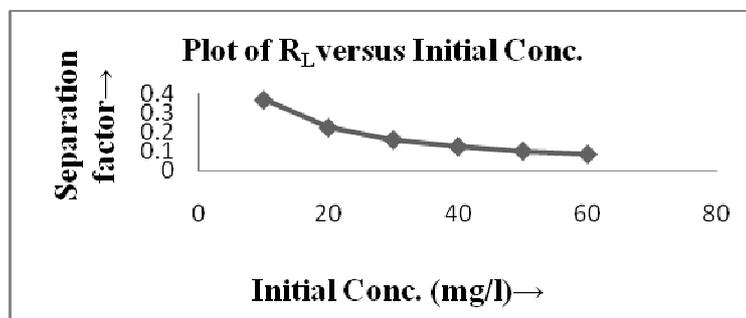
Fig.11 [Separation factor For Cd (II) adsorption by FMPGP]

Table-5 Maximum Adsorption capacities for Cd(II) adsorption to different adsorbents

Adsorption	q_{max} (mg/g)	Reference
Wheat bran	15.7	20
Spent grain	17.3	60
Sugarcane bagasse	6.79	19
Rice husk	21.28	16
Sesamum Indica	35.32	17
Modified coconut chaff	0.50	61
Unmodified coconut chaff	0.229	61
Rice husk ash	20.24	62
peanut hulls	5.96	63
FMPGP	18.52	This Study

3.8 Thermodynamic Studies
The K_D values thus obtained (Eq.10) are used to determine ΔG^0 by using Eq 11.The values of ΔG^0 was found to be -2645, -4.453, and -11.335 kJ/mol for Cd(II) biosorption at 288, 295, 303K respectively. The decrease in Gibbs energy indicates the degree of spontaneity of the adsorption process and the higher negative value reflects a more energetically favorable adsorption [58, 59]. The decrease in (ΔG^0) with increase in temperature shows an increase in feasibility of biosorption at higher temperature. ΔH^0 and ΔS^0 values were obtained from the slope and intercepts of van't Hoff plot, $\ln g_{10} K_D$ versus 1/T (figure-12). The values of ΔH^0 and ΔS^0 for Cd(II), was obtained as 19.77, kJ/mol and 69.15 J/mol K^{-1} respectively. The positive value of ΔH^0 indicates endothermic nature of adsorption while positive ΔS^0 value confirms the increased randomness at the solid-liquid interface during adsorption [58, 59].
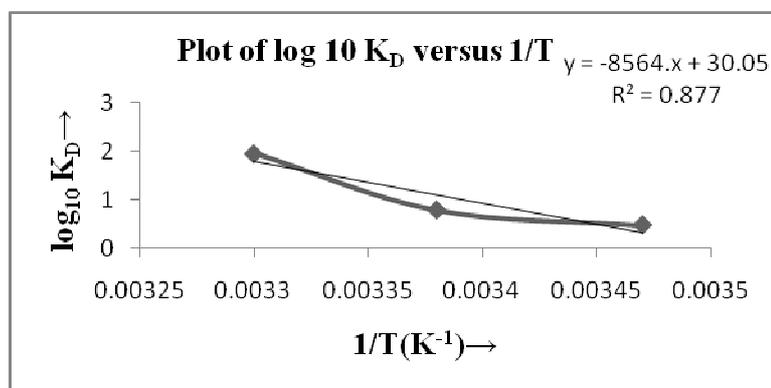
Fig.12 [Van't Hoff plot for Cd(II) adsorption onto FMPGP]

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Table-6 Thermodynamic parameter for adsorption of Cd(II) onto FMPGP

Temp.(K)	Thermodynamic parameter			
	$\log_{10} K_D$	ΔG^0(kJ/mol)	ΔS^0(J/mol K)	ΔH^0(kJ/mol)
288	0.4794	-2.645		
295	0.7884	-4.453	69.15	19.77
303	1.9538	-11.335		

3.8.1 Activation Energy

The increase in the pseudo-second order rate constant with temperature may be described by the Arrhenius equation which is shown in Eq. 13. When $\log_{10} k_2$ is plotted versus $1/T$, a straight line with slope E / 2.303 R is obtained. The magnitude of the activation energy may give an idea about the type of sorption. The activation energy for the sorption of Cd(II), was found as 11.20, kJ/mol from the slope of figure-13 indicating chemisorptions, as chemical adsorption is specific and involves forces much stronger (between 8.4 and 83.7 kJ/mol) than physical adsorption (usually no more than 4.2 kJ/mol) is also reported by U. Kumar [15].
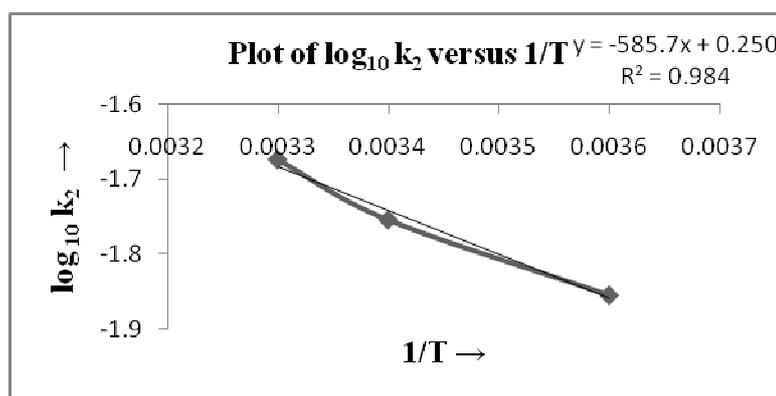
Fig.13 [Activation energy plot for removal of Cd (II) by FMPGP]

CONCLUSION

This study indicates that FMPGP has rapid adsorption rate and good adsorption capacity for cadmium. The major findings of this research are:

➢ The cadmium adsorption was found be dependent on agitation rate, pH and contact time.

➢ Higher percent removal is observed at low concentration of Cd (II) ions (10 mg/l).

➢ The pH has pronounced effect on the removal of Cd (II) ions by adsorption on FMPGP (98.9%) at pH 6-8.

➢ The adsorption of cadmium was found to be fitted the Langmuir isotherm model which suggests monolayer coverage of the adsorbent surface.

➢ Kinetic study however obeyed pseudo-second order model, which indicates chemisorptions as the rate limiting step in adsorption process. Chemisorption nature was further supported by high value of activation energy (11.37kJ/mol)

➢ The decrease in (ΔG^0) with increase in temperature shows an increase in feasibility of biosorption at higher temperature.

➢ Batch kinetic studies showed a rapid removal of Cd (II) process was endothermic and it was further confirmed by the positive value of ΔH^o (19.77 kJ/mol) and further positive value of ΔS^o (69.15 J/mol K) confirms the increased randomness at the solid-liquid interface during adsorption.

➢ Intraparticle diffuse plays important role in the adsorption of cadmium in the present study.

This work showed that formaldehyde modified pomegranate peel is inexpensive, highly available, effective Cd (II) ion adsorbent from natural waste as alternative to existing commercial adsorbent.

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REFERENCES

[1] JD Zuane. Handbook of Drinking Water Quality Standard and Controls, Van Nostrand   Reinhold, New York, **1990,** 64-69.

[2] CW Cheung; JF Porter; G Mckay, *Water Res*., **2001**, 605-612.

[3] S Liang; XY Guo; NC Feng; QH Tian, *J. Hazardous Materials*. **2009,** 170(1), 425–429.

[4] RP Dhakal; KN Ghimirek; K Inoue, *J. Hydrometallurgy*, **2005,** 79, 182–190.

[5]D Parajuli; K Inoue; K Ohto; T Oshima; A Murota; M Funaoka; K Makino, *J .Ractive and Functional Polymers*. **2005**, 62**,** 129-130.

[6]MA Mohammed; A Shitu; MA Tadda; M Ngabura, *Int. Res. J. Environ.,* **2014,** 3 (3), 62-71.

[7] NA Khan; S Ibrahim; P Subramaniam, *Malaysian Journal of Science.* **2004**, 23, 43-51.

[8]YE Sherif; A Ashmawy; S Badr, *J. Appl. Sci. Res*., **2008,** 4, 391-396.

[9] JIN Kumar; C Oommen, *J. Environ. Biol*., **2012**, 33, 27-31.

[10]F Pagnanelli; A Esposito; L Toro; F. Veglio, *J. Water Res.*, **2003,** 37, 627–633.

[11]YC Sharma; V Srivastava, *Indian Journal of Chemical Technology.* **2006***,* 13, 218-221.

[12] P Zhang; H Ma; Y. Zhang; G. Zhu; B Ren, *J. Chem. & Pharm. Res.,* **2014,** 6(7), 2175-2181.

[13] Y Iman; El-Sherif; A Nady*, Environ. Rese., Eng. and Management.* **2013**, 2(64), 19-28.

[14] G Zhengjm; T Congcong; T Lu; C Jun, *International Conferenceon Agricultural and Natural Resources Engineering Advances in Biomedical Engineering.* **2011***,* 3-5, 190-193.

[15] U Kumar, *International Journal of Environmental Science and Development*, **2011**, 2(5).

[16] PS Kumar; K Ramakrishnan; SD Kirupha; S Sivanesan, *Braz. J. Chem. Eng.,* **2010**, 27(2), 347-355.

[17] T Venkateesan; D Thangaraj; N Bommannan; K   Kulanthai; S Krishnamoorthy, *Research Journal of Chemical Sciences.* **2014***,* 4(3), 36-44.

[18] ZAA Othman; A Hashan; A Habila, *Molecule* **2011,** 16, 10443-14456.

[19] SC Ibrahim; MAKM Hanafiah; MZA Yahya, *Am. - Euras. J. Agric & Enviorn. Sci.,* **2006,** 1(3), 170-184.

[20] L Nouri; I Ghodbane; O Hamdaoui; M Chiha, *J. Hazard Mater.* **2007***,* 149, 115-125.

[21] N Seeram; R Lee; M Hardy; D Heber, *Separ. Purif. Technol*., **2005**, 41, 49–55.

[22] MR Moghadam; N Nasirizadeh; Z Dashti; E Babanezhad, *Int. J. Ind. Chem. (IJIC)* **2013**, 4(19), 1-6.

[23] SD Deosarkar, *J. Chem. Pharm. Res.,* **2012,** 4(6), 3319-3323.

[24] ESZE Ashtoukhy; NK Amen; O Abdelwahab, *Desalination*. **2008**, 223, 162-173

[25] SM Shartooh; MNAA Azzawi; SAKA Hiyaly, *Iraqi J. of Sci.,* **2013,** 54(4): 823-831.

[26] MA Ahmad; NAA Puad; OS Bello, *Water Resources and Industry*. **2014**, 6, 18-35**.**

[27]AM Yeneneh; S.Maitra; U Eldermerdash, *Journal of Applied Sciences.* **2011**, 11**,** 3555-3562.

[28] TS Anirudhan; BF Noeline; DM Manohar, *Environment Sci. Technol.,* **2006,** *40*, 2740-2745.

[29] CB Nasr; N Ayed; M Metche, *Z Lebensm unters Forsch* **1996,** 203, 374 -378.

[30] N Artik, *Fruit Processing.* **1998**, 8, 492-499.

[31] MA Nawwar; SA Hussein; I Merfort, *Phytochem.* **1994**, 36, 793-798.

[32]Y Noda; T Kaneyuki; A Mori; L Packer, *J. Agric. Food Chem.,* **2002,** 50,166-171

[33] AA Saiful; AL Ghaniey; D Suhardy; HK Faizul; MD Irfan*, Am. J.Appl. Sci*., **2005,** 2(11), 1499-1503.

[34] S Lagergren. Kungliga Svenska Veternskapsakd, *Handlingar*. **1898,** 24(4)**,** 1-39.

[35] G McKay; YS Ho, *Proc. Biochem.* **1999,** 34, 451-465.

[36] WJ Weber; JC Morris, *J. Sanit. Eng. Div*. **1962**, 89, 31-39.

[37] HMF Freundlich, *J. Phys. Chem.* **1906,** 57, 85-471.

[38] I. Langmuir, *J. Am. Chem. Soc*., **1918**, 40**,** 1361-1403.

[39] V Tharanitharan; K Srinivasan, *Asian J. Chem*., **2010**, 22(4), 3036-3046.

[40] Z Aksu; E Kabasakal, *Sep. Purif. Technol*., **2004,** 35, 223-240.

[41] A Agrawal; KK Sahu; BD Pandey, *Colloids and Surfaces A: Physicochem. Eng. Aspects*, **2004,** 237, 133-140.

[42] YS Ho; WT Chiu; CS Hsu; CT Huang, *Hydrometallurgy.* **2004,** 73, 55-61.

[43] R Saravanane; T Sundararajan; S Sivamurthyreddy, *Indian J. Env. Hlth.,* **2002***,* 44, 78-81.

[44] H Ucun; Y K Bayhan; Y Kaya; A Cakici; OF Algur, *Bio. Technol.,* **2002,** 85, 155-158.

[45] B Volesky**.** BV -Sorbex Inc., St. Lambert, Quebec, Canada. **2003.**

[46]Z Baysal; E Cınar; Y Bulut; H Alkan ; M. Dogru, *J. Hazard. Mater.* **2009,** 161, 62-67.

[47] M Ajmal; RA Rao; S Anwar; J Ahmad; R Alunad, *Bioresource Technol*., **2003**, 86, 147-149.

[48] C Namasivayam; K Ranganathan, *Water Research,* **1995,** 29, 1737-1744.

[49] NC Feng; XY Guo; S Liang, *J. Hazardous Materials.***2009***, 164* (2/3).1286–1292.

[50]S Mandina; F Chigondo; M Shumba; BC Nyamunada; E Sebata, *J. Appl. Chem. (IOSR-JAC)*, **2013**, 6 (2), 66-75.

[51] M Rio; AV Parwate; AG Bhole, *Waste Manage.* **2002,** 22, 821-830.

[52] PW Atkin. Physical Chemistry 5th Edition Oxford, Oxford University. **1995.**

[53] A Ayranci ; O Duman , *J. Hazard. Mater.* **2005**, 124, 125-132.

[54] JP Poot; G McKay; J J Healy, *J. Water Pollut. Control Fed.,* **1978,** 50, 926-935.

[55] FC Wu; RI Tseng; RS Jung, *Water Res.,* **200**1, 35, 613-618.
[56] V Tharanitharan; K Srinivasan, *Asian J Chem.*, **2009,** 21 (9), 7163-7172.
[57] S Arivoli; BR Venkatraman; T Rajchandrasekar; M Hema, *Res. J. Chem. Environ.,* **2007,** 17, 70-78.
[58] AA   Asem; D M Ahmed; YM Ahmed, Sep*. and Purif. Technol.,* **2008,** 61, 348–357.
[59] S. Chegrouche; A Mellah; M Barkat, *Desalination, 2009, 235***,** 306–318.
[60] KS Low; CK Lee SC Liew, *Process Biochem.,* **2000**, 36, 59-64.
[61] MT Osobamiro; OO Adewuyi, *Continental J. Environ. Sci*., **2012**, 6(3), 1-7.
[62] U Kumar; M Bandyopadhyay, *Biores. Technol*., **2006**, 97, 104-109.
[63] R Zacaria, *Environment Sci. Technol.,* **2002,** 36, 2067-2073.