

Removal of mercury (II) ion from the aqueous solution using a synthetic terpolymer

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The terpolymer has been prepared using the monomers *p*-hydroxybenzoic acid, thiourea and *para*-formaldehyde. Physicochemical properties of terpolymer have been investigated to explore adsorption process. The effectiveness of such a terpolymer in adsorbing mercury ion from aqueous solution containing 10 ppm Hg (II) ion has been studied as a function of agitation time, adsorbent dosage, initial metal ion concentration, and pH. Adsorption equilibrium studies are carried out in order to optimize the experimental conditions. The adsorption of mercury ion onto the terpolymer follows pseudo second order kinetic model. Adsorption data are modeled using both Langmuir and Freundlich classical isotherms. The adsorption capacity is found to be 53.48 mg/g at optimum pH of 4.5. Equilibrium time is found to be 3 h for all initial concentration studied. Desorption studies are performed with NaCl and show ion exchange predominant for mercury ion adsorption. The adsorbent is found to be both effective and economically viable.

Keywords: Adsorption Isotherm, Diffusion model, Equilibrium kinetic, Mercury ion, Terpolymer (4-HBTUPF)

The increased use of heavy metals has resulted in an increased flux of metallic substances in different environmental segments. The metals are of special concern due to their recalcitrant and persistency properties in nature. However ion exchange process can remove heavy metals by techno-economical manner and give ultra pure water. Ion exchange process may be defined as the reversible exchange of ions between the substrate and the surrounding medium¹.

Many methods have been developed to remove heavy metals from wastewater, namely adsorption, chemical oxidation/reduction, precipitation, ion exchange, electrochemical processes, membrane filtration and reverse osmosis. Among these methods, the metal cation adsorption is quite promising due to its high efficiency, easy handling, availability of different adsorbents and cost effectiveness².

However, the metal ion removal by chelating ion-exchange resin using batch equilibration method has gained rapid acceptance because of its wide variety of sorbent phases, high degree of selectivity, high loading capacity and enhanced hydrophilicity³⁻⁶. Ion-exchangers are widely used for the treatment of radioactive wastes from nuclear power stations⁶⁻⁸. The chelating ion-exchange behavior of the poly (2-hydroxy-4- acryl-oxyloxybenzophenone) resin

towards the divalent metal ions was studied by batch equilibration method as a function of contact time and pH⁸. A cross-linked styrene/maleic acid chelating matrix has been reported for its higher ability to remove the metal ions such as Cr³⁺, Fe³⁺, Ni²⁺, Cu²⁺ and Pb²⁺⁹. Acidic polymers such as poly (methacrylic acid) and poly (acrylic acid) have the tendency to remove the metal ions, e.g., Ag⁺, Cu²⁺, Co²⁺, Ni²⁺ and Cr³⁺ at different pH and polymer/metal ion ratios¹⁰. Salicylic acid and melamine with formaldehyde terpolymer found to have higher selectivity for Fe³⁺, Cu²⁺ and Ni²⁺ ions rather than Co²⁺, Zn²⁺, Cd²⁺ and Pb²⁺ ions¹¹. Resins synthesized by condensation of mixtures of phenol or hydroxybenzoic acid with formaldehyde and various amines have also been reported¹². The metal ion uptake capacity increases with increasing mole proportions of the terpolymer synthesized from substituted benzoic acid¹³. O-Nitrophenol and thiourea with paraformaldehyde terpolymer was identified as an excellent cation exchanger for Zn²⁺ and Co²⁺ ions¹⁴. Salicylic acid/formaldehyde/resorcinol resin has been synthesized and explored its use for the removal and separation of heavy metal ions from their binary mixtures¹⁵. 8-Hydroxyquinoline/formaldehyde/catechol copolymer is found to have lower moisture

content, an indication of high degree of cross-linking in the resin¹⁶. Phenolic schiff bases derived from hydroxybenzaldehydes and 4,4'-diamino-diphenyl ether have been reported as better chelating resins for Cu (II) leading to its separation from mixtures of Cu (II) and Ni (II) ions¹⁶. Recently, our research group has synthesized a chelating terpolymer resin using an eco-friendly technique and reported its good binding capacity for Ba²⁺ and Zn²⁺ ions¹⁷. A chelating resin with iminodiacetate functional group has been reported for its higher ability to remove the metal ions such as Pb (II), Cd (II), Zn (II), Ca (II) and Hg (II) ions¹⁸. Ion exchange resin synthesized by condensation of 4-hydroxybezaldehyde and biuret with formaldehyde was identified as an excellent cation exchanger for Pb (II), Ni (II) and Hg (II) ion from aqueous solution¹⁹. A cross-linked polyethyleinimine functionalized with ethylene sulphide showed high efficiency and selectivity towards Hg (II) adsorption from aqueous solution²⁰.

This study gives a background to a wider study intended to introduce polymers of these types for use in household filter systems. It has emerged that, due to the scarcity of water, certain households use water of Kodai Lake in Tamil Nadu which is contaminated by Hg (II) by thermometer manufacturing industry²¹. However, a literature survey revealed that no terpolymer ion exchange resins have been synthesized from 4-hydroxybenzoicacid-thiourea-parafomaldehyde. Therefore, we have carried out synthesis and characterization of these terrpolymer and it has been studied for the removal of Hg (II) from aqueous. The effects of some parameters on adsorption of Hg (II) were studied, namely pH, adsorbent amount, contact time, and the presence of competing ions. Regeneration of the terpolymer resin was also done so as to assess its reusability.

Experimental Section

Materials

4-Hydroxybenzoic acid (Nice, India) and thiourea (Merck, India) were purified by rectified spirit. *Parafomaldehyde* (Ranbaxy, Punjab) and sodium chloride (SD fine, India) were used as received. All other chemicals, solvent and indicators were analytical grade produced from Qualigens fine chemicals, India. Double distilled water was used for all experiments.

Preparation of synthetic wastewater

Hg (II) solution (1000 mg/L) was prepared by dissolving 1.356 g of HgCl₂ in distilled water and diluted

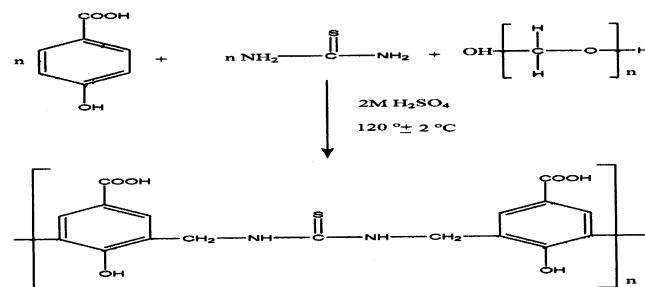
to 1000 mL. Appropriate volume of stock solutions were suitably diluted with distilled water to obtain a concentration of 10 mg/L of Hg(II) ion in the solution.

Preparation of adsorbent

Terpolymer was synthesized by condensation of the monomers, 4-hydroxybenzoicacid and thiourea with parformaldehyde at 2:3:5 ratios in the presence of 100 mL of catalyst 2M H₂SO₄ at 120°±2°C for 4 h. The resulting mixture was poured into ice with constant stirring and kept overnight as such. The pale yellow resin obtained was washed with water and ether then air dried. The dried resin was further purified by dissolving in 10% NaOH and regenerated in 1:1 (v/v) HCl. This process was repeated twice to separate the pure polymer. The purified terpolymer was finely ground well to the particle size of 270 to 400 mesh size and kept in vacuum over silica gel. The yield of the terpolymer (4-HBTUPF) was found to be 80-82%. The reaction route has been shown in Scheme 1. In order to increase the efficiency of terpolymer resin to adsorb metal ion from aqueous solution, it is modified by equilibrating 5 g of polymer with 200 mL of 5% of NaCl solution for 24 hr and washed with deionized water till it was free from chloride by testing with silver nitrate^{1,15,22,23}.

Characterization of terpolymer

FTIR spectrum of synthesized terpolymer (4-HBTUPF) and Hg (II) loaded terpolymer had been scanned in KBr pellets on a Broker (Model Tensor 27) spectrophotometer to identify the linkage and functional groups. The FTIR spectra with assignment of peaks are shown in Figs 1 (a and b). The average molecular weight of 4-HBTUPF terpolymer was determined by gel permeation chromatography (GPC) in Shimadzu using DMSO column, it is shown in Table 1. The surface of the terpolymer 4-HBTUPF was examined by scanning electron microscope Hitachi (Model S- 3000H) at different magnifications and the resulting pattern is shown in



Scheme 1

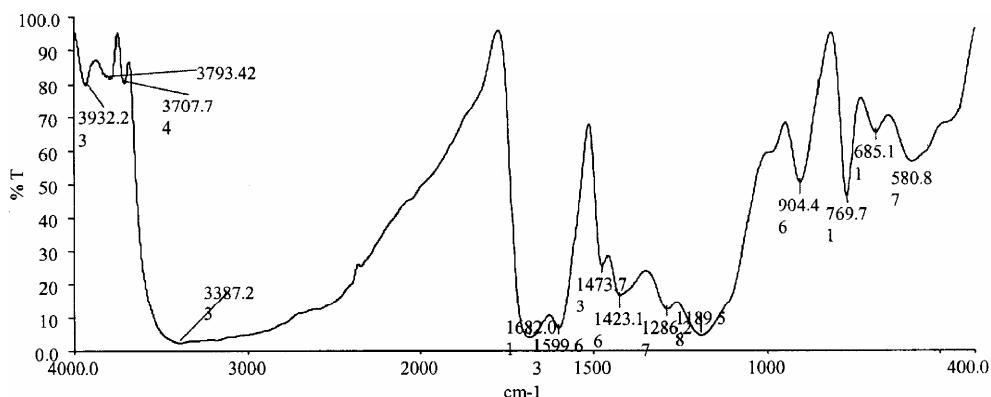


Fig. 1(a) — FTIR spectrum of 4-HBTUPF

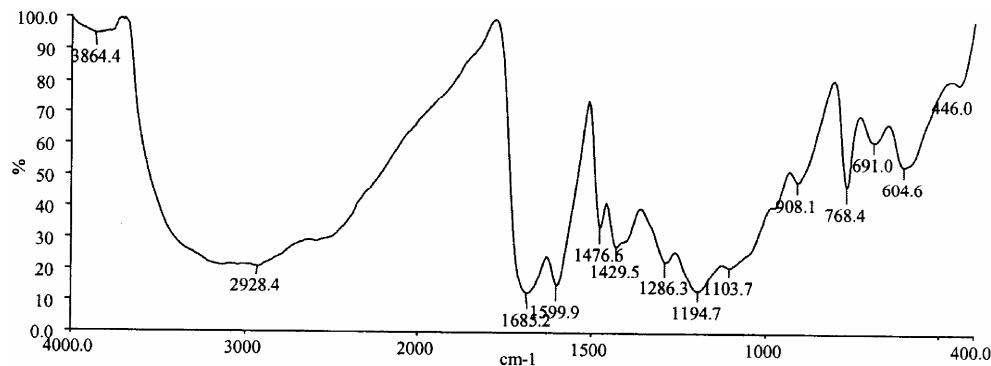


Fig. 1(b) — FTIR spectrum of 4-HBTUPF after adsorbing Hg (II) Ion

Table 1 — GPC for molecular weight measurement of 4-HBTUPF terpolymer.

Compound	\overline{M}_n	\overline{M}_w	\overline{M}_z	Polydispersity $\overline{M}_w / \overline{M}_n$	Polydispersity $\overline{M}_z / \overline{M}_n$
4-HBTUPF	4579	5427	5762	1.1458	1.2584

Table 2 — Physicochemical characteristics of 4-HBTUPF terpolymer.

Properties	Value (SD)
Moisture (%)	10.4 ± 0.25
Solid (%)	89.6 ± 0.25
True density(dry resin) g/cm ³	1.498 ± 0.25
Void Volume fraction	0.765 ± 0.025
Sodium ion exchange capacity (mmol/g)	6.78 ± 0.40

Figs 2(a and b). According to the literature methods¹⁵ the physicochemical properties like moisture and solid contents, apparent density, true density, void volume fraction and sodium exchange capacity were studied and they are given in Table 2.

Batch experiment

Hg (II) solution (100 mL) with desired concentration adjusted to desired pH was taken in Erlenmeyer glass flasks of 200 mL capacity and 0.1 g

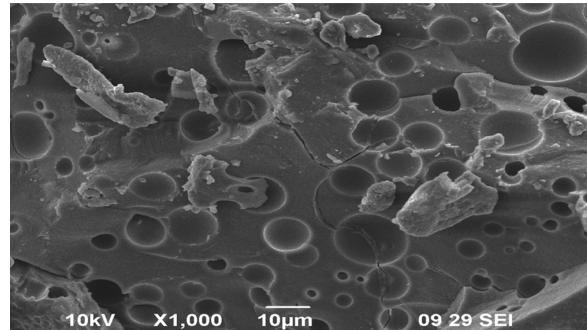


Fig. 2(a) — SEM photograph of 4-HBTUPF

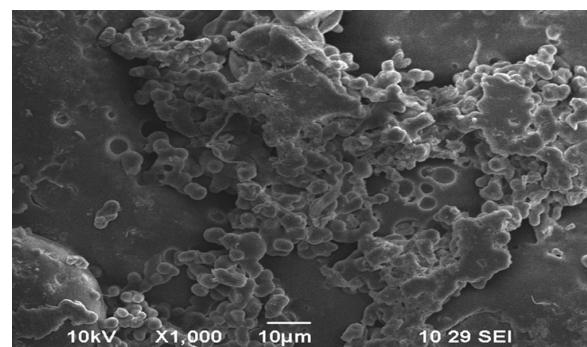


Fig. 2(b) — SEM photograph of 4-HBTU PF after adsorbing Hg (II) Ion

of sodium loaded 4-HBTUPF terpolymer was added to it. The solutions were agitated for a predetermined period at $30\pm2^\circ\text{C}$ and the polymer were separated by filtration and the filtrate was analyzed for Hg (II) by AAS. Adsorption isotherm and kinetic studies were carried out with different initial concentrations of Hg (II) by maintaining the modified terpolymer with sodium at constant level. Adsorption isotherm studies were made after completing period of 24 hr²⁴⁻²⁷.

Results and Discussion

FTIR spectral studies

The spectrums of 4-HBTUPF terpolymer before and after loading with Hg (II) ion are depicted in Fig. 1(a) and Fig. 1(b). A strong band at 1189 cm^{-1} is assigned for aromatic –OH bending of phenolic group¹⁵. The spectrum shows brad band at 3387 cm^{-1} may be assigned to the $\nu(\text{O}-\text{H})$ stretching of Ar-OH group merged with –NH stretching mode¹⁷. The medium strong band at 1682 cm^{-1} can be assigned to $\nu(\text{C}=\text{O})$ stretching of aromatic acid group²³. The sharp, medium/weak bands have appeared between 1200 cm^{-1} and 761 cm^{-1} for resin which is due to the $\delta(\text{C}-\text{H})$ bending tetra substituted benzene ring¹⁷. The medium band at 1473 cm^{-1} is due to $\delta(\text{C}-\text{H})$ deformation of methylene group¹⁵. The consistent appearance of the band at 904 cm^{-1} is due to $-\text{C}=\text{S}$ stretching¹⁷. The shift in adsorption band of functional groups in metal loaded terpolymer in compare with metal free 4-HBTUPF has been observed. This shows that metal ions are adsorbed on polymer surface by binding with these functional groups.

Morphological studies

The typical SEM photograph of the 4-HBTUPF is shown before and after loading loaded with mercury ion in Fig. 2(a) and Fig. 2(b). SEM image shows fringed model of crystalline and amorphous structure with less close packed surface. Due to the presence of deep pits, large size hydrated Hg (II) ions can easily adsorbed on the polymer surface. Loading of the terpolymer surface with Hg (II) is presumably leading to formation of white layer of uniform thickness^{15,24}.

Effect of agitation time

The effect of contact time on the adsorption of Hg (II) was studied for an initial concentration of 100 mg L^{-1} . The contact time of experiments were carried out at 30°C (time interval, 15 min). It was observed that the adsorption consists of two phases:

a primary rapid phase and a second slow phase. The first rapid phase lasted approximately 45 min and accounted for the major part in the total Hg (II) adsorption. Adsorption reached a plateau value in approximately 180 min, which showed saturation of the active sites on the adsorbent. Therefore, for further experiments, the shaking time was set to 180 min²⁴⁻²⁷.

Effect of pH

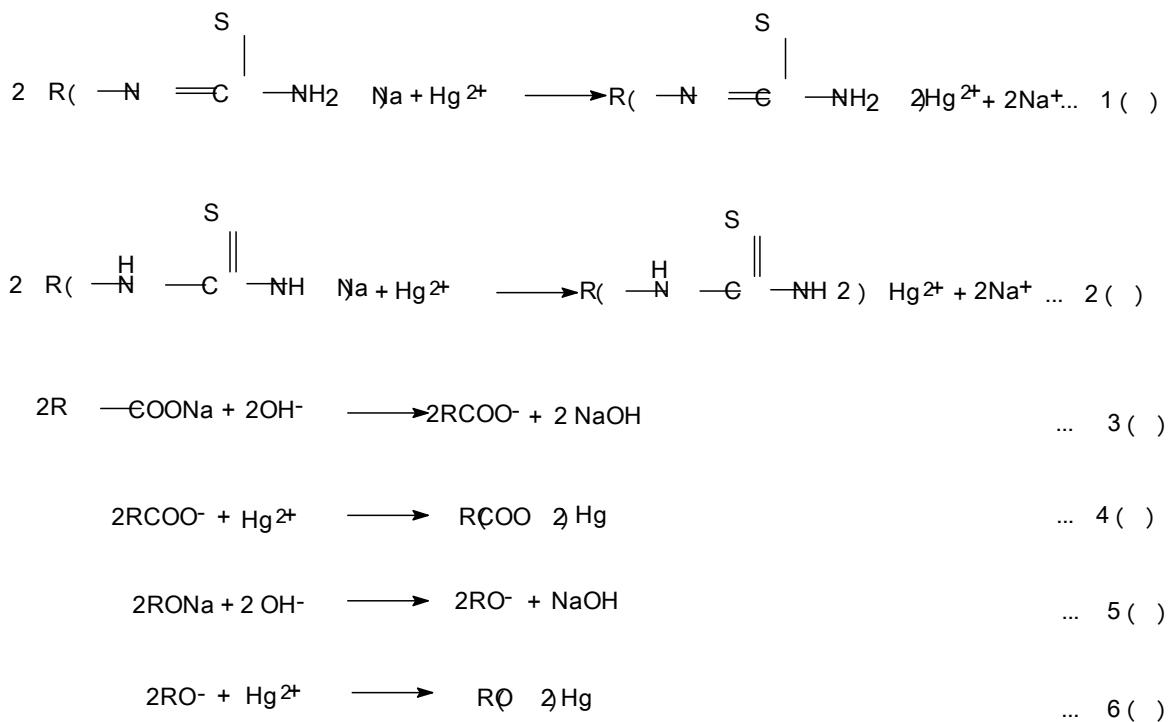
The most important single parameter influencing the sorption capacity is the pH of adsorption medium. The effect of pH on removal of Hg (II) ion by 4-HBTUPF terpolymer sorbent for the pH ranging from 2 to 10. It could be seen that quantitative removal of Hg (II) is achieved by the sodium loaded terpolymer over the pH range of 4.0-5.0 for an initial Hg (II) ion concentration of 10 mg/L and sodium loaded terpolymer dosage of $0.1\text{ g}/100\text{ mL}$. The perusal of the literature on Hg (II) ion speciation diagram shows that in presence of chloride ion, the dominant Hg (II) species at $\text{pH} > 4.0$ is $\text{Hg}(\text{OH})_2$. The species such as HgCl_2 or $(\text{HgCl}_2)_2$ and HgOHC are also present in small concentrations. The high affinity sodium loaded of 4-HBTHUPF terpolymer on Hg (II) ion in the pH range of 4.0-5.0 is explained by Pearson rule because terpolymer and the metal Hg (II) ion are soft base and soft acid respectively. Neutral molecules are softer acids than metal cations and as a rule, the interaction of Hg (II) species such as HgCl_2 or $(\text{HgCl}_2)_2$ and HgOHC with sulphur group is highly favoring at pH range 4.0-5.0. At low pH surface of the terpolymer is positive, due to electrostatic repulsion Hg (II) and $\text{Hg}(\text{OH})^+$ ions are not significantly adsorbed²⁸. Scheme of reactions for adsorption of mercury onto terpolymer adsorbent surface by various functional groups are given in equations (1 to 6).

Effect of sorbent dosage

The removal of Hg (II) as a function of sodium loaded 4-HBTUPF polymer. A quantitative removal of Hg (II) could be found at an optimum sorbent dosage of 0.5 g per 100 mL for an initial concentration of 10 mg/L of Hg (II) ion^{24,25}.

Adsorption isotherm studies

The commonly used adsorption isotherm, such as Langmuir and Freundlich adsorption isotherm^{24-27,29-31} has been employed for this study. The Langmuir equation is given as in equation (7):

Table 3 — Adsorption isotherm parameters for the adsorption of Hg (II) on sodium loaded 4-HBTUPF at optimum pH

Adsorbent	Langmuir model				Freundlich model		
	Q_0 (mg/g)	b (l/mg)	R^2	ΔG^0 (kJ/mol)	K_f (mg/g)	n (L/mg)	R^2
4-HBTUPF	53.48	1.0564	0.9762	-136.9	49.20	2.99	0.9524

$$\frac{C_e}{q_e} = \frac{1}{Q_0 b} + \frac{C_e}{Q_0} \dots (7)$$

where C_e is the equilibrium concentration of metal ion in mg/L. q_e is amount of metal ion adsorbed at equilibrium (mg/L). Q_0 and b is Langmuir constants related to adsorption capacity and energy of adsorption, respectively. Langmuir isotherm show good fit to the experimental data with good correlation coefficient ($R^2 = 0.9762$), shows that the adsorption obeys the Langmuir model. Q_0 and b were determined from slope and intercept of C_e/q_e versus C_e and are presented in the Table 3. From the values, we can conclude that the maximum adsorption corresponds to a saturated monolayer of adsorbate molecules on the adsorbent surface with constant energy and no transmission of adsorbate in the plane of the adsorbent surface³⁰. To confirm the favorability of the adsorption process, the separation factor (R_L) has calculated and presented in Table 4. The values were found to be between 0 and 1 and confirm that the ongoing adsorption process is favorable^{24-27,30,31}.

Table 4 — Equilibrium parameter R_L

Initial conc. Hg (II) Ion	R_L Values Sodium loaded 4-HBTUPF
3	0.2399
5	0.1592
7	0.1191
10	0.0865

The Freundlich equation has also been employed for the adsorption of mercury ion on the adsorbent. The Freundlich isotherm was represented as in equation (8):

$$\log(x/m) = \log K_f + 1/n \log C_e \dots (8)$$

where C_e is the equilibrium concentration (mg/L) and x/m is amount adsorbed per unit weight of sorbent. The linear plot of $\log(x/m)$ versus $\log C_e$ shows that adsorption of mercury ion on the terpolymer obeys the Freundlich isotherm. The K_f (adsorption capacity in mg/g) and n (sorption intensity) values are calculated from the intercept and slope respectively and given in Table 3. The values of $1 < n > 10$ shows favorable adsorption of mercury ion on the sorbent.

The R^2 (Table 3.) values suggest that Langmuir model is well fit than Freundlich isotherm model^{24-27,30,31}.

The free energy ΔG^0 for this adsorption process is given in the Table 3. It is calculating from Langmuir constant 'b', by the following equation (9)^{24,25}:

$$\Delta G^0 = -RT \ln(b) \quad \dots (9)$$

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

Adsorption kinetics

Kinetic models of pseudo-first order and pseudo-second-order^{25,26,31-33} are used for the purpose of investigating the sorption mechanism of Hg (II) on 4-HBTUPF terpolymer. The pseudo-first order kinetic model is expressed as in equation (10).

$$\ln(q_e - q_t) = -Kt + \ln q_e \quad \dots (10)$$

where q_e and q_t is the amount of metal adsorbed (mg/g) at equilibrium and at time t, respectively and K_1 is the pseudo first order equilibrium rate constant (h^{-1}). A plot of $\ln(q_e - q_t)$ versus t gives straight line [Fig. 3(a)]. The applicability of the rate equation was confirmed by using their R^2 values are given in the Table 5.

Pseudo second order adsorption rate equation is expressed as in equation (11):

$$\frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \frac{1}{q_e t} \quad \dots (11)$$

where K_2 is rate constant of pseudo-second-order adsorption reaction (g/mg/h). A plot of t/q_t versus t produces straight line [Fig. 3(b)] and indicates the applicability of pseudo second order model³¹⁻³³. Constants of rate equations and correlation coefficient values R^2 are given in Table 5. Correlation coefficient values are higher for pseudo second order model than for pseudo first order model. In order to compare quantitative applicability of kinetic models in fitting to the data, the percent relative deviation (P), was calculated as per the expression³²:

$$P = \frac{100}{N} \sum \frac{q_e(\text{exp}) - q_e(\text{theo})}{q_e(\text{exp})}$$

$q_e(\text{exp})$ and $q_e(\text{theo})$ is experimental and theoretical value of amount of metal adsorbed at

equilibrium. N is number of observation. The percentage deviation of experimental and theoretical data (Table 6) is less for pseudo second order kinetics. Therefore it could be concluded that the adsorption of Hg(II) on the 4-HBTUPF adsorbent is governed by pseudo-second order kinetics predominantly³².

In order to understand the nature of diffusion process responsible for the pore and film diffusion coefficient for various concentrations of Hg(II) is using the following equations (12)^{32,33}.

$$D_p = 0.03 * r_0^2 / t_{1/2} \quad \dots (12)$$

where D_p is the pore diffusion coefficient expressed in cm^2/s , r_0 is radius of the sorbent expressed in cm and $t_{1/2}$ is half life period in sec.

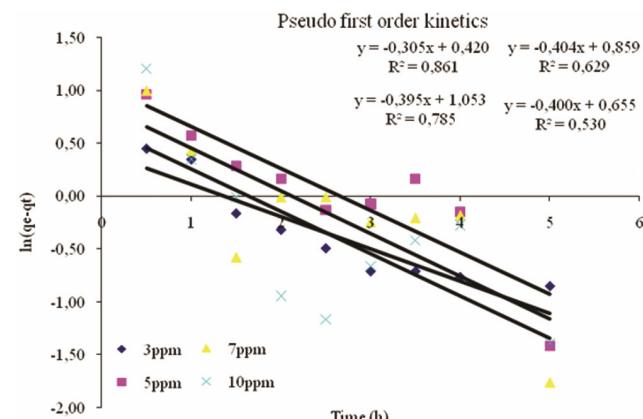


Fig. 3(a) — Pseudo first order kinetic model for adsorption of Hg (II) on sodium loaded 4-HBTUPF (Adsorbent dosage of 0.5g/100mL, temp at 30°C, Hg(II) conc. 3,5,7, and 10mg/L, contact time 24 hr and pH = 4.5)

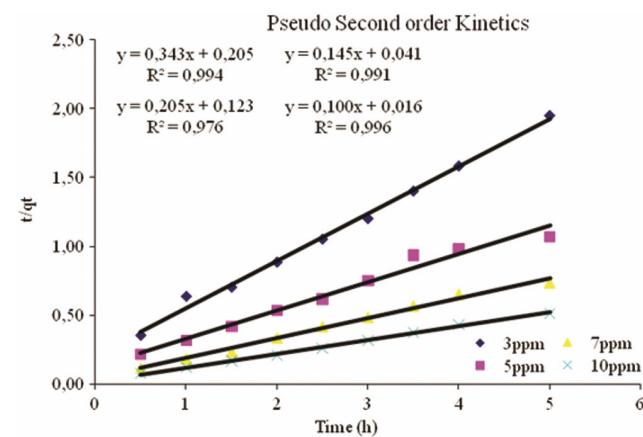


Fig. 3(b) — Pseudo second order kinetic model for adsorption of Hg (II) on sodium loaded 4-HBTUPF (Adsorbent dosage of 0.5g/100mL, temp at 30°C, Hg(II) conc. 3,5,7 and 10mg/L, contact time 24 hr and pH = 4.5)

Table 5 — Pseudo first order and pseudo second order kinetic constants and diffusion coefficient for the adsorption of Hg (II) on sodium loaded 4-HBTUPF at optimum pH

Adsorbent	Hg(II) (mg/L)	Pseudo first order kinetics			R^2
		$K_1 \text{ h}^{-1}$	$D_f (\text{cm}^2 \text{s}^{-1})$	$D_p (\text{cm}^2 \text{s}^{-1})$	
4-HBTUPF	3	0.305	3.3999×10^{-7}	2.4777×10^{-7}	0.8618
	5	0.395	7.2354×10^{-7}	3.2064×10^{-7}	0.7855
	7	0.404	1.0414×10^{-7}	3.2550×10^{-7}	0.6297
	10	0.400	1.4839×10^{-7}	3.2550×10^{-7}	0.5306

Adsorbent	Hg(II) (mg/L)	Pseudo second order kinetics			R^2
		$K_2 (\text{g/mg/h})$	$D_f (\text{cm}^2 \text{s}^{-1})$	$D_p (\text{cm}^2 \text{s}^{-1})$	
4-HBTUPF	3	0.5740	1.3305×10^{-6}	9.6960×10^{-7}	0.9948
	5	0.3367	3.2288×10^{-6}	1.4309×10^{-6}	0.9761
	7	0.5128	6.3246×10^{-6}	1.9796×10^{-6}	0.9915
	10	0.6250	3.4678×10^{-7}	3.4678×10^{-6}	0.9969

$$D_f = 0.23 * r_0 * \delta * \frac{\bar{c}}{c} / t_{1/2} \quad \dots (13)$$

where D_f is the film diffusion coefficient expressed in $\text{cm}^2 \text{s}^{-1}$, δ is film thickness expressed in cm and $\frac{\bar{c}}{c}$ is equilibrium loading of sorbent. According to Michelson *et al.* if film diffusion to be the rate determining process^{32,33}, its value should be in the order of 10^{-6} to $10^{-8} \text{ cm}^2 \text{s}^{-1}$, if pore diffusion to be the rate determining process, its value should be in the order of 10^{-11} to $10^{-13} \text{ cm}^2 \text{s}^{-1}$. It is evidence from the Table 5. The adsorption of Hg (II) of terpolymer surface follows film diffusion process, since the coefficient values are closer to the range of 10^{-6} to $10^{-8} \text{ cm}^2 \text{s}^{-1}$.

Desorption studies

Desorption experiment were conducted to recover the Hg(II) ion from the spent terpolymer using 1-10% NaCl solution. The values are shown in the Table. Results showed that 99% of Hg(II) ion desorbed from the terpolymer under optimum concentration of 5% NaCl. After the extraction the adsorption capacity of the terpolymer was again and again tested and about five cycles of operation. Results indicate that 5% NaCl solution is suitable for regeneration of terpolymer²⁴.

Conclusion

The present investigation shows that the 4-HBTUPF terpolymer can be employed as an effective sorbent for removal of Hg(II) from aqueous solution. Equilibrium of adsorption process reaches at 180 min. About 0.5 g of polymer is required for

Table 6 — Relative percent deviation experimental and theoretical values of pseudo first order and pseudo second order kinetic data for the adsorption of Hg (II) on sodium loaded 4-HBTUPF at optimum pH

Adsorbent	Hg(II) (mg/L)	Pseudo first order kinetics			P
		$q_e (\text{theo})$ (mg/g)	$q_e (\text{exp})$ (mg/g)	P	
4-HBTUPF	3	1.52	2.95	48.75	
	5	2.87	4.57	37.20	
	7	2.36	6.84	65.50	
	10	1.93	9.76	79.98	

Adsorbent	Hg(II) (mg/L)	Pseudo second order kinetics			P
		$q_e (\text{theo})$ (mg/g)	$q_e (\text{exp})$ (mg/g)	P	
4-HBTUPF	3	2.91	2.95	1.36	
	5	3.99	4.57	12.69	
	7	6.88	6.84	0.58	
	10	9.93	9.76	1.74	

maximum removal Hg(II). Terpolymer is effective for the quantitative removal of Hg(II) ion over the pH range of 4.0-5.0. The experimental data correlates reasonably well by the Langmuir and Freundlich adsorption isotherms and the isotherm parameters are calculated. Pseudo first order and pseudo second order rate equations have been used to describe the kinetics of sorption of Hg (II) on 4-HBTUPF terpolymer at different initial concentration of Hg (II) ion in the solution. The kinetic data and correlation coefficient value shows that this adsorption process follow pseudo second order kinetic model. Desorption of Hg (II) from the terpolymer has been effectively achieved with 5% NaCl.

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