

Adsorption of Cadmium(II) Ion from Aqueous Solutions onto Synthetic Terpolymer: Isotherm and Kinetic Study

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The adsorption of cadmium(II) onto a terpolymer 4-HBTUPF synthesized by condensation of 4-hydroxybenzoic acid and thiourea with paraformaldehyde in 2:3:5 ratios. The effect of experimental parameters such as pH, metal ion concentration, contact time and adsorbents dosage on cadmium(II) removal were studied. The data were analyzed using Langmuir and Freundlich equations to describe the equilibrium isotherms. The kinetic data fitted well with pseudo second order model than with pseudo first order model. The maximum adsorption capacity for the adsorption of cadmium(II) on the 4-HBTUPF adsorbent calculated from Langmuir isotherm was found to be 44.64 mg/g for the adsorption of cadmium(II) on 4-HBTUPF terpolymer. R² values shows that Langmuir model fit better than Freundlich model. FTIR analysis was used to obtain information on the nature of possible interaction between adsorbents and metal ions. SEM images confirmed the adsorption of cadmium onto the terpolymer through morphological observations. Thermodynamic study showed the feasibility of process and spontaneous nature of the adsorption. The results indicate that terpolymer 4-HBTUPF could be used effectively for the removal of cadmium from aqueous solution.

Keywords: Terpolymer (4-HBTUPF), Cadmium ion, Adsorption isotherm, Kinetic, Diffusion model.

INTRODUCTION

The presence of heavy metals in the environment poses a serious and complex pollution problem that has been still is a focus of attention all over the world. Heavy metals are main pollutants of surface and groundwater. The environmental impact due their toxicity has lead to the enforcement of stringent standards for the maximum allowable limits of their discharge into open landscapes and water. Cadmium is one of heavy metals, which is highly toxic to humans, plants and animals. The metal is of special concern because it is non-degradable and therefore persistent. The major sources of cadmium release into the environment by waste stream are electroplating, smelting, alloy manufacturing, pigments, plastic, battery, mining and refining processes¹.

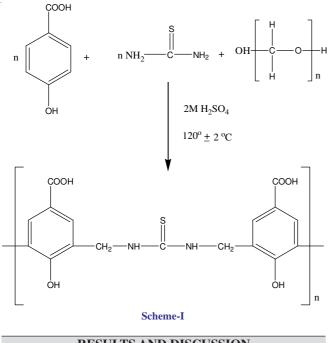
Over the past few decades, significant research work has been done on enhancing the properties of newly synthesized ion-exchange terpolymers for the treatment of wastewater and pollution control. The necessity to reduce the amount of heavy metal ions pollutant in wastewater streams has led to an increasing interest in ion-exchange terpolymer²⁻⁷. Therefore, attempt has been made to synthesize terpolymer and to evaluate the ion-exchange properties. Various combinations of 8hydroxyquinoline-5-sulfonic acid-thiourea-formaldehyde, *ortho*-nitro phenol-thiourea-*para*-formaldehyde and anthranilic acid-thiourea-*para*-formaldehyde have been synthesized by condensation polymerization and reported for their chelation ion-exchange properties toward selective metal ions⁸⁻¹⁰. Ion exchange technique can be used to remove traces of ionic impurities from water and give ultra pure quality in a simple efficient and techno-economically viable manner. In the present work, effectiveness of adsorption of cadmium ion on the terpolymer derived from condensation of 4-hydroxybenzoic acid and thiourea with *para*-formaldehyde was studied by determining maximum adsorption capacity of cadmium by batch mode process. The kinetic studies of cadmium(II) adsorption onto 4-HBTUPF were also studied.

EXPERIMENTAL

Preparation of synthetic wastewater: Analytical grade of cadmium solution, $Cd(NO_3)_2.4H_2O$ (1000 mg/L) supplied by Merck was used in preparing synthetic wastewater. The synthetic wastewater was prepared by diluting the stock solution of Cd^{2+} with distilled water to desired concentrations. The pH of the wastewater was then adjusted to 5 using 0.1 M NaOH and 0.1 M HNO₃.

Preparation of adsorbent: Terpolymer was synthesized by condensation of 4-hydroxybenzoic acid and thiourea with para-formaldehyde at 2:3:5 ratios in the presence of 100 mL of catalyst 2M H_2SO_4 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 4-HBTUPF terpolymer was found to be 80-82 %. The reaction rout has been shown in Scheme-I. To convert hydrogen form of terpolymer (4-HBTUPF) in to Na⁺ form, 5 g of polymer was equilibrated with 200 mL of 5 % of NaCl solution for 24 h and washed with deionized water till it was free from chloride by testing with silver nitrate.

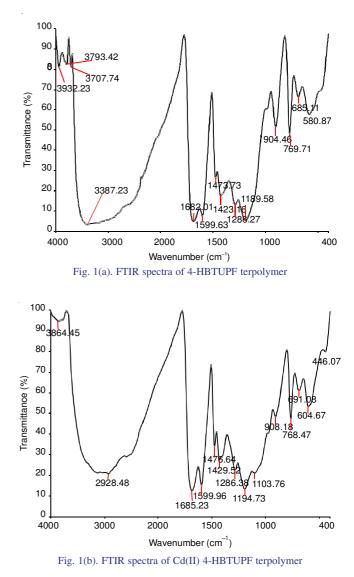
Batch experiment: 100 mL of cd(II) solution with desired concentration adjusted to desired pH were taken in Erlenmeyer flasks of 200 mL capacity and 0.2 g of sodium loaded 4-hydroxybenzoic acid thiourea *para*-formaldehyde terpolymer was added to it. The solutions were agitated for predetermined time at room temperature. After adsorption, the mixture was filtered through whatman filter paper (No.40). The concentration of cadmium in the solutions before and after equilibrium was determined by atomic absorption spectrophotometer (Model: SL 163, ELICO Ltd from Hyderabad, India) using air acetylene flame.



RESULTS AND DISCUSSION

Characterization of adsorbent: FTIR spectrum of the terpolymer (4-HBTUPF) and Cd(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 spectrums of 4-HBTUPF polymer before and after loading with Cd(II) ion are depicted in Fig.1(a) and 1(b). A strong band at 1189 cm⁻¹ is assigned for aromatic -OH

bending of phenolic group¹¹. The spectrum shows brad band at 3387 cm⁻¹ may be assigned to the v(O-H) stretching of Ar-OH group merged with -NH stretching mode¹². The medium strong band at 1682 cm⁻¹ can be assigned to v(C=O) stretching of aromatic acid group¹³. The sharp, medium and weak bands have appeared between 1200 and 761 cm⁻¹; this is for resin which is due to the δ (C-H) bending tetra substituted benzene ring¹². The medium band at 1473 cm⁻¹ is due to δ (C-H) deformation of methylene group¹¹. The consistent appearance of the band at 904 cm⁻¹ is due to -C=S stretching¹². The shift in adsorption band of the functional groups in metal loaded terpolymer (Fig. 1(b)) in compare with metal 4-HBTUPF has been observed. This shows that metal ions are adsorbed on polymer surface by binding with these functional groups¹². The surface morphology of the 4-HBTUPF and Cd(II)-loaded was examined by scanning electron microscope Hitachi (Model S-3000H) at different magnifications which is shown in Fig. 2(a) and 2(b). SEM image shows fringed model of crystalline and amorphous structure with less close packed surface. Due to the presence of deep pits Cd²⁺ can easily adsorbed on the polymer surface. Loading of the terpolymer resin surface with Cd²⁺, presumably leading to formation of white layer of uniform thickness.



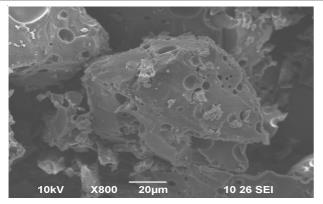


Fig. 2(a). SEM photograph of 4-HBTUPF terpolymer

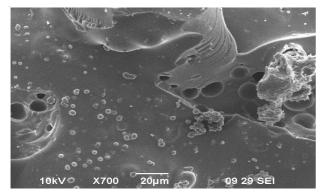


Fig. 2(b). SEM photograph of sodium loaded 4-HBTUPF terpolymer

Effect of contact time and optimum cadmium concentration: Study on the effect of contact time and concentration, on adsorption of Cd²⁺ on sodium loaded 4-HBTUPF shows that increases from 70.2 to 99.9 % (Fig. 3) as the concentration of cadmium in solution decreases from 100 mg/L to 10 mg/L at pH 6, temperature 30 °C. The adsorption of Cd²⁺ ion is rapid in initial stages and then gradually decreases and acquires equilibrium in 180 min. This finding reveals two important features: the process is highly dependent on initial concentration of cadmium and independent of the equilibrium time of the initial solute concentration. The findings have number of practical importance. The contact of solute and the adsorbent must be eliminated after the equilibrium time. This is probably due to large surface area of polymer with exchangeable. Sodium ion available at the beginning for the adsorption of Cd^{2+} ions. As the surface area of the adsorption site become exhausted, the uptake rate is controlled by the rate at which the adsorbate is transported from the exterior to the interior sites of the adsorbent particles13.

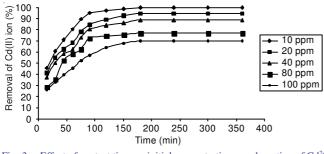


Fig. 3. Effect of contact time on initial concentration on adsorption of Cd²⁺ ion (pH = 6, Adsorbent dosage = 0.2 g/100 mL)

Influence of pH on adsorption capacity: The pH plays an important role in most adsorption processes and in the present system also the effect of this parameter was studied on the process of removal. The adsorption of cadmium was found to be maximum 99.9 % at pH 6 (Fig. 4) out of the different values of pH from 2 to 10. It was, however found to be minimum at pH 2. It is expected that the adsorbent surface in the alkaline range would favour the uptake of Cd²⁺ ion and the same has been found to be applicable in the present studies. In aqueous environments, at low pH, Cd²⁺ ions had to compete with H⁺ ions for adsorption sites on the adsorbent surface. As the pH increased, this competition weakens and more Cd²⁺ ions were able to replace H⁺ ions bound to the adsorbent surface. A similar trend of dependency of Cd²⁺ on pH was reported by Taty-Costodes et. al.14. At higher pH adsorption of Cd2+ on 4-HBTUPF decreases, this is due to precipitation of Cd²⁺ starts at pH 8.2 according to Namasivayam and Ranganathan¹⁵. Mechanism of adsorption of Cd²⁺ on the 4-HBTUPF polymer surface is given in the Scheme-II.

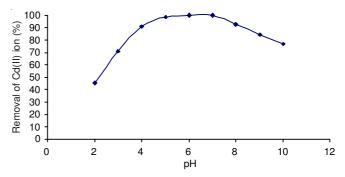
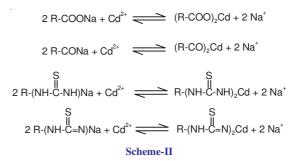


Fig. 4. Effect of pH on adsorption of Cd²⁺ ion [Concentration of Cd(II) 10 ppm, Adsorbent dosage 0.2 g/100 mL]



Effect of adsorbent dose: Effect of the adsorbent dose was studied at room temperature (30 °C) by varying the sorbent amount from 25 to 500 mg/100 mL. For all these runs, initial concentration of Cd^{2+} ions was fixed as 10 ppm. Fig. 5 shows the adsorption of limited availability of the number of adsorbing species for a relatively larger number of surface sites on the adsorbent at higher dosage of adsorbent. It is reasonable that with higher dosage of adsorbent there would be greater availability of exchangeable sites for the metal ions. The significant increase in uptake was observed when the adsorbent dose was increased from 100 to 500 mg/100 mL, any further addition of adsorbent beyond this did not cause any significant change in the adsorption. This may be due to overlapping of adsorption sites as a result of overcrowding of adsorbent particles¹⁶. The maximum removal of Cd²⁺ was

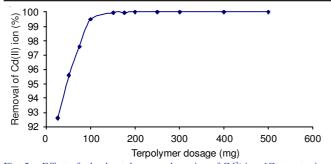


Fig. 5. Effect of adsorbent dose on adsorption of Cd²⁺ ion, [Concentration of Cd(II) 10 ppm, Adsorbent dosage 0.2 g/100 mL, pH = 6]

obtained in the adsorbent dose of 200 mg/100 mL. On considering this fact for the subsequent studies, the amount of adsorbent was taken as 200 mg/100 mL.

Adsorption isotherm: The maximum adsorption capacity of the sodium loaded terpolymer 4-HBTUPF for cadmium was investigated over a range of concentration of Cd^{2+} ion. Fig. 6 shows the plot of adsorption capacity, $q_e (mg/g)$ versus the equilibrium concentration of cadmium ions in the solution, $C_e(mg/L)$. The amount of cadmium adsorbed was found to increase with increasing cadmium concentration until the maximum adsorption capacity was achieved. Langmuir and Freundlich adsorption models can be used to describe the equilibrium between adsorbed cadmium ions and cadmium ion in solution. The Langmuir model assumes monolayer coverage of adsorbent surface and no interaction of adsorbate in the plan of the adsorbent surface. The linear form of Langmuir isotherm is given by the following equation.^{1,17}:

$$\frac{C_e}{q_e} = \frac{C_e}{Q_0} + \frac{1}{bQ_0} \tag{1}$$

where q_e is the amount adsorbed (mg/g), C_e is the equilibrium concentration of adsorbate (mg/L), Q_0 and b are Langmuir constants related to maximum adsorption capacity (mg/g) and energy of adsorption (mg/L), respectively. The values of Q_0 and b can be obtained from the intercept and slope of the plot $C_e/q_e vs. C_e$ Fig. 7.

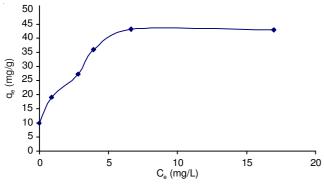


Fig. 6. Adsorption isotherm plot for cadmium adsorption by 4-HBTUPF terpolymer, (Concentration of Cd(II) 10 ppm, Adsorbent dosage 0.2 g/100 mL, pH = 6)

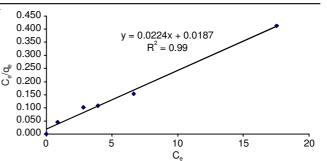


Fig. 7. Langmuir adsorption isotherm for Cd(II) adsorption by 4-HBTUPF terpolymer. (Adsorbent dosage 0.2 g/100 mL, pH = 6)

Magnitude of Langmuir constant b and the maximum adsorption capacity Q_0 was determined and shown in Table-1. The essential feature of the Langmuir isotherm can be expressed by means of R_L , a dimensionless constant referred to as a separation factor or equilibrium parameter. R_L is calculated using the following equation^{18,19}:

$$R_{L} = \frac{1}{1 + bC_0} \tag{2}$$

where, C_0 is the initial Cd^{2+} concentration (mg/L) and b is obtained from Langmuir plot. The parameter R_L indicates the shape of isotherm accordingly, as explained in Table-2. The values of R_L in the range of 0 to 1 at all initial cadmium concentrations confirm the favourable uptake of cadmium process.

TABLE-2 EQUILIBRIUM PARAMETER R _L VALUES AT OPTIMUM pH CONDITION			
Initial concentration Cd(II) ion	R _L values		
10	0.077		
20	0.040		
30	0.027		
40	0.020		
50	0.016		
60	0.013		

Freundlich equation can be described by the linearized form¹⁸:

$$\log q_e = \log K_f + (1/n) \log C_e$$
(3)

where, $K_f (mg/g)$ and N_f are the Freundlich constant of the system, indicating the adsorption capacity and adsorption intensity, respectively. The values of n and K_f can be calculated from the slope and intercept of the plot, respectively. The Freundlich equation assumes a logarithmic decrease in the enthalpy of adsorption with the increase in the fraction of occupied sites. Fig. 8 shows Freundlich adsorption isotherm obtained by plotting Log q_e versus Log C_e . The values of N_f and K_f determined from Freundlich plot are 4.81 and 24.4 mg/g, respectively (Table-1). However, the higher correlation coefficient obtained from Langmuir plot ($R^2 = 0.99$) compared to Freundlich plot ($R^2 = 0.9333$) suggested monolayer coverage of the adsorbent by cadmium ions.

TABLE-1 ADSORPTION ISOTHERM PARAMETER ADSORPTION FOR THE ADSORPTION OF Cd(II) ON SODIUM LOADED 4-HBTUPF AT OPTIMUM pH 6							
Adsorbent	Langmuir model			Freundlich method			
	$Q_0 (mg/g)$	b (L/mg)	\mathbb{R}^2	$\Delta G^{\circ} (KJ/mol^{-1})$	K_{f} (mg/g)	N _f (L/mg)	\mathbb{R}^2
Na-4HBTUPF	44.64	1.1978	0.9900	-48.02	24.3	4.81	0.9333

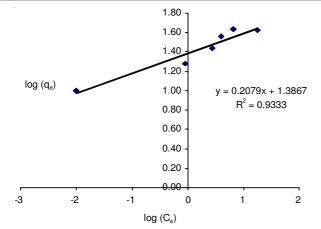


Fig. 8. Freundlich adsorption isotherm for Cd(II) adsorption by 4-HBTUPF terpolymer (Adsorbent dosage 0.2 g/100 mL, pH = 6)

Kinetic study: In order to investigate the controlling mechanism of adsorption process such as mass transfer and chemical reaction, a suitable kinetic model is needed to analyze the data. Adsorption kinetic describes the solute adsorption rate, is an important characteristic in evaluating the efficiency of adsorption. The adsorption data (at pH 5) for initial concentrations of 2, 5, 7 and 10 mg/L is shown in Fig. 9. The plot shows that kinetic of adsorption of Cd²⁺ consist of two phases; an initial rapid phase where adsorption was fast and a second slower phase where equilibrium uptake was achieved. The first phase is related to external surface adsorption and adsorption occurs instantaneously. The second phase is the gradual adsorption stage before the metal uptake reaches equilibrium. The

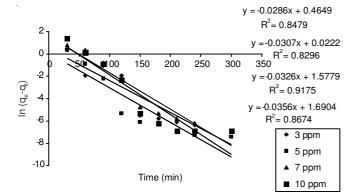


Fig. 9. Pseudo first order plot for adsorption of cadmium on 4-HBTUPF terpolymer, (Adsorbent dosage 0.2 g/100 mL, pH = 6)

The time to reach equilibrium is 180 min for all the five samples. Kinetic data were treated with the Lagergren first order model; the equation is given as follow¹⁸,

$$\ln(q_e - q_t) = \ln(q_e) - K_1 t \tag{4}$$

where, q_e and q_t are the amount of metal adsorbed (mg/g) at equilibrium and at any time *t*, respectively. Values of rate constant, K_1 , equilibrium adsorption capacity, q_e and the correlation coefficient, R^2 , were calculated from the plot $\ln(q_e-q_t)$ versus *t* (inset of Fig. 8) for all the samples (Table-3). The pseudo first order rate equation did not adequately describe the adsorption result since the correlation coefficient values, R^2 is low, the calculated equilibrium adsorption capacity q_e do not agree with experimental values (Table-3). The pseudo second order rate equation is expressed as²⁰,

$$\frac{t}{q_{t}} = \frac{1}{K_{2}q_{e}^{2}} + \frac{1}{q_{e}}t$$
(5)

The plot of t/q_t *versus* t gives a straight line; indicate the pseudo second order kinetics is applicable and q_e and K_2 can be calculated from the slope and intercept of the plot, respectively (Table-3). The plot of linearized form of pseudo second order reaction is shown in Fig. 10. Correlation coefficient R^2 for second order kinetic model is higher than first order kinetic and equilibrium adsorption capacity, q_e , values agree very well with the experimental data (Tables 3 and 4). This suggests that the adsorption of Cd²⁺ ions by 4-HBTUPF polymer follows pseudo second order model, which relies on the assumption that chemisorptions is the rate determining step^{1,21,22,25}.

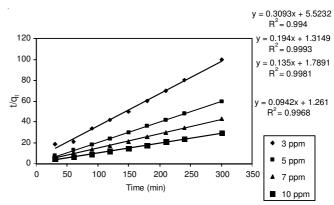


Fig. 10. Pseudo second order plot for adsorption of Cd(II) on 4-HBTUPF terpolymer (Adsorbent dosage 0.2 g/100 mL, pH = 6)

PSEUDO FIRST ORDER AND PSEUDO SECOND ORDER A KINETIC CONSTANTS AND DIFFUSION COEFFICIENT FOR THE ADSORPTION OF CADMIUM(II) ON SODIUM LOADED 4-HBTUPF AT OPTIMUM pH						
Adsorbent	Cd(II) (mg/L) —	Pseudo first order kinetic				
		$K_1(min^{-1})$	$D_{f}(cm^{2}s^{-1})$	$D_{p} (cm^{2}s^{-1})$	\mathbb{R}^2	
	3	0.0286	1.9664×10^{-8}	1.3895×10^{-10}	0.8479	
Sodium loaded	5	0.0307	3.3436×10^{-8}	1.4915×10^{-10}	0.8296	
4-HBTUPF	7	0.0326	3.4145×10^{-8}	1.5838×10^{-10}	0.9175	
	10	0.0356	3.7582×10^{-8}	1.7295×10^{-10}	0.8674	
	Cd(II) (mg/L) –	Pseudo second order kinetic				
Sodium loaded 4-HBTUPF		$K_2(mg g^{-1}min^{-1})$	$D_{f}(cm^{2}s^{-1})$	$D_{p} (cm^{2}s^{-1})$	\mathbb{R}^2	
	3	0.0173	1.3199×10^{-8}	3.4979×10^{-11}	0.9940	
	5	0.0286	1.0793×10^{-8}	4.8144×10^{-10}	0.9993	
	7	0.0102	5.1027×10^{-8}	2.4039×10^{-10}	0.9981	
	10	0.0070	5.1211×10^{-8}	2.3567×10^{-10}	0.9968	

TABLE-3

TABLE-4 RELATIVE PERCENT DEVIATION OF EXPERIMENTAL AND THEORETICAL VALUES OF PSEUDO FIRST ORDER AND PSEUDO SECOND ORDER KINETIC DATA FOR THE ADSORPTION OF CADMIUM(II) ON SODIUM LOADED 4-HBTUPF AT OPTIMUM pH

Adsorbent	Cd(II) (mg/L)	Pseudo first order kinetic			
		q_e (theo) (mg/g)	$q_e(exp)(mg/g)$	%P deviation	
Sodium loaded 4-HBTUPF	3	8.97	2.997	22	
	5	1.02	4.998	8.8	
	7	4.84	6.999	3.4	
	10	5.42	9.999	5.0	
	Cd(II) (mg/L) —	Pseudo second order kinetic			
		q_e (theo) (mg/g)	$q_e(exp)(mg/g)$	%P deviation	
Sodium loaded	3	3.26	2.997	0.97	
4-HBTUPF	5	5.15	4.998	0.33	
	7	7.41	6.999	0.65	
	10	10.62	9.999	0.69	

TABLE-5 DESORPTION OF CADMIUM(II) FROM 4-HBTUPF SURFACE WITH NaCl				
S.No	Concentration of NaCl (%)	% Recovery of Cd(II) ion from 4-HBTUPF resin surface		
1	1	93.20		
2	2	95.50		
3	3	97.70		
4	4	99.80		
5	5	99.90		
6	6	99.90		
7	7	99.91		
8	8	99.92		
9	9	99.90		
10	10	99.91		

Chemisorptions involve valency forces through sharing or exchange of electron between adsorbent and adsorbate.

Film and pore diffusion modeling for adsorption: In adsorption process of Cd²⁺ on solid surface, the Cd²⁺ species migrate towards the surface of the adsorbent. This type of migration proceeds till the concentration of the adsorbate species, adsorbed, on to the surface of the adsorbent. Once equilibrium is attained, the migration of the solute species from the solution stops. Under this situation, it is possible to measure the magnitude of the distribution of solute species between the liquid and solid phases. The magnitude of this kind of distribution is measure of the efficiency of the chosen adsorbent in the adsorbate species.

When a powdered solid adsorbent material is made in contact with a solution containing Cd²⁺, the Cd²⁺ first migrate from the bulk solution to the surface of the liquid film. This surface exerts a diffusion barrier. This barrier may be more significant or less significant²³. The involvement of a significant quantum of diffusion barrier indicates the dominant role taken up by the film diffusion in the adsorption process. Furthermore, the rate of an adsorption process is controlled either by external diffusion, internal diffusion or by both types of diffusions.

The external diffusion controls the migration of solute species from the solution to the boundary layer of the liquid phase. However, the internal diffusion controls the transfer of the solute species from the external surface of the adsorbent to the internal surface of the pores of the adsorbent material²³. It is now well established, that during the adsorption of Cd²⁺

over a porous adsorbent, the following three consecutive steps were taken place.

(i) Transport of ingoing adsorbate ions to external surface of the adsorbent (film diffusion).

(ii) Transport of the adsorbate ions within the pores of the adsorbent except for a small amount of adsorption, which occurs on external surface (particle diffusion).

(iii) Adsorption of the ingoing adsorbate ions on the interior surface of the adsorbent.

Out of these three processes, the third process is considered to be very fast and is not the rate limiting step. The remaining two steps impart the following three possibilities:

Case 1: External transport > internal transport, where the rate is governed by particle diffusion.

Case 2: External transport < internal transport, where the rate is governed by film diffusion.

Case 3: External transport = internal transport, which account for the transport of the adsorbate ions to the boundary and may not be possible within a significant rate, which later on gives rise to the formation of a liquid film surrounded by the adsorbent particles with a proper concentration gradient.

In the batch mode contact time adsorption experiment, rapid stirring was maintained. This Cd²⁺ to the transport of the adsorbed species from the solution to the pores of the adsorbent material and this step may control the rate of the adsorption process.

According to Michelson *et al.*²⁴, for film diffusion to be rate determining step, the value of the film diffusion coefficient, D_f , should be in the range 10^{-6} to 10^{-8} cm²/sec. If pore diffusion were to the limiting, the pore diffusion coefficient, D_p , should be in the range 10^{-11} to 10^{-13} cm²/sec.

In order to understand the nature of diffusion process responsible for the pore and film diffusion coefficient for various concentrations of cd(II) using the following equations²³.

$$D_{\rm p} = 0.03 * r_0^2 / t_{1/2}$$

where D_p is the film diffusion coefficient expressed in cm²s⁻¹, r_0 is radius of the sorbent expressed in cm and $t_{1/2}$ is half life period in sec.

$$D_{f} = 0.23 * r_{0} * \delta * \frac{\bar{c}}{c} / t_{1/2}$$

where D_f is the film diffusion coefficient expressed in cm² s⁻¹, δ is film thickness expressed in cm and is equilibrium loading of the adsorbent and $t_{1/2}$ is half life period in sec.

Since the adsorbent 4-HBTUPF used were of the size range (270 to 400 μ m), the film diffusion coefficients and pore diffusion coefficient were calculated. The values of D_p and D_f were calculated, It is evident from the Table-4, The adsorption of Cd²⁺ on terpolymer surface follows film diffusion process, since the coefficient values are closer to the range of 10⁻⁶ to 10⁻⁸ cm² s⁻¹.

Desorption studies: Desorption experiment were conducted to recover the Cd^{2+} from the spent terpolymer using 1 to 10 % NaCl solution. The values are shown in the Table-5. Results showed that 99.9 % of Cd^{2+} 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 terpolymer.

Conclusion

This study indicates a terpolymer synthesized by condensing 4-hydroxybenzoic acid and thiourea with *para*formaldehyde in 2:3:5 ratios are considerably efficient for removal of Cd²⁺ from aqueous solution. The adsorption is highly dependent on contact time, adsorbent dose and pH. From the above studies the following conclusions may be drawn:

• High percent removal of Cd^{2+} observed at low concentrations of Cd^{2+} ion in solutions.

• pH has prominent effect on adsorption of Cd(II) ion onto 4-HBTUPF sorbent surface with maximum removal at pH 6.

• Adsorption of cadmium was found to be fitted with Langmuir isotherm model, which suggests monolayer coverage of adsorbent surface.

• Kinetic study however obeyed pseudo-second order model, which indicates chemisorption as the rate limiting step in adsorption process.

• Adsorption of cd(II) on 4-HBTUPF showed film diffusion model.

• Since the terpolymer has been recycled efficiently with 5 % NaCl, removal of Cd²⁺ by 4-HBTUPF is economical.

ACKNOWLEDGEMENTS

The authors are thankful to The Principal, Government College of Engineering, Salem, Anna University-Chennai for providing facilities.

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