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Polymer-Grafted a Nano-TiO₂ as an Adsorbent for the Removal of Lead (II) and Mercury (II) Ions from Aqueous Solutions: Kinetic and Equilibrium **Studies**

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Abstract

The aim of present research is to removal of Pb (II) and Hg (II) heavy metal ions from aqueous solution using a nano-TiO₂-phenol-formaldehyde composite resin (TPFR). The resulting adsorbent TPFR was characterized by SEM with EDS, BET, FT-IR, XRD and TGA analyses and tested for metal adsorption. The particle size of adsorbent was 65-70 µ. The adsorption behavior of Pb (II) and Hg (II) ions from aqueous solution by TPFR was investigated as a function of some parameters such as initial metal ion concentration, contact time, dose and temperature. Adsorption equilibrium data for the removal of Pb (II) and Hg (II) ions were examined by various isotherm models. Kinetic studies indicated that Pb (II) and Hg (II) ions adsorption followed the pseudo-second-order model. The thermodynamics parameters of adsorption systems indicated spontaneous and endothermic process.

Keywords: FT-IR; TiO₂; Thermodynamics; Adsorption; Kinetics

Introduction

Pollution from heavy metal ions has become a serious problem for human health and for environment. The heavy metal ions are not biodegradable and tend to accumulate in organisms causing various diseases [1]. Due to the discharge of large amounts of metalcontaminated waste water, heavy metal ions, such as Cd, Cr, Cu, Ni, As, Pb and Zn [2] are being released as a consequence of several industrials activities like chemical manufacturing, paint pigments, plastics, metallurgy and nuclear industry [3]. Although few natural sources are concerned for lead existence, such as soil-erosion, volcanic emissions, mining, but industrial activities delivered about 90% of lead into environment, where lead-containing dust particles are significantly polluted the air as well as soils [4,5]. Because of their high solubility in the aquatic environments, heavy metals can be absorbed by living organisms. Once they enter the food chain, large concentrations of heavy metals may accumulate in the human body. The accumulation of lead in the human body causes chronic poisoning which include mental retardation to infants and kidney problem to adults [6]. Mercury has very tendency of binding with proteins and it mainly affects the renal and nervous systems [7].

Several methods and materials have been proposed and used for the removal of heavy metal ions from water namely: chemical precipitation, ion exchange, chemical oxidation/reduction, reverse osmosis, electro dialysis, and ultrafiltration. However, these techniques have inherent disadvantages, such as less efficiency, high costs, and further generation of toxic sludge or other waste products [8]. Therefore, developing cheaper, higher efficient and more environment-friendly adsorbents or technologies are attracting considerable attention of scientists.

Recently, numerous approaches have been studied for the development of cheaper and more effective technologies, both to decrease the amount of wastewater produced and to improve the quality of the treated effluent. Adsorption has become one of the alternative treatments, in recent years; the search for low-cost adsorbents that have metal-binding capacities has intensified [9]. The adsorbents may be of mineral, organic or biological origin, zeolites, industrial by-products, agricultural wastes, biomass, and polymeric materials [10].

The aim of this investigation is to evaluate the utility and the analytical efficiency of a nano TiO2-PFR composite as adsorbent in terms of selectivity and adsorption capacity of toxic Pb (II) and Hg (II) metal ions. It was systematically investigated with varying metal ion concentrations, dose, contact time and temperature. Equilibrium, kinetics and thermodynamic studies were performed to describe the adsorption process.

Materials and Methods

Materials

The chemicals used in the present study were Con. Sulfuric acid (Specific gravity = 1.82), Formaldehyde (37-40% solution) and Phenol (Density = 1.057gm-1). Titanium Dioxide (250 nm, molecular weight, 79.87) was supplied by SRL chemicals, Mumbai, India. The Mercury chloride (HgCl,, M.W. 271.50) and Lead nitrate (Pb(NO₃), M.W. 331.21) was obtained from RANKEM chemicals New Delhi, India. All the chemicals used were analytical grade. The double distilled (DD) water was used throughout the investigation.

Preparation of nano TPFR composites

Phenol and Con. Sulfuric acid (1:1) and 0.5 mg of nanoTitanium dioxide were mixed slowly with constant stirring in an ice bath. The mixture was then, heated to 70°C for three hours, cooled and kept overnight. The product was polymerized with formaldehyde solution (12 ml) in an ice bath, and then heated to 70°C for three hours and the product was cured, then ground washed with DD water, to remove the free acid. Then the sample was dried at 70°C for 16 h. Then the composite resin were sieved and preserved for characterization and further studies.

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Adsorption experiments

Batch mode adsorption studies were carried out by adding certain amount of adsorbent and 40 ml of metal ion solutions of certain concentrations, dose, contact time and temperatures in a thermo stated water bath shaker with a shaking of 200 rpm. The samples were withdrawn from the shaker at predetermined time intervals and solutions were separated from the adsorbent by centrifugations at 4000 rpm for 5 min. To determine the residual metal ion concentration, the absorbance of the supernatant solution was measured before and after treatment using atomic absorption (Elico SL-173) spectrometry at wavelength of 283.3 253.7 nm for Pb (II) and Hg (II) respectively. Experiments were carried out twice and the concentrations given were average values. The initial metal ion concentrations in the test solution and the contact time were varied to investigate their effect on the adsorption kinetics. The pH of the metal ion solution was adjusted by using NaOH or HCl solution and a pH meter. The adsorption studies were carried out at different temperatures (308, 313K and 318K). This was used to determine the effect of temperature on the thermodynamic parameters.

The amount of adsorption in batch experiments and adsorption efficiency were calculated as follows:

$\mathbf{q} = (\mathbf{C}_{a} - \mathbf{C}_{a}) \mathbf{V} / \mathbf{m}$	(1)
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Efficiency (%) = $(C_o - C_e) / C_o \times 100$ (2)

Where C_0 is the initial concentration (mg/L)

C_e is the equilibrium concentration (mg/L)

- V is the volume of solution (mL)
- m is the mass of adsorbent (g)
- q is the amount of adsorbed (mg/g)

Desorption experiments

Desorption of metal ions was performed by mixing TPFR-metal complexes and HCl eluent solutions of different concentrations, and stirred at 200 rpm for 12 h at room temperature. The final metal ion concentrations in the aqueous phase were similarly analyzed as described above. The desorption ratio (E) was calculated as follows:

$$E(\%) = C_{d} V_{d} / (C_{o} - C_{o}) \times 100$$
(3)

Where, E is the desorption ratio,

Cd is the concentration of the solutes in the desorption solutions,

Vd is the volume of the desorption solution and

Co, Ce and V are the same as defined above.

Results and Discussion

Effect of adsorbent activity

The activity of adsorbent for the adsorption of Pb (II) and Hg (II) was studied with an initial concentration of 20 ppm, adsorbent dose of 0.200 g and contact time of 120 min and the results were displayed in Figure 1. Noticeably as shown in the figure, the order of adsorption activity for the removal of Pb (II) and Hg (II) was TPFR > PFR > TiO₂. TPFR composite resin exhibited higher adsorption activity (68.1% & 91.5%) than PFR resin (33.5% & 27.6%) and TiO₂ (12.6% & 22.8%) of Pb (II) and Hg (II) respectively. TPFR composite resin had high removal efficiency than PFR resin and TiO₂ due to high surface area and more exposed active sites resulted in high metal ion adsorption.

B.E.T: The surface area of TPFR was determined by nitrogen sorption measurement. The surface area of TPFR was 23.65 m^2/g . The average pore radius of TPFR was 9.90 nm and total pore volume was 0.11 cm³/g shown in Figure 2. The relative adsorption performance of different adsorbent is highly dependent on the internal pore structure of each material. With the increase of pore radius, more adsorbate is easier to be adsorbed. Therefore, carbon activation offered some attractive advantages. It is not only able to increase the surface area and average pore radius but also reinforce the chemical strength of adsorbents in acidic medium.

FTIR: FTIR spectra of the TiO₂, TiO₂-PFR, TPFR-Pb (II) and TPFR-Hg (II) were shown in Figure 3. The main bands observed in the IR spectra of TiO₂, Figure 3a, showed only one major peak observed at 433.8 cm⁻¹, this band corresponding to TiO₂. Figure 3b showed the FTIR spectrum of TPFR. The absorption peak at 3392.7 cm⁻¹ indicated the presence of OH groups on the surface of TPFR. The characteristic bands at 1631.7 cm⁻¹ and 1020 cm⁻¹ correspond to the C=C and





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C-O-C stretching vibrations. The bands at 1463.9 and 869.9 cm⁻¹ were attributed to the C=C and C-H stretching in the aromatic ring, respectively. FTIR data of TPFR-Pb showed that characteristic band at 3558.3, 1613.8, 1450.3 and 1123.4 cm⁻¹ correspond to the OH, C=C, C-H and C-O-C stretching vibrations respectively (Figure 3c). Figure 3c indicated that mostly the bonded OH groups, C=C stretching, C-H bending vibrations and C-O-C vibrations were involved in Pb (II) ion adsorption. There were clear band shifts and intensity decrease in Figure 3c. These findings suggest that there is attachment of Pb (II) on the TPFR.

FTIR data of TPFR-Hg showed that characteristic bands at 3738.1, 3043.5, 1703.2, 1515 and 1205 cm⁻¹ corresponding to OH, =C-H, C=O and C=C stretching vibrations respectively (Figure 3d). The two new peaks were observed at 3043.5 and 1703.2 cm⁻¹ which revealed the adsorption of Hg (II) onto TPFR.

XRD: The XRD patterns as shown in Figure 4 were performed to analyze the crystalline nature. The characteristic 15°-30° peaks of TPFR are discernible in carbon; these indicate that they are amorphous carbon.

SEM: Figure 5 showed the SEMs of TPFR, TPFR-Pb (II) and TPFR-Hg (II) ions. However, the particles of TPFR (Figure 5a) had a rough surface with heterogeneous holes and pores that make a large surface area, which indicated that metals can be adsorbed onto its surface. Figures 5b and 5c showed micrographs of the TPFR surface after adsorbed Pb (II) ions and Hg (II) ions, the surface of TPFR was relatively smoother and less porous because of the formation of a layer over the adsorbent surface after adsorption of metal ions.

EDX: Further confirmation of the adsorption of Hg (II) and Pb (II) on TPFR composite was done by energy dispersive X-ray analysis (EDS). Figure 6a for the unloaded TPFR, did not show any characteristic signal for metal ions, but only showed for the four major constituents, i.e., C, O, Ti and S. Whereas for Hg (II) and Pb (II) loaded TPFR (Figures 6b and 6c) signals of presence of Hg(II) and Pb (II) were observed. This showed the diffusion or accumulation of metal ions onto the surface of TPFR.

TGA: The TGA thermo grams for the TPFR samples were shown in Figure 7. The thermo gravimetric profile revealed that the mass

loss occurs in three stages. The first weight loss about 12.32% in the temperature range 50-129°C, which may be the combined water existed in TPFR composite. The second weight loss occurred in the temperature range 129-426°C, a typically high enough temperature to induce thermal degradation of ordinary carbon polymers which about 37.74%. The final weight loss was determined above 426-700°C, which





Figure 5: The SEM images of (a) TPFR (b) PFR-Pb (II) (c) TPFR-Hg (II).



100

90

80



Hg(II)

Pb(II)

60



about 17.7%. Finally, no mass loss was detected when the temperature was increased to 700°C. This result indicated that the TPFR are stable at higher temperature. The char residue of PTFR content was 33.6%.

The characterization results confirmed that the formation of the adsorbent TPFR occurred successfully.

Effect of initial concentrations

Effect of initial lead and mercury ion concentration was studied at different initial metal ion concentrations in the range of 20 -60 mg/L at 298 K with 0.200 g TPFR at 180 min. The percentage of Pb (II) and Hg (II) ions adsorption at different metal concentrations using TPFR, decreased with increase in metal ion concentration. This may be due to saturation of active adsorption sites onto TPFR. The effect of initial concentration on the removal of Pb (II) and Hg (II) by the adsorbent was indicated in Figure 8.

Effect of contact time

The effect of contact time on the adsorption of Pb (II) and Hg (II) at 20 mg/L. The Pb (II) and Hg(II) adsorption increased with increasing the contact time, the maximum removal of both lead and mercury ions occurred at 180 min, after which there were no significant changes. The equilibrium was reached at 240 min for the both metal ions. Following this, the adsorption rate was uniform as there was no significant change in adsorption with the increasing time. The initial fast adsorption is due to the availability of more active sites and more functional groups which participate in the lead and mercury uptake till equilibrium is attained and thereafter, there was no further adsorption. All the results were presented in Figure 9.

Effect of adsorbent mass

The effect of adsorbent dosage on lead and mercury removal was studied by varying the amount TPFR between 0.050-0.250g. It is evident from Figure 10, that the removal of lead and mercury was increased with increase in TPFR dose until a constant value was achieved. That is, the percentage removal increased from 41.8% to 98.3% for lead and mercury was increased from 58.6% to 71.3% as the TPFR adsorbent. This can be associated with higher available surface area and more available sorption sites at higher sorbent doses. The optimum adsorbent dosage was found to be 0.250 g for lead and mercury. The adsorption







efficiency of both lead and mercury was observed at 98.3% and 71.3% respectively.

Adsorption isotherms

The adsorption isotherm shows how the adsorbate molecules are distributed between the liquid phase and solid phase. The analysis of the isotherm data by fitting them to different isotherm model is an important step to find the suitable model that can be used for design purposes.

The Langmuir model [11] assumes that the uptake of Pb (II) and Hg (II) ions occurs on a homogeneous surface by monolayer adsorption without any interaction between adsorbed ions. The linear form of Langmuir isotherm is given by:

$$\frac{C_e}{q_e} = \frac{1}{K_L \times q_m} + \frac{C_e}{q_m}$$
(4)

Where, q_m is the maximum adsorption capacity, KL is the Langmuir bonding energy coefficient. The K_L and q_m can be calculated from the intercept and slope of the linear plot of C_e/q_e against C_e shown in Figure 11.

It is obvious that the Langmuir adsorption isotherm is more suitable to describe the adsorption equilibrium (R2 > 0.975). Therefore, monolayer coverage of Hg (II) on TPFR particles is assumed with the maximum adsorption capacity of 20.83 mg/g.

According to [12], the essential characteristics of Langmuir isotherm can be explained in terms of dimensionless constant separation factor (RL), which is defined by following equation:

$$\mathbf{R}_{\mathrm{L}} = 1/1 + \mathbf{K}_{\mathrm{L}} \mathbf{C}_{\mathrm{o}} \tag{5}$$

Where, KL (L/mg) is the Langmuir constant related to the energy of adsorption and Co (mg/L) is the initial concentration of both Pb (II) and Hg (II) ions. The RL value indicates the type of the isotherm to be either unfavorable (RL>1), linear (RL=1), favorable (0<RL<1), irreversible (RL=0). It is clear from that all RL values lies between 0 and 1 indicating the favorable sorption of Pb (II) and Hg (II) ions by the TPFR.

The Freundlich isotherms is an empirical equation and is one



of the most widely used isotherms for the description of multi-site adsorption. The linear form as follows:

$$\log q_{e} = \log K_{F} + 1/n \log C_{e}$$
(6)

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Where, 'KF' and 'n' are the Freundlich isotherm constants indicating the adsorption capacity and adsorption intensity, respectively [13,14]. The KF and n can be calculated from the intercept and slope of the linear plot of log q_e against log C_e . The value of n >1 indicates (2.5 and 1.492) favorable and heterogeneous adsorption of Pb (II) and Hg (II) onto TPFR. Both the metals did not follow the Freundlich isotherm as closely as the Langmuir isotherm.

Temkin isotherm models assume that the fall in the heat of sorption is linear rather than logarithmic. The data were analyzed according to the linear form of the Temkin model [15].

$$\mathbf{q}_{e} = \mathbf{B}_{1} \ln \mathbf{K}_{T} + \mathbf{B}_{1} \ln \mathbf{C}_{e} \tag{7}$$

The isotherm constants B_1 and K_r are related to the maximum binding energy and heat of adsorption. The B_1 and K_r can be calculated from the intercept and slope of the linear plot of q_e against ln C_e .

The Freundlich and Langmuir isotherm models could not elucidate clearly the type of biosorption behavior (physical or chemical). So, the equilibrium data were further tested by the D-R model using the following equation [16].

$$\ln q_e = \ln q_m - \beta \epsilon^2 \tag{8}$$

Where, β a constant related to the adsorption energy (mol²/kJ²), q_m is a constant that indicates the sorption degree characterizing the sorbent (mg/g) and ϵ is the Polanyi potential shown in Eq.8:

$$\boldsymbol{\varepsilon} = \operatorname{RT} \ln \left(1 + 1/C \right) \tag{9}$$

The biosorption type based on the D-R model can be predicted by the mean free energy (kJ/mol) employing Eq.10 [17]:

$$\mathbf{E} = 1/(2\beta)^{1/2} \tag{10}$$

The magnitude of E may characterize the type of the adsorption as chemical ion exchange (E=8-16 kJ/mol), or physical adsorption (E<8 kJ/mol). The mean free energy of adsorption for the present study was found to be 0.42 kJ/mol for Pb (II) and 9.208 kJ/mol for Hg (II). This implies that, the adsorption of Pb (II) on TPFR may be considered as physical adsorption process, the Hg (II) was chemical adsorption process.

The Jovanoic isotherm [18], which is based on the same assumptions of the Langmuir isotherm, also considers the possibility of some mechanical contacts between the adsorbing and desorbing molecules on the homogeneous surface and can be represented in a linear form as follows:

$$\ln qe = \ln q_m + K_1 C_e \tag{11}$$

Where, q_m is the maximum amount adsorbed (in mg/g) and KJ (in L/mg) is the constant related to the energy of adsorption. The q_m and K_J can be calculated from the intercept and slope of the linear plot of $\ln q_e$ against C_e (Figure 12).

To understand the adsorption equilibrium behavior, five isotherms, namely Langmuir, Freundlich, Temkin, D-R and Jovanoic isotherm models were tested, and the Table 1 summarized the isotherm parameter values. The best fitted models were selected on the basis of coefficient Langmuir isotherm and Jovanoic isotherm model. The Langmuir isotherms were best fit model for the adsorption of Hg (II);



Figure 12: Jovanoic isotherm plots for the adsorption of Pb(II) and Hg(II) onto TPFR.

Mathematical models	Parameters	Pb(II)	Hg(II)
Langmuir isotherm	R ²	0.881	0.974
	K	39.46	15.74
	q _m (mg/g)	23.25	20.83
	R ²	0.831	0.942
Freundlich isotherm	K _F	388.1	292.4
	n	2.5	1.492
	R ²	0.922	0.956
Temkin isotherm	B ₁	17.76	25.68
	Κ _T	84.61	108.3
	R ²	0.935	0.954
D-R isotherm	β	2.752	0.005
	q _m (mg/g)	188.01	30.75
	E kJ/mol	0.426	9.208
Jovanoic isotherm	K _J (L/mg)	4.33	4.53
	q _m (mg/g)	4.37	4.347

Table 1: Different adsorption isotherm model parameters for the adsorption of Pb(II) and Hg(II) on PTFR.

the maximum adsorption capacity of Hg (II) was 20.83 mg/g. The Jovanoic isotherm model well described in Hg (II) onto TPFR. The maximum amount adsorbed was 4.347 mg/g for Hg (II).

Kinetic Studies

In order to investigate the mechanism and to determine the rate controlling step of adsorption of Pb (II) and Hg (II) on TPFR, kinetic models were used. The rate constants

were calculated by using pseudo-first-order and pseudo-secondorder kinetic models and the rate controlling step was determined by intra-particle diffusion model.

Pseudo-first-order model

The pseudo-first-order kinetic model was described by Lagergren [19] and might be represented by Eq. 12:

$$\mathbf{l}_{n} \left(\mathbf{q}_{e} - \mathbf{q}_{t} \right) = \ln \mathbf{q}_{e} - \mathbf{k}_{1} \mathbf{t}$$
(12)

Where, $q_e (mg/g)$ and $q_t (mg/g)$ are the adsorption capacity at equilibrium and time t (min), respectively; k1 (min⁻¹) is the rate

constant of pseudo-first-order kinetic model. Values of k_1 and q_e can be obtained from the slope and intercept of the plot ln (q_e-q_e) versus t.

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Pseudo-second-order model

The linear form of pseudo-second-order kinetic model was expressed by Eq. 13 [20]:

$$\frac{t}{q_{t}} = \frac{1}{k_{2} \times q_{e}^{2}} + \frac{t}{q_{e}}$$
(13)

Where, k_{2} (g/mg/min) is the second-order rate constant of adsorption.

The plot of t/qt versus t shows a linear relationship. Values of k_2 and equilibrium adsorption capacity qe were calculated from the intercept and slope of the plot shown in Figure 13.

Intra-particle diffusion model

For a solid-liquid adsorption process, the solute transfer is usually characterized by external mass transfer, or intra-particle diffusion, or both. The intra-particle diffusion model proposed by Weber and Morris [21] was used to identify the mechanism involved in the adsorption process:

$$\mathbf{q}_{t} = \mathbf{k}_{id} \mathbf{t}^{0.5} + \mathbf{C} \tag{14}$$

Where, kid (mg g-1min-0.5) is the rate constant of the intra-particle diffusion model and C (mg/ g) reflects the boundary layer effect. The kid and C can be determined from the slope and intercept of the linear plot of q_t against t^{0.5}.

The pseudo-first-order, pseudo-second-order and intra-particle diffusion models were used to understand the kinetic nature of Pb (II) and Hg (II) onto TPFR adsorption system. All the values were presented in Table 2. All the experimental data showed better agreement with pseudo-second-order model in terms of higher correlation coefficient value ($\mathbb{R}^2 > 1$), which suggested the adsorption rate of Pb (II) and Hg (II) onto TPFR might be controlled by chemisorptions mechanism. The rate controlling step consisted valence forces through sharing or exchange of electrons between the adsorbent surface and adsorbate ions and no involvement of mass transfer in solution [22]. The value of pseudo- second-order rate constant, k_2 , was 0.032 g/mg/min for Pb (II) was and 0.891 g/mg/min for Hg (II).



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Mathematical models	Parameters	Pb(II)	Hg(II)	
First-order kinetics	R ²	0.711	0.749	
	k1 (min ⁻¹)	0.009	0.018	
	q _e (mg/g)	72.74	30.41	
Second-order kinetics	R ²	0.97	1	
	k ₂ g/mg/min	0.032	0.891	
	q _e (mg/g)	44.64	76.33	
Intra-particle diffusion	R ²	0.851	0.960	
	k _{id} g/mg/min ^{1/2}	1.380	1.882	
	C (mg/g)	18.7	73.28	

Table 2: Kinetic parameters for the adsorption of Pb(II) and Hg(II) on PTFR.

Effect of Temperature and Thermodynamic dData

The adsorption tests were performed by batch technique in single system at 308K, 318K, and 328K, respectively. For kinetic studies, a series of 250ml flask were used and each flask was filled with TPFR at mass loadings 0.200g for both Pb (II) and Hg (II) solution at 20 ppm metal solutions. The percentage removal of Pb (II) and Hg (II) are presented in Figure 14.

Thermodynamic parameters, such as changes in Gibbs free energy (ΔG°), enthalpy (ΔH°) and entropy (ΔS°) are the actual indicators for practical applications. Adsorption thermodynamics was evaluated with respect to different temperatures (308K, 318K and 328K). The thermodynamic parameters were calculated by the following equations [23]:

$$K_{L} = \frac{q_{e}}{C_{e}}$$
(15)

Where, K_L is the Langmuir constants; C_e is the concentration of solute adsorbed on the resin at equilibrium, mg/ L.

$$\Delta G^{\circ} = -RT \ln K_{r} \tag{16}$$

The change in enthalpy (ΔH°) and entropy (ΔS°) was determined from the slope and intercept of van't Hoff plot of ln K_L versus 1/T plot (Figure 15), according to the following equation:

$$\ln K_{\rm L} = \frac{\Delta S^{\rm o}}{R} - \frac{\Delta H^{\rm o}}{RT}$$
(17)

Where, R is the gas constant (8.314 J/mol K), T is the temperature (in K). The correlation coefficient for the linear plot for Pb (II) and Hg (II) was R2=0.883 and R2=0.991 respectively. Values of the standard Gibbs free energy change for the adsorption process obtained from Eq. (16) were listed in Table 3.

The negative values of ΔG° at all temperatures indicated the spontaneous nature of the adsorption of Pb (II) and Hg (II) on TPFR. In Hg (II), ΔG° was negative and increased towards negative side with rise in temperature, indicating the adsorption process to be spontaneous in nature without any induction period and more favorable at higher temperature.

The standard enthalpy and entropy changes of adsorption determined from the Eq. (17) were 27.25 kJ/ mol and 101.9 J/mol/K for Hg (II), 2.13 kJ/ mol and 36.22 J/mol/K for Pb (II), respectively. The positive value of Δ H° suggests the endothermic nature of adsorption. The positive value of Δ S° confirmed the increased randomness at the solid-solute interface during adsorption process, which suggests that Pb (II) and Hg (II) ions replace some water molecules from the solution previously adsorbed on the surface of adsorbent. These displaced molecules gain more translation entropy than lost by the adsorbate ions, thus allowing the prevalence of randomness in the system [24].

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Desorption Studies

Whether an adsorbent is an appropriate material in removal of metal ions from aqueous solutions depends not only on its adsorptive capacity, but also on its regeneration ability. For repeated use of an adsorbent, adsorbed metal ions should be easily desorbed under suitable conditions. In this work, desorption of metal ions with various concentrations of eluent solution was carried out. The results showed that the elution ratio is different under various eluent concentrations. Maximum recovery of Hg (II) and Pb (II) at 100%, was achieved with 2 and 3M HCl eluent solutions, respectively. In order to show the reusability of the adsorbent, adsorption-desorption cycle of metal ion was repeated five times by using the same beads. The adsorption capacities for the TPFR resin did not noticeably change (only a maximum 5% change was observed) during the repeated adsorptiondesorption operations. This can be attributed to decomposition effect of HCl used as stripping agent on adsorbent. These results show that the TPFR resin has good regeneration ability (Figure 15).



Metal ions	R ²	ΔH° J/mol	ΔS° J/mol K	-ΔG°(kJ/mol) ×102		
				308K	318K	328K
Hg(II)	0.991	27.25	101.9	41.80	50.67	62.24
Pb(II)	0.883	2.13	36.22	88.74	96.96	95.79

Table 3: Thermodynamic parameters for the adsorption of $\mathsf{Pb}(\mathsf{II})$ and $\mathsf{Hg}(\mathsf{II})$ on TPFR.





Conclusion

The present study reported the mechanism of adsorption of Hg (II) and Pb (II) onto nanoTPFR prepared via polymerization method. Adsorption of the metal ion was dependent on metal ion concentration, contact time, dose and temperature. The Langmuir and Jovanoic model provided the best fit for the Hg (II) ion, revealing the maximum adsorption capacity of 20.83 mg/g and 4.347 mg/g respectively. The lower values of RL and n < 1 indicated that the adsorption process was favored for nanoTPFR.

Adsorption of Hg (II) and Pb (II) ions was shown to be dependent on the dose and the optimum dose for the better adsorption was found to be 0.200 g for both metal ions. Kinetic studies demonstrated that the mechanism for adsorption of metal ions followed the pseudo-secondorder rate model, which provided the best fit for the both metal ion.

The thermodynamic studies revealed that the adsorption is spontaneous and endothermic for Hg (II) and Pb (II) ions onto nanoTPFR. The positive entropy indicated increase in the degree of freedom for the adsorbed species and suggests that there is an increase in the concentration of adsorbate in solid-solution interface.

References

- Inglezakis VJ, Loizidou MD, Grigoropoulou HP (2003) Ion exchange of Pb(2+), Cu(2+), Fe(3+), and Cr(3+) on natural clinoptilolite: selectivity determination and influence of acidity on metal uptake. J Colloid Interface Sci 261: 49-54.
- 2. Barakat MA (2011) New trends in removing heavy metals from industrial wastewater. Arabian Journal of Chemistry 4: 361-377.
- Quintelas C, Rocha Z, Silva B, Fonseca B, Figueiredo H, et al. (2009) Removal of Cd(II), Cr(VI), Fe(III) and Ni(II) from aqueous solutions by an E. Coli biofilm supported on kaolin. Chem Eng J 149: 319-324.
- Siegel FR (2002) Environmental geochemistry of potentially toxic metals. Berlin Springer-Verlag 218.
- Spiro TG, Stigliani WM (2002) Chemistry of the environment, Upper Saddle River, NJ Prentice- Hall 356.
- Kawasaki N, Bun-el R, Ogata F, Nakamura T, Tanei S, et al. (2006) Water treatment technology using carbonaceous materials produced from vegetable biomass, Journal of water and environmental technology 4: 73-82.
- Denizli A, Senal S, Alsancak G, Tuzmen N, Say R (2003) Mercury removal from sunthetic solutions using poly(2-hydroxy ethylmethacrylate) gel beads modified with Poly(ethyleneamine). Reactive and Functional polymers 55: 121-130.

 Ahluwalia SS, Goyal D (2005) Removal of heavy metals from waste tea leaves from aqueous solution. Eng Lite Sci 5: 158-162.

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- Laung WC, Wong MF, Chua H, Lo W, Leung CK (2000) Removal and recovery of heavy metals by bacteria isolated from activated sludge treating industrial effluents and municipal waste-water, Water Sci. Technol, 41: 233-240.
- Kurniawan TA, Chan GY, Lo WH, Babel S (2006) Comparisons of low-cost adsorbents for treating wastewaters laden with heavy metals. Sci Total Environ 366: 409-426.
- Langmuir I (1918) The adsorption of gases on plane surfaces of glass, mica and platinum, Journal of American chemical society 40: 1361-1403.
- Hall KR, Eagleton LC, Acrivos A, Vermevlen T (1966) Pore and Solid diffusion kinetics in fixed bed adsorption under constant pattern conditions. Indian Engineering & chemistry Fundamentals 5: 212-219.
- Febrianto J, Kosasih AN, Sunarso J, Ju YH, Indraswati N, et al. (2009) Equilibrium and kinetic studies in adsorption of heavy metals using biosorbent: a summary of recent studies. J Hazard Mater 162: 616-645.
- Ngah WSW, Endud CS, Mayanar R (2002) Removal of copper (II) ions from aqueous solution onto chitosan and cross-linked Chitosan beads. React Funct Polym 50: 181-190.
- 15. Temkin MJ, Pyzhev V (1940) Kinetics of ammonia synthesis on promoted iron catalysts. Acta Physiochim URSS 12: 217-222.
- Dubinin MM, Radushkevich LV (1947) Equation of the characteristic curve of activated charcoal. Proc Acad Sci USSR 55: 331-333.
- Foo KY, Hameed BH (2010) Insights into the modeling of adsorption isotherm systems. Chem Eng J 156: 2-10.
- Jovanoic DS (1969) Physical adsorption of gases I. Colloid and Polymer science 235I: 1203-1214.
- Lagergren S (1898) About the theory of so-called adsorption of soluble substance, K. Svenska Vetenskapsakad Handl 24: 1-39.
- 20. Ho YS, Mckay G (1998) The kinetics of sorption of basic dyes from aqueous solution by sphagnum moss peat Can J Chem Eng 76: 822-827.
- Weber Jr WJ, Morris JC (1963) Kinetic of adsorption on carbon from solution. J Sanit Eng Div Am Soc Civ Eng 89: 31-60.
- Ho YS, Mckay G, Wase, Forster CF (1963) Study of the adsorption of divalent metal ions onto peat, Adsorption science and Technology Am Soc Civ Eng 89: 31-60.
- Biswas K, Saha SK, Ghosh VC (2007) Adsorption of fluoride from aqueous solution by a synthetic iron(III) aluminum(III) mixed oxide. Ind Eng Chem Res 46: 5346- 5356
- Malkoc E, Nuhoglu Y (2007) Determination of kinetic and equilibrium parameter of the batch adsorption of *Quercus itnaburensis*. Chemical Engineering Process 46: 1020-1029.