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RESEARCH ARTICLE

STUDIES ON THE REMOVAL OF Cd (II), Hg (II), AND Bi (III) METAL IONS USING NANO Fe₂O₃ COMPOSITE MICRO RETICULAR RESINS

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ABSTRACT

Phenol-Formaldehyde resin (PFR) grafted Nano-Fe₂O₃ (nFe₂O₃) was fabricated for Bi(III), Hg(II) and Cd(II) removal using a novel polycondensation method. The present materials were carefully examined by FT-IR spectra (FT-IR), Scanning electron microscope (SEM), energy-dispersive microanalysis (EDX), and thermo gravimetric analysis (TGA). PFR-nFe₂O₃ showed excellent uptake effects for Bi(III), Hg(II) and Cd(II) removal with a pseudo-second order model. The Freundlich models well described the equilibrium isotherm than the Langmuir model. Thermodynamic parameters showed that adsorptions were feasible, spontaneous and endothermic. These suggested that both electrostatic adsorption and chemisorptions were involved. The results indicated that PFR-nFe₂O₃ could well be used as a high performance sorbent for the heavy metal ions removal from aqueous solution with a list of Bi(III), Hg(II) & Cd(II) ions.

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INTRODUCTION

Water pollution with heavy metals are a very important problem all over the world. Nickel, Bismuth, lead and cadmium are typical widespread heavy metal pollutants in the natural water environment. The main anthropogenic pathway which Bismuth, lead and cadmium entering environment is via wastes from industrial processes such as electroplating, alloy manufacturing, pigments, batteries and textile operations [1-8]. Nickel entering body could cause cancers of the lungs, nose and bone [1-2]. Cadmium entering body could cause serious damages of the kidneys, lungs, bones and hypertension [4-5]. Lead could cause brain damage in children even at extremely low concentration [6-9]. The conventional methods for heavy metal removal from water and wastewater include oxidation, reduction, precipitation, membrane filtration, ion exchange and adsorption [1]. Among these methods, adsorption is highly effective and economical. Many adsorbents such as various activated carbon [1-8,10-14], agricultural waste including chitosan, orange peel and various hell, barley straw and grape bagasse [15]; industrial products including lignin, waste slurry, silica gel [16-17], polymeric ion exchange resins [18] and polymeric chelating resins [19-25]; natural materials including zeolites, clay and lignite, [16,26] have been used for the heavy metals removal.

Among these materials, the low-cost adsorbents such as agricultural waste, industrial waste slurry and natural materials are unquestionable interesting compared to expensive commercial activated carbon due to higher the quality. While polymeric chelating resins such as chemically modified melamine chelate resins with functional groups of sulfur and nitrogen donor atoms are very efficient for heavy removal of Fe(II), Fe(III), Cr(III), Cr(VI), Cu(II), Ag(I) and Ni(II) with a high selectivity [19-25,27,28]. The importance of chelating resins are usually greater than carbonaceous adsorbents with good selectivity to metal ions, make them very attractive candidates for heavy metal removal, but the expensive costs at capital and operation limit the application in industrial scale. To decrease capital expense, various cheaper activated carbons derived from agricultural waste such as coconut shell charcoal, pecan shells, hazelnut shell, rice husk and almond husk was utilized to the heavy metal removal in decades [14, 29, 30]. For example, the adsorption capacities of Ni(II) were 10.11 and 62.5 mg g⁻¹ at hazelnut shell and coir-pith activated carbon [14,30]. Moreover, rice husk and hazelnut shell activated carbon could be used to other heavy metal removal including Cr(VI), Cu(II), Hg(II) and Zn(II) [14,15]. Further these activated carbons have been treated by various methods to enhance sorption capacity or selectivity. They were respectively treated by inorganic acid for Cr(III), Cu(II), Ni(II) and Cd(II) removal [1,2,4], ethylenediamine and triethylenetetramine for Cd(II), Cr(III), Fe(III) and Pb(II) ions

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adsorption [7], amine for Cu(II) uptake [11], sulfurized steam for Pb(II) and Hg(II) removal [12].

From above facts, it always is significant to develop low-cost and high effective activated carbon materials in terms of the heavy metal ions removal. In this work, PFR resin grafted nFe₂O₃ (PFR-nFe₂O₃) was fabricated using a novel polycondensation method. The adsorption behaviors of Bi(III), Hg(II) and Cd(II) ions were investigated at PFR-nFe₂O₃ using batch methods in detail. To perform this study the experimental tests carried out were SEM, nitrogen adsorption isotherms, FT-IR, XRD, E-dax and TGA and aqueous solutions adsorption isotherms of the heavy metals.

2. Materials and Methods

2.1. MATERIALS

Phenol and formaldehyde used were Fischer reagents (India). LR grade of Conc. H₂SO₄ was used. The other chemicals and reagents were of chemically pure grade (AnalaR) procured from SD Fine Chemicals, India.

2.2. METHODS

Phenol (10 mL) and Conc. H₂SO₄ (11.5 mL) were blended gradually with continuous stirring and cooling, heated to about 70 °C on a hot water bath for 6 h, cooled directly in the ice-cold water and set aside overnight [31]. 2 % and 0 % nFe₂O₃ was mixed to phenol sulphonic acid and these constitute samples labeled as PFR-nFe₂O₃ and PFR. This mixture was polymerized with formaldehyde (12.5 mL) at 70 °C and treated at this temperature for 3 h to yield a dark brown chunky mass. It was subsequently ground, cleaned with distilled water and finally with double distilled (DD) water to remove excess free acid, dried, sieved (250– 300 μm) using Jayant sieves (India) and preserved for characterization [32].

2.3. Characterization of the samples

FT-IR (SHIMADZU MODEL FT-IR spectrometer) spectra was used to the study the before and after heavy metal ions adsorption on resins using the IR-grade KBr pellets in the ratio of 1:200 at the wave number ranging from 400 to 4000 cm⁻¹. The morphology of free and heavy metal ions loaded resins were studied by SEM (Vega3 Tescan SEM instrument). For studying the elemental constitute of free and heavy metal ions loaded of adsorbent, X'Pert Pro Materials Research diffractometer system and EDX (Bruker machine) were used. The thermal degradation of the free and heavy metal ions treated resins were found out using TGA (SII MODEL 6000 thermal analyzer).

2.4. Batch studies

Batch adsorption experiments were carrying out by introducing a preferred amount of PFR and PFR-nFe₂O₃ resin in 250 mL glass bottles separately containing heavy metal ion solutions of various concentrations (0.01M-0.05M). The mixtures were stirring at 200 rpm using a Remi rotator water bath shaking machine at 303 K to attain the equilibrium. The agitation time was varied from 10 to 60 min in the succeeding periods like

10, 20, 30, 40, 50 and 60 min at 303 K to find the equilibrium. The residual concentration of the heavy metal ions in the aqueous medium was determined by using standard titration techniques as per the literature [33]. The equilibrium adsorption capacity (q_e) of the adsorbents was estimated with the help of following equation:

$$q_e = (C_o - C_e) \times V / M \quad \text{----- (1)}$$

Where q_e is the equilibrium adsorption capacity (mg g⁻¹), C_e is the concentration of metal ion (mg L⁻¹) at equilibrium, V is the volume of solution (L) and M is the weight (g) of adsorbent.

2.5 Specific surface area and pore properties of Resins

The specific surface area and pore structure of the carbon samples were determined by N₂ adsorption-desorption isotherms at 77 K (Micrometrics ASAP 2020 system) after being vacuum-dried at 100°C overnight. The specific surface areas were calculated by the conventional BET (Brunauer–Emmett–Teller) method. The pore size distribution (PSD) plots were recorded from the adsorption branch of the isotherm based on the Barrett–Joyner–Halenda (BJH) model.

3. RESULTS AND DISCUSSION:

3.1. Characterization of PFR and PFR-nFe₂O₃

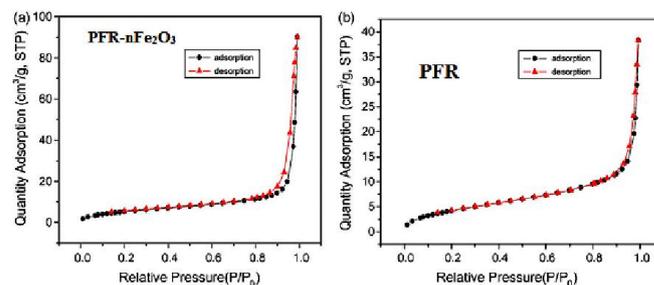


Fig.1. N₂ adsorption–desorption isotherms of PFR and PFR-nFe₂O₃

An abrupt increase in nitrogen volume adsorbed at higher P/P_0 suggested a quite large contribution in micropore and macropore range in the both resins. Micropore surface area is extremely small and tends to zero which is preferred from the metal ion adsorption point of view. In the entire region of relative pressure, the nitrogen volume adsorbed by PFR was smaller than that by PFR-nFe₂O₃, testifying a lower porosity for PFR. Both the isotherms have the characteristic feature of the type IV isotherm with almost the same inflection points around $P/P_0 = 0.9$ and hysteresis loops, indicating that the pore shape of the resins was similar, that is, the pores had not been destroyed significantly during the reaction.

The FT-IR spectra of the PFR-nFe₂O₃, Bi (III) – PFR-nFe₂O₃, Hg (II) – PFR-nFe₂O₃ and Cd (II) – PFR-nFe₂O₃ were shown in Fig.2. These showed a shift in wave number of dominant peaks related with the loaded metal and confirmed the metal binding process occurring at the exterior of resin [34]. This information gives confirmation that the functional groups of

SO_3^- are implied in binding the heavy metal ions onto the ion exchange resins (IERS). SEM images of the free and heavy metal ions loaded adsorbents are shown in Fig 3a, 3b, 3c and 3d respectively. As observed from Figures, a visible change of the surface morphology in the heavy metals loaded PFR and PFR- nFe_2O_3 exhibited that the adsorption of heavy metal ions has happened on the resin.

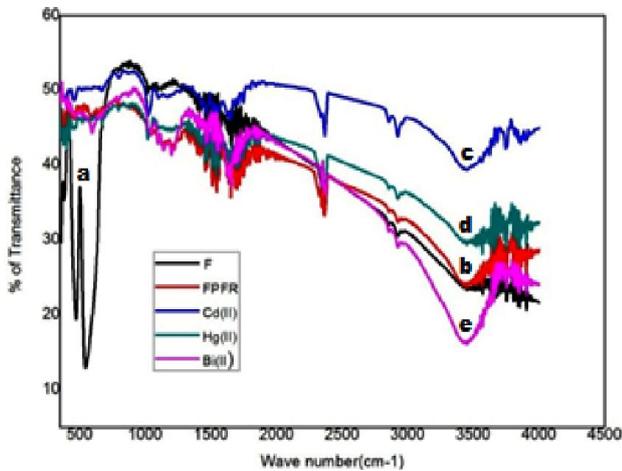


Fig.2. FTIR spectra of (a) Fe_2O_3 (b) PFR- nFe_2O_3 (c) PFR- nFe_2O_3 -Cd(II) (d) PFR- nFe_2O_3 -Hg(II) and (e) PFR- nFe_2O_3 -Bi(III)

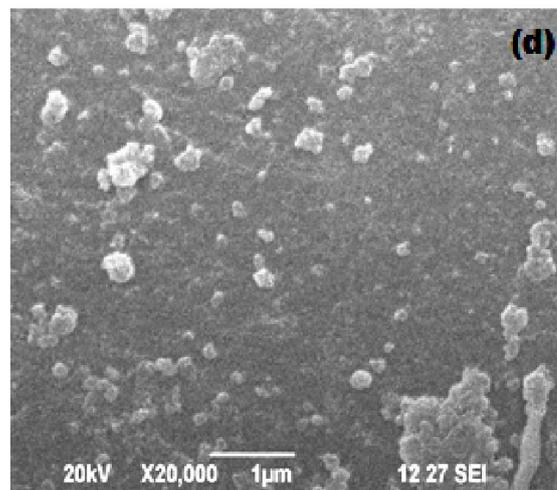
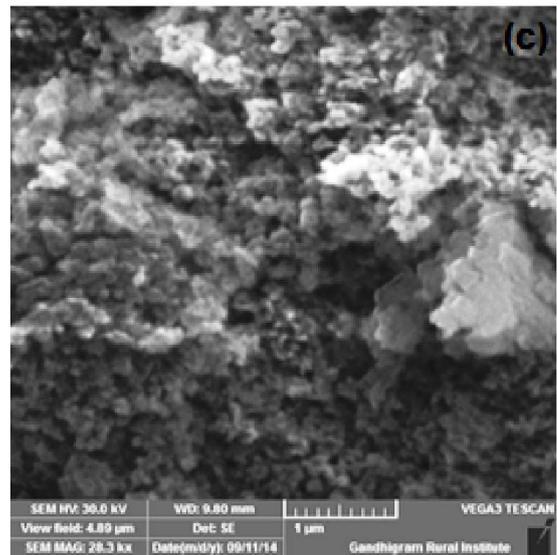
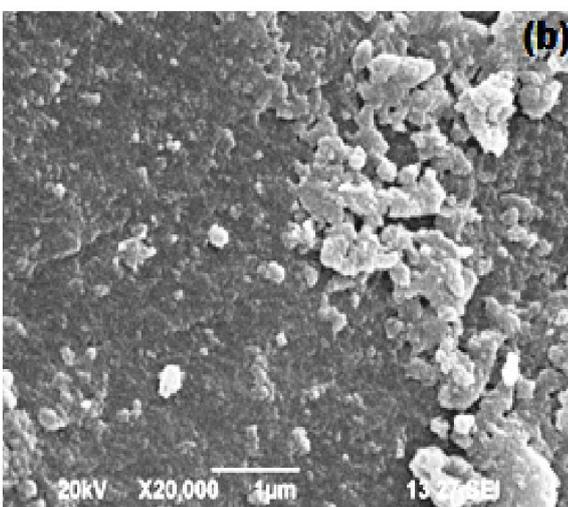
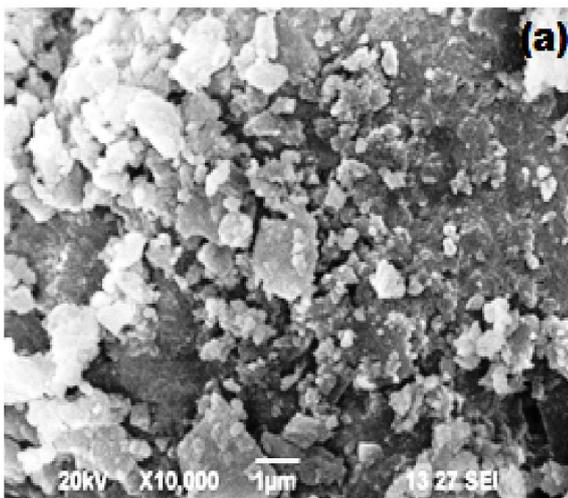


Figure 3. The SEM images of (a) PFR- nFe_2O_3 (b) PFR- nFe_2O_3 -Cd(II) (c) PFR- nFe_2O_3 -Hg(II) (d) PFR- nFe_2O_3 -Bi(III)

The XRD spectrum of free and Hg (II) loaded adsorbent are shown in Fig 4a and b. These showed that disappear (or) change of peaks in the spectrum after adsorption confirms the adsorption of Hg (II) onto PFR- nFe_2O_3 .

3.2. Adsorption isotherm study

Fig.5 indicated that the C_0 increases from 30 to 150 mg L^{-1} as well as the adsorption capacity of IER at 30°C for Bi(III), Hg(II) and Cd(II) ions raises in the cycle as the initial concentration creates essential driving force to rout the dispute to the mass transfer of metal ions between the adsorbate and the adsorbent. The relation between Bi(III), Hg(II) and Cd(II) and IER can be found out with the various adsorption isotherm representations like Freundlich [35] and Langmuir's isotherm [36] models. The limits were determined from fig.6a and b and are tabulated in Table 1:

$$\text{Freundlich isotherm: } \log q_e = \log K_F + (1/n) \log C_e \quad \text{----- (2)}$$

$$\text{Langmuir's isotherm: } (C_e/q_e) = (1/Q_0b) + (C_e/Q_0) \quad \text{----- (3)}$$

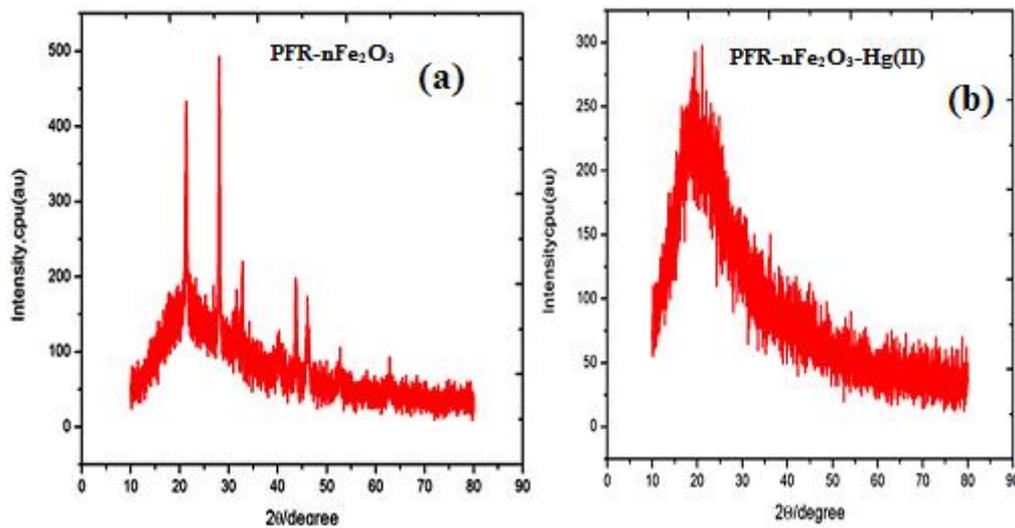
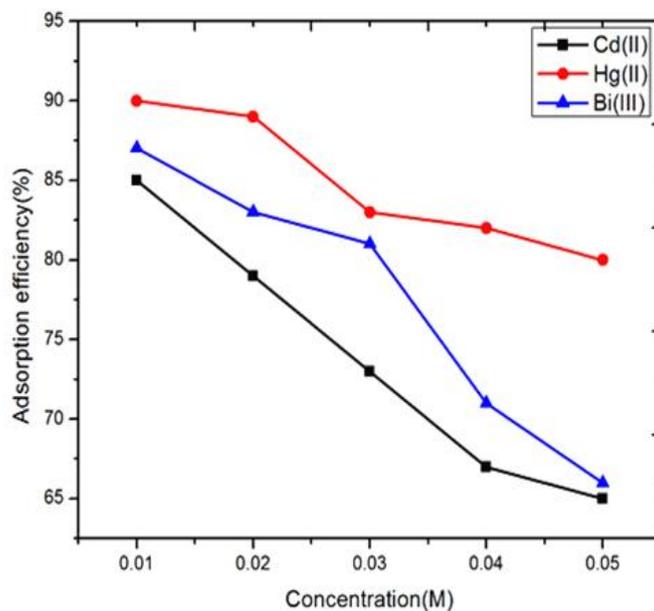
Figure 4. XRD Pattern of free (a) and Hg (II) loaded (b) PFR-n Fe_2O_3 

Fig.5. Effect of concentration on the removal of Bi(III), Hg(II) and Cd(II) from aqueous solution

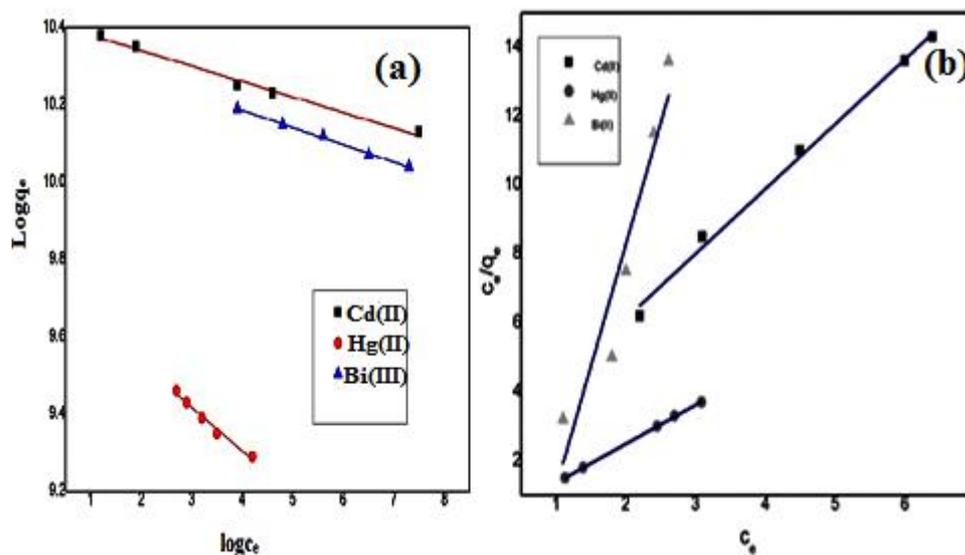


Fig. 6. Freundlich (a) and Langmuir's plots (b) for Bi(III), Hg(II) and Cd(II) removal

Where K_F (mg g^{-1}) is the Freundlich constant and 'n' the Freundlich exponent. Where, q_e (mg g^{-1}) is the adsorbed amount of Hg (II) at equilibrium, C_e (mg L^{-1}) is the equilibrium concentration of Bi(III), Hg(II) and Cd(II), Q_0 (mg g^{-1}) and b (L mg^{-1}) are Langmuir constants related to adsorption capacity and energy of adsorption. As depicted in Table 1, the trial data could be well fitted with Freundlich ($R^2=0.946, 0.985 \text{ \& } 0.991$) as compared to the Langmuir's isotherm models ($R^2=0.962, 0.975 \text{ \& } 0.942$). The value of the exponent $1/n$ consisting between 0 and 1 and then the value of n greater than 1 indicated sympathetic atmospheres for adsorption [37].

Table 1. Adsorption isotherm factors for Bi(III), Hg(II) and Cd(II) removal from aqueous solution onto the PFR-nFe₂O₃

Mathematical models	Parameters	Cd(II)	Bi(III)	Hg(II)
Langmuir isotherm	R^2	0.962	0.975	0.942
	K_L	79.70	70.03	60.35
	q_m (mg/g)	0.0097	0.0108	0.0112
Freundlich isotherm	R^2	0.946	0.985	0.991
	K_F	1.3304	1.7418	2.924
	n	0.0961	0.0950	0.1007

3.3. Adsorption Kinetics and Intraparticle diffusion rate

Fig.7 obviously showed that the adsorption process was prompt at the starting of reaction and over within 20 min. Consequently a prolonged next stage for the Hg^{2+} adsorption on PFR-nFe₂O₃ was ceased within 60 min. Hence the equilibrium time was 20 min for this adsorption. Further, no major change was detected owing to the occurrence of more active sites on PFR-nFe₂O₃ at begin of the reaction and more active sites were not available on PFR-Fe₂O₃ after 20 min. The efficiency of the IERs was valued through analyzing adsorption kinetics. The rate constant was calculated from Lagergren pseudo - first order equation which is commonly expressed as [38].

$$\text{Log}(q_e - q_t) = \text{log } q_e - [K_1 / 2.303] t \text{----- (4)}$$

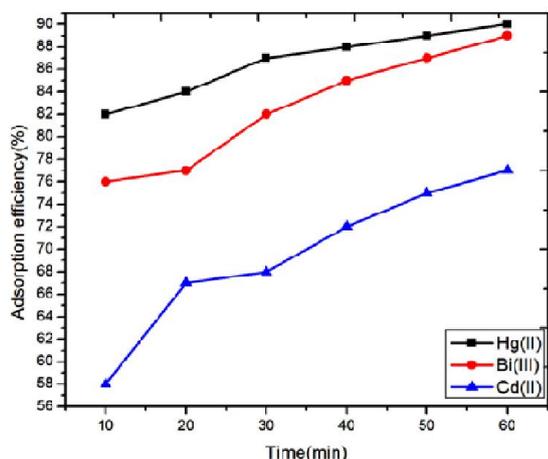


Figure 7. Effect of contact time on the removal of Hg(II), Bi(III) & Cd(II) from aqueous solution

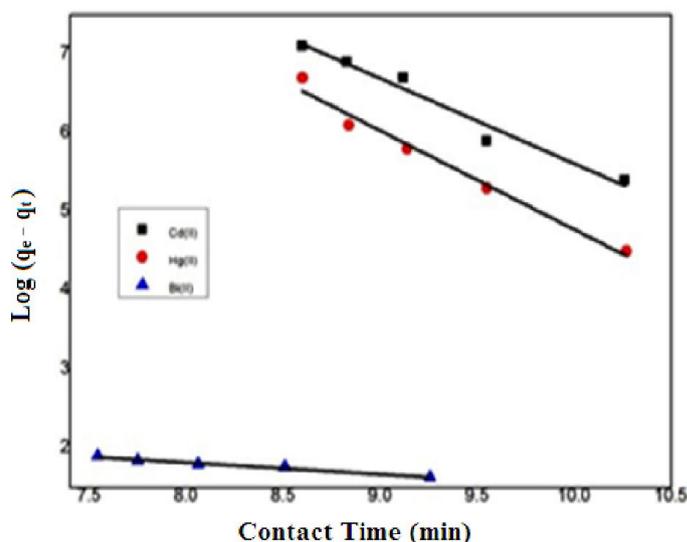


Fig.8. pseudo first order plot for the removal of Cd (II), Hg (II) and Bi(III) from aqueous solution

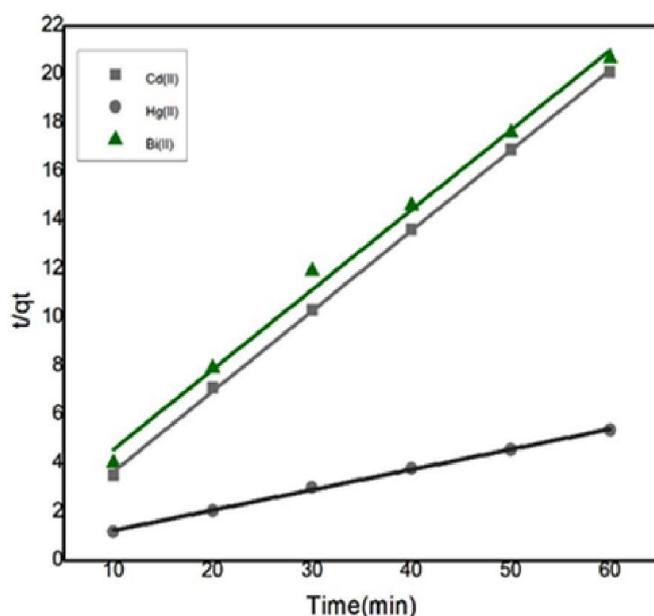


Fig.9. pseudo second order plot for the removal of Cd (II), Hg (II) and Bi(III) from aqueous solution

Where K_1 is the pseudo-first-order rate constant (min^{-1}) and q_e (mg g^{-1}) is the adsorption capacity at equilibrium and q_t (mg g^{-1}) is the adsorbed amount of metal ion after time t (min). The all values are calculated from Fig.8 and are presented in Table 2.

The linear form of pseudo - second order kinetic model can be expressed as [39]:

$$t / q_t = 1 / K_2 q_e^2 + t/q_e \text{----- (5)}$$

Where K_2 is the rate constant of second order adsorption (g/mg/min). K_2 and q_e were determined from the Fig.9 and are tabulated in Table.2. The R^2 values for pseudo second-order kinetic model are relatively higher than pseudo-first order kinetic model. The correlation between predicted and

experimental q_e values pointed out that the adsorption system studied goes to pseudo second-order kinetic model.

This model was to the highlight the rate-limiting step of the adsorption process and recommended by Weber and Morris [40]. If the plot q_t versus $t_{1/2}$ makes a straight line and exceed throughout the origin, intra-particle diffusion is the source of rate-limiting step. This equation can be expressed as

$$q_t = K_{id} t^{1/2} + C \quad \text{----- (6)}$$

Where, q_t is the adsorption capacity at any time t and K_{id} is the intra particle diffusion rate constant and C is the film thickness. The calculated K_{id} , C and correlation coefficient (R^2) values are tabulated in Table.2. Larger the value of C greater is the effect of boundary layer on adsorption process. The deviation of the plot from the linearity indicates the rate-limiting step have to be controlled boundary layer diffusion. These two straight lines describe the points, the sharp first linear portion is because of the film diffusion and the second linear portion is because of the pore diffusion. Non-linearity of the plots had revealed the multi stage adsorption for adsorbing Cd (II), Hg (II) and Bi(III) ions through PFR-nFe₂O₃.

3.4. Effect of temperature

The effect of temperature on the adsorption of heavy metal ions by PFR-nFe₂O₃ was studied from 303 K to 323 K. Thermodynamic parameters tell feasibility and the spontaneous nature of the adsorption process. The thermodynamic parameters, specifically free energy change (ΔG^0), entropy change (ΔS^0) and enthalpy change (ΔH^0), were studied using the equilibrium constants at different temperatures. The adsorption equilibrium constant (K_C) was calculated by the following equation:

$$K_C = C_{ad}(\text{solid}) / C_e(\text{solution}) \quad \text{----- (7)}$$

C_{ad} is the amount of metal (mg) adsorbed on the adsorbent per liter (L) of the solution at equilibrium, and C_e is the equilibrium concentration (mg L⁻¹) of the metal in the solution. The free energy change (ΔG^0) of the adsorption was calculated by the following equation:

$$\Delta G^0 = -2.303 RT \log K_C \quad \text{----- (8)}$$

Table 2. Kinetic parameters for the adsorption of Hg(II) ion, Bi(III) ion and Hg(II) on PFR-nFe₂O₃

Mathematical models	Parameters	Hg(II)	Bi (III)	Cd (II)
	R^2	0.869	0.966	0.946
First-order kinetics	k_1 (min ⁻¹)	0.005	0.003	0.001
	q_e (mg/g)	0.110X10 ¹⁰	1.006	1.62X10 ¹⁰
	R^2	0.998	0.993	0.999
Second-order kinetics	k_2 g/mg/min	0.082	0.328	0.330
	q_e (mg/g)	12.05	3.049	3.03
	R^2	0.902	0.977	0.913
Intra-particle diffusion	k_{id}	50.74	87.77	41.37
	g/mg/min ^{1/2}	8.384X10 ³	2.3888X10 ⁴	2.744X10 ⁴

The correlation between equilibrium constant (K_C) and temperature (T) is indicated using the van't Hoff's equation:

$$\log K_C = - [\Delta H^0 / 2.303 RT] + (\Delta S^0 / 2.303R) \quad \text{----- (9)}$$

The enthalpy change (ΔH^0) and entropy change (ΔS^0) values were calculated from the slope and intercept of the linear plot $\log K_C$ versus $1/T$ (Fig.10). The calculated all values were tabulated in Table.3. The negative values of ΔG^0 show the endothermic nature of the ion exchange process between heavy metals and PFR-nFe₂O₃, as the negative value of ΔG^0 indicates the spontaneous nature of heavy metals sorption [41]. The positive entropy change (ΔS^0) value represents to an increase in the degree of freedom of the adsorbed metal ions.

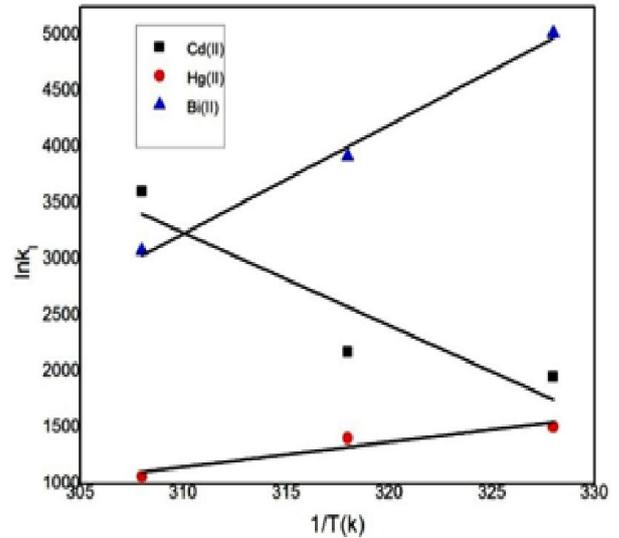


Figure 10. van't Hoff's plots of ln K versus 1/T for the adsorption of Cd(II) ion, Hg(II) and Bi(III) onto PFR-nFe₂O₃

Table 3. Thermodynamic parameters

Metal Ion	Thermodynamics parameters					
	R^2	ΔH^0 J/mol	ΔS^0 J/mol K	$-\Delta G^0$ (kJ/mol) $\times 10^2$		
Hg(II)	0.977	87.77	23888	308K	318K	328K
Bi(III)	0.913	41.37	27445	-79.3	-83	-86.2
Cd(II)	0.902	50.74	8384	-70.9	-73	-81.8
				-57	-63	-66

4. Conclusion

nFe₂O₃ were tightly impregnated within a polymeric matrix PFR through a polycondensation process, using formaldehyde as the cross-linking agent and a novel composite micro porous cation exchanger PFR-nFe₂O₃ was obtainable for selective heavy metals removal. As Compared to PFR, PFR-nFe₂O₃ displayed more preferable heavy metals confiscation from aqueous medium. The kinetic studies show that the adsorption of heavy metals onto PFR-nFe₂O₃ followed the pseudo-second order rate expression.

The adsorption isotherm studies confirmed a good fit with the Freundlich isotherm model. The exchanges between heavy metals and PFR-nFe₂O₃ are thermodynamically favorable and endothermic in nature. The current study concludes that micro porous cation exchange resin PFR-nFe₂O₃ could be applied for the removal of heavy metal ions from aqueous solution as well as waste water.

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