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RESEARCH ARTICLE

FABRICATION OF NEW MODIFIED CROSS LINKED POLYIMERIC RESINS COMPOSITE WITH NANO TiO₂ & NANO Fe₂O₃ FOR THE REMOVAL OF SELECTIVE METAL IONS

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ABSTRACT

Phenol-Formaldehyde resin (PFR) grafted Nano-Fe₂O₃ & Nano-TiO₂ (nFe₂O₃ & nTiO₂) was fabricated for Cd(II), Zn(II) & Hg(II) removal using a novel polycondensation method. The present resources were carefully examined by FT-IR spectra (FT-IR), Scanning electron microscope (SEM), Energy-dispersive microanalysis (EDX), and Thermo gravimetric analysis (TGA). PFR/nFe₂O₃ & nTiO₂ showed excellent uptake effects for Cd(II), Zn(II) and Hg(II) removal with a pseudo-second order model. The D-R isotherm models well described the equilibrium isotherm than the Langmuir's 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 & nTiO₂ could well be used as a high concert sorbent for the heavy metal ions removal from aqueous solution with a list of Cd(II), Zn(II) & Hg(II).

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INTRODUCTION

Water contamination with heavy metals is a very significant problem all over the world. Nickel, lead and cadmium are three distinctive extensive heavy metal pollutants in the natural water environment. The main anthropogenic pathway which nickel, lead and cadmium entering environment is via wastes from industrial processes such as electroplating, alloy manufacturing, pigments, batteries and textile operations. Nickel entering body could cause cancers of the lungs, nose and bone (Baraka et al., 2007; Duran et al., 2008). Cadmium entering body could cause serious damages of the kidneys, lungs, bones and hypertension (Beatty, 1999; Kołodynska et al., 2008). Lead could cause brain damage in children even at extremely low concentration (Shukla et al., 2006; Pramanik et al., 2004; Li et al., 2002; Dakova et al., 2007). The conservative methods for heavy metal removal from water and wastewater include oxidation, reduction, precipitation, membrane filtration, ion exchange and adsorption. Among these methods, adsorption is highly effective and economical. Many adsorbents such as various activated carbon (Liu et al., 2005; Atia et al., 2005; Donia et al., 2006; Navarro et al., 2001; Kantipuly et al., 1990), agricultural waste including

chitosan, orange peel and various hell, barley straw and grape bagasse (Mathew, 1994); industrial products including lignin, waste slurry, silica gel (Lezzi et al., 1994; Roy et al., 2003), polymeric ion exchange resins (Juang and Wang, 2003) and polymeric chelating resins (Atzei et al., 2001; Chen et al., 2007; Denizi, 2004; Gode, 2003; Reddy, 2003; Chen, 2007; Eloueara and Bouzida, 2008); natural materials including zeolites, clay and lignite, (Pehlivan, 2006) 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 (Lin et al., 2000; Leinonen 2000). 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 (Chen, 2005; Chen, 2003).

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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. 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). 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, ethylenediamine and triethylenetetramine for Cd(II), Cr(III), Fe(III) and Pb(II) adsorption, amine for Cu(II) uptake, sulfurized steam for Pb(II) and Hg(II) removal. 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 & nTiO₂) was fabricated using a novel polycondensation method. The adsorption behaviors of Cd(II), Zn(II) and Hg(II) were investigated at PFR/ nFe₂O₃ & nTiO₂ 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.

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.

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 (Sarkar *et al.*, 2010). 2 % and 0 % nFe₂O₃ & nTiO₂ was mixed to phenol sulphonic acid and these constitute samples labeled as PFR/ nFe₂O₃ & nTiO₂ and PFR. This mixture was polymerized with formaldehyde (12.5 mL) at 70 °C and treated at this temperature for 3 hrs 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 (Siva *et al.*, 2014).

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).

Batch studies

Batch adsorption experiments were carrying out by introducing a preferred amount of PFR and PFR/nFe₂O₃ &

nTiO₂ resin in 250 mL glass bottles separately containing heavy metal ion solutions of various concentrations (0.01–0.05M). 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 (Vasudevan and Sharma, 1979). 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.

Specific surface area and pore properties of Activated Carbon

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.

RESULTS AND DISCUSSION

Characterization of PFR and PFR/nFe₂O₃ & nTiO₂

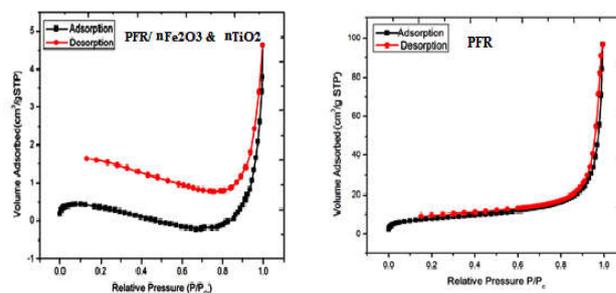


Figure 1. N₂ adsorption–desorption isotherms of PFR and PFR/nFe₂O₃ & nTiO₂

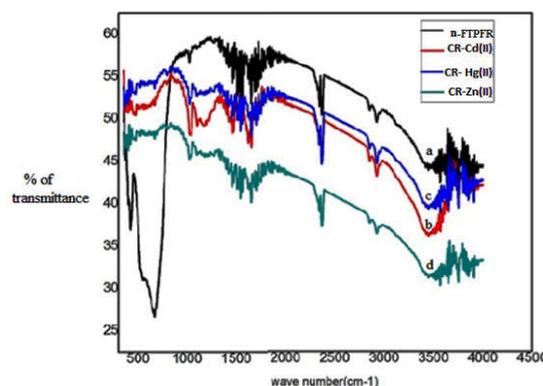


Figure 2. FTIR spectra of (a) PFR/nFe₂O₃ & nTiO₂ (b) PFR/nFe₂O₃ nTiO₂Cd (II) (c) PFR/nFe₂O₃ & nTiO₂- Hg (II) & (d) PFR/nFe₂O₃ & nTiO₂ Zn(II)

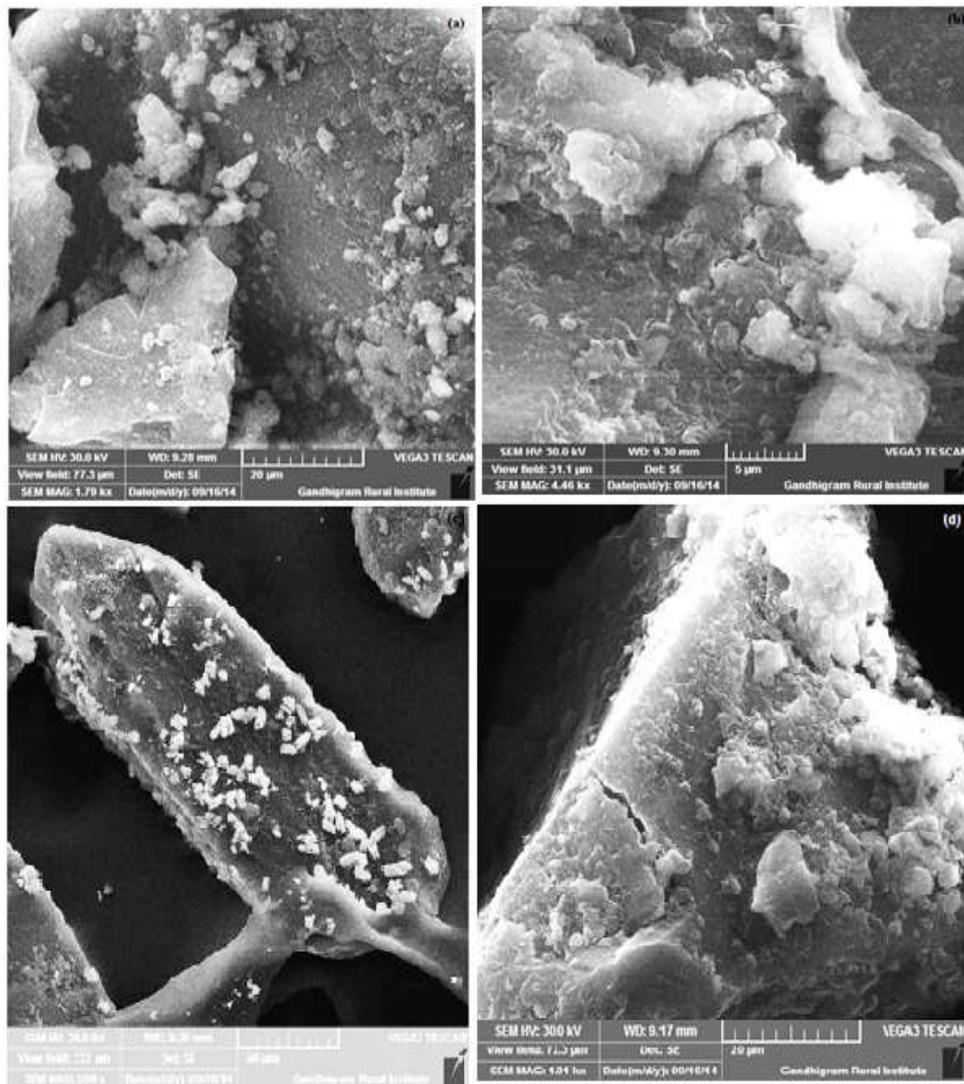


Figure 3. The SEM images of (a) PFR/nFe₂O₃ & nTiO₂ (b) PFR/nFe₂O₃ & nTiO₂ Cd (II) (c) PFR/nFe₂O₃ & nTiO₂ -Zn(II) (d) PFR/nFe₂O₃ & nTiO₂ Hg(II)

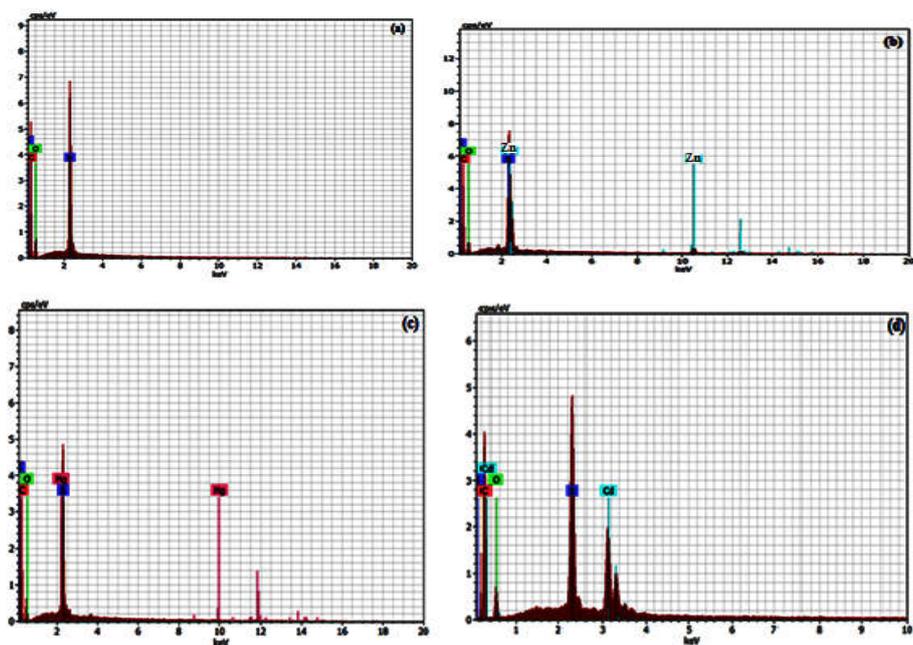


Figure 4. Energy dispersive spectra of a) n-TiO₂ b) CR-Cd (II) c) CR-Hg (II) d) CR-Zn (II)

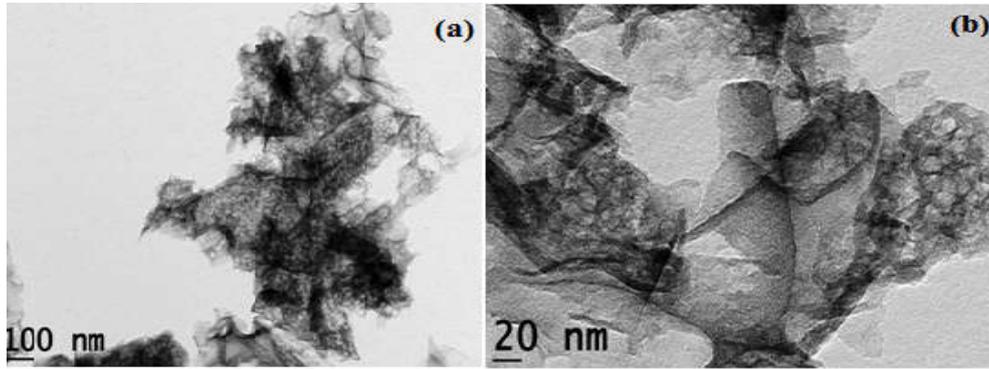


Figure 5. TEM image of free a) and Hg(II) loaded n-FTPFR

An abrupt increase in nitrogen volume adsorbed at higher P/P_0 suggested a quite large contribution in mesopore 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/ $n\text{Fe}_2\text{O}_3$ & $n\text{TiO}_2$, 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/ $n\text{Fe}_2\text{O}_3$ & $n\text{TiO}_2$, Zn(II) – PFR/ $n\text{Fe}_2\text{O}_3$ & $n\text{TiO}_2$, Hg (II) – PFR/ $n\text{Fe}_2\text{O}_3$ & $n\text{TiO}_2$ and Cd (II) – PFR/ $n\text{Fe}_2\text{O}_3$ & $n\text{TiO}_2$ 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 (Natarajan and Krishnamoorthy, 1993). 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 / $n\text{Fe}_2\text{O}_3$ & $n\text{TiO}_2$ exhibited that the adsorption of heavy metal ions has happened on the resin.

TEM

The morphology and size of nanoparticles were studied by (TEM). The image revealed that the particle size of the composite was 20 nm (Fig 5a and 5b).

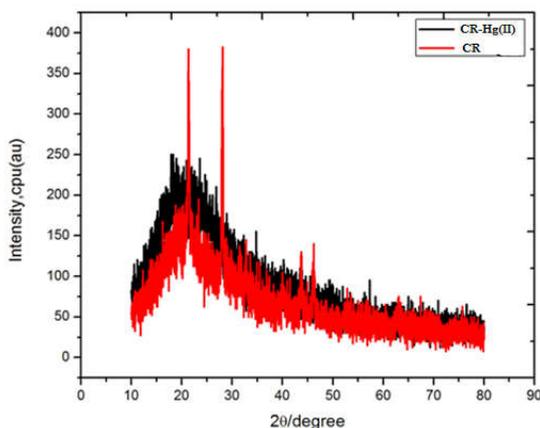


Figure 6. XRD Pattern of free (a) and Hg (II) loaded (b) PFR/ $n\text{Fe}_2\text{O}_3$ & $n\text{TiO}_2$

The XRD spectrum of free and Hg (II) loaded adsorbent are shown in Fig 6a and b. These showed that disappear (or) change of peaks in the spectrum after adsorption confirms the adsorption of Hg (II) onto PFR/ $n\text{Fe}_2\text{O}_3$ & $n\text{TiO}_2$.

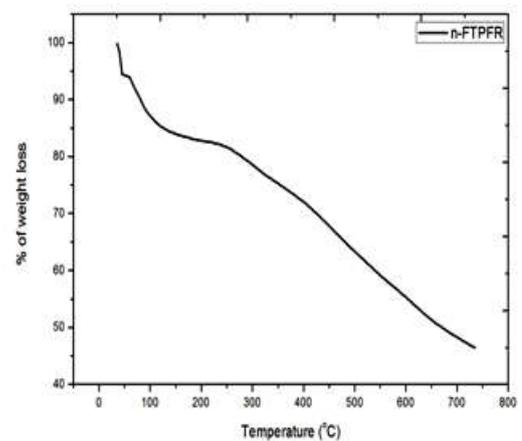


Figure 7. TGA curve of n-FTPFR

TGA

The TGA thermo grams for the n-FTPFR samples were shown in figure 7. The weight loss of nFTPFR during the heating process was investigated in figure7. The TGA curve of nFTPFR revealed weight loss at two regions corresponding to the loss of water (8% by weight) at temperature around 100 Cand the loss of organic binder (50% by weight) at the temperature range of 200- 500°C. No further significant weight loss peak was observed in the temperature range above 500°C. It can be concluded that nFTPFR exhibited thermal stability during the heating process at the temperature range 750°C

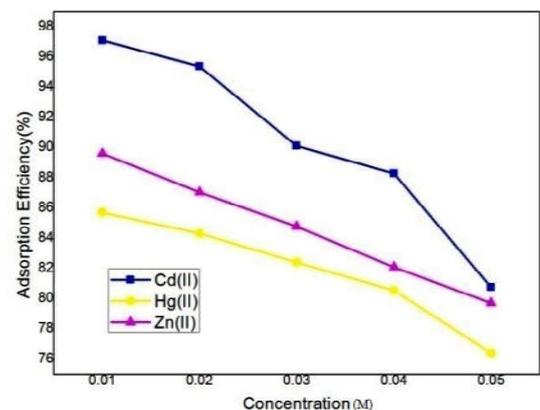


Figure 7. Effect of concentration on the removal of Zn(II), Cd(II) and Hg(II) from aqueous solution

Adsorption isotherm study

Fig.7 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 Cd(II), Zn(II) and Hg(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 Cd(II), Zn(II) and Hg(II) and IER can be found out with the various adsorption isotherm representations like D-R isotherm (Bassett *et al.*, 1989) and Langmuir isotherm (Sosa *et al.*, 2003) models. The limits were determined from fig.8a and b and are tabulated in Table 1:

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

Langmuir isotherm : $(C_e/q_e) = (1/Q_0b) + (C_e/Q_0)$ ----- (3)

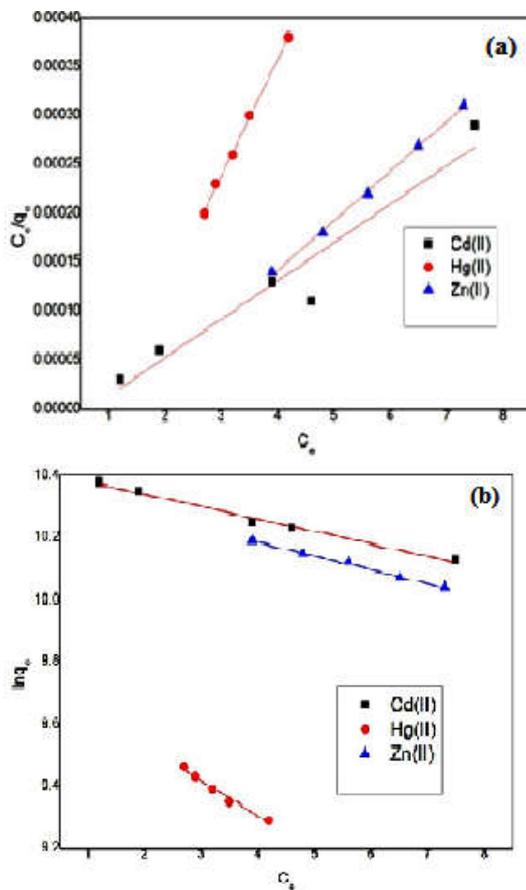


Fig. 8. (a) Langmuir plots (b) D-R isotherm for Cd(II), Zn(II) and Hg(II) removal

Where K_L (mg g⁻¹) is the Langmuir constant and ‘n’ the Langmuir 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 Cd(II), Zn(II) and Hg(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 D-R Isotherm ($R^2=0.909, 0.984$ & 0.991) as compared to the Langmuir isotherm models ($R^2=0.962, 0.975$ & 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 (Srivastava *et al.*, 2006).

Table 1. Adsorption isotherm factors for Cd(II), Zn(II) and Hg(II) removal from aqueous solution onto the PFR/nFe₂O₃ & nTiO₂

Mathematical models	Parameters	Cd(II)	Zn(II)	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
D-R isotherm	R^2	0.984	0.994	0.991
	B	21.96	114.5	91.98
	E kJ/mol	10.980	57.250	45.910

Adsorption Kinetics and Intraparticle diffusion rate

Fig.9 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 heavy metal ions removal adsorption on PFR/nFe₂O₃ & nTiO₂ 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 at begin of the reaction and more active sites were not available on PFR / nFe₂O₃ & nTiO₂ 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 (Aroua *et al.*, 2008).

$\log (q_e - q_t) = \log q_e - (K_1 / 2.303) t$ ----- (4)

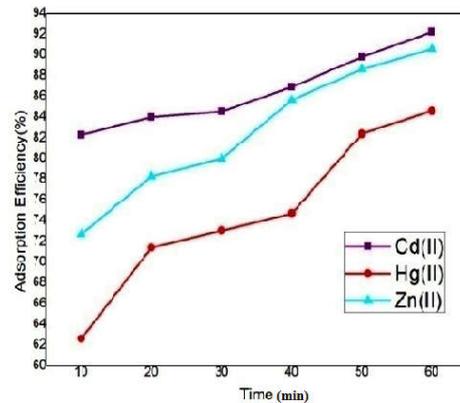


Figure. 9. Effect of contact time on the removal of Cd(II), Zn(II) & Hg(II) from aqueous solution

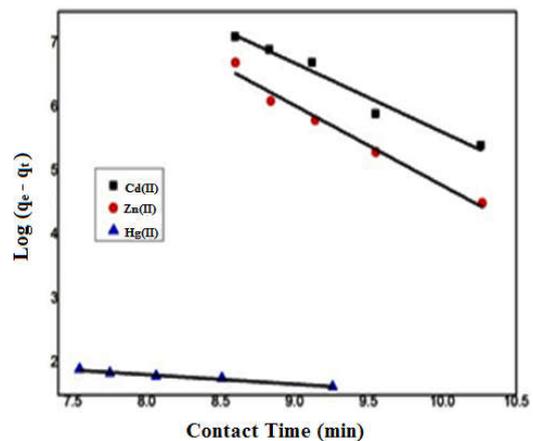


Fig. 10. Pseudo first order plot for the removal of Cd (II), Zn (II) and Hg(II) from aqueous solution

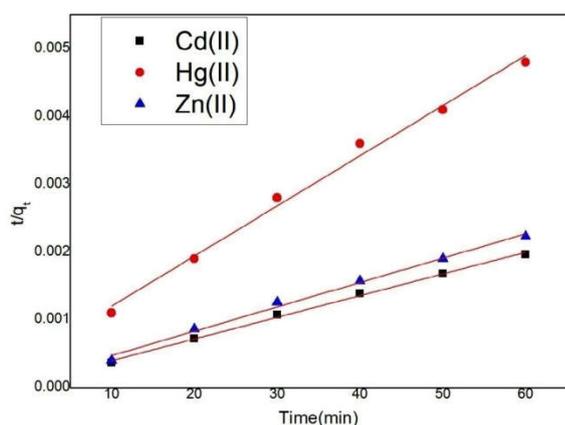


Fig. 11. Pseudo second order plot for the removal of Cd (II), Hg (II) and Zn(II) from aqueous solution

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.10 and are presented in Table.2. The linear form of pseudo - second order kinetic model can be expressed as (Shubha *et al.*, 2001):

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

Where K_2 is the rate constant of second order adsorption (g/mg/min). K_2 and q_e were determined from the Fig.11 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 (Freundlich, 1906). 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 Zn(II) ions through PFR/nFe₂O₃ & nTiO₂.

Effect of temperature

The effect of temperature on the adsorption of heavy metal ions by PFR/nFe₂O₃ & nTiO₂ was studied form 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 Cd(II) ion , Zn(II) ion and Hg(II) on PFR/nFe₂O₃ & nTiO₂

Mathematical models	Parameters	Cd(II)	Zn(II)	Hg(II)
First-order kinetics	R^2	0.962	0.975	0.942
Second-order kinetics	k_1 (min^{-1})	79.70	70.03	60.35
Intra-particle diffusion	q_e (mg/g)	1.5776	2.2908	2.5882
	R^2	0.992	0.995	0.994
	k_2 g/mg/min	80.00	70.422	60.606
	q_e (mg/g)	0.0125	0.0142	0.0165
	R^2	0.962	0.975	0.942
	k_{id} $\text{g/mg/min}^{1/2}$	79.70	70.03	60.35
	C (mg/g)	0.198	0.360	0.413

The correlation between equilibrium constant (K_C) and temperature (T) is indicated using the van't Hoff 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.12). The calculated all values were tabulated in Table.3. The negative values of ΔH^0 show the exothermic nature of the ion exchange process between heavy metals and PFR/nFe₂O₃, nTiO₂ as the negative value of ΔG^0 indicates the spontaneous nature of heavy metals sorption (Lagergren *et al.*, 1898). The negative entropy change (ΔS^0) value represents to a decrease in the degree of freedom of the adsorbed metal ions.

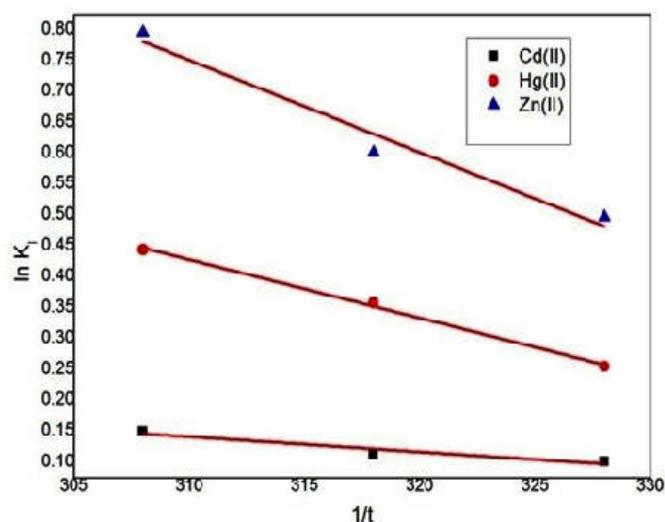


Figure 12. Van't Hoff plots of $\ln K$ versus $1/T$ for the adsorption of Cd(II) ion, Hg(II) and Zn(II) onto PFR/nFe₂O₃ & nTiO₂

Table 3. Thermodynamic Parameters

Metal Ions	Thermodynamics parameters					
	R ²	ΔH° J/mol	ΔS° J/mol K	-ΔG°(kJ/mol) × 10 ²		
Cd(II)	0.909	21.96	0.211	308K	318K	328K
				-86.92	-89.83	-90.79
Zn(II)	0.984	91.82	0.522	-69.23	-73.62	-79.67
Hg(II)	0.991	114.5	0.554	-55.67	-62.43	-66.75

Conclusion

nFe₂O₃ & nTiO₂ were tightly impregnated within a polymeric matrix PFR through a polycondensation process, using formaldehyde as the cross-linking agent and a novel composite nano porous cation exchanger (20nm) PFR/nFe₂O₃ & nTiO₂ was obtainable for selective heavy metals removal. As Compared to PFR, PFR/nFe₂O₃ & nTiO₂ displayed more preferable heavy metals confiscation from aqueous medium. The kinetic studies show that the adsorption of heavy metals onto PFR/nFe₂O₃ & nTiO₂ followed the pseudo-second order rate expression. The adsorption isotherm studies confirmed a good fit with the D-R isotherm model. The exchanges between heavy metals and PFR/nFe₂O₃ & nTiO₂ are thermodynamically feasible, spontaneous and endothermic in nature. The current study concludes that nano porous cation exchange resin PFR/nFe₂O₃ & nTiO₂ could be applied for the removal of heavy metal ions from aqueous solution as well as waste water.

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