Effective removal of heavy metal ions from aqueous solutions using a new chelating resin poly [2,5-(1,3,4-thiadiazole)-benzalimine]: kinetic and thermodynamic study

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ABSTRACT

A novel poly [2,5-(1,3,4-thiadiazole)-benzalimine] abbreviated as TDPI adsorbent was synthesized using simple polycondensation technique. The synthetic route involves the preparation of 2,5-diamino-1,3, 4-thiadiazole from 2,5-dithiourea and subsequent condensation with terephthalaldehyde. The resin was chemically characterized using Fourier transform infrared (FT-IR), ^{1}H-NMR, and ^{13}C-NMR spectroscopic analysis. Surface morphology and thermal stability were analyzed using scanning electron microscopy (SEM) and thermo-gravimetric analysis (TGA). The effect of the pH value of solution, contact time, adsorbent dose, and initial metal ion concentration were investigated by batch equilibrium adsorption experiments. Kinetic studies show that the adsorption of metal ions onto the resin proceeds according to the pseudo-second-order model and the equilibrium data were best interpreted by the Redlich–Peterson isotherm. The experimental values of the adsorption capacities of Pb^{2+}, Cu^{2+}, Ni^{2+}, and Cd^{2+} on to TDPI could reach up to 437.2, 491.6, 493.7, and 481.9 mg.g^{-1} respectively. The exothermic nature of the process, the affinity of the adsorbent towards the metal ions and the feasibility of the process are explained in the thermodynamic parameters. The resin stability and re-usability studies suggest that the resin is chemically stable (0.3 N HCl and H$_2$SO$_4$) and could be regenerated without any serious decline in performance.

Key words | adsorption studies, isotherm, kinetics, polyimine, regeneration studies, thaiadiazol

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INTRODUCTION

Activated carbon is one of the most widely used adsorbents in the adsorption process. Adsorption is one of the most effective and simplest approaches to remove toxic heavy metal pollutants from aqueous systems. Even though activated carbon seems to be economically attractive, it suffers from costly regeneration and low adsorption capacity. Therefore, the search for alternative adsorbents has resulted in the development of polymer-based adsorbents for pollutant removal from water (Pan *et al.* 2009). General methods, such as chemical precipitation and reverse osmosis, results in incomplete removal of metal ions. The most promising technique for the removal of metal ions is their adsorption on organic sorbent containing chelating functional groups. An organic chelating sorbent consists of a polymer matrix and chelating functional group attached to it. Broadly, polymer-based adsorbents can be classified into the following categories: polymeric adsorbents, chemically modified polymeric adsorbents, polymeric chelating adsorbents, polymer-based inorganic hybrid adsorbents. Commercially available polymeric adsorbents are based on

cross-linked polystyrenes and polyacrylic esters. Such polymer-based adsorbents have been mainly used for organic chemical removal, such as phenol, amine acids, carbon tetrachloride, nitrophenol, etc. (Gusler *et al.* 1993; Xu *et al.* 1997; Abburi 2003; Deosarkar & Pangarkar 2004; Lee *et al.* 2005; Freitas *et al.* 2008; Zhang *et al.* 2008). Cross-linked polystyrene adsorbents do not have any functional group and hence are not used for removal of heavy metal ions. Similarly, polyacrylic acid esters have been used mainly for the removal of organic chemicals (Bohra *et al.* 1994; Yang *et al.* 2007; Pan *et al.* 2008).

Chemical modification is an effective approach to increase the adsorption performance of a polymer adsorbent towards some specific pollutants. In this type of adsorbent, mostly a polystyrene matrix is used, in which functional groups such as carboxylic acid, amine, and sulfonic acids are introduced into the polymeric matrix by means of chemical reactions (Chen *et al.* 2002; Zheng *et al.* 2007; Chang *et al.* 2008).

Functional groups such as 1,2-bis(o-aminophenylthio) ethane (Mondal & Das 2003), catechol (Bernard *et al.* 2008), 2-napthol-3,6-disulfonic acid (Mondal *et al.* 2002), 1-(2-thioazoalylazo)2-napthol (Lee *et al.* 2001), and amino group (Rivas *et al.* 2001) chemically introduced into a polystyrene matrix have been reported for the removal of heavy metal ions. However, the adsorption capacities of these modified polymeric adsorbents did not meet the expected level.

Polymeric chelating adsorbents are generally designed adsorbents which consist of two sections: the polymeric matrix and the immobilized chelating groups to absorb the toxic heavy metals from industrial streams or other aqueous systems. The nature of the chelating group is of particular interest and is expected to offer specific interactions with targeted metals through complex formation. Chelating groups like ethylene diamine (Leinonen & Lehto 2000), 2,3-dihydroxybenzoic acid (Hosseini *et al.* 2006), benzethiazol (Meesri *et al.* 2007) in a polymeric adsorbent were used for selective removal of Pt^{2+}, Cu^{2+}, Pb^{2+}, Cd^{2+}, and Fe^{3+}. Recently, aminomethyl pyridine functional group in a silica matrix was reported for selective adsorbent of Cu^{2+} (Bai *et al.* 2012). A functional group such as dihydroxy imidazole was used for efficient and selective extraction of uranium from aqueous solution (Yuan *et al.* 2012).

Major drawbacks in polymeric chelating adsorbents are: involves multiple synthetic routes such as preparation of polymer matrix; introduction of chelating monomer into the polymer matrix; and immobilization of the chelating group. Only carbon chain polymers such as polystyrene, methyl methacrylate, glyceraldehyl methacrylate were used as polymeric chelating adsorbent and lack environmental and chemical stability.

An alternative to this problem is to use chemically and thermally stable polymers for metal ion adsorption. Even though such polymers possess excellent environmental stability, introduction of a chelating group is challenging work.

In the recent past, polyamides, polyesters, and polyimides have been emerging as potential alternatives to carbon chain containing polymeric chelating adsorbents. Chemically resistance polymers are synthesized in which the chelating groups are part of the polymeric repeating units that can be effectively used as an adsorbent for heavy metal ions and dyes (Murugesan *et al.* 2011; Ravikumar *et al.* 2011; Kirupha *et al.* 2013; Vidhyadevi *et al.* 2013). We have investigated potential alternatives to carbon chain polymers with polyamides, polythioamides, and polyimides bearing different functional groups which are present in the polymer backbone which could be utilized for metal ion adsorption. Polyamide bearing azomethine and thiourea as the functional group was found to be an effective adsorbent for the removal of Pb^{2+}, Cu^{2+}, Ni^{2+}, and Cd^{2+} (Kirupha *et al.* 2013). Polyamides in which the azomethine group is present as pendant chlorobenzylidine rings was found to be highly effective under competitive conditions in which the adsorption capacities were in the order $Cu^{2+} > Pb^{2+} > Cr^{3+} > Cd^{2+}$ (Murugesan *et al.* 2011). Polyimine with thiourea as the functional group was an equally effective adsorbent for the removal of Zn^{2+} and Ni^{2+}. Introduction of the pyridyl functional group in addition to azomethine and thiourea functional groups in a polyamide backbone has resulted in higher adsorption capacities for the removal of Cu^{2+} and Pb^{2+} (Kirupha *et al.* 2013).

Therefore, introduction of different functional groups in a polyamide or polyimide backbone, which can effectively bind with metal ions could be an effective alternative to chemically modified chelating polymers. Major advantages of such types of adsorbents include being chemically resistant, very low percentage of swelling in the aqueous media, and higher binding

capacity. More importantly, these resins have higher regener-
ation ability and are easy to recycle (washing with 0.1 N
H_2SO_4 or HCl). In the present investigation, we have designed
and synthesized a new and effective adsorbent poly[2,5-(1,3,4-
thiadiazole)-benzalimine] for the removal of Pb(II), Cu(II),
Ni(II), and Cd(II) from aqueous solutions.

MATERIALS AND METHODS

Materials

2,5-dithiourea (Aldrich), hydrogen peroxide (SRL), ter-
ephthalaldehyde (Aldrich) were used without purification.
Dimethylformamide (DMF) (Himedia) was stored over
anhydrous CaS_2 for 72 hours, filtered and distilled under
reduced pressure and the middle fraction was collected
and stored over type 4-A molecular sieves. All the reagents
used for synthesis and experiments were of analytical grade.

2,5-Diamino-1,3,4-thiadiazole monomer (Melenchuk
et al. 2008) was prepared as follows: a suspension containing
25 g of 2,5-dithiourea in 150 mL of water was added to
35 mL of hydrogen peroxide and the mixture was allowed
to stir at ambient temperature overnight. The completion
of the reaction was monitored by UPLC (ultra-performance
liquid chromatography). The resulting solid was collected by
filtration, washed with water and finally with methanol. The
diamine 2,5-diamino-1,3,4-thiadiazole was dried under
vacuum prior to polymer formation.

Synthesis of the adsorbent poly [2,5-(1,3,4-thiadiazole)-benzalimine]

The polymeric adsorbent was synthesized using a simple con-
densation technique (Tsai *et al.* 2005). Equimolar quantities
of 2,5-diamino-1,3,4-thiadiazole and terephthalaldehyde
were heated under reflux condition in DMF solvent. After
15 minutes, the system was connected to a vacuum pump
and the aziotrope was distilled out. The contents were
heated in an oil bath with magnetic stirrer at 140 °C for 72
hours. The contents were poured into water along with stirrer
and the precipitated polyimine was filtered, washed with hot
water and finally with ethanol. The vacuum dried adsorbent
was used for batch-wise adsorption experiments.

Adsorption experiments

The Pb^{2+}, Cu^{2+}, Ni^{2+}, and Cd^{2+} uptake capacities of the adsor-
bent TDPI (poly [2,5-(1,3,4-thiadiazole)-benzalimine]) were
determined in dissolved solutions of $Pb(NO_3)_2$, $CuSO_4.5H_2O$,
$NiSO_4.6H_2O$, and $3Cd(SO_4).8H_2O$, respectively, using double
distilled water. The concentration of all the stock solutions
was kept at $1.0\ g.L^{-1}$. Adsorption experiments were per-
formed by mixing TDPI (20–100 mg) with 20 mL of the
desired metal ion concentration of Pb^{2+}, Cu^{2+}, Ni^{2+}, and
Cd^{2+} separately in a flask kept at the desired temperature
and shaken in a horizontal bench shaker for 60 minutes.
The pH value of each metal ion solution was adjusted with
0.4 N acetic acid and sodium hydroxide solution. When the
adsorption experiments were complete, the mixture was fil-
tered and the metal ion concentration was determined
using atomic adsorption spectrophotometer (AAS).

The adsorption kinetics on the uptake of metal ions was
studied by placing 1 g of TDPI with 100 mL working solution
in a flask shaken at 35 °C. The initial pH of the working sol-
ution was adjusted to 6 and the solutions were taken at
different time intervals for analysis. In the adsorption isotherm
experiments, the initial pH was adjusted to the value of 6 at a
dosage of 0.02 g of adsorbent equilibrated with 20 mL of metal
ion solution with different initial metal ion concentrations. All
suspensions were shaken at 35 °C for 60 minutes and the solid
was separated by filtration. Initial and equilibrium metal ion
concentrations in the aqueous solutions were determined by
using AAS. The amount of metal ion adsorbed by the adsor-
bent was calculated according to the following equation:

$$q_e = \frac{(C_i - C_e)V}{W} \tag{1}$$

where q_e is the adsorption capacity of the polymer, C_e and C_o
are the equilibrium and initial metal ion concentration taken,
V is the volume of aqueous phase, and W is the weight of the
dried adsorbent (g). All the experiments were conducted
four times and the average value was taken.

Analytical method

Infra-red (IR) spectra were carried out on a Spectrumone,
Perkin Elmer ATR spectrophotometer using KBr pellets

around the 4,000–400 cm^{-1} region. The solution ^{1}H-NMR spectra were recorded on a Bruker-500 MHz instrument with DMSO-d$_6$ solvent. ^{13}C-NMR spectra were obtained using Bruker-500 Mhz. The morphology of the adsorbent and the metal ion adsorbed adsorbent was examined on a Leo Gemini 1530 scanning electron microscope (SEM) at an accelerating voltage of 15 kV.

Stability tests

In order to examine the re-usability of TDPI, the metal ion adsorption–desorption cycles were repeatedly performed five times using the same adsorbent by batch operations. The adsorption was carried out by shaking 0.02 g adsorbent with 20 mL of 1 g.L^{-1} of Pb(NO$_3$)$_2$, CuSO$_4$.5H$_2$O, NiSO$_4$.6H$_2$O, and Cd(SO$_4$).8H$_2$O with pH 6 at 35 °C for 60 minutes. The adsorbent was then separated by filtration and treated with 0.1 N H$_2$SO$_4$ or HCl and de-ionized water until equal equilibrium was reached for subsequent adsorption tests.

RESULTS AND DISCUSSION

Characterization of monomer and polymer TDPI

The chemical scheme for the synthesis of monomer and polymer are shown in Figures 1 and 2, respectively.

The structure of monomer 2,5-diamino-1,3,4-thiadiazole and polymer TDPI are characterized using spectroscopic analysis. The IR spectrum of monomer and the polymer TDPI is shown in Figure 3. In the monomer the –NH$_2$ stretching frequency is observed around 3,100 cm^{-1}. Formation of –N=CH— (imine) links between free –NH$_2$ of monomer and –CHO of terephthaldehyde is clearly observed at 1,694 cm^{-1} (stretching frequency of –N=CH—) in the polymer. The formation of polyimine between
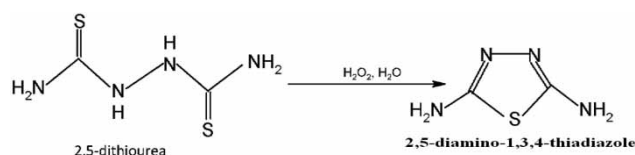

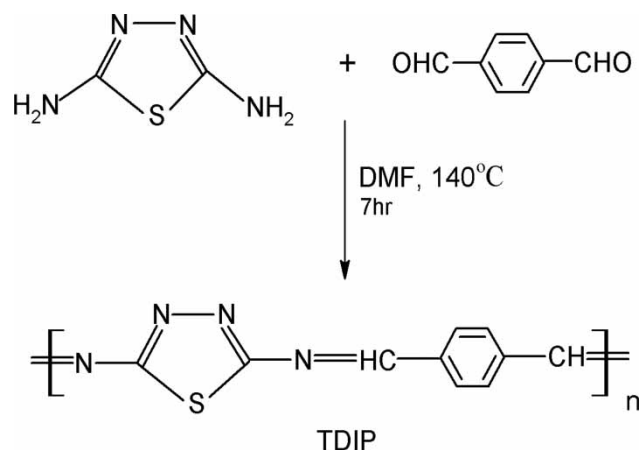Figure 1 | Synthesis of 2,5-diamino-1,3,4-thiadiazole monomer.
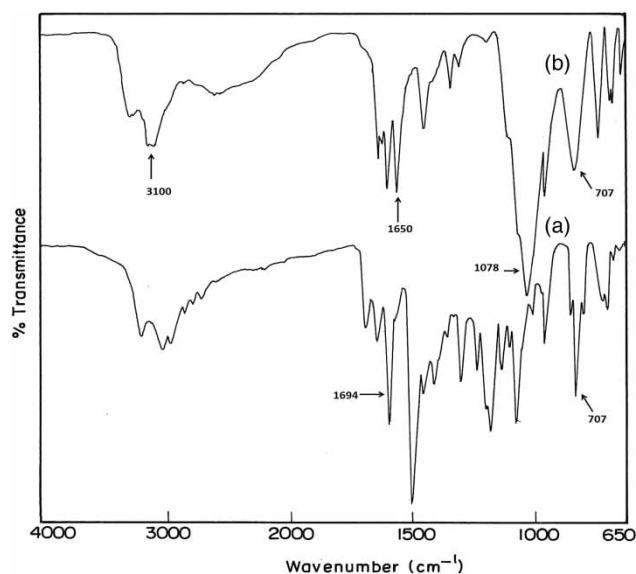

Figure 2 | Synthesis of TDPI polymer.

Figure 3 | IR spectra of monomer 2,4-diaminothiadiazole and TDPI polymer.

primary amine and the aldehyde of terephthalaldehyde is a well-established reaction by our group (Murugesan et al. 2012). Other IR observations in the monomer and polymer are: C=N, N—N, C—S—C— appearing near 1,650, 1,078, and 707 cm^{-1}, respectively.

^{1}H-NMR allowed the validation of the polymer synthesis step. The ^{1}H-NMR spectrum of the polymer is shown in Figure 4. The four hydrogens of the primary amine group in the monomer were observed at δ = 7.13 ppm. Aromatic protons of the polymer appeared as a broad signal in the region 7.9–7.2 ppm. The first indication of a material to be a polymer
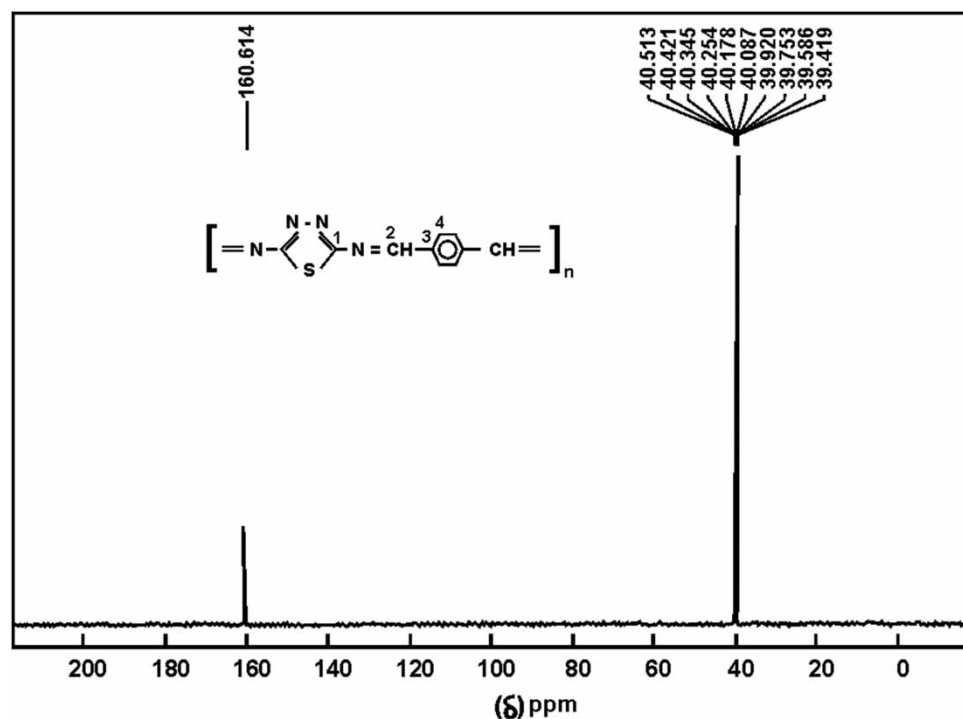
Figure 4 │ ¹H-NMR of TDPI polymer.

comes from significantly broad and ill-resolved peaks. This is due to the entanglement of chains that distort the shielding effect (Mohanty *et al.* 1998).

The –N=CH– protons appeared at $\delta = 8.73$ ppm. The structure of the polymer was further subjected to ^{13}C-NMR analysis. ^{13}C-NMR spectrum of polymer TDPI is shown in Figure 5. The C_1, C_2, C_3, and C_4 of the polymer corresponds to $\delta = 164$, 130, 129, and 115 ppm, respectively, which clearly confirms the structure explained in Figure 2.

Adsorption behavior of TDPI

Effect of pH on adsorption

The solution pH is an important parameter for metal ion sorption, because it has a remarkable effect on the speciation of metal ions as well as the surface charge and binding sites for the adsorbent. The adsorption capacities of Pb^{2+}, Cu^{2+}, Ni^{2+}, and Cd^{2+} onto TDPI adsorbent were determined in the range of 3.0–7.0 as shown in Figure 6. From the results it is evident that the adsorption capacities increase within the pH range 5.0–6.0 and the maximum metal uptake was obtained

at pH 6 for all metal ions investigated. This increase was expected because the thiadiazole groups are weakly basic and have good affinity for H^+ ions. At lower pH, there is competition between M^{2+} and H^+ ions, which results in lower adsorption capacities. When the pH increased, the competitive effect of H^+ ions decreased due to the replacement of H^+ ions by OH^- ions. This leads to increasing the affinity of adsorption sites towards metal ions. At pH 6, all the metal ions remain in solution. Only beyond a pH value of 10 does precipitation of metal ions take place. At the optimum pH of 6 only the adsorption process is in operation rather than precipitation.

Effect of adsorbent dosage on adsorption

Adsorption dosage is also an important factor in batch adsorption studies to determine the optimum dose. The effect of adsorbent amount on the removal of Pb^{2+}, Cu^{2+}, Ni^{2+} and Cd^{2+} ions is presented in Figure 7. It is clear from the figure that there was a rapid increase in adsorption when the adsorbent dose is increased from 40 to 60 mg. At 60 mg, the percentage removal was almost 90%. This significant change in adsorption capacity can be explained as such,
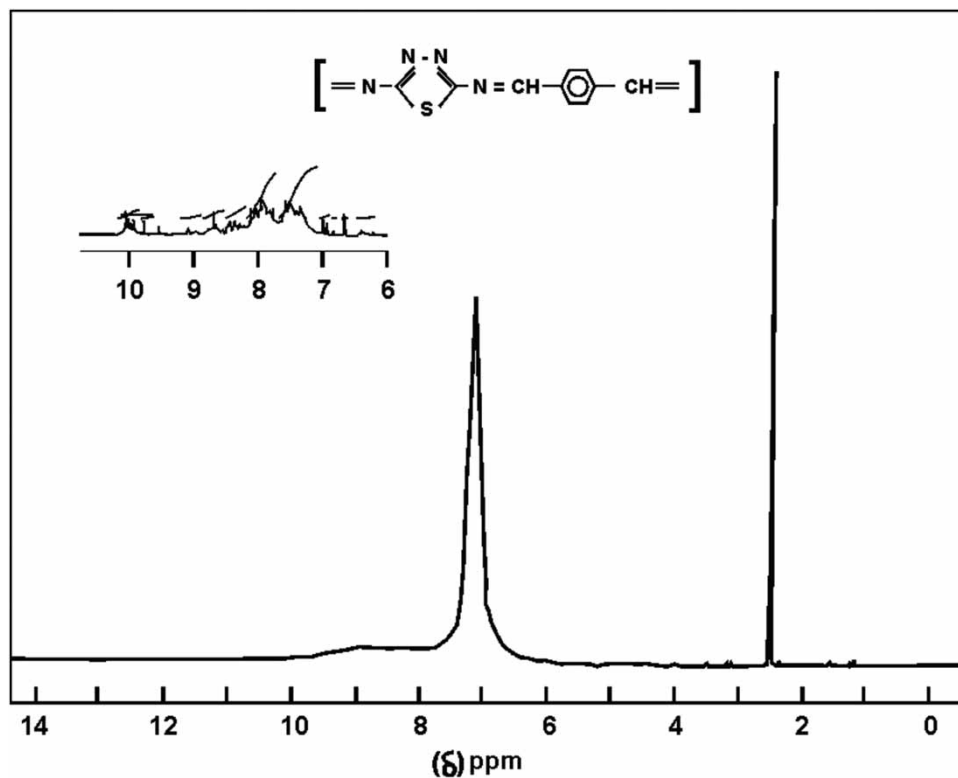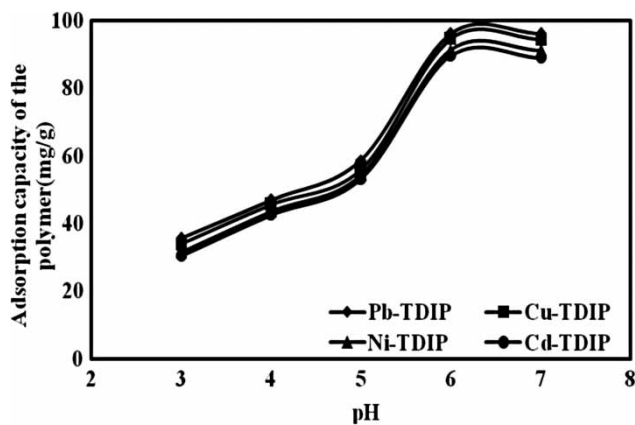
Figure 5 | ^{13}C-NMR of TDPI polymer.

Figure 6 | Effect of pH onto metal sorption (initial metal ion concentration = 100 mg/L, dose = 20 mg, and contact time = 60 min).

Figure 7 | Effect of adsorbent dosage onto metal ion sorption (initial metal ion concentration = 100 mg/L, solution pH = 6.0, and contact time = 60 min).

Effect of contact time on adsorption, kinetics, and adsorption mechanism

In order to evaluate the rate of adsorption reaction for Pb^{2+}, Cu^{2+}, Ni^{2+}, and Cd^{2+} ions onto TDPI, adsorption experiments covering different contact times (10–100 minutes) were performed at an initial individual metal ion concentration of 100 mg/L. The adsorption capacities of Pb^{2+},

that at higher adsorbent dose, functional groups present in the adsorbent also increase, consequently better adsorption takes place. Maximum removal was gained at 60 mg and no further substantial increase was noted beyond 60 mg adsorbent dose. Therefore, an optimum adsorbent dosage of 60 mg was kept for all subsequent experiments.
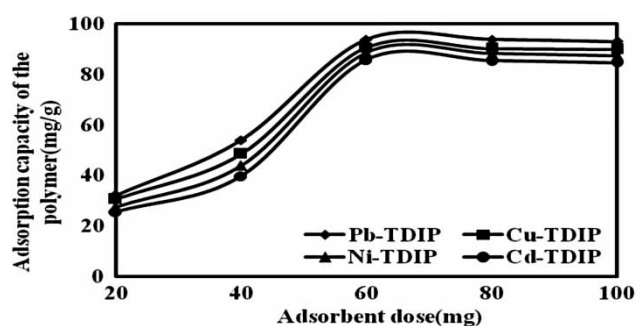
Cu^{2+}, Ni^{2+}, and Cd^{2+} ions onto TDPI were investigated with varying contact times and the results are presented in Figure 8. The adsorption equilibrium was attained within 50–70 minutes. To ensure the equilibrium condition was achieved, the contact time of 60 minutes was chosen.

Adsorption kinetics provides information about the rate controlling mechanism of the adsorption process. The reaction rate of the adsorbate uptake, which is required for selecting the optimum operating conditions for the full-scale batch process, can be elucidated with adsorption kinetic studies. To interrupt the kinetic studies of the metal adsorption process, Lagergren pseudo-first-order model, pseudo-second-order model, and intraparticle diffusion model were used to evaluate the experimental data.
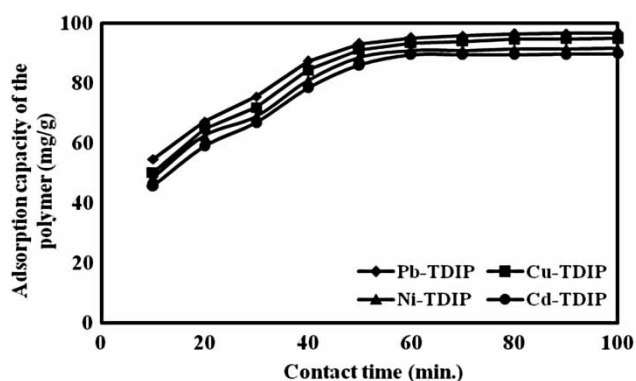
The literalized form of pseudo-first-order rate equation by Lagergren and Svenska (Lagergren 1898) is given as:

$$\log(q_e - q_t) = \log q_e - \frac{K_{ad}}{2.303}t \tag{2}$$

where q_e and q_t are the amount of metal ion adsorbed at equilibrium and at contact time t (min) and K_{ad} (min^{-1}) is the rate constant. From the plot of $\log(q_e - q_t)$ versus time t, the rate constant k_1 and correlation co-efficient R^2 are calculated and listed in Table 1.

The experimental data were also fitted by the pseudo-second-order kinetic model which is given by the equation below:

$$\frac{t}{q_t} = \frac{1}{h} + \frac{1}{q_e}t \tag{3}$$

where $h = kq_e^2$ ($mg.g^{-1}\ min^{-1}$) can be regarded as the initial adsorption rate as $t \to 0$ and k is the rate constant of pseudo-second-order adsorption ($g.mg^{-1}\ min^{-1}$).

The intraparticle diffusion model is expressed by the equation given by Weber & Morris (1963)

$$q_t = K_p t^{1/2} + C \tag{4}$$

where C is the intercept and K_p is the intraparticle diffusion rate constant ($mg/gmin^{1/2}$), and t is the time (min). The R^2 values and other kinetic parameters of pseudo-second-order and intraparticle diffusion kinetic models are presented in Table 1.

Figure 8 │ Effect of contact time onto transition metal ion sorption (initial metal ion concentration = 100 mg/L, solution pH = 6.0, and adsorbent dose = 60 mg).

Table 1 │ Kinetic models and other statistical parameters for metal ions sorption onto TDPI polymer

Kinetic model	Parameters	Concentration of lead(II) solution = 100 (mg/L)	Concentration of copper(II) solution = 100 (mg/L)	Concentration of nickel(II) solution = 100 (mg/L)	Concentration of cadmium(II) solution = 100 (mg/L)
Pseudo-first-order equation	k_{ad} (min^{-1})	0.0716	0.0776	0.0672	0.0621
	q_e, cal (mg/g)	131.21	168.96	113.92	110
	R^2	0.9891	0.9838	0.9867	0.9880
Pseudo-second-order equation	k ($g\ mg^{-1}\ min^{-1}$)	8.58×10^{-4}	7.06×10^{-4}	7.79×10^{-4}	7.14×10^{-4}
	q_e, cal (mg/g)	108.69	109.89	105.26	104.1
	h($mg.g^{-1}\ min^{-1}$)	10.14	8.53	8.64	7.74
	R^2	0.9966	0.9946	0.9956	0.9957
Intraparticle diffusion	K_p ($mg/g.\ min^{1/2}$)	6.2933	6.8158	6.4047	6.5874
	C	41.101	34.649	35.05	31.4
	R^2	0.8790	0.8793	0.879	0.8898

From the R^2 values, it is suggested that the adsorption of Pb^{2+}, Cu^{2+}, Ni^{2+}, and Cd^{2+} onto TDPI followed a second-order-type kinetics. The pseudo-second-order model is based on the assumption that the rate determining step may be a chemical adsorption involving valence forces through sharing or exchanging of electrons between adsorbent and the adsorbate (Reddad *et al.* 2002).

Effect of initial metal ion concentration and adsorption isotherm

The effect of initial metal ion concentration has a significant influence in determining the adsorption capacity of the resin. With the initial metal concentration in the range of 100–500 mg/L and at optimum conditions, percentage adsorption studies were carried out and the behavior is shown in Figure 9. It was clear from the results that with an increase in initial metal ion concentration adsorption capacity increases due to the presence of a large number of active sites available initially in the adsorbent. The initial concentration may provide the driving force to overcome the resistance to the mass transfer of metal ions between liquid and solid phases (Srivastava *et al.* 2006). The initial concentration is higher, and then the driving force was higher, and therefore the adsorption capacity would be higher.

It is not appropriate to use the coefficients in the determination of the linear regression method for comparing the best fit in isotherms. Due to inherent bias, resulting from linearization, alternative isotherm parameter sets were determined by non-linear regression. The non-linear method is a better way to obtain the isotherm parameters (Ho 2006; Ho *et al.* 2002). The adsorption isotherm data
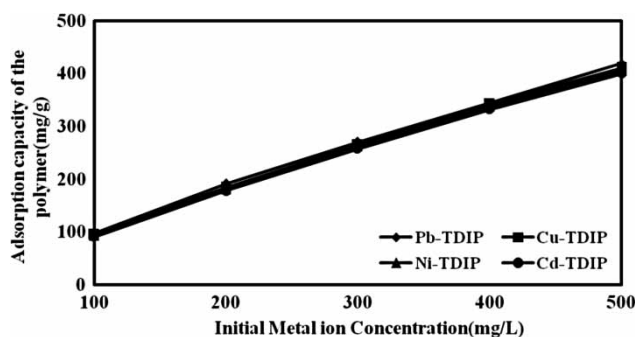

Figure 9 │ Effect of initial metal ions concentration onto metal ion sorption (initial metal ion concentration = 100–500 mg/L, pH = 6.0, dose = 60 mg/L, and time = 60 min).

were analyzed by fitting non-linear forms of Langmuir (Langmuir 1918), Freundlich (Freundlich 1906), and Redlich–Peterson (Redlich & Peterson 1959) adsorption isotherm models. The Langmuir isotherm model assumes a monolayer adsorption which takes place at specific homogeneous sites within the adsorbent and all the adsorption sites are energetically identified. In this model, a metal ion monolayer was formed on a modified adsorbent with a metal complex formation (Unlu & Ersoz 2007).

The non-linear equation of Langmuir isotherm model was expressed as follows:

$$q_e = \frac{q_m K_L C_e}{1 + K_L C_e} \tag{5}$$

where C_e is the supernatant concentration at the equilibrium state of the system (mg/L), q_m (mg/g) and K_L (L/mg) are the Langmuir constants, representing the maximum adsorption capacity for the solid phase loading and the energy constant related to the heat of adsorption, respectively.

The plot of C_e versus q_e was plotted and the values of q_m and K_L are presented in Table 2. In general, $K_L \geq 1$ indicates the unusability of the resin. $K_L = 1$ means reversible process, $K_L = 0$ indicates irreversible process and $1 > K_L > 0$ indicates the suitability of resin for the adsorption process. The values of K_L of Pb^{2+}, Cu^{2+}, Ni^{2+}, and Cd^{2+} ions at room temperature are in the range 0.0254–0.0911 (Table 2), indicating the suitability of TDPI for the adsorption of the metal ions from aqueous solution.

The Freundlich sorption isotherm model is the earliest known relationship describing the sorption process. The model applies to adsorption on interaction between the heterogeneous surface and the adsorbed molecule, and the application of the Freundlich equation also suggests that sorption energy exponentially decreases on completion of the sorptional centers of an adsorbent. The isotherm is an empirical equation which can be employed to describe the heterogeneous systems and is expressed as follows:

$$q_e = K_f C_e^{1/n} \tag{6}$$

where K_f is the Freundlich constant $((mg/g)(L/mg)(1/n))$ related to the bonding energy. K_f can be defined as the adsorption or distribution coefficient and represents the quantity of

Table 2 | Isotherm parameters and other constants obtained from non-linear model

Adsorbent	Isotherm model	Parameters	Lead	Copper	Nickel	Cadmium
TDPI	Langmuir	q_m (mg/g)	437.2	491.6	493.7	481.9
		k_L (L/mg)	0.0911	0.0377	0.0284	0.0254
		R^2	0.9780	0.9916	0.9963	0.9949
	Freundlich	K_f [(((mg/g)(L/mg)(1/n))]	96.25	55.76	44.41	40.78
		n (g/L)	3.105	2.323	2.145	2.159
		R^2	0.9710	0.9811	0.9821	0.9752
	Redlich–Peterson	K_R (L/g)	78.62	26.64	17.30	13.42
		α_R (L/mg)	0.4099	0.1307	0.0650	0.0394
		β (Constant)	0.8237	0.8217	0.8728	0.932
		R^2	0.9934	0.9964	0.9978	0.9953

metal ions adsorbed onto the adsorbent for unit equilibrium concentration. $1/n$ (g/L) is the heterogeneity factor and n is a measure of the deviation from linearity of adsorption. The values of K_f and n are calculated and listed in Table 2.

The Redlich–Peterson isotherm is a hybrid isotherm featuring both Langmuir and Freundlich models (Redlich & Peterson 1959) which incorporates three parameters into an empirical equation and can be applied either in homogeneous or heterogeneous systems due to its versatility (Foo & Hameed 2010). It approaches the Freundlich isotherm model at high concentrations and is in accordance with the low concentration limit of the ideal Langmuir condition. The equation is given as:

$$q_e = \frac{K_R C_e}{1 + \alpha_R C_e^{\beta}} \tag{7}$$

where q_e is the amount of adsorbate in the sorbent at equilibrium (mg/g), C_e is the equilibrium concentration (mg/L); K_R is the Redlich–Peterson isotherm constant (L/g), α_R is the Redlich–Peterson isotherm constant (L/mg), and β is the exponent which lies between 0 and 1. The Redlich–Peterson isotherm exponent which lies between 0 and 1, has two limiting behaviors: Langmuir form for $\beta = 1$ and Freundlich form for $\beta = 0$. The R^2 values of all the isotherms are given in Table 2. The R^2 values of Redlich–Peterson approach 1 and are 0.99 for all the metal ions examined. This value suggests that the Redlich–Peterson isotherm is best suited for the TDPI adsorbent which accounts for both the Freundlich and Langmuir possibilities, such as multilayered adsorption (SEM evidence: Figure 10) and

adsorption onto more than one type of binding site (Figure 11) proposed.

Certain inorganic metal ions co-ordinate with the organic functional groups present in the polymer through ionic bonds, co-ordinate bonds and ion–dipole interaction leading to the co-ordination of metal complexation. An important application of metal complexation with polymer is used in wastewater treatment for selective removal of toxic metal ions. However, their mechanism of complexation with the organic functional groups present in the polymer is still a matter of speculation. Cu^{2+} consists of a d^9 configuration and is known to form 1:1 and 1:2 complexes with polymeric adsorbents (Espana et al. 1987; Sirola et al. 2010). Hence the possible chelating form between Cu^{2+} metal ion and TDPI represented as shown in Figure 11. Similar conclusions may be drawn for the other investigated metal ions. To further corroborate the findings, the bare and metal ion adsorbed TDPI were subjected to solid state UV studies and the results are shown in Figure 12. It is clear from the UV spectra that the metal ion adsorbed TDPI shows absorption in the region of 650 nm when compared to the raw TDPI, which supports the formation of metal complexes with TDPI.

Thermodynamics of adsorption

The effect of temperature on the adsorption of Pb^{2+}, Cu^{2+}, Ni^{2+}, and Cd^{2+} ions onto the chelating resin TDPI has been studied over the temperature range of 303–333 K under optimum condition. It can be observed that the amounts of Pb^{2+}, Cu^{2+}, Ni^{2+}, and Cd^{2+} ion adsorption
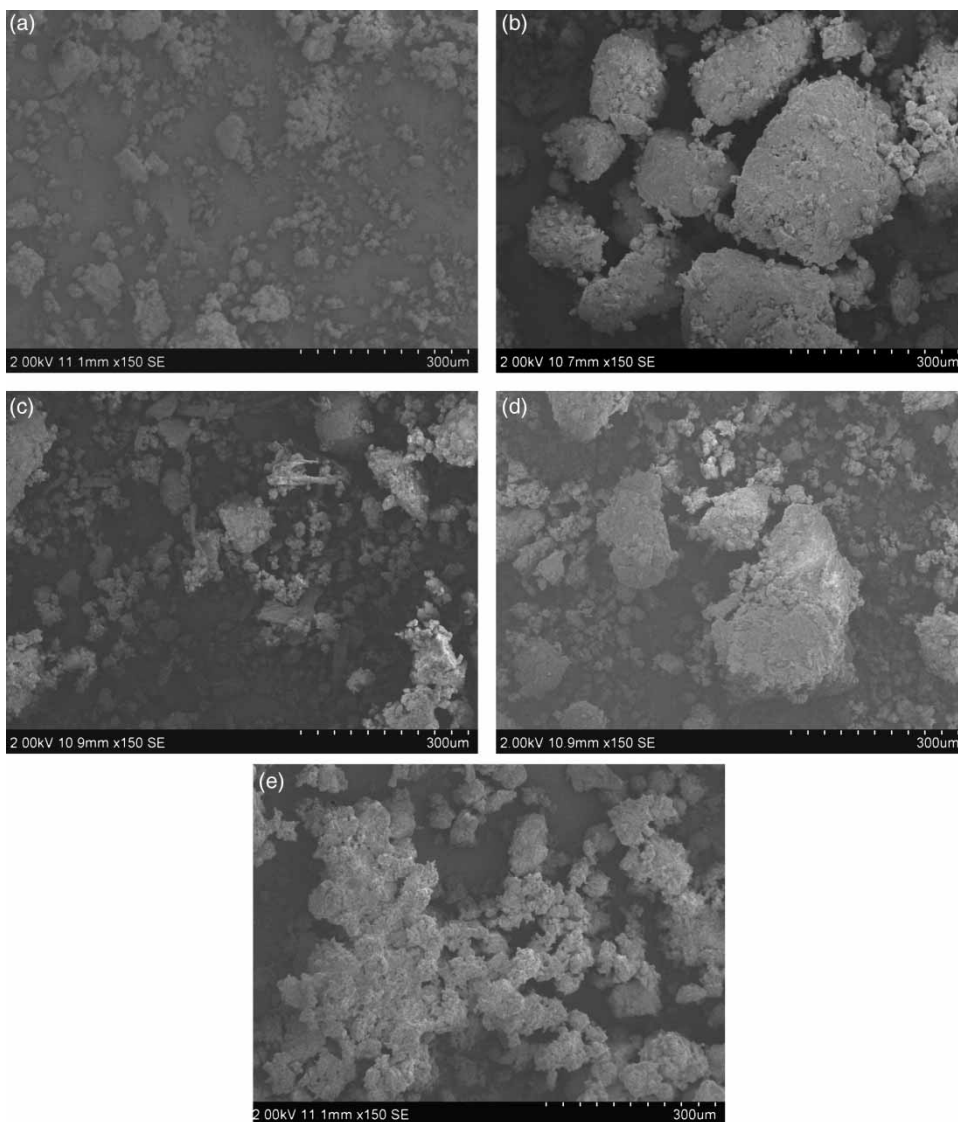
Figure 10 │ Comparison of raw and metal loaded SEM images of TDPI adsorbent: (a) SEM micrographs polymer resins TDPI; (b) SEM micrographs of Pb adsorbed TDPI; (c) Cu adsorbed TDPI; (d) Ni adsorbed TDPI; (e) Cd adsorbed TDPI.

decreased with an increase in temperature, which indicates that the process is exothermic in nature (Figure 13). The value of thermodynamic parameters such as Gibbs energy (ΔG), enthalpy (ΔH), and entropy (ΔS) are estimated using the relation:

$$\Delta G = -RT \ln K_d \tag{8}$$

$$\Delta H = \Delta G - T \quad \Delta S \tag{9}$$

$$\Delta G^\circ = -RT \ln\left(\frac{C_{Ae}}{C_e}\right) \tag{10}$$

$$\log K_d = \frac{\Delta S^\circ}{2.303R} - \frac{\Delta H^\circ}{2.303RT} \tag{11}$$

where K_d is the distribution coefficient, C_e is the equilibrium metal ion concentration in solution (mg/L), C_{Ae} is the amount of metal ion adsorbed onto TDPI per liter of solution at equilibrium (mg/L), R is the gas constant
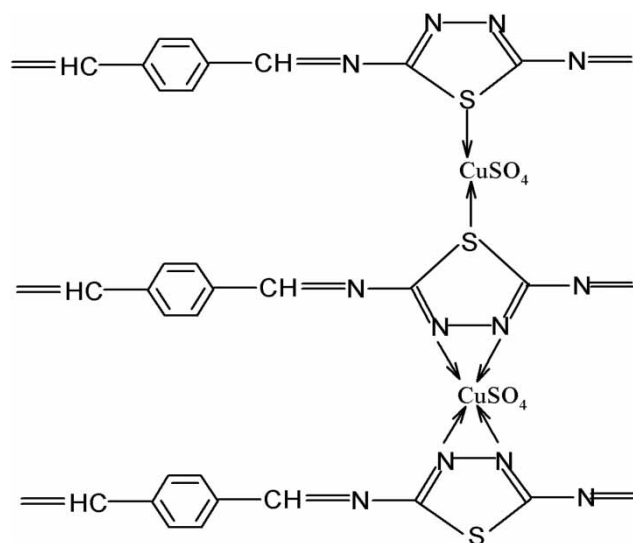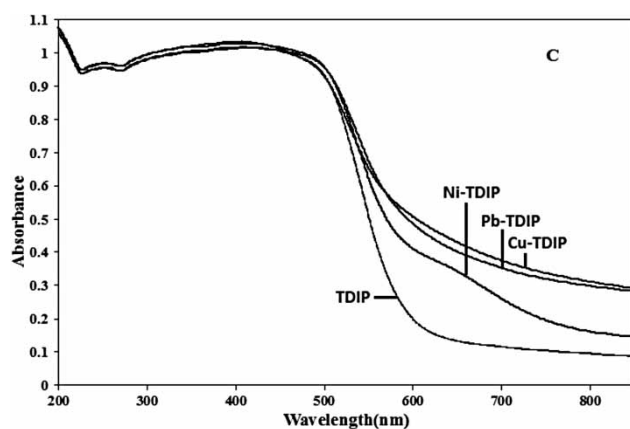
Figure 11 | Adsorption mechanism of TDPI polymer.

Figure 12 | Solid state UV spectra of raw TDPI and Cu^{2+}, Pb^{2+}, and Ni^{2+} adsorbed TDPI.
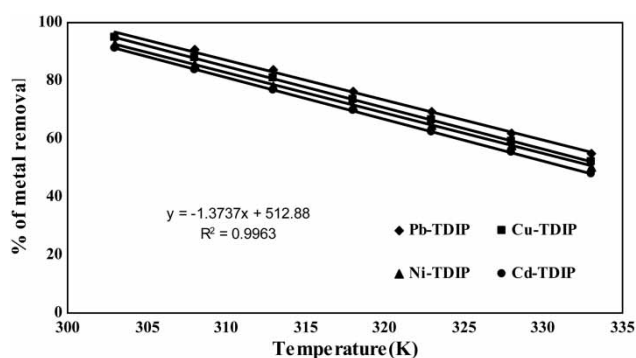

Figure 13 | Temperature studies (K vs % of metal removal).

(8.314 J/mol/K), and T is the temperature (K). The values of (ΔG_{ads}), (ΔH_{ads}), and (ΔS_{ads}) are calculated and listed in Table 3. The exothermic nature of the process is further confirmed by the negative value of enthalpy change ΔH_{ads}. The negative entropy of adsorption ΔS_{ads} confirms the decreased randomness at the solid–solution interface during adsorption which reflects the affinity of the TDPI adsorbent towards metal ions. The feasibility of the process and its spontaneous nature is reflected in the negative energy values ΔG_{ads}.

Resin stability and re-usability

For the development of a good quality adsorbent, the regeneration ability, chemical stability, and thermal stability are the key features. These adsorbents which show high stability and do not collapse when used in different conditions are good candidates. The stability of the TDPI chelating resin has been studied in 0.1–0.3 N H_2SO_4 and HCl. The resin was shaken in acid solution of a range of concentrations for 60 minutes at room temperature and filtered. The resin was washed with distilled water until it was free from acidic solution and dried under vacuum at 60 °C for 10 hours. The adsorption capacity of the acid-treated resin was found to be similar to the untreated one with a small variation of 1–4%. This indicates that TDPI is stable in acid medium up to 0.3 N. The adsorbent when tested with common organic solvents like benzene, toluene, carbon tetrachloride, DMAc, etc., was found to be insoluble and does not swell. The thermal stability of the adsorbent was evaluated using thermo-gravimetric analysis (TGA), and the thermogram of TDPI is represented in Figure 14. The resin undergoes major decomposition only beyond 300 °C and the decomposition starts at 200 °C (initial weight loss up to 5% is due to the occluded solvent and moisture). The char yield at 763 °C is 64.3% which is a much higher value when compared to the carbon chain polymers usually used as chelating cross-linked polymers.

Concentrations of 0.1 N H_2SO_4 or HCl were sufficient enough for regeneration of metals. 0.1 N solution of H_2SO_4, HCl, and CH_3COOH were used as eluent for the regeneration of metals. It can be seen from Figure 15 that this resin was more effective and can be re-used after five cycles for adsorption–desorption with
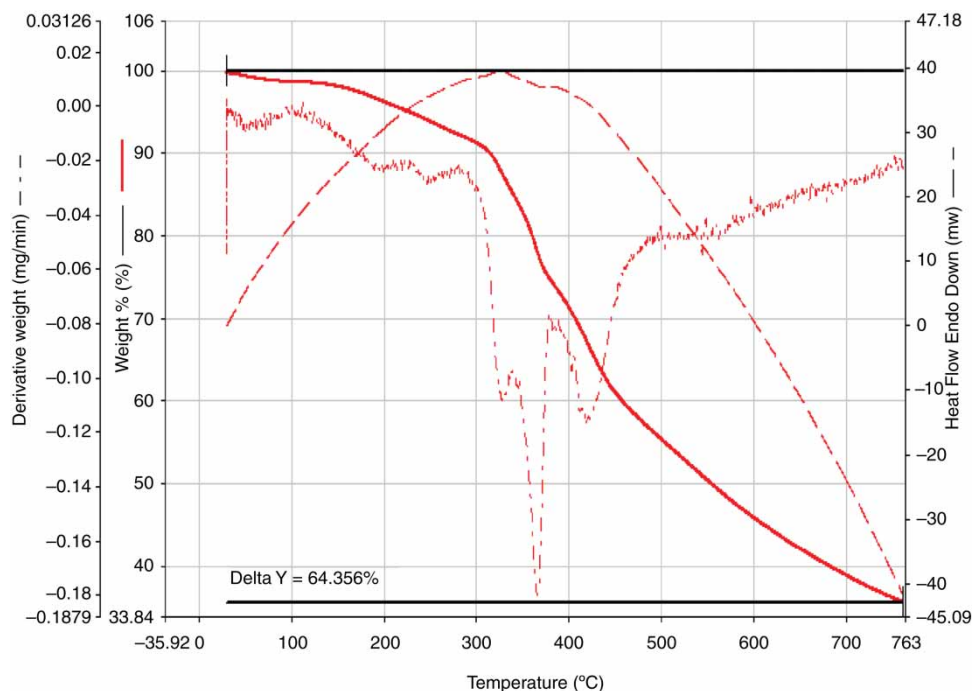
Figure 14 │ TGA of TDPI adsorbent.

Table 3 │ Thermodynamic parameters onto metal sorption by TDPI polymer

Adsorbent TDPI polymer	ΔH (kJ/mol)	ΔS (J/mol/K)	ΔG (kJ/mol)						
			303 K	308 K	313 K	318 K	323 K	328 K	333 K
Lead	−76.359	−228.99	−7.43	−5.87	−4.25	−3.12	−2.17	−1.35	−0.55
Copper	−74.788	−225.36	−7.30	−5.07	−3.74	−2.71	−1.83	−1.02	−0.23
Nickel	−66.900	−201.61	−6.37	−4.52	−3.32	−2.37	−1.64	−0.83	−0.05
Cadmium	−64.52	−195.30	−5.82	−4.21	−3.09	−2.18	−1.36	−0.57	−0.02

a 3.0–7.0% change in the adsorption capacity. Among the eluents used, acetic acid was least effective because it is a weak acid when compared to mineral acids. These results indicate that the adsorbent TDPI could be regenerated for re-use without a serious decline in performance.

CONCLUSION

Poly [2,5-(1,3,4-thiadiazole)-benzalimine] (TDPI) resin was prepared as a new adsorbent for removing Pb^{2+},

Cu^{2+}, Ni^{2+}, and Cd^{2+} ions from an aqueous solution. The maximum adsorption capacities of TDPI adsorbent for all four metal ions calculated from the Langmuir isotherm were found to be 437.2 mg/g for Pb^{2+}, 491.6 mg/g for Cu^{2+}, 493.7 mg/g for Ni^{2+}, and 481.9 mg/g for Cd^{2+}, respectively, which are higher than other polymeric chelating adsorbents (Table 4). The adsorption process for the metal ions onto TDPI fits well to pseudo-second-order kinetic model, and the best adsorption isotherm was found to be the Redlich–Peterson model. The adsorption process is spontaneous ($\Delta G_{ads} < 0$), exothermic ($\Delta H_{ads} < 0$), and reversible ($\Delta S_{ads} < 0$). For regeneration
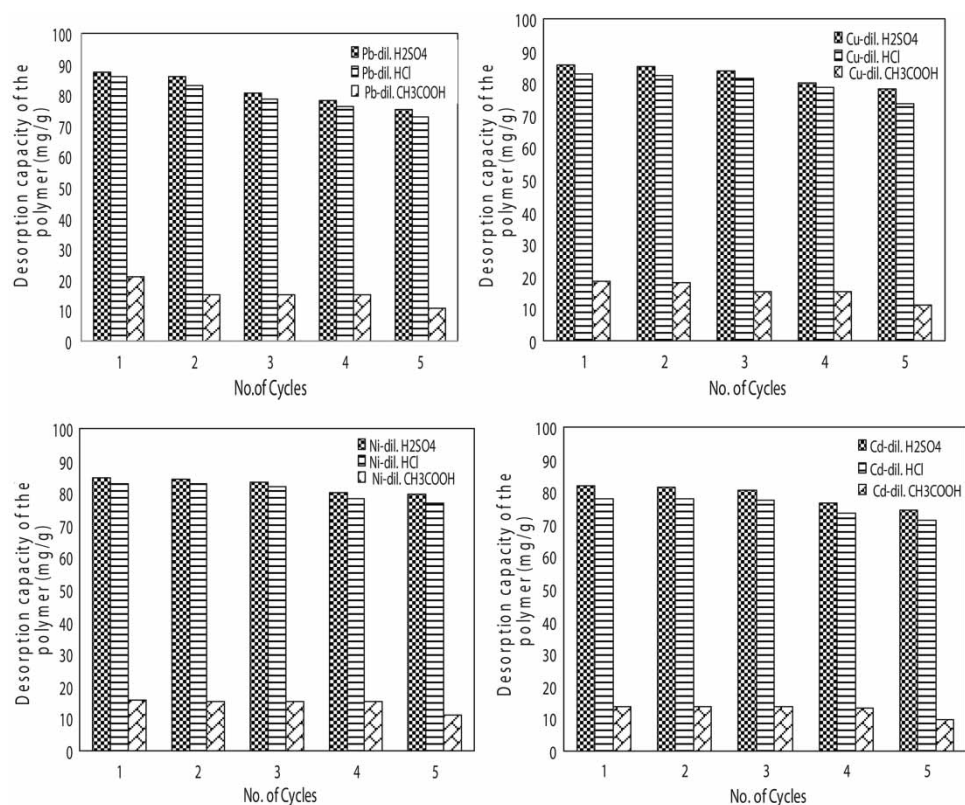
Figure 15 │ Desorption studies of adsorbent TDPI at 30 °C (metal ion concentration = 100 mg/L, adsorbent dose = 20 mg, and pH = 6.0).

Table 4 │ Comparison of adsorption capacities of various polymeric adsorbents with different functional groups for Pb^{2+}, Cu^{2+}, Ni^{2+}, and Cd^{2+} ions

Adsorbents	Functional groups	Adsorption capacity (mg/g)				Reference
		Pb(II)	Cu(II)	Ni(II)	Cd(II)	
SBA-15	3-Aminopropytriethoxy silane	–	–	14.10	23.70	Shahbazi *et al.* (2011)
NH_2–MCM–41	$-RNH_2-$	–	–	40.50	79.80	Lam *et al.* (2007)
NH_2–MCM–41	$-NH_2$	57.74	–	12.36	18.25	Heidari *et al.* (2009)
NH_2–SNHS	3-Aminopropyltriethoxy-silane (APTES)	96.79	–	40.73	31.29	Najafi *et al.* (2012)
Mercerized cellulose (DIPCI)	Triethylenetetramine	147.1	56.8	–	68.0	Gurgel & Gil (2009)
Present work	Thiadiazole, imine	437.2	491.6	493.7	481.9	TDPI

purposes, 0.1 N H_2SO_4 was found to be sufficient. Due to its good thermal, chemical stability, high adsorption capacities, and re-usability, TDPI exhibits potential application for efficient removal of Pb^{2+}, Cu^{2+}, Ni^{2+}, and Cd^{2+} ions from aqueous effluents.

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