

## 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

Selvaraj Dinesh Kirupha, Selvaraj Kalaivani, Thangaraj Vidhyadevi, Periyaraman Premkumar, Palanithamy Baskaralingam, Subramanian Sivanesan and Lingam Ravikumar

### 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),  $^1\text{H-NMR}$ , and  $^{13}\text{C-NMR}$  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  $\text{Pb}^{2+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Ni}^{2+}$ , and  $\text{Cd}^{2+}$  on to TDPI could reach up to 437.2, 491.6, 493.7, and 481.9  $\text{mg.g}^{-1}$  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  $\text{H}_2\text{SO}_4$ ) and could be regenerated without any serious decline in performance.

**Key words** | adsorption studies, isotherm, kinetics, polyimine, regeneration studies, thiadiazol

**Selvaraj Dinesh Kirupha**  
Department of Chemistry,  
Coimbatore Institute of Technology,  
Coimbatore 641 014,  
India

**Selvaraj Kalaivani**  
**Thangaraj Vidhyadevi**  
**Periyaraman Premkumar**  
**Palanithamy Baskaralingam**  
**Subramanian Sivanesan**  
Department of Applied Science and Technology,  
Anna University,  
Chennai 600025,  
India

**Lingam Ravikumar** (corresponding author)  
Department of Chemistry,  
CBM College (Affiliated to Bharathiar University),  
Coimbatore 641042,  
India  
E-mail: [ravikumarcbm@rediffmail.com](mailto:ravikumarcbm@rediffmail.com)

### 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-naphthol-3,6-disulfonic acid (Mondal *et al.* 2002), 1-(2-thioazalylazo)2-naphthol (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  $\text{Pt}^{2+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Pb}^{2+}$ ,  $\text{Cd}^{2+}$ , and  $\text{Fe}^{3+}$ . Recently, aminomethyl pyridine functional group in a silica matrix was reported for selective adsorbent of  $\text{Cu}^{2+}$  (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  $\text{Pb}^{2+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Ni}^{2+}$ , and  $\text{Cd}^{2+}$  (Kirupha *et al.* 2013). Polyamides in which the azomethine group is present as pendant chlorobenzylidene rings was found to be highly effective under competitive conditions in which the adsorption capacities were in the order  $\text{Cu}^{2+} > \text{Pb}^{2+} > \text{Cr}^{3+} > \text{Cd}^{2+}$  (Murugesan *et al.* 2011). Polyimine with thiourea as the functional group was an equally effective adsorbent for the removal of  $\text{Zn}^{2+}$  and  $\text{Ni}^{2+}$ . 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  $\text{Cu}^{2+}$  and  $\text{Pb}^{2+}$  (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 regeneration ability and are easy to recycle (washing with 0.1 N H<sub>2</sub>SO<sub>4</sub> 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), terephthalaldehyde (Aldrich) were used without purification. Dimethylformamide (DMF) (Himedia) was stored over anhydrous CaS<sub>2</sub> 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 condensation 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 azeotrope 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<sup>2+</sup>, Cu<sup>2+</sup>, Ni<sup>2+</sup>, and Cd<sup>2+</sup> uptake capacities of the adsorbent TDPI (poly [2,5-(1,3,4-thiadiazole)-benzalimine]) were determined in dissolved solutions of Pb(NO<sub>3</sub>)<sub>2</sub>, CuSO<sub>4</sub>·5H<sub>2</sub>O, NiSO<sub>4</sub>·6H<sub>2</sub>O, and 3Cd(SO<sub>4</sub>)·8H<sub>2</sub>O, respectively, using double distilled water. The concentration of all the stock solutions was kept at 1.0 g.L<sup>-1</sup>. Adsorption experiments were performed by mixing TDPI (20–100 mg) with 20 mL of the desired metal ion concentration of Pb<sup>2+</sup>, Cu<sup>2+</sup>, Ni<sup>2+</sup>, and Cd<sup>2+</sup> 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 filtered 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 solution 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 adsorbent was calculated according to the following equation:

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

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



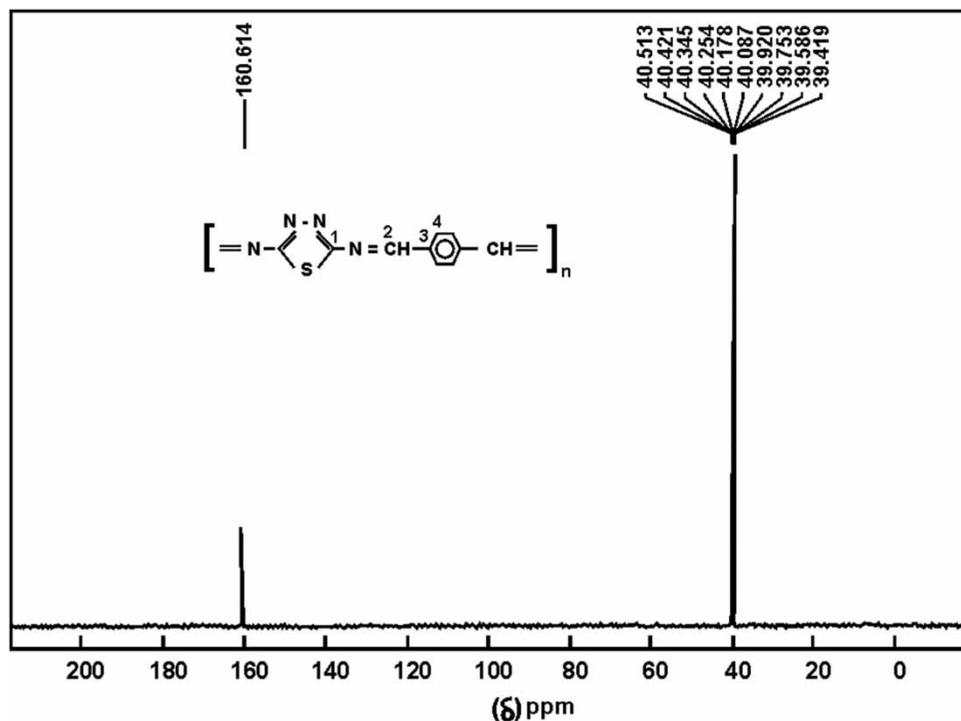


Figure 4 |  $^{13}\text{C}$ -NMR of TDPI polymer.

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  $-\text{N}=\text{CH}-$  protons appeared at  $\delta = 8.73$  ppm. The structure of the polymer was further subjected to  $^{13}\text{C}$ -NMR analysis.  $^{13}\text{C}$ -NMR spectrum of polymer TDPI is shown in Figure 5. The  $\text{C}_1$ ,  $\text{C}_2$ ,  $\text{C}_3$ , and  $\text{C}_4$  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  $\text{Pb}^{2+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Ni}^{2+}$ , and  $\text{Cd}^{2+}$  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  $\text{H}^+$  ions. At lower pH, there is competition between  $\text{M}^{2+}$  and  $\text{H}^+$  ions, which results in lower adsorption capacities. When the pH increased, the competitive effect of  $\text{H}^+$  ions decreased due to the replacement of  $\text{H}^+$  ions by  $\text{OH}^-$  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  $\text{Pb}^{2+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Ni}^{2+}$  and  $\text{Cd}^{2+}$  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,

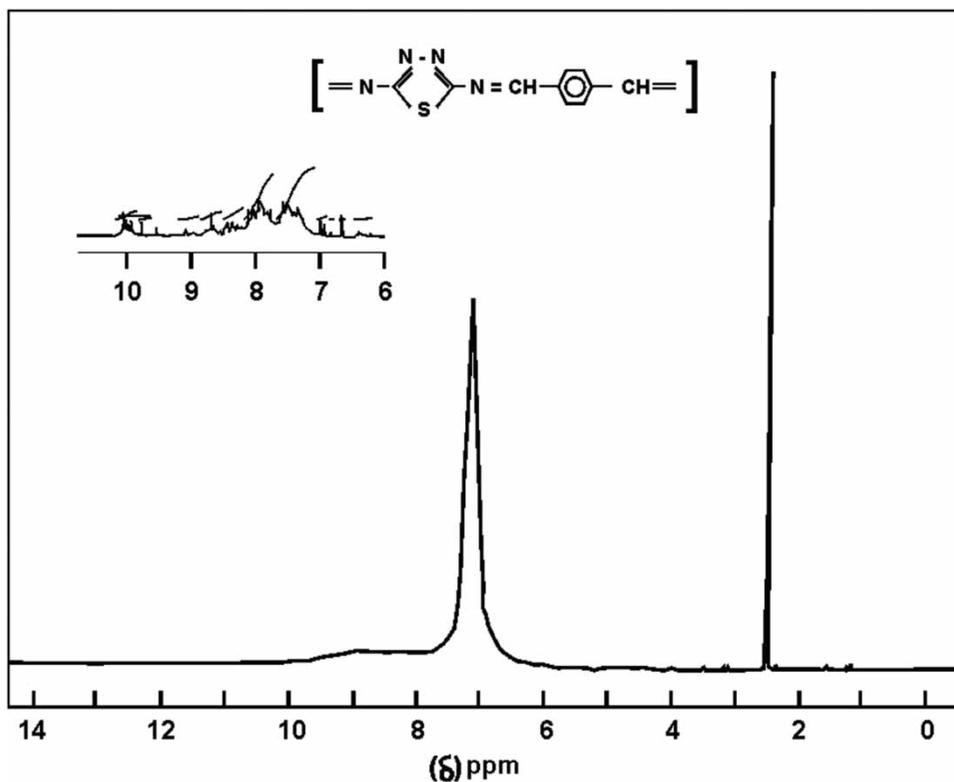


Figure 5 |  $^{13}\text{C}$ -NMR of TDPI polymer.

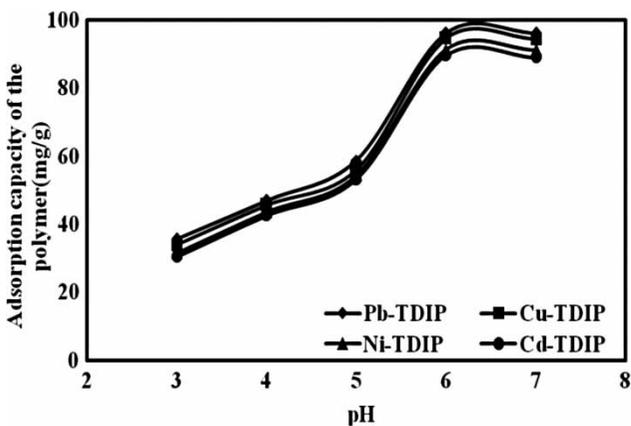


Figure 6 | Effect of pH onto metal sorption (initial metal ion concentration = 100 mg/L, dose = 20 mg, and contact time = 60 min).

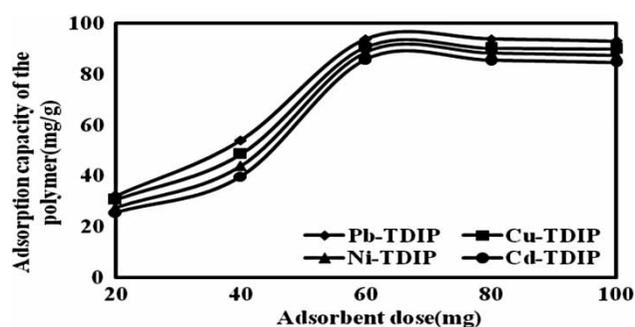


Figure 7 | Effect of adsorbent dosage onto metal ion sorption (initial metal ion concentration = 100 mg/L, solution pH = 6.0, and contact time = 60 min).

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.

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

In order to evaluate the rate of adsorption reaction for  $\text{Pb}^{2+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Ni}^{2+}$ , and  $\text{Cd}^{2+}$  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  $\text{Pb}^{2+}$ ,

$\text{Cu}^{2+}$ ,  $\text{Ni}^{2+}$ , and  $\text{Cd}^{2+}$  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.

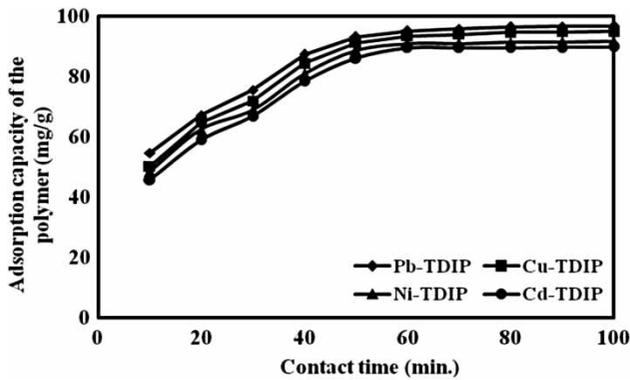


Figure 8 | Effect of contact time onto transition metal ion sorption (initial metal ion concentration = 100 mg/L, solution pH = 6.0, and adsorbent dose = 60 mg).

The literalized form of pseudo-first-order rate equation by Lagergren and Svenska (Lagergren 1898) is given as:

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

where  $q_e$  and  $q_t$  are the amount of metal ion adsorbed at equilibrium and at contact time  $t$  (min) and  $K_{ad}$  ( $\text{min}^{-1}$ ) 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:

$$\frac{t}{q_t} = \frac{1}{h} + \frac{1}{q_e}t \quad (3)$$

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

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

$$q_t = K_p t^{1/2} + C \quad (4)$$

where  $C$  is the intercept and  $K_p$  is the intraparticle diffusion rate constant ( $\text{mg/gmin}^{1/2}$ ), 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.

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

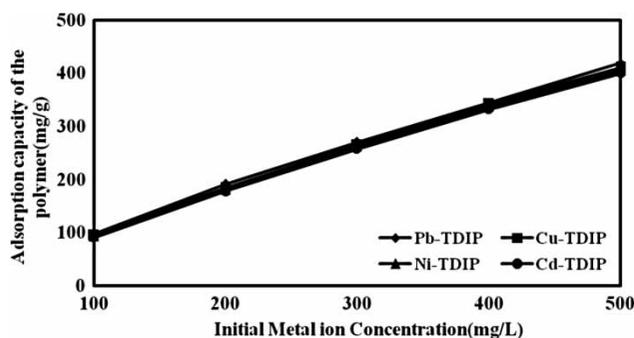
Kinetic model	Parameters	Concentration of lead(II)	Concentration of copper(II)	Concentration of nickel(II)	Concentration of cadmium(II)
		solution = 100 (mg/L)	solution = 100 (mg/L)	solution = 100 (mg/L)	solution = 100 (mg/L)
Pseudo-first-order equation	$k_{ad}$ ( $\text{min}^{-1}$ )	0.0716	0.0776	0.0672	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	$k$ ( $\text{g mg}^{-1} \text{min}^{-1}$ )	$8.58 \times 10^{-4}$	$7.06 \times 10^{-4}$	$7.79 \times 10^{-4}$	$7.14 \times 10^{-4}$
	$q_e$ , cal (mg/g)	108.69	109.89	105.26	104.1
	$h$ ( $\text{mg.g}^{-1} \text{min}^{-1}$ )	10.14	8.53	8.64	7.74
	$R^2$	0.9966	0.9946	0.9956	0.9957
Intraparticle diffusion	$K_p$ ( $\text{mg/g. min}^{1/2}$ )	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:

$$q_e = \frac{q_m K_L C_e}{1 + K_L C_e} \quad (5)$$

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:

$$q_e = K_f C_e^{1/n} \quad (6)$$

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
		$R^2$	0.9934	0.9964	0.9978	0.9953
	Redlich–Peterson	$K_R$ (L/g)	78.62	26.64	17.30	13.42
		$\alpha_R$ (L/mg)	0.4099	0.1307	0.0650	0.0394
		$\beta$ (Constant)	0.8237	0.8217	0.8728	0.932
		$R^2$	0.9934	0.9964	0.9978	0.9953
		$R^2$	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:

$$q_e = \frac{K_R C_e}{1 + \alpha_R C_e^\beta} \quad (7)$$

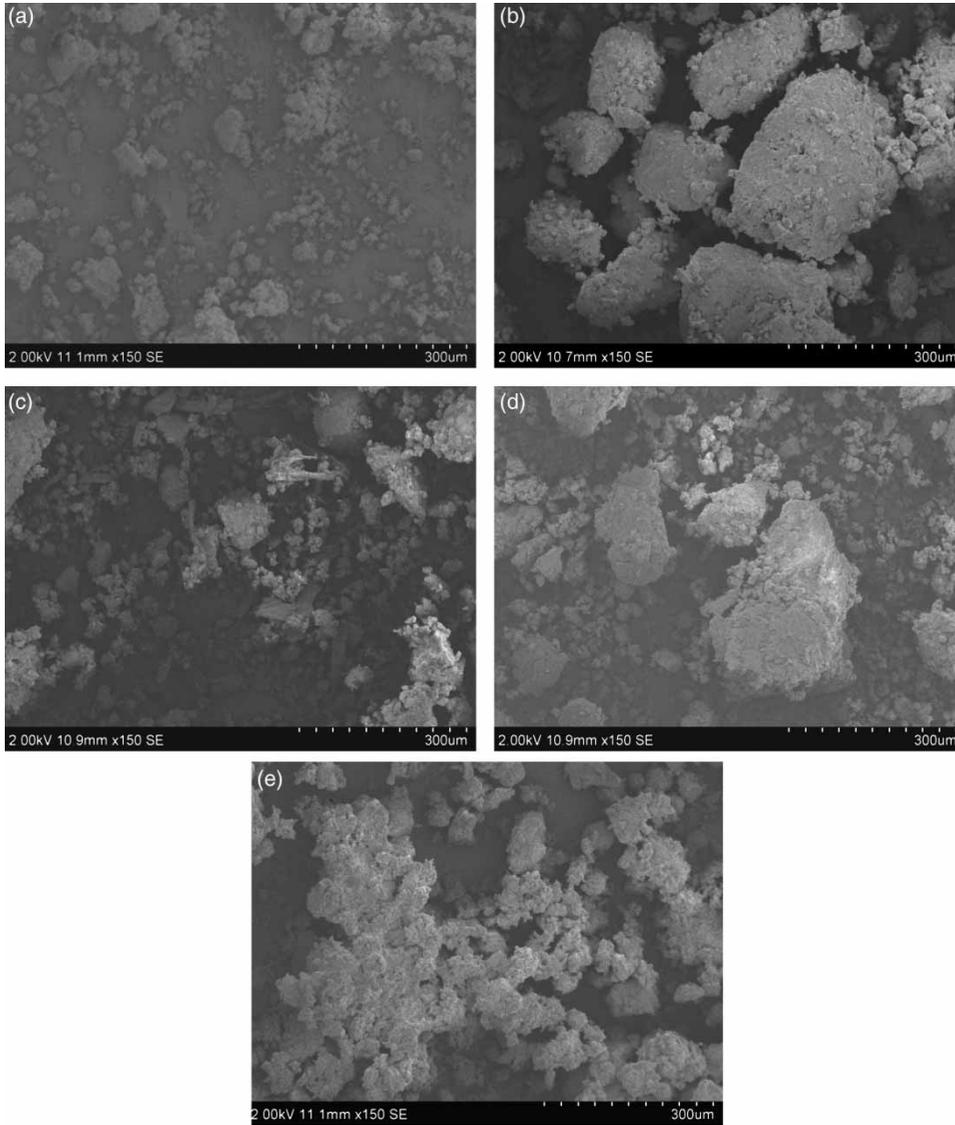
where  $q_e$  is the amount of adsorbate in the sorbent at equilibrium (mg/g),  $C_e$  is the equilibrium concentration (mg/L);  $K_R$  is the Redlich–Peterson isotherm constant (L/g),  $\alpha_R$  is the Redlich–Peterson isotherm constant (L/mg), and  $\beta$  is the exponent which lies between 0 and 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 (España *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 ( $\Delta G$ ), enthalpy ( $\Delta H$ ), and entropy ( $\Delta S$ ) are estimated using the relation:

$$\Delta G = -RT \ln K_d \quad (8)$$

$$\Delta H = \Delta G - T \Delta S \quad (9)$$

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

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

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

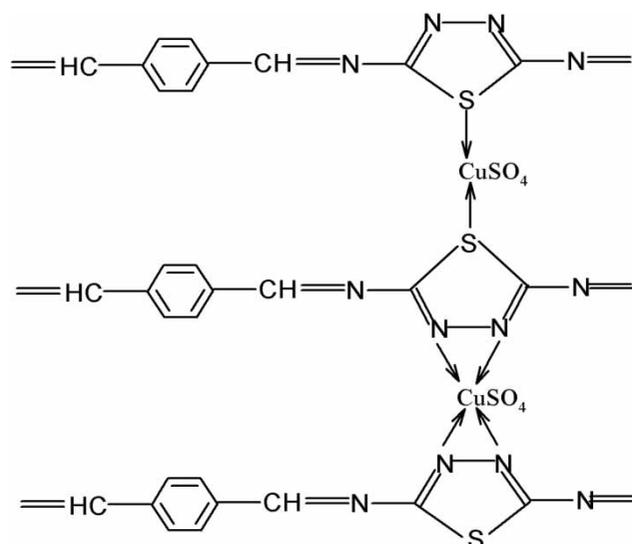


Figure 11 | Adsorption mechanism of TDPI polymer.

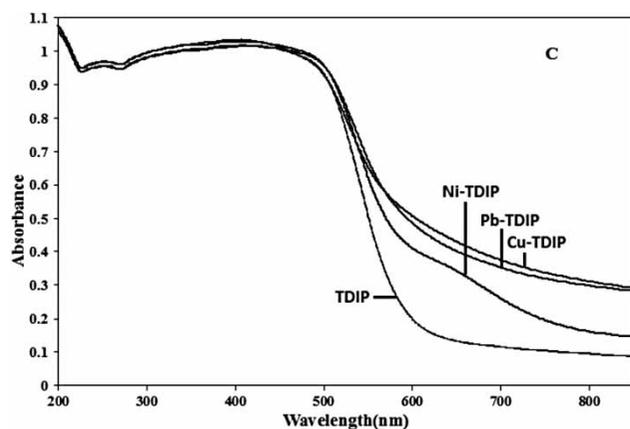


Figure 12 | Solid state UV spectra of raw TDPI and  $\text{Cu}^{2+}$ ,  $\text{Pb}^{2+}$ , and  $\text{Ni}^{2+}$  adsorbed TDPI.

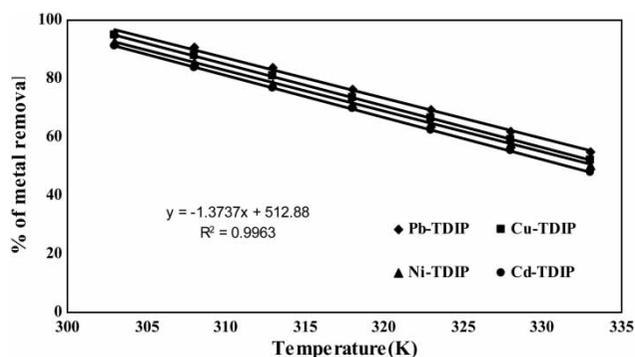


Figure 13 | Temperature studies (K vs % of metal removal).

(8.314 J/mol/K), and  $T$  is the temperature (K). The values of ( $\Delta G_{ads}$ ), ( $\Delta H_{ads}$ ), and ( $\Delta S_{ads}$ ) are calculated and listed in Table 3. The exothermic nature of the process is further confirmed by the negative value of enthalpy change  $\Delta H_{ads}$ . The negative entropy of adsorption  $\Delta S_{ads}$  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  $\Delta G_{ads}$ .

### 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  $\text{H}_2\text{SO}_4$  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  $\text{H}_2\text{SO}_4$  or HCl were sufficient enough for regeneration of metals. 0.1 N solution of  $\text{H}_2\text{SO}_4$ , HCl, and  $\text{CH}_3\text{COOH}$  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

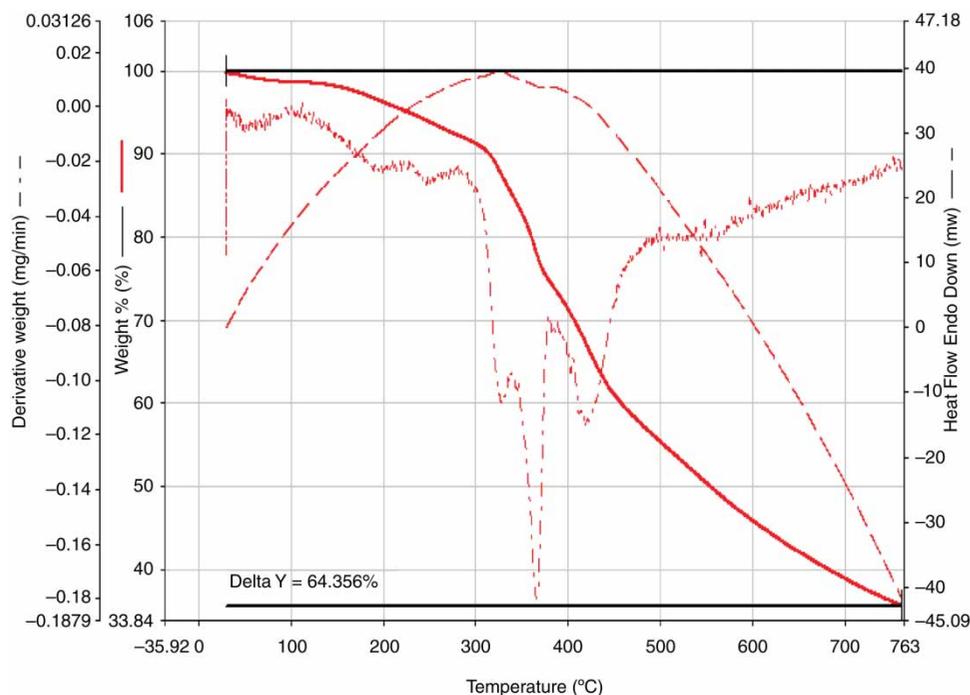


Figure 14 | TGA of TDPI adsorbent.

Table 3 | Thermodynamic parameters onto metal sorption by TDPI polymer

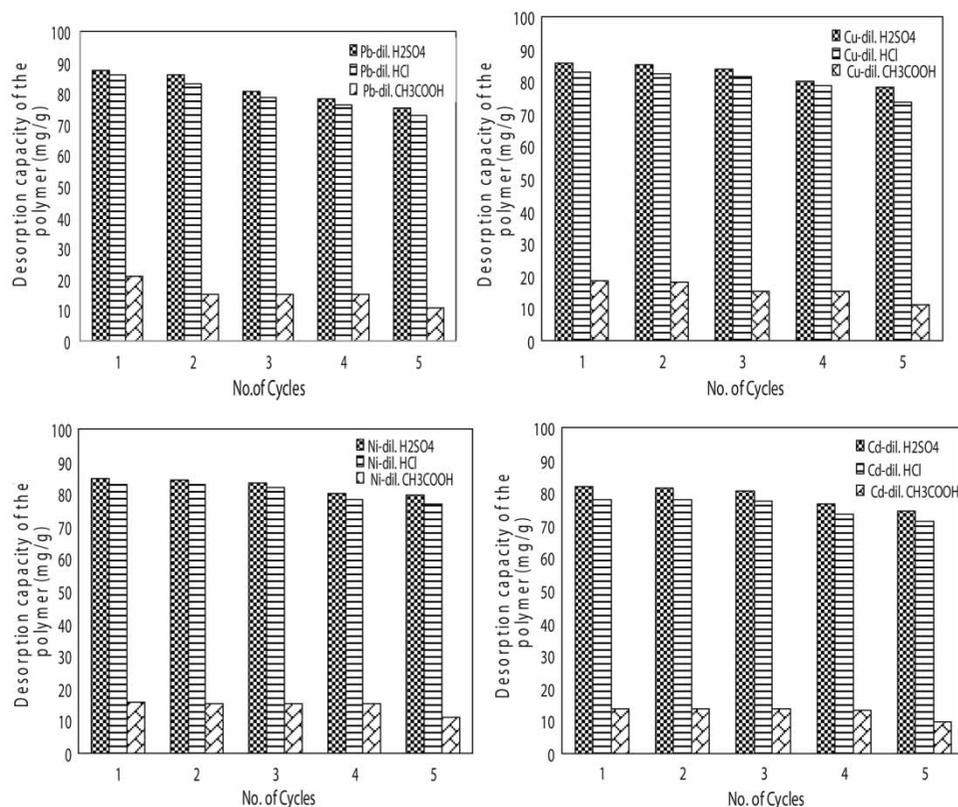
Adsorbent TDPI polymer	$\Delta H^\circ$ (kJ/mol)	$\Delta S^\circ$ (J/mol/K)	$\Delta G^\circ$ (kJ/mol)						
			303 K	308 K	313 K	318 K	323 K	328 K	333 K
Lead	-76.359	-228.99	-7.43	-5.87	-4.25	-3.12	-2.17	-1.35	-0.55
Copper	-74.788	-225.36	-7.30	-5.07	-3.74	-2.71	-1.83	-1.02	-0.23
Nickel	-66.900	-201.61	-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<sup>2+</sup>, Cu<sup>2+</sup>, Ni<sup>2+</sup>, and Cd<sup>2+</sup> ions

Adsorbents	Functional groups	Adsorption capacity (mg/g)				Reference
		Pb(II)	Cu(II)	Ni(II)	Cd(II)	
SBA-15	3-Aminopropyltriethoxy silane	–	–	14.10	23.70	Shahbazi et al. (2011)
NH <sub>2</sub> -MCM-41	-RNH <sub>2</sub> -	–	–	40.50	79.80	Lam et al. (2007)
NH <sub>2</sub> -MCM-41	-NH <sub>2</sub>	57.74	–	12.36	18.25	Heidari et al. (2009)
NH <sub>2</sub> -SNHS	3-Aminopropyltriethoxy-silane (APTES)	96.79	–	40.73	31.29	Najafi et al. (2012)
Mercurized 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<sub>2</sub>SO<sub>4</sub> 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<sup>2+</sup>, Cu<sup>2+</sup>, Ni<sup>2+</sup>, and Cd<sup>2+</sup> ions from aqueous effluents.

## REFERENCES

- Abburi, K. 2003 Adsorption of phenol and p-chlorophenol from their single and bisolute aqueous solutions on amberlite XAD-16 resin. *J. Hazard. Mater.* **105**, 143–156.

- Bai, L., Hu, H., Zhang, W., Fu, J., Lu, Z., Liu, M., Jiang, H., Zhang, L., Chen, Q. & Tan, P. 2012 [Amine/acid catalyzed synthesis of a new silica-aminomethyl pyridine material as a selective adsorbent of copper](#). *J. Mat. Chem.* **22**, 17293–17301.
- Bernard, J., Branger, C., Nguyen, T. L. A., Denoyel, R. & Margailan, A. 2008 [Synthesis and characterization of a polystyrenic resin functionalized by catechol: application to retention of metal ions](#). *React. Funct. Polym.* **68**, 1362–1370.
- Bohra, P. M., Vaze, A. S. & Pangarkar, V. G. 1994 [Adsorptive recovery of water soluble essential oil components](#). *J. Chem. Tech. Biot.* **60**, 97–102.
- Chang, C. F., Chang, C. Y., Hsu, K. E., Lee, S. C. & Holl, W. 2008 [Adsorptive removal of the pesticide methomyl using hyper crosslinked polymers](#). *J. Hazard. Mater.* **155**, 295–304.
- Chen, J. L., Pan, B. C., Xiong, Y., Li, A. M., Long, C., Han, Y. Z., Sun, Y. & Zhang, Q. X. 2002 Chinese patent: CN1384069.
- Deosarkar, S. P. & Pangarkar, V. G. 2004 [Adsorptive separation and recovery of organics from PHBA and SA plant effluents](#). *Sep. Purif. Technol.* **38**, 241–254.
- Espana, E. G., Nuzzi, F., Sabatini, A. & Vacca, A. 1987 [Reactions of 2-\(aminomethyl\)pyridine with hydrogen ion and divalent transition metal ions. II. Thermodynamic functions and visible spectra](#). *Gazz. Chim. Ital.* **117**, 273–275.
- Foo, K. Y. & Hameed, B. H. 2010 [Insights into the modeling of adsorption isotherm systems](#). *Chem. Eng. J.* **156**, 2–10.
- Freitas, P. A. M., Iha, K. & Felinto, M. C. F. C. 2008 [Adsorption of di-2-pyridyl ketone salicyloylhydrazone on amberlite XAD-2 and XAD-7 resins: characteristics and isotherms](#). *J. Coll. Interf. Sci.* **323**, 1–5.
- Freundlich, H. M. F. 1906 [Uber die adsorption in losungen](#). *Z. Phys. Chem.* **57**, 385–470.
- Gurgel, L. V. A. & Gil, L. F. 2009 [Adsorption of Cu\(II\), Cd\(II\) and Pb\(II\) from aqueous single metal solutions by succinylated mercerized cellulose modified with triethylenetetramine](#). *Carbohydr. Polym.* **77**, 142–149.
- Gusler, G. M., Browne, T. E. & Cohen, Y. 1993 [Sorption of organics from aqueous solution onto polymeric resins](#). *Ind. Eng. Chem. Res.* **32**, 2727–2735.
- Heidari, A., Younesi, H. & Mehraban, Z. 2009 [Removal of Ni\(II\), Cd\(II\), and Pb\(II\) from a ternary aqueous solution by amino functionalized mesoporous and nanoporous silica](#). *Chem. Eng. J.* **153**, 70–79.
- Ho, Y. S. 2006 [Isotherms for the sorption of lead onto peat: comparison of linear and non-linear methods](#). *Pol. J. Environ. Stud.* **15** (1), 81–86.
- Ho, Y. S., Porter, J. F. & McKay, G. 2002 [Equilibrium isotherm studies for the sorption of divalent metal ions onto peat: copper, nickel and lead single component systems](#). *Water Air Soil Poll.* **141**, 1–33.
- Hosseini, M. S., Raissi, H. & Madarshahian, S. 2006 [Synthesis and application of a new chelating resin functionalized with 2,3-dihydroxy benzoic acid for Fe\(III\) determination in water samples by flame atomic absorption spectrometry](#). *React. Funct. Polym.* **66**, 1539–1545.
- Kirupha, S. D., Murugesan, A., Vidhyadevi, T., Baskaralingam, P., Sivanesan, S. & Ravikumar, L. 2013 [Novel polymeric adsorbents bearing amide, pyridyl, azomethine and thiourea binding sites for removal of Cu\(II\) and Pb\(II\) ions from aqueous solution](#). *Separ. Sci. Technol.* **48**, 254–262.
- Lagergren, S. 1898 [About the theory of so-called adsorption of soluble substances](#). *K. Sven. Vetensk. Handl.* **24**, 1–39.
- Lam, K. F., Yeung, K. L. & McKay, G. 2007 [Efficient approach for Cd<sup>2+</sup> and Ni<sup>2+</sup> removal and recovery using mesoporous adsorbent with tunable selectivity](#). *Environ. Sci. Technol.* **41**, 3329–3334.
- Langmuir, I. 1918 [Adsorption of gases on plain surface of glass mica platinum](#). *J. Am. Chem. Soc.* **40**, 1361–1403.
- Lee, W., Lee, S. E., Lee, C. H., Kim, Y. S. & Lee, Y. I. 2001 [A chelating resin containing 1-\(2-thiazolylazo\)-2-naphthol as the functional group; synthesis and sorption behavior for trace metal ions](#). *Microchem. J.* **70**, 195–203.
- Lee, J. W., Jung, H. J., Kwak, D. H. & Chung, P. G. 2005 [Adsorption of dichloromethane from water onto a hydrophobic polymer resin XAD-1600](#). *Water Res.* **39**, 617–629.
- Leinonen, H. & Lehto, J. 2000 [Ion-exchange of nickel by iminodiacetic acid chelating resin Chelex 100](#). *React. Funct. Polym.* **43**, 1–6.
- Meesri, S., Praphairaksit, N. & Imyim, A. 2007 [Extraction and pre-concentration of toxic metal ions from aqueous solution using benzothiazole-based chelating resins](#). *Microchem. J.* **87**, 47–55.
- Melenchuk, T. V., Danilva, E. A., Stryapan, M. G. & Islyaikin, K. S. 2008 [Synthesis and properties of diaminothiadiazoles](#). *Russ. J. Gen. Chem.* **78** (3), 480–484.
- Mohanty, A. K., Das, D., Panigrahi, A. K. & Mishra, M. 1998 [Synthesis and characterization of a novel polyamide: polycondensation of 2,5-diaminothiazole with terephthalic acid](#). *Eur. Polym. J.* **34** (12), 1889–1898.
- Mondal, B. C. & Das, A. K. 2003 [Determination of mercury species with a resin functionalized with a 1,2-bis\(o-aminophenylthio\) ethane moiety](#). *Anal. Chim. Acta* **477**, 73–80.
- Mondal, B. C., Das, D. & Das, A. K. 2002 [Synthesis and characterization of a new resin functionalized with 2-naphthol-3,6-disulfonic acid and its application for the speciation of chromium in natural water](#). *Talanta* **56**, 145–152.
- Murugesan, A., Ravikumar, L., SathyaSelvaBala, V., SenthilKumar, P., Vidhyadevi, T., Kirupha, S. D., Kalaivani, S. S., Krithiga, S. & Sivanesan, S. 2011 [Removal of Pb\(II\), Cu\(II\) and Cd\(II\) ions from aqueous solution using polyazomethineamides: equilibrium and kinetic approach](#). *Desalination* **271**, 199–208.
- Murugesan, A., Vidhyadevi, T., Kalaivani, S. S., Premkumar, M. P., Ravikumar, L. & Sivanesan, S. 2012 [Kinetic and thermodynamic studies on the removal of Zn<sup>2+</sup> and Ni<sup>2+</sup> from their aqueous solution using poly\(phenylthiourea\) imine](#). *Chem. Eng. J.* **197**, 368–378.
- Najafi, M., Yousefi, Y. & Rafati, A. A. 2012 [Synthesis, characterization and adsorption studies of several heavy](#)

- metal ions on amino-functionalized silica nano hollowsphere and silica gel. *Sep. Purif. Technol.* **85**, 193–205.
- Pan, B. J., Pan, B. C., Zhang, W. M., Zhang, Q. R., Zhang, Q. X. & Zheng, S. R. 2008 Adsorptive removal of phenol from aqueous phase by using a porous acrylic ester polymer. *J. Hazard. Mater.* **157**, 293–299.
- Pan, B. J., Pan, B. C., Zhang, W. M., Zhang, Q. R., Zhang, Q. X. & Zheng, S. R. 2009 Development of polymeric and polymer-based hybrid adsorbents for pollutants removal from waters. *Chem. Eng. J.* **151**, 19–29.
- Ravikumar, L., Kalaivani, S. S., Murugesan, A., Vidhyadevi, T., Karthik, G., Kirupha, S. D. & Sivanesan, S. 2011 Synthesis, characterization and heavy metal ion adsorption studies of polyamides, polythioamides having pendent chlorobenzylidene rings. *J. App. Polym. Sci.* **122**, 1634–1642.
- Reddad, Z., Gerente, C., Andres, Y. & Cloirec, P. L. 2002 Adsorption of several metal ions onto a low-cost biosorbent: kinetic and equilibrium studies. *Environ. Sci. Technol.* **36**, 2067–2073.
- Redlich, O. & Peterson, D. L. 1959 A useful adsorption isotherm. *J. Phys. Chem.* **63**, 1024–1026.
- Rivas, B. L., Pooley, S. A., Maturana, H. A. & Villegas, S. 2001 Sorption properties of poly(styrene-co-divinylbenzene) amine functionalized weak resin. *J. Appl. Polym. Sci.* **80**, 2123–2127.
- Shahbazi, A., Younesi, H. & Badiei, A. 2011 Functionalized SBA-15 mesoporous silica by melamine-based dendrimer amines for adsorptive characteristics of Pb(II), Cu(II) and Cd(II) heavy metal ions in batch and fixed bed column. *Chem. Eng. J.* **168**, 505–518.
- Sirola, K., Laatikainen, M. & Paatero, E. 2010 Effect of temperature on sorption of metals by silica-supported 2-(aminomethyl)pyridine. Part I: Binding equilibria. *React. Funct. Polym.* **70**, 48–55.
- Srivastava, V. C., Swamy, M. M., Mall, I. D., Prasad, B. & Mishra, I. M. 2006 Adsorptive removal of phenol by bagasse fly ash and activated carbon: equilibrium, kinetics and thermodynamic study. *Colloid. Surface. A* **272**, 89–104.
- Tsai, F. C., Chang, C. C., Liu, C. L., Chen, W. C. & Jenekhe, S. A. 2005 New thiophene-linked conjugated poly(azomethine)s: Theoretical, electronic structure, synthesis and properties. *Macromolecules* **38**, 1958–1966.
- Unlu, N. & Ersoz, M. 2007 Removal of heavy metal ions by using dithiocarbamated sporopollenin. *Sep. Purif. Technol.* **52**, 461–469.
- Vidhyadevi, T., Murugesan, A., Kirupha, S. D., Baskaralingam, P., Ravikumar, L. & Sivanesan, S. 2013 Adsorption of Congo red dye over pendent chlorobenzylidene rings present on polythioamide resin: kinetic and equilibrium studies. *Separ. Sci. Technol.* **48**, 1450–1458.
- Weber, W. J. & Morris, J. C. 1963 Kinetics of adsorption on carbon from solution. *J. Sanit. Eng. Div. Am. Soc. Civ. Eng.* **89**, 31–60.
- Xu, Z. Y., Zhang, Q. X., Wu, C. & Wang, L. 1997 Adsorption of naphthalene derivatives on different macroporous polymeric adsorbents. *Chemosphere* **35**, 2269–2276.
- Yang, W. B., Li, A. M., Fu, C. E., Fan, J. & Zhang, Q. X. 2007 Adsorption mechanism of aromatic sulfonates onto resins with different matrices. *Ind. Eng. Chem. Res.* **46**, 6971–6977.
- Yuan, L. Y., Liu, Y. L., Shi, W. Q., Li, Z. J., Lan, J. H., Feng, Y. X., Zhao, Y. L., Yuan, Y. L. & Chai, Z. F. 2012 A novel mesoporous material for uranium extraction, dihydroimidazole functionalized SBA-15. *J. Mater. Chem.* **22**, 17019–17026.
- Zhang, W. M., Xu, Z. W., Pan, B. C., Hong, C. H., Jia, K., Jiang, P. J., Zhang, Q. J. & Pan, B. J. 2008 Equilibrium and heat of adsorption of diethyl phthalate on heterogeneous adsorbents. *J. Coll. Interf. Sci.* **325**, 41–47.
- Zheng, K., Pan, B. C., Zhang, Q. J., Zhang, W. M., Pan, B. J., Han, Y. H., Zhang, Q. R., Du, W., Xu, Z. W. & Zhang, Q. X. 2007 Enhanced adsorption of p-nitroaniline from water by a carboxylated polymeric adsorbent. *Sep. Purif. Technol.* **57**, 250–256.

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