



# Adsorption performances and mechanisms of the newly synthesized N,N'-di (carboxymethyl) dithiocarbamate chelating resin toward divalent heavy metal ions from aqueous media

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## ABSTRACT

N,N'-di (carboxymethyl) dithiocarbamate chelating resin (PSDC) was synthesized by anchoring the chelating agent of N,N'-di (carboxymethyl) dithiocarbamate to the chloromethylated PS-DVB (Cl-PS-DVB) matrix, as a new adsorbent for removing divalent heavy metal ions from waste-stream. The physicochemical structures of Cl-PS-DVB and PSDC were elaborately characterized using Fourier transform infrared spectroscopy (FT-IR), elemental analysis (EA), and were further morphologically characterized using BET and BJH methods. The adsorption performances of PSDC towards heavy metals such as Cu(II), Pb(II) and Ni(II) were systematically investigated, based upon which the adsorption mechanisms were deeply exploited. For the above target, the classic batch adsorption experiments were conducted to explore the kinetics and isotherms of the removal processes with pH-value, initial concentration, temperature, and contact time as the controlling parameters. The kinetic and isotherm data could be well elucidated with Lagergren-second-order equation and Langmuir model respectively. The strong affinity of PSDC toward these target soft acids could be well demonstrated with the electrostatic attraction and chelating interaction caused by IDA moiety and sulphur which were namely soft bases on the concept of hard and soft acids and bases (HASB). Thermodynamic parameters, involving  $\Delta H^\circ$ ,  $\Delta S^\circ$  and  $\Delta G^\circ$  were also calculated from graphical interpretation of the experimental data. The standard heats of adsorption ( $\Delta H^\circ$ ) were found to be endothermic and the entropy change values ( $\Delta S^\circ$ ) were calculated to be positive for the adsorption of Cu(II), Pb(II) and Ni(II) ions onto the tested adsorbents. Negative values of  $\Delta G^\circ$  indicated that adsorption processes for all tested metal ions onto PSDC were spontaneous.

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## 1. Introduction

The presence of heavy metals in the environment has been of great concern because of their high toxicity and susceptible carcinogenic effect [1]. Such well known toxic heavy metals as lead, copper, nickel, zinc, cadmium, can be distinguished from other pollutants, since they cannot be biodegraded but accumulated in living organisms, thus causing various diseases and disorders even in relatively lower concentrations. Heavy metal contamination exists in aqueous waste-streams from many industries such as chemical, plating, mining, tanneries, painting, plumbing, as well as agricultural sources where fertilizer and fungicidal spray are intensively used [2,3]. With views to both resources reuse and environment

protection, heavy metals should be effectively removed, separated and recovered from waste-streams prior to their discharge.

Nowadays, many separation methods, involving solvent extraction, ion exchange, co-precipitation, membrane process and carbon adsorption, have been developed and used to wipe off heavy metal ions from different aqueous solutions with a broad range of concentrations. However, no satisfactory removal ratio could be achieved by the above-mentioned techniques, with an inevitability of overrun upon interrelated pollution control limits. Moreover, applications of these technologies are even subjected to be so expensive that have been limited in an obvious extent [4]. Therefore, cost-effective and more efficient alternative technologies or adsorbents are well needed for the treatment to these wastewaters.

Recently, the selective adsorption technology with chelating resins has received an enormous attention and increasing application due to the remarkable simplicity, high efficiency and low cost during the following multi-adsorption interaction processes to heavy metal ions such as ion exchange, physical adsorption

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and chelation [5–7]. To develop this promising technology, several researchers have obtained some series of chelating resins through the polymerization of conventional chelating monomers such as acrylic acid, methacrylic acid and vinylpyridine [8–10]. In another procedure to invent chelating resins with different matrix structures and functional groups, synthetic polymers are firstly prepared, and the manifold low-molecular weight ligands are then grafted in succession by functionalization reactions [11–13].

According to the principle of hard and soft acids and bases (HSAB), sulphur-containing groups are namely soft bases and therefore it is reasonable to use sulphur-containing functional group materials to remove with much efficiency such soft acids like Cu(II), Pb(II) and Ni(II), etc. [14]. In many earlier literatures, various types of dithiocarbamate (DTC) which were widely used as sulphur-bearing complexing agents were anchored to diverse polymeric supports to remove and separate heavy metals from different systems [15–17]. Nevertheless, those synthesized chelating resins possessing DTC as sole functional group still suffer from disadvantages including the low adsorption selectivity and capacity toward divalent metals. Additionally, the adsorption mechanisms and separation behaviors were not systematically investigated and exploited. Recently, polymers containing the iminodiacetic acid (IDA) as the functional group have been synthesized and widely used for a range of treatment processes to eliminate heavy metal ions from different metal-loading wastewaters [18]. Such polymers with EDTA-like group structure, offer extremely high affinity and selectivity toward commonly encountered metal cations [19]. To our knowledge, chelating resins containing both DTC and IDA are expected to display a relatively excellent adsorption performances in terms of thermodynamics and selectivity comparing with those reported chelating resin functionalized by only DTC.

Thus, the focus of this paper is to synthesize a new PS-DVB copolymer (PSDC), consisting of DTC and IDA moiety, with the chemical functionalization with sodium *N,N'*-di (carboxymethyl) dithiocarbamate. The typical characters and the special performances of such typical divalent heavy metal ions like Cu(II), Pb(II) and Ni(II), are comprehensively investigated, based on which the natures and mechanisms of the adsorption processes are also deeply evaluated.

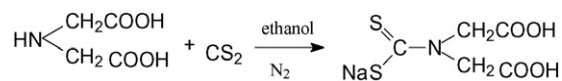
## 2. Experimental

### 2.1. Materials

Chloromethylated PS-DVB copolymer (cross-linking density 4%, Cl content 18%) was obtained from Jiangsu NanGe Environmental Technology Co., Ltd. (Jiangsu Province, PR China). Iminodiacetic acid was obtained from ACROS (Belgium). All of the cupric nitrate, lead nitrate, nickel nitrate, carbon disulfide, ethanol, DMF and sodium hydroxide were purchased from First Reagent Factory of Nanjing (Jiangsu Province, PR China). Deionized water was used for the synthesis of new resin and preparation of several metal stock solutions.

### 2.2. Preparation of *N,N'*-di (carboxymethyl) dithiocarbamate (*N*-DC)

Firstly, 40 g of iminodiacetic acid was successively added in a mixture of NaOH (25 g) and ethanol (250 ml). Excess solution of



Scheme 1. Preparation of *N*-DC.

carbon disulfide (40 ml) in ethanol (80 ml) was secondly added dropwise and the mixture was heated at 25 °C for 5 h under N<sub>2</sub> atmosphere. The reaction mixture was finally vaporized in rotary evaporator and di (carboxymethyl) dithiocarbamate was separated by crystallization under reduced pressure. The reaction form may be represented as in Scheme 1.

### 2.3. Preparation of *N,N'*-di (carboxymethyl) dithiocarbamate resin (PSDC)

20 g of chloromethylated PS-DVB (Cl-PS-DVB) copolymer were firstly added to 30 g of *N*-DC in 150 ml of DMF, the mixture was secondly stirred at 60 °C for 5 h. Beads were finally filtered and exhaustively washed with water, methanol and dried at 60 °C under vacuum to constant weight. The reaction form may be represented as in Scheme 2.

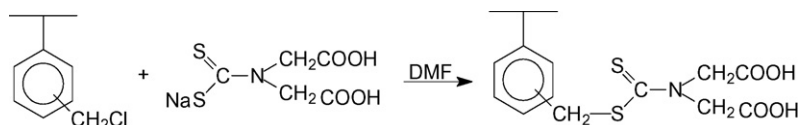
### 2.4. Characterization of PSDC

Elemental analysis (EA, CHN-O-Rapid Analyzer, Germany) of PSDC was carried out in order to determine the amount of ligands available in the chelating matrix. It is reported as equivalents of chelating groups by weight (g) of resin. The chelating functional groups of the resin were analyzed by Fourier transform infrared spectrometer (FT-IR, NEXUS 870, USA). The specific surface area and the pore distribution of Cl-PS-DVB and PSDC were respectively measured by BET and BJH methods using a Micrometrics TriStar 3000 analysis instrument (Micrometrics Instrument, Norcross, USA).

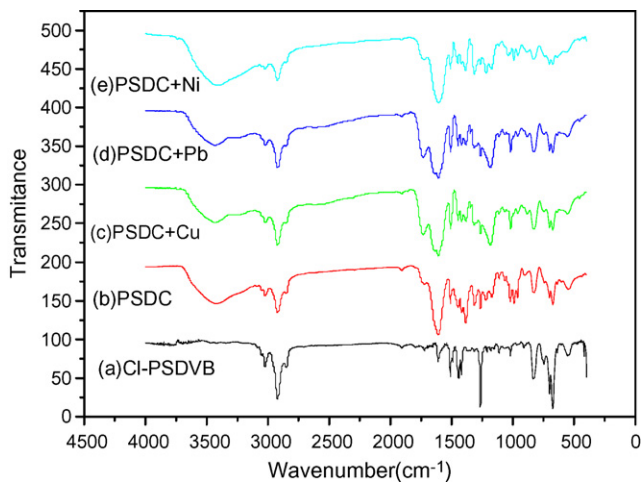
### 2.5. Adsorption studies

Equilibrium adsorption of Cu(II), Pb(II) and Ni(II) ions was performed at three different temperatures such as 288 K, 303 K, 318 K. Dose of 0.100 g of dry resin (30–40 mesh) was firstly weighed accurately and introduced directly into 250 ml conical flask. Then, 100 ml of aqueous solutions containing heavy metals with certain concentrations ( $C_0$ , mmol/l) ranging from 0.1 to 5.0 were added to each flask. The flasks were completely sealed and shaken in an incubator shaker at pre-settled temperatures under 120 rpm. The adsorption tests were conducted continuously till 24 h to attain the equilibrium. The concentration ( $C_e$ , mmol/l) of the residual aqueous phase was determined using an atomic adsorption spectrophotometer (AAS, TEHRMO, USA). HNO<sub>3</sub> solution (0.5 mol/l) and NaOH solution (0.5 mol/l) were properly used to adjust the solution to a desired initial pH-value and acetic acid–acetate buffer was only used to maintain solution at pH-value of 5 and 6. The amount of metal adsorbed per unit mass of resin was calculated with Eq. (1). The metal-removal ratio was calculated with Eq. (2).

$$Q_e = \frac{(C_0 - C_e)V}{M} \quad (1)$$



Scheme 2. Preparation of PSDC.



**Fig. 1.** The FT-IR spectra of (a) Cl-PS-DVB, (b) PSDC, (c) PSDC+ Cu(II), (d) PSDC+ Pb(II) and (e) PSDC+ Ni(II).

$$A = \frac{100(C_0 - C_e)}{C_0} \quad (2)$$

where  $C_0$  and  $C_e$  are the initial and equilibrium metal concentration (mmol/l),  $M$  is the mass of resins (g) and  $V$  is the volume of solution (l).  $Q_e$  is the equilibrium adsorption capacity (mmol/g), respectively.  $A$  is the metal-removal ratio in %.

In kinetic tests, known amounts of a concentrated metal bearing solution were added to a aqueous suspensions of PSDC (particle size 30–40 mesh, solid concentration 0.2 g/l, total volume 2000 ml) to have an initial metal concentration of 0.2 mmol/l. Solid suspension were also pH-adjusted using acetic acid–acetate buffer and mechanically stirred at a preset temperature under 120 rpm for 12 h. The samples (1 ml) were withdrawn at pre-settled time interval (2 min, 5 min, 10 min, etc.) and the metal-removal ratio was calculated as described above.

### 3. Results and discussion

#### 3.1. Characterization of PSDC

FT-IR spectra could be found in Fig. 1. In the spectra (a), the adsorption at  $625\text{ cm}^{-1}$  and  $800\text{ cm}^{-1}$  stood for C–Cl bond. In the spectra (b), the adsorption band near  $1100\text{ cm}^{-1}$  was caused by the stretching vibrations of the C=S in S–CS– structure. Two strong peaks were observed at  $1650\text{ cm}^{-1}$  and  $3465\text{ cm}^{-1}$ , which

**Table 1**  
Results of EA for PSDC.

Resin	Elemental analysis (%)				Fraction of functional group (mmol/g)
	C	H	N	S	
PSDC	63.20	5.89	1.49	7.37	1.06

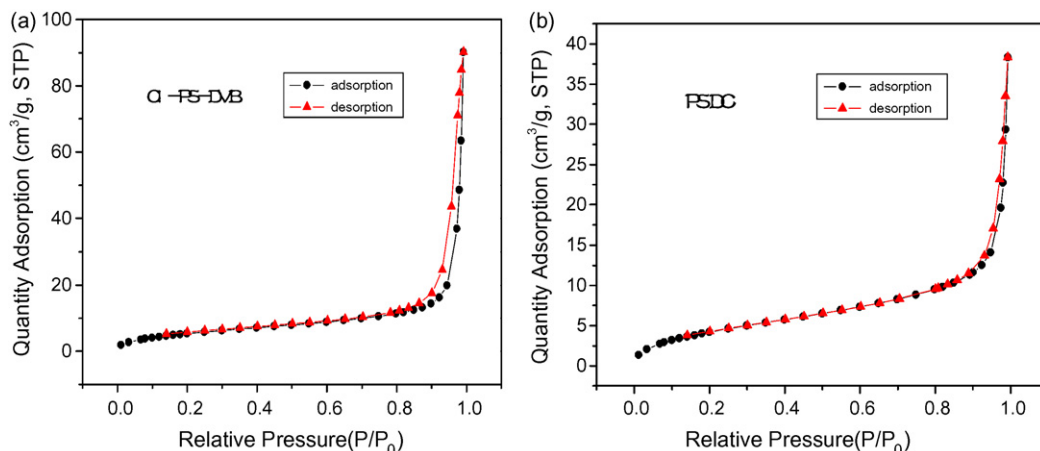
**Table 2**  
Porous structure parameters of Cl-PS-DVB and PSDC.

Designation	Cl-PS-DVB	PSDC
BET surface area ( $\text{m}^2/\text{g}$ )	21.43	16.85
BJH desorption average pore diameter (nm)	25.72	13.74
BJH desorption cumulative volume of pores ( $\text{cm}^3/\text{g}$ )	0.14	0.06

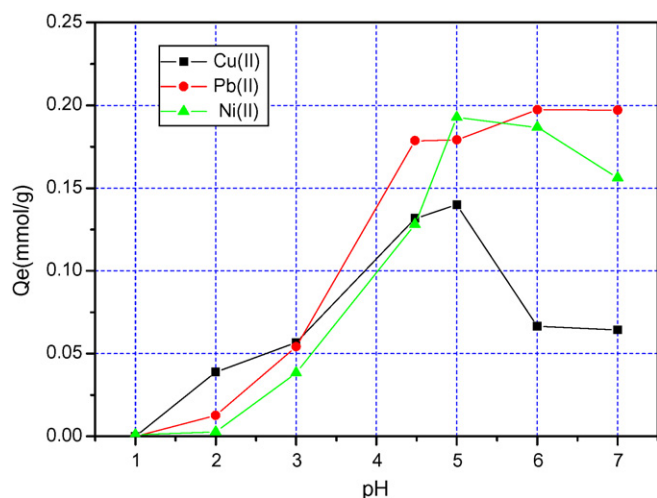
was ascribed to the stretching vibrations of C=O group in carboxyl ( $-\text{COO}$ ) and hydroxyl ( $-\text{OH}$ ), respectively [20]. So, Cl-PS-DVB functionalized with N-DC to form PSDC was carried out successfully. In the spectra (c–e), the peaks at  $1100\text{ cm}^{-1}$  and  $1650\text{ cm}^{-1}$  decreased, indicating a stronger metal–ligand bond has formed between metal ions and functional group in PSDC. EA-analyzed data for PSDC from Table 1 also testified that N-DC group was anchored onto the PS-DVB successfully.

Fig. 2 showed the  $\text{N}_2$  adsorption–desorption isotherms of Cl-PS-DVB and PSDC. 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 PSDC was smaller than that by Cl-PS-DVB, testifying a lower porosity for PSDC. 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 porous structure parameters of the resins summarized from the basis of the nitrogen adsorption data were listed in Table 2. As shown in Table 2, the values of BET surface area, BJH desorption average pore diameter and BJH desorption cumulative volume of pores for PSDC were all smaller than those of Cl-PS-DVB, which could be interpreted by that the larger pores were packed due to the cross-linking during the synthesis reaction and became smaller than before.



**Fig. 2.** Nitrogen adsorption–desorption isotherms of (a) Cl-PS-DVB and (b) PSDC.



**Fig. 3.** Effect of pH on the uptake of Cu(II), Pb(II) and Ni(II) (under the initial metal concentration of 0.2 mmol/l, resin dosage of 0.100 g, the solution volume of 100 ml, the temperature of 288 K, and the stirring rate of 120 rpm).

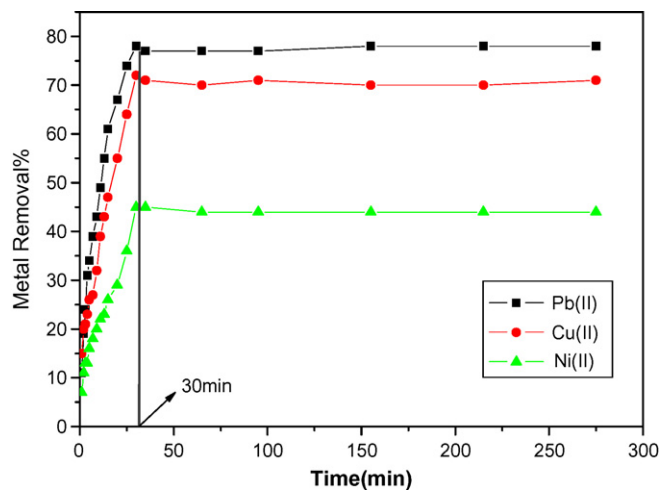
### 3.2. Effect of pH on the removal of metal ions

It is well known that the adsorption of heavy metal ions by resins is dependent on pH which extremely affects the chelation as well as physisorption processes [21]. Thus, the effect of pH on the adsorption capacities should be investigated. Fig. 3 shows the uptake of Cu(II), Pb(II) and Ni(II) as the function of hydrogen ion concentration in the pH range of 1–7, with the initial metal concentration of 0.2 mmol/l.

There was an abrupt increase in metal adsorption amount when pH was raised from 1 to 5. The adsorption of Cu(II) and Ni(II) ions on the resin was clearly more favorable at the pH-value of 5, compared with Pb(II) ion at 6. These adsorption trends could probably be affected by the competitive interaction between metal and hydrogen ions with the active sites on the surface of the resins [22–24]. At lower pH, an excess of hydrogen ions can compete effectively with metal ions for binding sites, resulting in a lower level of metal uptake. At the pH-value higher than 6, three metal ions might precipitate, the presence of alkaline ions help to form the hydroxyl complexes [25].

### 3.3. Adsorption kinetics

The effects of contact time on the adsorption of PSDC for Cu(II), Pb(II) and Ni(II) ions were shown in Fig. 4. In single metal systems, the removal percentage increased sharply during the first 30 min and then tended to the equilibrium. Numerous researchers thought the decrease of free chelating site resulted in polymer chains shrink with the adsorption occurring. So a cation with bigger ionic radius was difficult to diffuse toward the adsorption site, thus



**Fig. 4.** Effect of contact time on the adsorption of Cu(II), Pb(II) and Ni(II) (under the initial metal concentration of 0.2 mmol/l, the resin dosage of 0.400 g, the volume of 2000 ml, the temperature of 288 K, the stirring rate of 120 rpm, and the pH-value for Cu(II), Ni(II), Pb(II) of 5, 5, 6, respectively).

lead to a lower removal achievement [26–30]. However, the uptake percentage of heavy metals in present study were in the order of Ni(II) < Cu(II) < Pb(II), with the same trend of hydrated radius as Ni(II) (0.2025 nm) < Cu(II) (0.2065 nm) < Pb(II) (0.2655 nm) [31]. Obviously, the matrix structure of PSDC could not play easily much influence upon the tested adsorption processes.

In order to interpret the mechanisms of metal adsorption processes, intraparticle diffusion model, Lagergren first-order equation and second-order equation models were all used to describe the kinetic processes. From the linear form of these three models, equations can be written as follows:

$$\text{First-order kinetic equation: } \log(Q_e - q) = \log Q_e - \frac{k_1 t}{2.303} \quad (3)$$

$$\text{Second-order kinetic equation: } \frac{t}{q} = \frac{1}{k_2 Q_e^2} + \frac{t}{Q_e} \quad (4)$$

$$\text{Intraparticle diffusion equation: } q = k_{\text{int}} t^{1/2} \quad (5)$$

where  $Q_e$  and  $q$  are the amounts of the metal ions adsorbed ( $\text{mg g}^{-1}$ ) at equilibrium and at time  $t$  (min), respectively,  $k_1$  ( $\text{min}^{-1}$ ),  $k_2$  ( $\text{g mmol}^{-1} \text{min}^{-1}$ ) and  $k_{\text{int}}$  ( $\text{mmol g}^{-1} \text{min}^{-1/2}$ ) are the rate constants.

The parameters of the three equations were tabulated in Table 3. The second-order equation appeared to be the best-fitting model ( $r^2 > 0.99$ ). The fitting curves for the adsorption of Cu(II), Pb(II) and Ni(II) by second-order equation were shown in Fig. 5. From Table 3 and Fig. 5, the calculated amount of equilibrium adsorption capacity was similar to the actual tested adsorption capacity. The adsorption rate was related to the content of active adsorption site on the matrix of adsorbent.

**Table 3**  
Kinetic parameters for the adsorption of Cu(II), Pb(II) and Ni(II).

Equations	Parameters	Pb(II)	Cu(II)	Ni(II)
First-order kinetic equation	$Q_e$ (mmol/g)	0.58	0.61	0.43
	$k_1$ (1/min) $\times 10^{-2}$	7.87	7.65	7.07
	$r^2$	0.8545	0.7208	0.8063
Second-order kinetic equation	$Q_e$ (mmol/g)	0.85	0.83	0.54
	$k_2$ ( $\text{g mmol}^{-1} \text{min}^{-1}$ ) $\times 10^3$	1.62	0.11	1.29
	$r^2$	0.9981	0.9943	0.9945
Intraparticle diffusion equation	$k_{\text{int}}$ ( $\text{mmol g}^{-1} \text{min}^{-1/2}$ )	0.13	0.11	0.06
	$r^2$	0.8201	0.8821	0.9118
	$Q_{e,\text{exp}}$ (mmol/g)	0.77	0.78	0.51



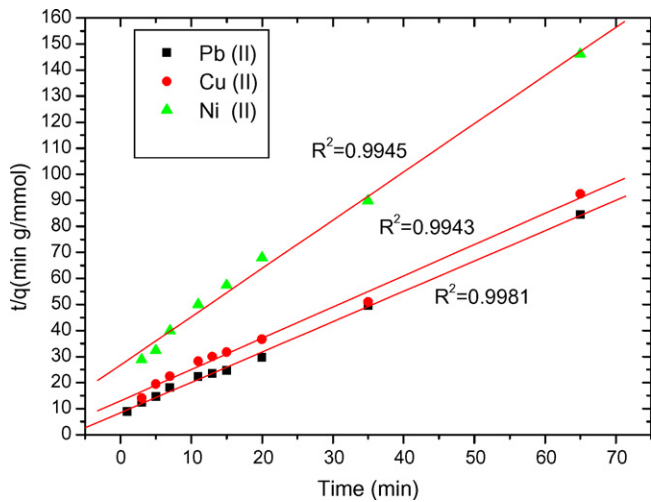


Fig. 5. Linear fitting curves of  $t/q$  versus  $t$  for the metal adsorption onto PSDC at 288 K.

### 3.4. Adsorption isotherms

The isotherm curves for the adsorption of PSDC towards Cu(II), Pb(II) and Ni(II) ions were shown in Fig. 6. The isotherm results reveal the good adsorption capacity of PSDC for Cu(II), Pb(II) and Ni(II). In addition, the sharp increase in capacity was observed in the initial concentration range of 0.1–1 mmol/l. There was a ten-fold increase in concentration, and accordingly there was a nearly tenfold increase in adsorption capacity. Whereas, according to the metal ion concentration of 1–5 mmol/l, there was only less than 50% increase in the adsorption capacity. The remarkably different trends demonstrate the variety in the adsorption interactions involving physical and chemical mechanisms [32]. The adsorption is more sensitive under the lower concentration of metal ions, which shows that the adsorption is dominated by the electrostatic attraction (physical adsorption). Consequently, the electrostatic attraction does play a primary role in the complex formation between metal ions and functional group in the resin. On the other hand, in the higher concentrations of 1–5 mmol/l, the adsorption is relatively insensitive, although the resin displays high affinity toward the metals, which indicates that the adsorption is dominated by the chelating interaction (chemical adsorption).

To quantify the sorption capacity of the resin studied for the removal of Cu(II), Pb(II) and Ni(II), the two most commonly used isotherms, namely Freundlich and Langmuir, have been adopted. From the linear form of these two isotherms, equations can be written as follows:

$$\text{Langmuir isotherm : } \frac{C_e}{Q_e} = \frac{1}{Q^0 b} + \frac{C_e}{Q^0} \quad (6)$$

Table 4

Fitting results with Langmuir and Freundlich isotherm model for Cu(II), Pb(II) and Ni(II).

Adsorbates	T (K)	Langmuir constants			Freundlich constants		
		$Q^0$ (mmol/g)	$b$ (l/mmol)	$r^2$	$K_f$ (mmol/g)	$n$	$r^2$
Pb(II)	288	1.40	21.65	0.9981	0.15	5.2145	0.9502
	303	1.67	38.45	0.9990	0.20	3.1578	0.9204
	318	1.88	85.48	0.9904	0.63	6.3214	0.9052
Cu(II)	288	1.08	17.64	0.9970	0.13	3.6254	0.9145
	303	1.30	8.62	0.9984	0.52	5.2140	0.9008
	318	1.57	10.05	0.9980	0.23	3.6521	0.8356
Ni(II)	288	0.97	5.98	0.9998	0.63	5.6254	0.8011
	303	1.30	5.95	0.9990	0.27	4.6521	0.9024
	318	1.46	4.39	0.9993	0.85	8.5102	0.9057

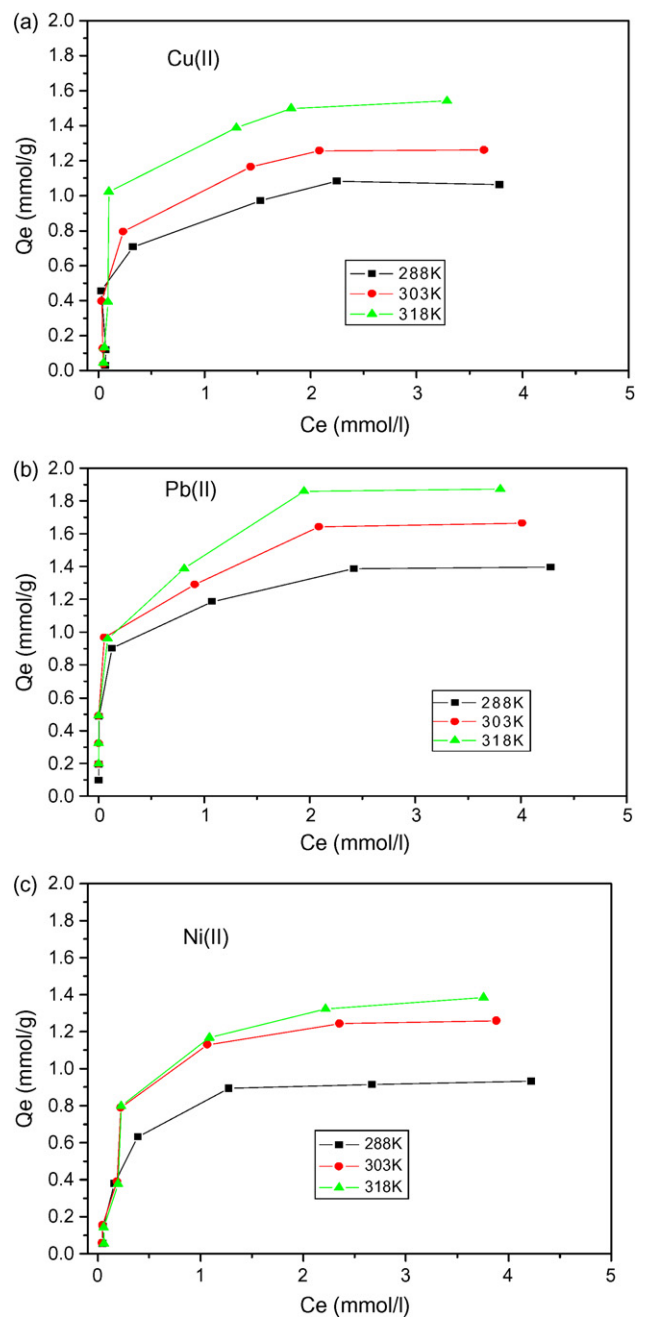


Fig. 6. Adsorption isotherms of (a) Cu(II), (b) Pb(II) and (c) Ni(II) at 288 K, 303 K, 318 K (under the initial metal concentration of 0.1–5 mmol/l, the resin dosage of 0.100 g, the volume of 100 ml, the stirring rate of 120 rpm, and the pH-value for Cu(II), Ni(II), Pb(II) of 5, 5, 6, respectively).

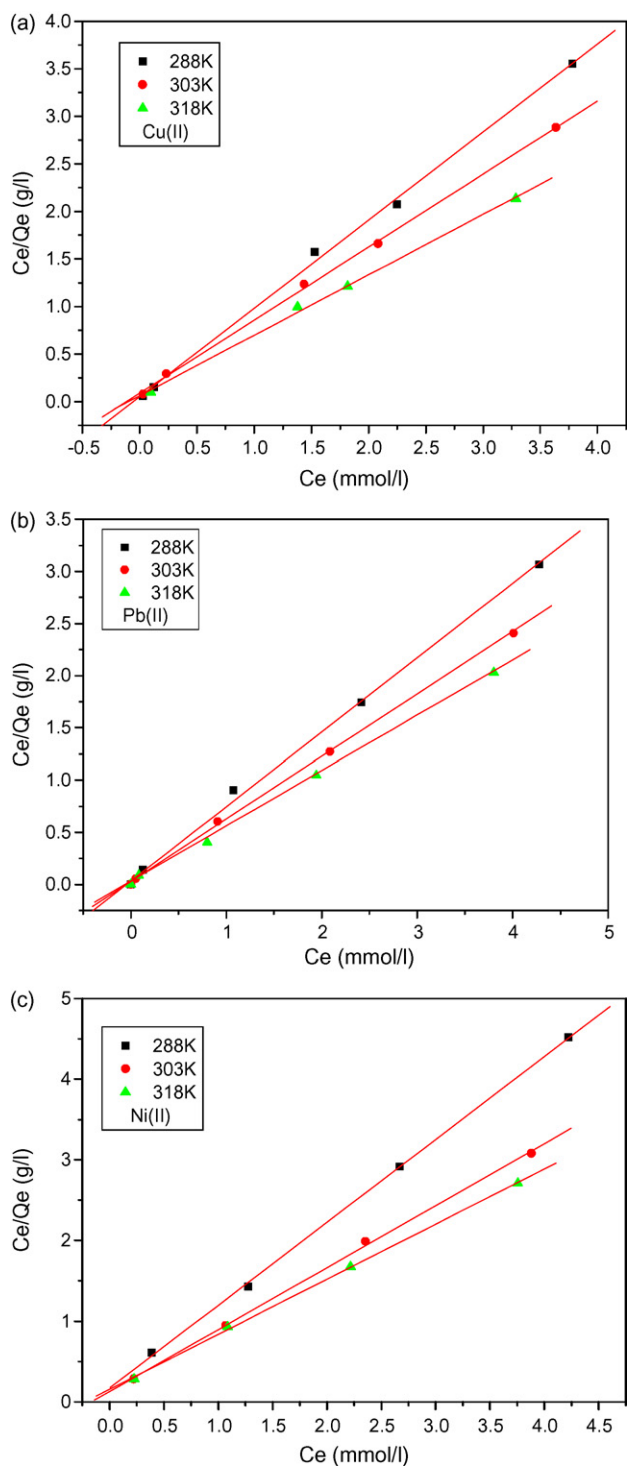


Fig. 7. Linear fitting curves with Langmuir model for (a) Cu(II), (b) Pb(II) and (c) Ni(II).

$$\text{Freundlich isotherm: } Q_e = K_f C_e^{1/n} \quad (7)$$

where  $Q_e$  is the amount of solute adsorbed on the surface of the adsorbent (mmol/g),  $C_e$  the equilibrium ion concentration in the solution (mmol/l),  $Q^0$  the maximum surface density at monolayer coverage,  $b$  (l/mmol) is the Langmuir sorption constant,  $K_f$  the Freundlich constant (mmol/g) which indicates the sorption capacity and represents the strength of the adsorptive bond and  $1/n$  is the heterogeneity factor which represents the bond distribution.

As shown in Table 4 and Fig. 7, the experimental data could be well fitted by Langmuir isotherm model ( $r^2 > 0.99$ ). The higher temperature promotes the adsorption processes for three metals, which indicates the endothermic phenomena. The calculated adsorption capacity ( $Q^0$ ) and energy of the adsorption ( $b$ ) are in the order of Pb(II) > Cu(II) > Ni(II) and Pb(II) < Cu(II) < Ni(II), respectively. In general, the values of  $Q^0$  and  $b$  reflect the metal ion removal priorities. Hereby, the chelating interaction is in the order of Pb(II) > Cu(II) > Ni(II), the same trend with the kinetic performance in the above section. In addition, the calculated adsorption capacity of PSDC toward Pb(II) is far greater than that of DTC-resin reported earlier, which should be attributed to the introduction of IDA moiety and increase in sulphur fraction in the chelator supported material [15–18]. And the predicted  $Q^0$  for three metals is greater than those observed, with the reason of the difficulties for metal ions to access all of the potential binding sites on the matrix.

### 3.5. Adsorption thermodynamics

The effect of temperature on the adsorption of heavy metal ions onto PSDC is given from the plots and curves of the distribution coefficient values  $K_d$  versus temperatures in Fig. 8. It can be found that  $K_d$  increased with temperature increasing, a certification of the endothermic adsorption nature. Thermodynamic parameters including free energy change ( $\Delta G^\circ$ ), enthalpy change ( $\Delta H^\circ$ ) and entropy change ( $\Delta S^\circ$ ) are respectively estimated in Eqs. (8)–(10) [14]. The Gibb's free energy change of the process is related to the distribution coefficient ( $K_d$ ) in the linear form of Eq. (8).

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

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

$$\log K_d = \frac{\Delta S^\circ}{2.303 R} - \frac{\Delta H^\circ}{2.303 RT} \quad (10)$$

where  $K_d$  is the distribution coefficient (ml/g), and  $R$  is the gas constant (J/mol K). According to the linear form of Eq. (10), the values of  $\Delta H^\circ$  and  $\Delta S^\circ$  can be calculated respectively from the slope and intercept of  $\log K_d$  versus  $1/T$  plots. The calculated values of thermodynamic parameters are tabulated in Table 5. As it can be seen from Table 5, positive values of  $\Delta H^\circ$  represent the endothermic natures of adsorption processes. The heat of adsorption values between 20.9 kJ/mol and 418.4 kJ/mol are frequently assumed as the comparable values for the chemical sorption processes [33]. From Table 5,  $\Delta H^\circ$  values are respectively 16.80 kJ/mol, 17.49 kJ/mol and 12.54 kJ/mol for Cu(II), Pb(II) and Ni(II), which reveals that physisorption and chemisorption coexist during adsorption processes. Negative values of  $\Delta G^\circ$  indicate the spontaneous natures

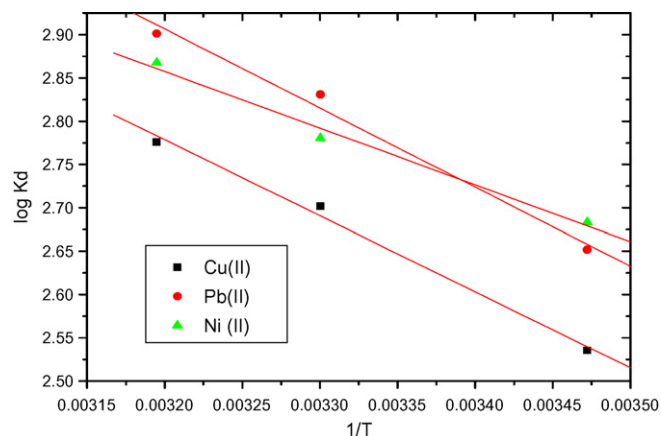


Fig. 8. Plots of  $\log K_d$  versus  $1/T$  for the adsorption of Cu(II), Pb(II) and Ni(II).

**Table 5**  
Thermodynamic parameters for the adsorption of Cu(II), Pb(II) and Ni(II) onto PSDC.

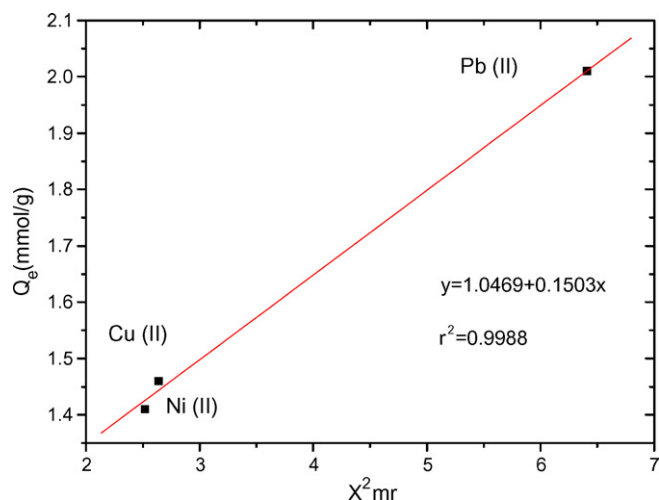
Metals	$C_0$ (mmol/l)	$\Delta H^\circ$ (kJ/mol)	$\Delta S^\circ$ (J/K mol)	$T$ (K)	$\Delta G^\circ$ (kJ/mol)	$r^2$
Cu(II)	1	16.80	106.96	288	-3.87	0.9937
				303	-4.34	
				313	-4.61	
Pb(II)	1	17.49	111.61	288	-4.05	0.9882
				303	-4.55	
				313	-4.81	
Ni(II)	1	12.54	94.83	288	-4.45	0.9889
				303	-4.61	
				313	-4.76	

of the reactions. In addition, the reaction is favored and getting easier at higher temperatures. All of entropy change values  $\Delta S^\circ$  are positive, due to the liberation of water molecules of hydrated-M(II) with the exchange of mobile metal ions in the flux with more ions present on the solid-phase.

### 3.6. Adsorption mechanism

To account for the following decreasing trend in the adsorption capacities as  $\text{Pb(II)} > \text{Cu(II)} > \text{Ni(II)}$ , both of the functional group characteristics and the metal ion properties should be taken into consideration. According to HASB theory, as a Lewis soft acid, lead ion has precedence, over copper and nickel ions which could be regarded as middle-soft acid, in the interaction with PSDC which could be regarded a Lewis soft base. Thus, PSDC show stronger affinity to Pb(II), versus weaker interaction to Cu(II) and Ni(II).

Several properties of metal ions are certainly important affecting factors towards the adsorption capability onto the same adsorbent. Because it is difficult to array the metal ions just by such single factor as atomic number, ionic potential and ionic radius, and so on, a concept of covalent index was thus proposed by Nieboer and Richardson [34], which was a complex parameter computed by the expression of  $X_m^2 \cdot r$ , where  $X_m$  is the electro-negativity and  $r$  is the ionic radius. Covalent index could reflect the importance of chelating interactions with ligands relative to ionic interactions. The metal uptake capacity has been found close relativity with the covalent index [35]. The relationship between adsorption capacities and the covalent indexes corresponding to different metal ions, was demonstrated in Fig. 9. The linear-curve with a perfect relative parameter of  $r^2 > 0.99$ , indicated that the chelating interaction did play an important role during the adsorption processes.



**Fig. 9.** Plots of the adsorption capacities versus the covalent indexes.

## 4. Conclusion

N,N'-di (carboxymethyl) dithiocarbamate (N-DC) consisting of DTC and IDA moiety was anchored successfully to the chloromethylated PS-DVB to form PSDC. The adsorption behavior of Pb(II), Cu(II) and Ni(II) by PSDC was pH-dependent with the most effective uptake at pH of 5–6. PSDC displayed quick adsorption performance (30 min) toward Pb(II), Cu(II) and Ni(II) and adsorption kinetic processes for three heavy metal ions were found to follow Lagergren-second-order model. Adsorption isotherms correlated well with the Langmuir equation and the maximum adsorption capacities were in order of  $\text{Pb(II)} > \text{Cu(II)} > \text{Ni(II)}$ . Higher adsorption capacity for Pb(II) was attributed to introduction of IDA moiety and sulphur in PSDC, which was further elucidated by higher covalent index and soft acid property of the cation. Two adsorption mechanisms were concluded from the experimental results, that is electrostatic attraction in the range of 0.1–1 mmol/l and the chelating adsorption in the range of 1–5 mmol/l. Enthalpy change values were respectively 16.80 kJ/mol, 17.49 kJ/mol and 12.54 kJ/mol for Cu(II), Pb(II) and Ni(II), which revealed that the sorption processes including physisorption and chemisorption was endothermic. Negative values of free energy change indicated the spontaneous natures of the reactions. Finally, this new material shows characteristics of a chelating exchanger and can therefore be used as an alternative adsorbent in selective separation processes.

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