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Synthesis of Graft Copolymer of Poly(acrylic acid) and Poly(vinyl alcohol) in the Presence of Methylene Bisacrylamide Crosslinker and Investigation of its Efficiency in Removing Lead Ion from Aqueous Solution

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# Synthesis of Graft Copolymer of Poly(acrylic acid) and Poly(vinyl alcohol) in the Presence of Methylene Bisacrylamide Crosslinker and Investigation of its Efficiency in Removing Lead Ion from Aqueous Solution

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A novel graft copolymer of acrylic acid onto poly(vinyl alcohol) has been synthesized and it is crosslinked by methylene bisacrylamide for the investigation of its efficiency in removing lead ion from aqueous solution. The chemical nature of the ion exchange resin has been elucidated with the help of chemical test, FTIR, TGA and DSC. Particle size (0.20 mm), surface area ( $85.6 \text{ m}^2/\text{g}$ ), ion exchange capacity (5.3 meq H<sup>+</sup>/g), optimum pH (4.5), time (60 min) and temperature ( $40^{\circ}$ C) for Pb(II) adsorption were determined. Metal ion adsorption kinetics, isotherms and thermodynamics have been studied. A plausible mechanism for lead ion exchange has been suggested.

Keywords: Graft copolymerization, crosslinking, lead ion, adsorption, isotherm, ion-exchange

## 1 Introduction

Lead, cadmium and mercury are the prior toxic metals. Lead is the most important because of its wide application as vessel, pipes, gasoline additives, ammunition, metal products, paints, pigments, storage batteries, printing materials and lead reinforced pencils (1). Lead restricts the synthesis of hemoglobin by interfering with enzymes (1). Its toxicological effects are weakness, weight loss, nausea, constipation, vomiting, chronic nephritis, impaired concentration, sleep disturbance, muscular aches and pains, anemia, and damage to the brain (2). Due to the abundant use of lead and its toxicity, it is necessary to develop reliable, efficient and cost effective methods for control or removal of lead from industrial and municipal waste prior to release into natural water systems.

There are many removal methods available for lead such as solvent extraction (3), ion-exchange (4), adsorption (5), etc. Metal ion adsorption onto solid polymer surface (Solid phase extraction, SPE) is now considered one of the most promising techniques for concentration, removal and recovery of metal ions from wide variety of sources (6) due to its cost effectiveness, eco-friendliness and rapidness. The selectivity of these materials towards metal ion can be controlled by immobilizing functional group, pH of the medium, presence of masking agents, temperature, etc. The polymeric matrix affects other properties, namely the ionexchange capacity, kinetic features, mechanical and chemical strength, and regeneration (6).

In the present decade, several researchers (7,8) are engaged in synthesizing suitable polymers having selective metal ion binding capacity. Very few of them (9–11) reported removal and recovery of lead ion from aqueous solutions. There are works (12,13) on the grafting of acrylic acid (AA) onto poly(vinyl alcohol) (PVA) in the absence of a crosslinker and its analytical application as selective extractor for metal ions. However, there are no reports on the grafting of AA onto PVA and subsequent crosslinking by methylene bisacrylamide. Crosslinked AA-g-PVA is expected to have better metal ion-binding capacity with faster kinetics than that of an uncrosslinked one. PVA is cheaper and its sorption properties can be enhanced by the graft copolymerization (14–17).

In the present work, a new procedure for concentrating lead (II) ion by AA-g-PVA (crosslinked by methylene bisacrylamide) has been developed. Under the sorption conditions, kinetic and thermodynamic parameters are evaluated. Different adsorption isotherms have been studied and possible mechanism of metal ion binding has been discussed.

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Nomenclature	Ce: Metal ion concentration at equilibrium
PVA: Polyvinyl alcohol	$K_a$ : Langmuir constant (L.mg <sup>-1</sup> )
PAA: Polyacrylic acid	$Q_m$ : Langmuir constant related to mono-layer capacity (mg.g <sup>-1</sup> )
MBA: Methylene bisacrylamide	n: Freundlich constant (dimensionless)
CAS: Ceric ammonium sulphate	K <sub>F</sub> : Freundlich constant
AA-g-PVA: Uncross-linked graft copolymer	a, b: Temkin constant
X-AA-g-PVA: Cross-linked graft copolymer	$\alpha$ , $\beta$ :, $\gamma$ : Redlich-Peterson isotherm constant (L.mg <sup>-1</sup> )
Sorbate: Lead ion	$Q'_{m}$ : Dubinin-Radushkevick constant related to adsorption capacity (mg.g <sup>-1</sup> )
Sorbent: Cross-linked graft copolymer	$K_{DR}$ : Dubinin-Radushkevick adsorption constant(mol <sup>2</sup> .KJ <sup>-2</sup> )
Qt: Metal ion adsorption capacity at time t	ε: Polyani potential
Qe: Metal ion adsorption capacity at equilibrium	$E_{DR}$ : Mean free energy of adsorption (KJ.mol <sup>-1</sup> )
$C_0$ : Initial metal ion concentration	

## 2 Experimental

### 2.1 Chemicals and Reagents

Poly(vinyl alcohol) (Burgoyne Burbidges, viscosity average molecular weight = 16100, degree of hydrolysis = 98.5–99.0 mol%, viscosity = 30 cps) was used. Acrylic acid (Sisco Research Laboratories Pvt. Ltd., Mol. Wt. = 72.06, Sp.gr. = 1.05) was purified by distillation and the middle fraction was used. Ceric ammonium sulphate (Himedia Laboratories Pvt. Ltd.), methylene bis acrylamide (Fluka, Buchs, Switzerland), lead nitrate (Merck, Mumbai, India) and sulfuric acid (Merck, Mumbai, India, 98%, Sp.gr. = 1.84, Mol. Wt. = 98.08) were used as received.

### 2.2 Equipments

Fourier transform infrared (FTIR) spectra of the polymer were recorded on Shimadzu FTIR (Model No.8400s) using KBr pellets. Thermal analysis was conducted using a Stantum Red Craft Thermal Analyzer (STA-780) in air at a rate of  $10^{\circ}$ C/min. The amount of metal ion in the solution was measured using atomic absorption spectrophotometer (AAS, Shimadzu, AA 6300) and complexometrically. An Elico L1-120 pH meter, thermostat and chromatographic column (internal diameter = 0.8 cm) were used.

## 2.3 Synthesis of Crosslinked Graft Copolymer

Graft copolymerization and crosslinking were carried out in a two-necked round-bottomed flask at 70°C. A definite amount of PVA (0.5 g) was mixed with AA (5 ml) monomer and stirred for 15 min at room temperature. Water (20 ml), concentrated sulfuric acid (2 ml) and CAS (0.2 g) were then added and stirred. Nitrogen atmosphere was maintained throughout the reaction period. After an hour, MBA (0.1 g) was mixed to crosslink the grafted product. Quenching with hydroquinone arrested polymerization and crosslinking reaction. The precipitated polymer was separated by filtration and washed several times with 1:10 H<sub>2</sub>SO<sub>4</sub>(v/v). The rest PVA were separated by prolonged (24 h) extraction with water in a Soxhlet apparatus. Finally, the sample was extracted with acetone for 72 h to dissolve all other impurities. The colorless product was dried under vacuum at 100°C for 72 h to a constant weight. The yield was 5.59 g, which indicated the small loss of monomer. The dried solid was grounded and screened through a set of sieves for the particles of the size ranged between 0.15 to 0.20 mm for conducting experiments.

#### 2.4 Sorption and Desorption Procedure

Adsorption by the batch method was carried out with suitable mechanical agitation (90-100 rpm) and temperature (5 to  $40^{\circ}$ C). To determine the retention of lead ion, 0.013 g of prepared polymer (X-AA-g-PVA) was taken into a 100 ml beaker with 10 ml metal solution. The concentration of lead (II) ion in aqueous solution was kept within 207 to 1242 mg/L (ppm). The pH of the solution was maintained at 4.5. One ml solution of the sample was withdrawn each time from the reaction mixture by a syringe at a gap of fixed time interval and analyzed for kinetic study. For isothermal study, the system was agitated for 60 min and then filtered for the analysis of residual metal ion complexometrically. The selectivity of the prepared resin among various metal ions (Pb<sup>II</sup>, Cd<sup>II</sup> and Ni<sup>II</sup>; commonly found in electroplating waste) was determined by a competitive batch method. Resin sample (0.013 g) was equilibrated for 60 min with 10 ml solution (3.3 ml of each metal ion solution, which contained 0.001 mole metal ion). The adsorbed metal ions were sequentially eluted (desorbed) with the selective striping agents.

#### 2.5 Treatment of Data

All the experiments were performed at least in triplicate at room temperature  $(27^{\circ}C)$ . The adsorption capacity (Q, mg/g), percentage of recovery (R), degree of grafting (G) and cross-link density (q) was calculated from the following relations (13–18).

Q = Metal adsorbed	(mg)/Adsorbent ad	ided (g)	(1)
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R = Metal ion eluted (g)

 $\times 100$ /Metal ion originally bound to polymer (g)

(2)

G = Polymer grafted (g)/PVA added (g)(3)  $q = M_0/M_c$ (4)

Where  $M_0$  = molecular weight of the repeating unit,  $M_c$  = average molecular mass between a consecutive crosslink (14).

#### **3** Results and Discussion

#### 3.1 Evidence for the Formation of Crosslinked Graft Copolymer

FTIR spectra of (a) PVA and (b) the crosslinked graft copolymer of PVA (X-AA-g-PVA) are shown in Figure 1. The spectrum of the grafted polymer exhibits all the characteristics peaks of PVA. In addition, two new peaks at 1723 and 1650 cm<sup>-1</sup> are observed in the spectrum b (these are not present in a). The bands at 1723 and 1650 cm<sup>-1</sup> are due to carbonyl stretching frequency of carboxylic acid and secondary amide respectively (19), which suggest the grafting of poly(acrylic acid) onto PVA and crosslinking by bisacry-



Fig. 1. FTIR spectra of (a) PVA and (b) crosslinked AA-g-PVA.



Sch. 1. Synthesis of crosslinked AA-graft-PVA

lamide (Scheme 1). Both polymers exhibit a peak at 3435 cm<sup>-1</sup> that corresponds to both polymeric —OH and —NH bonds (19). Since the crosslinked graft copolymer of PVA contains both —OH and —NH groups, the peak intensity is higher than that of PVA. The bonding of uncross-linked AA-g-PVA (synthesized in absence of MBA) has been reported earlier (13).

Thermo-gravimetric analysis (TGA) and differential thermal analysis (DTA) traces of PVA and (X-AA-g-PVA) are shown in Figure 2. TGA of PVA shows three steps weight loss while that of g-PVA gives rise to four steps. First stage (30–250°C,  $\approx 10\%$ ), second stage (250–300°C,  $\approx 65\%$ ) and third stage (>300°C, >20\%) weight loss of PVA are due to the removal of moisture, decomposition



**Fig. 2.** TGA and DTA traces of PVA and grafted PVA (X-AA-g-PVA)

of PVA (13) and loss of residual impurities, respectively. Similarly, first step (30–100°C,  $\approx$  35%), second step (100– 190°C,  $\approx$  20%), third step (190–225°C,  $\approx$  20%) and fourth step (>225°C, > 20%) weight loss of grafted PVA may be due to removal of water, carbon dioxide, nitrogen and the impurities respectively. The uncrosslinked AA-g-PVA (prepared in absence of MBA) like PVA exhibited three stages weight loss (13). Thus, the change in weight loss pattern from three steps for PVA to four steps for modified PVA clearly indicates the simultaneous grafting by PAA and crosslinking by MBA. The endothermic peak at 100°C of both the polymers justifies the evolution of water during heating. FTIR trace also confirms the presence of moisture in the polymer. The endothermic peak around 200°C of both the polymers may be due to melting of the polymers.

#### 3.2 Physical and Chemical Characteristics

The physicochemical characteristics of the synthesized polymer (X-AA-g-PVA) are given in Table 1. The surface area of crosslinked polymer was determined by methylene blue adsorption method (20) and was found to be  $85.6m^2/g$ . The exchange capacity of the exchanger (5.3 meq. H<sup>+</sup>/g) was superior to the literature value of commercially available many cation exchangers (21) such as SRS-100 (1.85), VERSATIC-10 (2.11), and uncrosslinked AA-g-PVA (13) (3.6). A higher specific surface area and greater pore size are the probable reasons for superior exchange capacity of a crosslinked polymer compared to an uncrosslinked one. Average molecular weight between two consecutive crosslink density (14), and pore size (14) of the material were 583 g mol<sup>-1</sup>, 0.122 and 39.33 A<sup>0</sup>, respectively.

## 3.3 Influence of pH on Lead Ion Adsorption and Adsorption Mechanism

The results on Pb(II) adsorption at various pH (2.5-5.5) are shown in Figure 3. The adsorption capacity of the polymer was increased with pH from 2.5 to 4.5 and then levels off

 Table 1. Some physical and chemical characteristics of the synthesized polymer

Parameters	Values	Measurement Process
Bulk density (g.cm <sup>-1</sup> )	1.45	Specific gravity bottle
Particle size (mm)	0.20	Screened
Surface area (m <sup>2</sup> .g <sup>-1</sup> )	85.6	Methylene blue adsorption method (20)
Exchange capacity (meqH <sup>+</sup> .g <sup>-1</sup> )	5.3	Volumetric method
Average molecular weight between two consecutive crosslink (g.mol <sup>-1</sup> )	583	Swelling studies (14)
Cross-link density	0.122	Swelling studies (14)
Pore size $(A^0)$	39.33	Swelling studies (14)
Degree of grafting	10	Chemical (13)

with the further increase of pH. The optimum pH was found to be 4.5.

The lead ion goes to the exchange site mainly through ion exchange process (Eq. 5). The presence of exchangeable H<sup>+</sup> (exchange capacity = 5.3 meq H<sup>+</sup>/g) favors the ion exchange process. The absence of sharp peak at 1723 cm<sup>-1</sup> and appearance of a new peak at 1595 cm<sup>-1</sup> in the FTIR spectrum of lead adsorbed exchanger (spectrum is not shown) clearly indicates the presence of carboxylate anion (19) in the metal loaded sample.

$$2 \operatorname{RCOO^-H^+}(\operatorname{Resin}) + \operatorname{Pb^{2+}}(\operatorname{aq}) \rightleftharpoons (\operatorname{RCOO})_2 \operatorname{Pb} (\operatorname{solid}) + 2 \operatorname{H^+}(\operatorname{aq})$$
(5)

At low pH (<4.5), the equilibrium shifts towards left. As a result, a lesser amount of Pb(II) was adsorbed at pH 2.5. While at relatively higher pH (>4.5), the lead ion undergoes hydrolysis and interferes with the exchange process. As a result, adsorption capacity levels off at pH beyond 4.5.



**Fig. 3.** Effect of pH on lead ion adsorption (Sorbent dose = 1.3 g/L, Sorbate dose = 207 ppm, Time = 1 h, Temperature =  $27^{\circ}$ C)



**Fig. 4.** Effect of sorbate (Pb<sup>II</sup>) dose on adsorption. (Sorbent dose = 1.3 g/L, pH = 4.5, Time = 1 h, Temperature =  $27^{\circ}$ C)

### 3.4 Effect of Sorbate Dose on Metal Ion Adsorption

The effect of sorbate dose (Pb<sup>II</sup> concentration) on adsorption, keeping the other conditions (pH = 4.5, temperature =  $27^{\circ}$ C, sorbent dose = 1.3 g/L and time = 1 h) fixed, was studied (Fig. 4). It was observed that lead ion uptake capacity of the sorbent increases sharply with the increase of metal ion concentration. The lead ion retention capacity of the resin (X-AA-g-PVA) was 12.48 mg/g at low level of sorbate (207 ppm) and became 50 mg/g at 1000 ppm of lead. The maximum uptake capacity was found to be 224.6 mg/g at relatively higher dose of sorbate (4500 ppm) and the value is fairly higher than reported values (22) (24, 44.2, 134.5 and 147.9 mg/g for resins of polyethylenimine, carboxylic, sulfonic and phosphoric acids respectively). Uncrosslinked AA-g-PVA showed inferior results (13) (probably due to lower exchange capacity).

#### 3.5 Retention of Pb(II) in the Competitive Condition

In this group of experiments, the competitive adsorption of nickel, cadmium and lead ions into the polymer were investigated. These experiments were performed at a constant pH (4.5), temperature (27°C), sorbent dose (1.3 g/L) and time (1 h) with the solution containing 0.001 mole of each metal ion. The adsorption capacities were 0.106, 0.081 and 0.065 m mol/g for lead, nickel and cadmium ions respectively (Table 2). The order of affinity under competitive condition was the same as that obtained for single ion solutions [i.e. Pb(II) > Ni(II) > Cd(II)]. Nickel, cadmium and lead were eluted sequentially and quantitatively from the resin by 0.002 M H<sub>2</sub>SO<sub>4</sub>, 0.1 M H<sub>2</sub>SO<sub>4</sub> and 0.01M



**Fig. 5.** Effect of time on Pb<sup>II</sup> adsorption. (Sorbent dose = 1.3 g/L, Sorbate dose = 207 ppm, pH = 4.5, Time = 1 h; 1, 2 and 3 represent 5, 27 and 40°C, respectively)

HNO<sub>3</sub>. Selection of eluent is based on solubility and solubility product principle. Lead sulfate is insoluble in aqueous medium. So sulfuric acid is not a suitable eluent for lead ion. Higher concentration of sulfuric acid is required to resist the hydrolysis of cadmium ion. Thus, cadium requires higher concentration of  $H_2SO_4$  for elution compared to nickel. Volume of eluent required for stripping is related to its concentration. The stability constants (K<sub>stability</sub>) for the various metal/resin complexes were investigated with Ruzic (23) method. The K<sub>stability</sub> values for the complexes were 794, 524 and 216 L/mol for Pb(II), Ni(II) and Cd(II), respectively. The maximum amount of the lead ion adsorbed was consistent with the higher stability constant values obtained.

## 3.6 Effect of Contact Time, Adsorption Kinetics and Transport Mechanism.

Figure 5 shows the amount of Pb(II) adsorbed ( $Q_t$ , mg/g) at a contact time, t (min). The results have indicated that ~90% adsorption took place in 30 min, and the time required to reach the equilibrium is 60 min; that is much less than reported values of commercially available carboxylic resins (22) and uncrosslinked AA-g-PVA (13). The rapid adsorption in the initial part may be attributed to the availability of the negatively charged surface of the sorbent (RCOO<sup>-</sup>). The slow adsorption in the later part may be due to electrostatic hindrance between adsorbed positively charged sorbate and available cationic sorbate in solution, and the slow pore diffusion of the solution into the bulk

Table 2. Competitive adsorption and elution of Ni(II), Cd(II) and Pb(II) ions

Metal ions	Metal ions adsorbed (mg/g of polymer	Metal ions adsorbed (m mol/g of polymer)	Eluent used	Volume of Eluent (ml)	Recovery (%)
Ni(II)	04.60	0.081	$0.002 MH_2 SO_4$	20	83.30
Cd(II)	07.25	0.063	$0.1 \text{M H}_2 \text{SO}_4$	20	74.07
Pb(II)	22.07	0.106	0.01M HNO3	40	94.07

of adsorbent. The similar types of results were observed by Denizil et al. (11).

The time dependent experimental adsorption data (Fig. 5) are used to fit various kinetic models by linear regression plots. The equations (24) used for fitting the data are: First order, pseudo first order, second order, pseudo second order, Bhattacharya-Venkobachor, power function and simple Elovich models. The present kinetic data could be best described by first order model:  $-Ln(C/C_{\circ}) = k_1 t (C_{\circ} \text{ and } C$  denote concentration of lead ion at t = 0 and t = t respectively;  $k_1$  refers first order rate constant, min<sup>-1</sup>). The plot of  $-Ln(C/C_{\circ})$  against t gives rise to straight line with very good correlation coefficient ( $R^2 = 0.993$ , 0.998 and 0.995 at 5, 27 and 40°C, respectively).

The transport (diffusion) mechanism of sorbate (Pb<sup>II</sup>) into the adsorbent follows three steps viz, film, pore and intra particle diffusion. The slowest of the three steps controls the overall rate process. The Weber and Morris (24) plot of log Q<sub>t</sub> vs. 0.5 log t is found to be linear ( $\mathbb{R}^2 > 0.95$ ) over the range of contact time, which implied that intra-particle diffusion was the rate limiting step during extraction of Pb(II) from water. The kinetic data have also been analyzed using the kinetic expression developed by Boyd et al. (24) to confirm the actual rate determination step involved in the lead ion adsorption process. The plot of -Ln(1-Q<sub>t</sub>/Q<sub>e</sub>) against t give rise to straight line ( $\mathbb{R}^2 > 0.95$ ), which indicates that the adsorption process was controlled by the intra-particle diffusion. The result obtained was found to be similar with that reported by Saeed et al. (1).



**Fig. 6.** Adsorption isotherm of  $(Pb^{II})$  (Sorbent dose = 1.3 g/L, Sorbate dose = 207 ppm, pH = 4.5, Time = 1 h; 1, 2 and 3 represent 5, 27 and 40°C, respectively)

#### 3.7 Adsorption Isotherm and Energy

Five isotherms (24) (Langmuir, Freundlich, Redlich, Toth and Temkin) were used for fitting the experimental data (Fig. 6) obtained at 5, 27 and 40°C (pH 4.5, time =1 h, sorbate dose = 1.3 g/L). The isotherm data have been analyzed using the linear equation of various models (Table 3). Among isotherms, the order of fitting the experimental data at 27°C is Langmuir (R<sup>2</sup> = 0.9974)> Temkin (R<sup>2</sup> = 0.9955)> Redlich-Peterson (R<sup>2</sup> = 0.9937)> Freundlich (R<sup>2</sup> = 0.9752)> Dubinn-Redushkevick (R<sup>2</sup> = 0.9752). In order to distinguish between physical and chemical adsorption, the isotherm data (Fig. 6) was subjected to the

**Table 3.** Isotherm model and related statistical parameters (Sorbent dose = 1.3 g/L, pH = 4.5, Time = 1 h; Temperature = 5, 27 and  $40^{\circ}$ C)

Isotherm Model	Parameters	$5^{\circ}C$	27° C	40° C
Langmuir (Linear form) $C_e/Q_e = 1/K_a .Q_m + C_e/Q_m$	<b>R</b> <sup>2</sup>	0.998	0.997	0.993
	Ka	0.0032	0.0038	0.0042
	Qm	75.18	87.72	105.26
Frendlich (Linear form) $LogQ_e = LogK_F + (1/n) Log C_e$	$\mathbf{R}^2$	0.976	0.975	0.986
	1/n	0.622	0.635	0.701
	$K_{\rm F}$	1.013	1.230	1.159
Temkin $Q_e = a + 2.303 b \text{ Log } C_e$	$\mathbb{R}^2$	0.996	0.995	0.989
	а	-56.52	-61.52	-63.65
	b	16.49	19.05	21.09
Redlich-Peterson(Linear form) $C_e/Q_e = 1/\alpha + (\beta/\alpha)C_e^{\gamma}$	$\mathbb{R}^2$	0.995	0.993	0.989
	α	0.265	0.366	0.467
	eta	0.0068	0.0079	0.0081
	γ	0.900	0.900	0.900
Dubinn-Redushkevick Ln $Q_e = Ln$ $Q'_m \cdot K_{DR} \varepsilon^2  \varepsilon = RT$ $Ln(1+1/C_e)$	$\mathbf{R}^2$	0.874	0.860	0.869
	$\mathbf{Q}_{\mathrm{m}}^{/}$	39.94	45.27	45.77
	K <sub>DR</sub>	0.0008	0.0005	0.0002
	E <sub>DR</sub>	25	31.62	50

Dubinn-Redushkevich (DR) isotherm model (24) (Table 3). The adsorption energy ( $E_{DR}$ ), which is the free energy change when one mole of ion is transferred to the surface of adsorbent from infinity in solution, was calculated using the relationship (24):  $E_{DR} = (-2K_{DR})^{-1/2}$ . The magnitude of  $E_{DR}$  is useful for estimating the type of adsorption. In the present case, values were observed in range 25–50 KJmol<sup>-1</sup>, which indicates that the adsorption of Pb(II) took place by ion exchange process (Eq. 5).

## 3.8 Effect of Temperature and Adsorption Thermodynamics

The effect of temperature on Pb(II) adsorption at various sorbate dose is shown in (Fig. 6). The adsorption capacity increases with the increasing temperature from 5 to  $40^{\circ}$ C. The adsorption and desorption occurred through ion exchange process (Eq. 5). Initial increase of temperature favors the adsorption, while increase of temperature above  $40^{\circ}$ C accelerates the desorption process.

Thermodynamic parameters such as free energy change  $(\Delta G^0)$ , enthalpy-change  $(\Delta H^0)$  and entropy change  $(\Delta S^0)$  were calculated to evaluate the thermodynamic feasibility of the process and to confirm the nature of adsorption process. The Van't Hoff equation (25) (Eq. 6) could be used for the estimation of thermodynamic parameters  $(\Delta H^0 \text{ and } \Delta S^0)$ , and  $\Delta G^0$  may be calculated through Equation 7.

$$Ln (Q_e/C_e) = (\Delta S^0/R) - \Delta H^0/RT$$
(6)  
$$\Delta G^0 = \Delta H^0 - T\Delta S^0$$
(7)

The value of  $\Delta H^0$  and  $\Delta S^0$  were calculated from the slope and intercept of the plot of Ln(Q<sub>e</sub>/C<sub>e</sub>) vs. 1/T. The negative values of  $\Delta G^0$  confirm the spontaneous nature and feasibility of the sorption process. The enthalpy change ( $\Delta H^0$ ) values are found to be +10.53 KJmol<sup>-1</sup>, which indicated the endothermic nature of adsorption process. The positive entropy change ( $\Delta S^0$ ) for the adsorption indicated the increase of number of species in the system through the release of H<sup>+</sup> ion during adsorption (Eq. 5).

## 4 Conclusions

The synthesized resin acts as cation exchanger with high exchange capacity. It has good chemical and thermal stability. Exchange bed could be used more than 40 cycles with little loss of exchange capacity. The developed technique could be applied for the selective extraction of lead(II) from environmental samples. The proposed method is highly efficient, cost effective, simple and rapid. The crosslinked AA-g-PVA has significantly higher lead ion uptake capacity and selectivity than that of uncrosslinked AA-g-PVA and commercially available carboxylic resins. The adsorption and desorption of lead ion took place mainly by ionexchange process. The synthesized exchanger has strong affinity with lead ion over nickel and cadmium ions. The adsorption process follows the first order kinetics and Langmuir adsorption isotherm.

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