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Study sorption and desorption of Cd^{+2} , Pb^{+2} ions by selected chelating resin to removal them from industrial and environmental wastes

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Abstract

A paper reports study of sorption and desorption behavior of Cd^{+2} , Pb^{+2} ions on selected chelating resin consists of (P-DETATA). It had converted to sodium form by treated with basic solution (0.5 M, NaOH). Sorption studies of Cd^{+2} and Pb^{+2} ions were carried out by using batch-column processing system, and total capacity (mmoles of M^{n+} /g dry resin) was designed as a function of pH values, time periods and constant temperature. As well, desorption of Cd^{+2} and Pb^{+2} ions were achieved using diverse concentrations of diluted HCl at flow rate of 1 ml/min using column method. The results obtained indicate that the (P-DETATA) resin has higher affinity towards the metal ions under the study. This may give opportunity to use it for removing of Cd^{+2} and Pb^{+2} ions from industrial and environmental wastes.

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1. Introduction

In industries, several operations like tanning, plating and mining discharge wastewater polluted with heavy and poisonous elements into the environment. Technological approaches with various ways were established to control the contamination of superficial and groundwater. Different functionalized chelating polymers have potential uses in the selective uptake ions from manufacturing discarded solutions [1–8].

For enrichment and separation of metal ions, using of chelating agent-loaded organic polymers have a great attention. hydroxamic acid, amidoxime, iminoacetic acid [9–12], Schiff bases [13,14], thiol [15,16], thiazole [17] and amines [18] are some particular patterns. Diverse amino resins came from glycidyl meth-acrylate with various matrix properties have been prepared and used to the recovery some metal ions from water medium

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[19,20]. Functionalization of polysiloxanes with organic group is typically used to present many chelating ligand groups [21–27]. It is finding that the fusion of chelating ligands onto polysiloxanes, its manner into an increasing number of uses in fields for instance extraction of metal ions from organic and aqueous solutions [28–34], use in chromatographic separation as stationary phases [25,33] and for the catalysis of reactions [35,36]. Sol–gel method at ambient temperatures has been used to synthesize Porous solid polysiloxanes [27–32].

For many decades, diethylenetriamine has been used as a chelating ligand. Substitution reaction was carried out to prepare diethylenetriamine with halogen-functionalized polysiloxanes [21,37].

In this article, selected chelating resin consist of the DETATA anchored poly-siloxane material was prepared according to modification method by El-Ashgar et al. [38]. Sorption and desorption studies were done by using batch and column processing system at diverse pH media, periods and constant temperature.

2. Experimental

2.1. Chemical and materials

Diethylenetriaminopropyltrimethoxysilane, Tetraethylorthosilicate, and ethyl-chloroacetate were supplied from Aldrich. Other chemicals were supplied by across. Stock solution of divalent (II) ions was made by using the metal (II) nitrate in D.W. The measurements of pH were monitored by using $\text{CH}_3\text{COOH}/\text{CH}_3\text{COONa}$ buffer solution (pH 3.4–6.0) and $\text{NH}_4\text{OH}/\text{NH}_4\text{Cl}$ (pH 9–10).

2.2. Preparation of DETATA anchored resin (P-DETATA)

The method described in literature was adapted to prepare the (P-DETATA) resin, the preparation was included the following steps [38]:

- i. Ethyl chloroacetate (24.51 g) was treated with stirred ethanoic solution of diethylenetriaminopropyltrimethoxysilane (13.27 g, in 15 mL of ethanol). The reaction was refluxed for about 48 h at 90 °C after that left to cool. The solvent was removed and diethylenetriaminetetraethylacetate silane agent was obtained.
- ii. Stirred ethanoic solution (0.05 mole) of product in step i in the presence of 4.95 g 0.042M HCl as catalyst was reacted with Tetraethylorthosilicate (20.8 g, in 25 mL ethanol) then the mixture was left to stir for about 1 h at room temperature. Polymerization was carried out within 3 days according to the method of El-Ashgar et al. [38].

2.3. Conversion of anchored resin to sodium form(Na-form)

A 5.0 g of resin form was shaken in 30 ml of (0.5 M) NaOH1 for 15 h at R.T. The mixture was decanted, and then the resin was filtered off, and wash with D.W. It was left in air to dry and stated as (Na-form).

2.4. Batch-processing system for metal sorption experiments

Batch method was using for Metal ion sorption experiments and employing the literature method [19,20]. The total capacity (T.C) was determined as M^{n+}/g dry resin. Sorption ion was qualified at diverse periods and pH. Flame atomic absorption technique (FAAs) was used to quantify the metal ions.

2.5. Column separation experiment

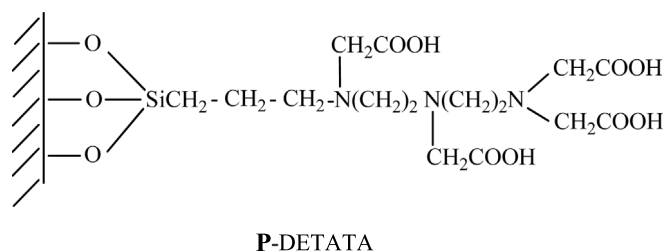
100 mg of the resin was packed in a small column. The solution of the ion with 5×10^{-3} M was allowed at rates 1, 2, and 3 ml/min. A 5.0 mL of the effluent was collected every 10 min and quantified.

2.6. Desorption experiment

100 mg of resin was packed on the column, which was previously buffered then loaded with the ions. After the maximum uptake, the loaded resin was washed with D.W. Elusion was done via using HCl (0.5, 1.5 and 3M). Ten ml of the effluent was collected consequently and the concentration of the unrestricted ion was quantified.

3. Results and discussion

As it was mentioned earlier, the chelating resin with DETATA ligand functionalized on polysiloxane material was synthesized according to the method as described by El-Ashgar et al. [38]. The proposed structure of the functionalized resin was illustrated in Fig. 1. The detail spectroscopic data of this structure were as in the literature [38] (see Scheme 1).



(Where **P** represents [Si-O]_n, DETATA represents diethylenetriaminetetraacetic Acid)

Scheme 1. Diethylenetriaminetetraacetic acid.

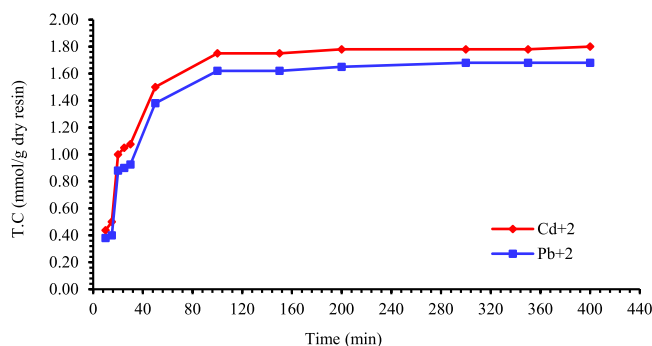


Fig. 1. Total capacity of metal ions under the study by resin (Na-form) versus of the time.

3.1. Sorption of metal ions using batch-processing system

A comparison between (T.C) of the sodium-forms and hydrogen-forms of the dry resin is represented in Table 1. The differences perhaps because the higher ionic nature of the sodium-form giving $-(COO^-)$ compared with hydrogen-form which are controlled by the pH buffer. T.C in both forms was the order ($Cd^{2+} > Pb^{2+}$). The higher removal of ions by resin (Na-form) can be elucidated by the higher affinity of $-(COO^-)$. This reveals that the resin could be favorable in the area of wastewater treatment. Conversely, modification of DETATA ligand functionalized on the resin may lead to improve the affinity of anchored resin in a wide spectrum of diverse ions in aqueous and non-aqueous solutions.

Table 1. (T.C) of resin (Na-form) and resin (H-form) at pH (Cd^{2+} 6.5, Pb^{2+} 6.1).

Metal ion	Total Capacity (T.C) of the anchored resin (mmol/g dry resin)	
	Resin (Na-form)	Resin (H-form)
Cd	1.52	1.28
Pb	1.20	1.10

Fig. 1 illustrates the variation of the (T.C) versus of the time for metal ions under study at pH (Cd^{2+} 6.5, Pb^{2+} 6.1). The (T.C) reached to 50% within 20 min while to 90% after 40 min. Equilibrium of adsorption (T.C) was done in 100 min for both ions under the study.

3.2. pH effect on the total capacity (T.C) of metal ion

Fig. 2 shows the influence of the pH medium on total capacity (T.C) of both metal ions under the study. At close to the natural pH of the metal ion solution, the maximum values of total capacity for both metal ions (Cd^{2+} 6.8, Pb^{2+} 6.2) were recorded. This may be due to that the electron pairs on N atom is unoccupied, the existence of carboxylic group may be also given a chance for making the corresponding resin–metal complex. Decreasing of total capacity in acidic solution belong to the protonation of electron pairs on nitrogen atom Also, the lower dissociation of the $-(\text{COO}^-)$ [19,20]. After the natural pH, the total capacity of both metal ions is unconvinced to be assigned individual to the interaction of the ions with the active positions on chelating polymer. Another reason may also relative to the formation of metal hydroxide as soluble or insoluble species. Nevertheless, chelation between the functional ligands on the solid surface and metal ions can be occurred in a diverse manner owing to static hinderance effects and the complexity of the solid matrix [39].

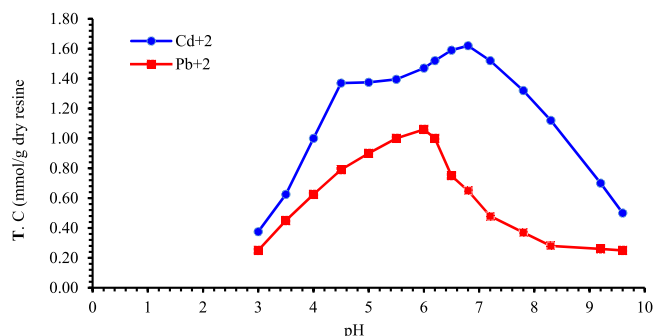


Fig. 2. pH effect on total capacity for ions under the study via resin (Na-form) at 25 °C.

To illustrate the correlation the quantity of adsorption with equilibrium concentration for both metal ions at certain temperature, isotherms of adsorption are used. Fig. 4 displays the isotherms of both ions at pH constant and 25 °C. It indicates that the total capacity increases with the rising of concentration until the overload value after that there is no longer effect of the concentration on the (T.C) (see Fig. 3).

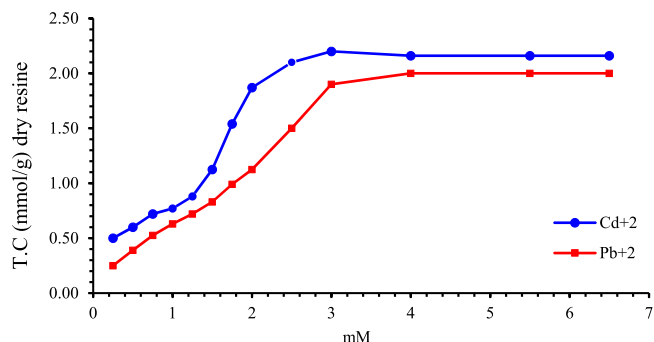


Fig. 3. Adsorption isotherms for both ions on resin (Na-form) at pH constant and 25 °C.

Fig. 4a and b reveal the total capacity of both ions (Cd^{2+} and Pb^{2+}) by resin versus of the time at 1, 2 and 3 mL/min. It was obviously found that the required time to reach the saturation (maximum total capacity) was longer when the flow rate had decreased. Conversely, at the same flowing time, while the flow rate increases, the total capacity will increase. This may assign to the big volume of the influent solution fleeting through the column at the higher rate reaching quick saturation of active positions. Briefly, using higher flow rate can be provide the saturation at short period while lower flow rate gives well interaction between the polymer and both ions. Consequently, the

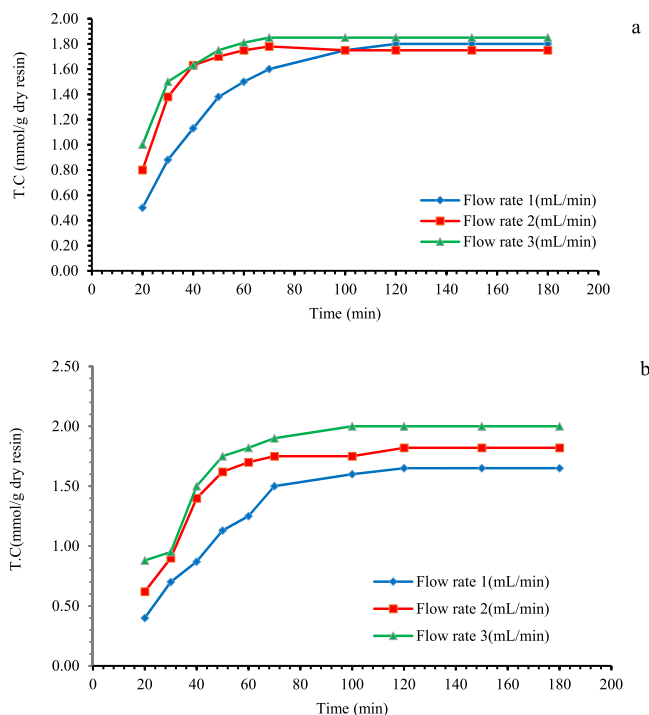


Fig. 4. Flow rate influence at the total capacity for both ions by resin (Na-form) with preliminary concentration 5×10^{-3} M: (a) Cd²⁺ and (b) pb²⁺.

process should be achieved in line with the priority. It is also evident that upper 2 mL/min flow rate is less effective to provide substantial variations in the values of total capacity.

3.3. Desorption experiment

Diverse concentrations (0.5, 1.5 and 3M of HCl) using column technique was used as eluent agent. Elution ratio was calculated by adapting the relation below [40]:

$$\frac{\text{Quantity of metal ion in eluent}}{\text{Quantity of metal ion adsorbed on the resin}} \times 100$$

Generally, Fig. 5(a and b) indicate the desorption data. Using 140–150 mL of 0.5M HCl gave more than 90% of the desorption efficiency for metal ions under the study. The eluent volume (35–60 mL of (3 M) HCl) gave (desorption efficiency 92%–100%). The generation of resin was carried out more than 5 cycles without losing its activity.

4. Conclusions

In summary, the prepared anchored resin (P-DETATA) exhibits high potential towards Cd²⁺ and Pb²⁺. Sodium form of the chelating polymer indicated the (T.C) slightly higher than the H-form. Sorption studies were achieved at different pH values, periods and certain temperature. The total capacity (T.C) gained by the batch processing system was relatively slighter than that found by the column one. Diverse concentrations (0.5, 1.5 and 3 M) of HCl were used as eluates and found to be the effective desorbed agents. The generation of resin more cycles without losing its activity may be made it suitable to use in industrial and environmental fields. In addition, this may make it possible to use as solid phase for removing the metal ions under the study from polluted water and industrial wastes.

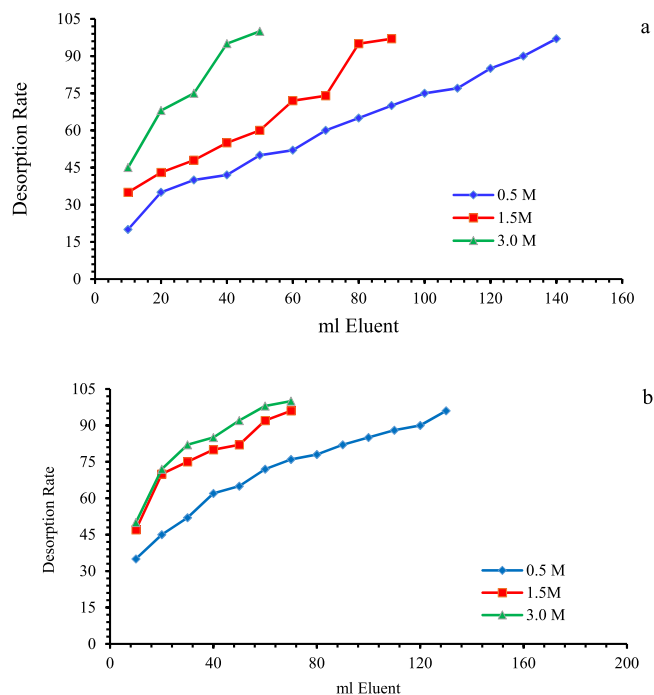


Fig. 5. Elution of ions from resin (Na-form) by HCl with various concentrations by column: (a) Cd²⁺ and (b) Pb²⁺.

References

- [1] Ramadani SA, Lekchiri Y, Morcellet M, Crini G, Morcellet J, Janus L. Preparation of pyrazole compounds for attachment to chelating resins. *Eur Polym J* 2000;36(9):1885.
- [2] Bicak N, Sherrington DC, Sungur S, Tan N. A glycidyl methacrylate-based resin with pendant urea groups as a high capacity mercury specific sorbent. *React Funct Polym* 2003;54(171).
- [3] Kawamura Y, Mitsuhashi M, Tanible H, Yoshida H. Adsorption of metal ions on polyaminated highly porous chitosan chelating resin. *Ind Eng Chem Res* 1993;32(2):386.
- [4] Navorro RR, Sumi K, Matsumura M. Improved metal affinity of chelating adsorbents through graft polymerization. *Water Res* 1999;33(9):2037.
- [5] Lezzi A, Cobianco S, Roggero A. Synthesis of thiol chelating resins and their adsorption properties toward heavy metal ions. *J Polym Sci Part A* 1994;32(10):1877.
- [6] Tewari PK, Singh AK. Preconcentration of lead with amberlite XAD-2 and amberlite XAD-7 based chelating resins for its determination by flame atomic absorption spectrometry. *Talanta* 2002;56(4):735.
- [7] Trochimczuk AW, Kolarz BN. Synthesis and chelating properties of resins with methylthiourea, guanlythiourea and dithiocarbamate groups. *Eur Polym J* 2000;36(11):2359.
- [8] Tewari PK, Singh AK. Thioisocyclic acid-immobilized amberlite XAD-2: metal sorption behaviour and applications in estimation of metal ions by flame atomic absorption spectrometry. *Analyst* 2000;125:2350.
- [9] Biack N, Senkal BF, Melekaslan D. Poly (styrene sulfonamides) with EDTA-like chelating groups for removal of transition metal ions. *J Appl Polym Sci* 2000;77(12):2749.
- [10] Yuchi A, Mukaie K, Sotomura Y, Yamada H, Wada H. Direct evidence for two interaction modes in adsorption of divalent metal ions to iminodiacetate-type chelating resins. *Anal Sci* 2002;18(5):575.
- [11] Chien WC, Yung CC, Yuan CC. Synthesis of chelating resins with iminodiacetic acid and its wastewater treatment application. *J Appl Polym Sci* 2002;84(6):1353.
- [12] Malla ME, Alvarez MB, Batistoni DA. Evaluation of sorption and desorption characteristics of cadmium, lead and zinc on amberlite IRC-718 iminodiacetate chelating ion exchanger. *Talanta* 2002;57(2):277.
- [13] Samal S, Das RR, Day RK, Acharya S. Chelating resins VI: Chelating resins of formaldehyde condensed phenolic schiff bases derived from 4, 4'-diaminodiphenyl ether with hydroxybenzaldehydes—synthesis, characterization, and metal ion adsorption studies. *Appl Polym Sci* 2000;77(5):967.
- [14] Syamal A, Singh M, Kumar D. Syntheses and characterization of a chelating resin containing ONNO donor quadridentate schiff base and its coordination complexes with copper(II), nickel(II), cobalt(II), iron(III), zinc(II), cadmium(II), molybdenum(VI) and uranium(VI). *React Funct Polym* 1999;39(1):27.

- [15] Antico E, Masana A, Salvado V, Hidalgo M, Valiente M. Adsorption of palladium by glycolmethacrylate chelating resins. *Anal Chim Acta* 1994;296(3):325.
- [16] Dominguez L, Yue Z, Economy J, Mangun CL. Design of polyvinyl alcohol mercaptal fibers for arsenite chelation. *React Funct Polym* 2002;53(2–3):205.
- [17] Chen Y, Zhao Y. Synthesis and characterization of polyacrylonitrile-2-amino-2-thiazoline resin and its sorption behaviors for noble metal ions. *React Funct Polym* 2003;55(1):89.
- [18] Burba P. Anion exchangers functionalized by chelating reagents (AnChel) for pre-concentration of trace elements: Capabilities and limitations. *Fresenius J Anal Chem* 1999;341(12):709.
- [19] Attia AA, Donia AM, Abou-EL-Enien SSA, Yousif AM. Studies on uptake behaviour of copper (II) and lead (II) by amine chelating resins with different textural properties. *Sep Purif Technol* 2003;33(3):295.
- [20] Attia AA, Donia AM, Yousif AM. Synthesis of amine and thio chelating resins and study of their interaction with zinc (II), cadmium (II) and mercury (II) ions in their aqueous solutions. *React Funct Polym* 2003;56(1):75.
- [21] El-Nahhal IM, Zaggout FR, El-Ashgar NM. Uptake of divalent metal ions (Cu^{2+} , Zn^{2+} and Cd^{2+}) by polysiloxane immobilized monoamine ligand system. *Anal Lett* 2000;33(10):2031.
- [22] Klonkowski AM, Widernik T, Grobelna B, Jóźwiak WK, Proga H, Szubiakiewicz E. Amino-modified silicate xerogels complexed with Cu(II) as Catalyst precursors, coordination state and thermal decomposition. *J Sol-Gel Sci Tech* 2001;20(2):161.
- [23] El-Kurd HM, El-Nahhal IM, El-Ashgar NM. Synthesis of new polysiloxane-immobilized ligand system di(amidomethyl) aminetetraacetic acid. *J Phosphorus Sulfur Silicon Rel Elem* 2005;180(7):1657.
- [24] Saadeh SM, El-Ashgar NM, El-Nahhal IM, Chehimi MM, Maquet J, Babonneau F. Synthesis, characterization and applications of polysiloxane networks with immobilized pyrogallol ligands. *Appl Organometal Chem* 2005;19(6):759.
- [25] El-Ashgar NM, El-Nahhal IM. Pre-concentration and separation of copper (II) by 3-aminopropylpolysiloxane immobilized ligand system. *J Sol-Gel Sci Tech* 2005;34(2):165.
- [26] El-Ashgar NM, El-Nahhal IM. Separation of Cu(II), Ni(II), and Co(II) ions using iminobis (N-2-aminoethylacetamide) polysiloxane-immobilized ligand system. *J Dispers Sci Technol* 2006;27(7):915.
- [27] Parish RV, El Nahhal IM, El-Kurd HM, Baraka RM. Synthesis of some new polysiloxane ligand systems (iminodiacetate) part i. *Asian J Chem* 1999;11(3):790.
- [28] Moawed EA, Zaid MAA, El-Shahat MF. Pre-concentration and determination of trace amounts of metal ions in cast iron, granite, and water using polyurethane foam functionalized with beta-naphthol. *Acta Chromatogr* 2005;15:220.
- [29] Kudryavtsev GV, Miltchenko DV, Yagov VV, Lopatkin AA. Ion sorption on modified silica surface. *Colloid Interface Sci* 1990;140(1):114.
- [30] Iamamoto MS, Gushikem Y. Adsorption and pre-concentration of some metal ions from ethanol on silica gel modified with pyridinium ion. *Analyst* 1989;114:983.
- [31] Sturgeon RE, Berman SS, Willie SN, Desauinier JAH. Pre-concentration of trace elements from seawater with silica-immobilized 8-hydroxyquinoline. *Anal Chem* 1981;53(14):2337.
- [32] Khatib IS, Parish RV. Insoluble ligands and their applications: I. A comparison of silica-immobilized ligands and functionalized polysiloxanes. *J Organomet Chem* 1989;369(1):9.
- [33] El-Nasser AA, Parish RV. Solid polysiloxane ligands containing glycine- or iminodiacetate-groups: synthesis and application to binding and separation of metal ions. *J Chem Soc Dalton Trans* 1999;19:3463.
- [34] Van Grieken R. Pre-concentration methods for the analysis of water by x-ray spectrometric techniques. *Anal Chim Acta* 1982;143:3.
- [35] Cermak J, Kviclova M, Blechta V, Capka M, Bastl Z. Hydrogenation catalytic activity of substituted cyclopentadienyl titanium complexes anchored on polysiloxanes prepared by a sol-gel procedure. *J Organomet Chem* 1996;509(1):77.
- [36] Price PM, Clark JH, Macquarrie DJ. Modified silicas for clean technology. *J Chem Soc Dalton Trans* 2000;2(2):101.
- [37] Ahmed I, Parish RV. Insoluble ligands and their applications: IV, Polysiloxane-bis (2-aminoethyl) amine ligands and some derivatives. *J Organomet Chem* 1993;452(1–2):23.
- [38] El-Ashgar NM, El-Nahhal IM, Chehimi MM, Babonneau F, Livage J. New strategy for the synthesis of diethylenetriaminetetraacetic acid functionalized polysiloxane ligand systems. *J Dispers Sci Technol* 2009;30(5):684.
- [39] Aguilar M, Cortina JL. Solvent extraction and liquid membranes. *Fundamentals and applications in new materials*, LLC: Taylor & Francis Group; 2008.
- [40] Ni C, Yi C, Feng Z. Studies of syntheses and adsorption properties of chelating resin from thiourea and formaldehyde. *J Appl Polym Sci* 2001;82(13):3127.