

Poly(vinyl pyridine-poly ethylene glycol methacrylate-ethylene glycol dimethacrylate) beads for heavy metal removal

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Abstract

Poly(vinyl pyridine-poly ethylene glycol methacrylate-ethylene glycol dimethacrylate) [poly(VP-PEGMA-EGDMA)] beads with an average size of 30–100 μm were prepared by suspension polymerization. Poly(VP-PEGMA-EGDMA) beads were characterized by swelling studies, scanning electron microscopy (SEM), elemental analysis, Fourier Transform Infrared Spectroscopy (FTIR). The beads with a swelling ratio of 65% were used for the heavy metal removal studies. Chelation capacity of the beads for the selected metal ions, i.e., Pb(II), Cd(II), Cr(III) and Cu(II) were investigated in aqueous media containing different amounts of these ions (5–80 mg/l) and at different pH values (2.0–10.0). The maximum chelation capacities of the poly(VP-PEGMA-EGDMA) beads were 18.23 mg/g for Pb(II), 16.50 mg/g for Cd(II), 17.38 mg/g for Cr(III) and 18.25 mg/g for Cu(II). The affinity order on mass basis was observed as follows: Cu(II) > Pb(II) > Cr(III) > Cd(II). pH significantly affected the chelation capacity of VP incorporated beads. Heavy metal adsorption on the poly(PEGMA-EGDMA) control microspheres was negligible. Regeneration of the chelating beads was easily performed with 0.1 M HNO_3 . It was shown that these beads can be used effectively for heavy metal removal from aqueous solutions with repeatedly adsorption–desorption operations. These features show that poly(VP-PEGMA-EGDMA) beads are potential candidate sorbent for heavy metal removal.

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1. Introduction

There is noticeable increase in heavy metal contaminant volume to those who make many serious environmental problems in the recent years [1]. Heavy metals are metabolic poisons and enzyme inhibitors [2]. They can cause mental retardation and semipermanent brain damage. Because of the reason that heavy metals can not be rendered harmless by chemical or biological remediation processes, they are classified as environmental toxic substances [3]. Toxic metals are released into the environment in a number of different ways. Coal combustion, sewage waste waters, automobile emissions, battery industry, mining activities, tanneries, alloy industries and the utilization of fossil fuels are just a few examples [4]. Many different methods for heavy metal removal from aqueous solu-

tion have been reported in the literature, such as adsorption, extraction, precipitation, neutralization, dialysis, ion exchange and complexing agent modified polymers, both in microbead and membrane forms [4–9]. Among these techniques, adsorption is generally preferred for the heavy metal removal due to availability of different adsorbents, its high efficiency, easy handling and low cost possibilities. So many researches dealing with toxic metal ion removal by using chelating polymers has a great importance in environmental applications [8–22]. A large number of polymers incorporating a variety of ligands including polyethyleneimine, amidoxime, acrylamide, thiazolidine, phosphoric acid, dithiocarbamate and amino acids have been prepared and their adsorption and analytical properties were investigated [18–28]. An expensive and critical step in this preparation process is coupling of a ligand to the adsorption matrix. The major issue is that of slow release of these covalently bonded chelators off the matrix. Release is a general problem encountered in any ligand chelation technique which caused a decrease in chelation capacity [19–24]. The time consuming and

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Table 1

Recipe and polymerization conditions for preparation of the poly(VP-PEGMA-EGDMA) beads with a swelling ratio of 65% and in the size range of 30–100 μm

Aqueous dispersion phase	Organic phase
50 ml of deionized water	1 ml VP
0.4 g poly(vinyl alcohol)	4 ml PEGMA 1 ml EGDMA 4 ml toluene 0.15 g BPO
Polymerization conditions	
Reactor volume	100 ml
Stirring rate	400 rpm
Temperature and time	85 °C and 4 h

high cost of chelating procedure has inspired a search for suitable low cost adsorbents.

Hence, in the presented study, we have tried to develop chelating beads for the assembly of a new class of novel heavy metal adsorbents. It is showed that poly(VP-PEGMA-EGDMA) beads can be used directly for heavy metal removal. This approach for the preparation of metal-chelating matrix has so many advantages over conventional preparation techniques; those needed the activation of the matrix for metal-chelating ligand immobilization. So, according to this procedure, comonomer VP has a role as the metal-chelating ligand, and there is no extra need to activate the matrix for the chelating-ligand immobilization. VP was polymerized with PEGMA and EGDMA without chelating-ligand immobilization step and also there is no leakage of the ligand.

In the presented work, possible usage of poly(VP-PEGMA-EGDMA) for heavy metal usage has been discussed.

2. Experimental

2.1. Materials

Poly (ethylene glycol) methacrylate (PEGMA) was supplied from Aldrich Chem. Co., USA and used as received. Vinyl pyridine (VP), selected as the reactive comonomer, was obtained from Merck AG (Darmstadt, Germany). Ethylene glycol dimethacrylate (EGDMA, Aldrich Chem. Co.) was used as the cross-linking agent as supplied. An initiator, benzoyl peroxide (BPO) was obtained from Fluka A.G. (Buchs, Switzerland). Toluene was supplied from Merck, Germany and used as diluent (as a pore former). Poly(vinyl alcohol) (PVAL; Mw: 85–146, 87–89% hydrolyzed) was supplied from Aldrich Chem. Co. (USA) and used as the stabilizer. All other chemicals were of reagent grade and were purchased from Merck AG (Darmstadt, Germany). Distilled-deionized water was used in the preparation of the media for polymerization and all adsorption experiments.

2.2. Preparation of poly(VP-PEGMA-EGDMA) beads

Poly(VP-PEGMA-EGDMA) gel beads were prepared by using a suspension polymerization method developed in previous studies [29,30]. Table 1 gives the recipe and polymerization

conditions for preparation of the poly(VP-PEGMA-EGDMA) beads with a swelling ratio of 65% and in the size range of 30–100 μm .

2.3. Characterization of poly(VP-PEGMA-EGDMA) beads

Water uptake ratio of the polymeric beads was determined in distilled water. The experiment was conducted as follows; initially dry beads were carefully weighed before being placed in a 50 ml vial containing distilled water. The vial was put into an isothermal water bath with a fixed temperature (25 °C) for 2 h. The bead samples were taken out from the water, wiped using a filter paper, and weighed. The weight ratio of dry and wet samples was recorded.

The surface morphology of the beads was examined using scanning electron microscopy (SEM). The samples were initially dried in air at 25 °C for 2 days before being analyzed. A fragment of the dried bead was mounted on a SEM sample mount and was sputter coated with gold for 2 min. The sample was then mounted in a scanning electron microscope (Model: Raster Electron Microscopy, Leitz-AMR-1000, Germany). The surface of the sample was then scanned at the desired magnification to study the morphology of the beads.

In order to evaluate the degree of VP incorporation, the synthesized poly(VP-PEGMA-EGDMA) beads were subjected to elemental analysis using a Leco Elemental Analyzer (Model CHNS-932, USA).

Infrared spectrum was recorded on Shimadzu FTIR 8000 Series, FTIR spectrophotometer (Japan), 16 scans were taken at 4 cm^{-1} resolution. Polymer samples were prepared by dispersing in dry KBr pellets and recorded between 4600 and 400 cm^{-1} .

2.4. Adsorption studies

Chelation of heavy metal ions from aqueous solutions was investigated in batch experiments. Effects of the initial heavy metal ion concentration and pH of the medium on the chelation rate and capacity were studied. 100 ml aliquots of aqueous solutions containing different amounts of heavy metal ions (in the range of 5–80 mg/l) were treated with the chelating beads. Chelation flasks were stirred magnetically at 250 rpm. The suspensions were brought to the desired pH by adding sodium hydroxide (NaOH) and hydrochloric acid (HCl). The pH was maintained in a range of ± 0.1 units until equilibrium was attained. The concentration of the sample was analyzed by using a PerkinElmer Model 3110 Flame Atomic Absorption Spectrophotometer (USA). The instrument response was periodically checked with known heavy metal solution standards. The experiments were performed in replicates of three and the samples were analyzed in replicates of three as well. Chelation experiments were carried out at 25 °C. The amount metal ions adsorbed q (mg/g polymer) was obtained as follows:

$$q = [(C_0 - C) \times V]/m \quad (1)$$

where, C_0 and C are the initial and equilibrium concentrations (mg/l), respectively; V is the volume of the aqueous phase (l); and m is the mass of the beads used (mg).

2.5. Elution and reuse

Elution efficiency from the polymer beads was measured for all the metals. Elution of the metals from the polymer beads was carried out in 100 ml of 0.1 M HNO_3 solution for 60 min. The chelating beads adsorbed metal ions were placed in the elution medium and stirred with a magnetic stirrer at 250 rpm at room temperature. The final metal ion concentration in the aqueous phase was determined by using a flame atomic absorption spectrometer according to the guidelines of the manufacturers. The elution ratio was calculated from the amount of metal ions adsorbed on the beads and the final metal ions concentration in the desorption medium, by using the following expression:

$$\text{Desorption ratio (\%)} = (A/B) \times 100 \quad (2)$$

Here, A is the amount of metal ions desorbed to the elution medium (mg) and B is the amount of metal ions adsorbed on the microbeads (mg).

In order to determine the reusability of the chelating beads, consecutive chelation and elution cycles were repeated 10 times by using the same chelating beads.

3. Results and discussion

3.1. Properties of polymer beads

The suspension polymerization procedure provided cross-linked poly(VP-PEGMA-EGDMA) beads in the spherical form in the size range of 30–100 μm . The surface morphology of polymer beads is investigated by the scanning electron micrographs in Fig. 1. As clearly seen in SEM images, the beads have a spherical form and have very few small pores on the surface. The roughness of the surface should be considered as a factor providing an increase in the surface area. In addition, these pores reduce mass transfer resistance and facilitate that

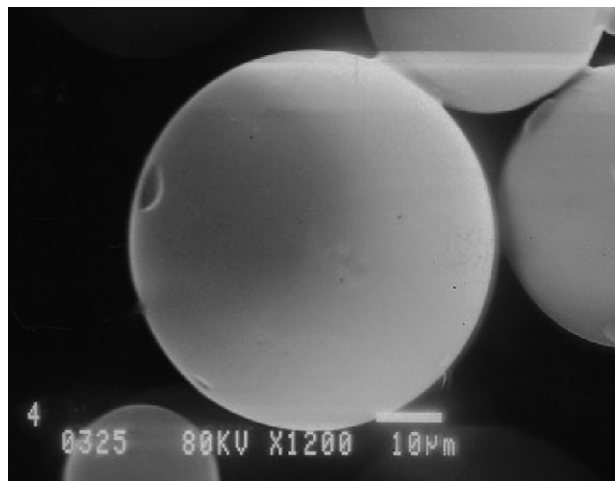


Fig. 1. SEM micrograph of poly(VP-PEGMA-EGDMA) beads.

the diffusion of metal ions because of high internal surface area. This also provides higher metal chelation capacity (Fig. 1). The poly(VP-PEGMA-EGDMA) beads are cross-linked hydrophilic matrices, i.e., hydrogels; therefore they do not dissolve in aqueous media, but do swell, depending on the degree of cross-linking and on the hydrophilicity of the matrix. The equilibrium swelling ratio of the beads used in this study, which are prepared with the recipe given in Table 1, is 65%. Compared with poly(PEGMA-EGDMA) (55%), the water uptake ratio of the poly(VP-PEGMA-EGDMA) beads increases (65%). Several possible factors may contribute to this result. First, incorporating vinyl pyridine actually introduces more hydrophilic functional groups into the polymer chain, which can attract more water molecules into the polymer matrices. Second, reacting vinyl pyridine with PEGMA and EGDMA could effectively decrease the molecular weight. Therefore, the water molecules penetrate into the polymer chains more easily, resulting in an improvement of polymer water uptake in aqueous solutions. It should be also noted that these beads are quite rigid and strong enough due to the highly cross-linked structure, so they are suitable for packed bed column applications.

Number-average diameter of poly(VP-PEGMA-EGDMA) and poly(PEGMA-EGDMA) were 57.66 and 54.55 μm , respectively. The coefficient of variation values of poly(VP-PEGMA-EGDMA) and poly(PEGMA-EGDMA) were 31.20% and 36.00%, respectively. Although, the suspension polymerizations were performed identical conditions, VP containing beads with slightly higher average size. This result probably originated from the higher viscosity of VP based beads with respect to the other. The determined coefficient of variation values indicated that poly(VP-PEGMA-EGDMA) beads had a narrower size distribution relative to the poly(PEGMA-EGDMA) beads. Note that the average size values and size distribution were determined in the aqueous medium since the swollen bead size was significant for the intended application.

In order to identify the polymeric structure, FTIR spectra of the poly(VP-PEGMA-EGDMA) and poly(PEGMA-EGDMA) were taken (Fig. 2). FTIR spectra of poly(VP-PEGMA-EGDMA) have the characteristic C=O stretching bands belongs to ester functional group in the structure of EGDMA, appear at 1745 cm^{-1} . The C–O stretching bands appear between 1290 and 1100 cm^{-1} with wide and medium effected peaks. Also, between 3525 and 3200 cm^{-1} O–H stretching bands and between 3000 and 2800 cm^{-1} aliphatic C–H stretching bands appear for all spectra. The most important point in these spectra is that it can be exactly seen the C–C and C–N bands in the structure of pyridine between 1600 and 1430 cm^{-1} . These peaks also can be seen in both surface and bulk structures. These data confirmed that the poly(VP-PEGMA-EGDMA) beads were formed with functional groups vinyl pyridine (Fig. 2).

To evaluate the amount of vinyl pyridine incorporation within the polymeric structure, elemental analysis of the synthesized poly(VP-PEGMA-EGDMA) beads was performed. C (%), H (%) and N (%) were found 59.92, 8.47 and 2.40, respectively. The incorporation percentage of vinyl pyridine was found to be 2.40%, from nitrogen stoichiometry. The nitrogen amount that was found in elemental analysis only comes from the incorpora-

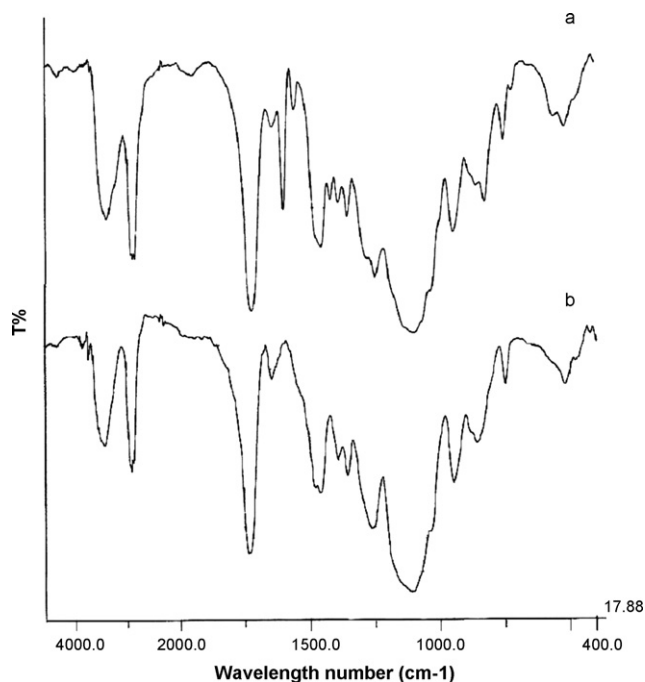


Fig. 2. (a) FTIR spectra of poly(VP-PEGMA-EGDMA) beads and (b) FTIR spectra of poly(PEGMA-EGDMA) beads.

tion of vinyl pyridine within the polymeric structure. Because, there is no nitrogen in the other monomers and chemicals used in the polymerization. This result also showed that the copolymerization reaction was exactly completed, as some vinyl pyridine monomers did not form part of the polymer and would have been removed during extensive washing.

3.2. Adsorption of heavy metal ions

Figs. 3–6 show the initial concentration of metal ions dependence of the adsorbed amount of the Pb(II), Cd(II), Cr(III) and Cu(II), relatively onto the both poly(VP-PEGMA-EGDMA) and poly(PEGMA-EGDMA) beads. Adsorption of metal ions onto the poly(PEGMA-EGDMA) beads was very low, around 0.7 mg/g. Because there is no any reactive functional groups in the poly(PEGMA-EGDMA) structure for complexation of metal

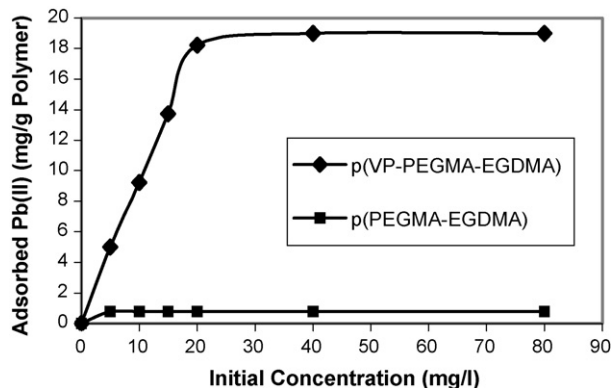


Fig. 3. Adsorption of Pb(II) ions on the poly(VP-PEGMA-EGDMA) and poly(PEGMA-EGDMA) beads; pH 6.0; temperature: 25 °C.

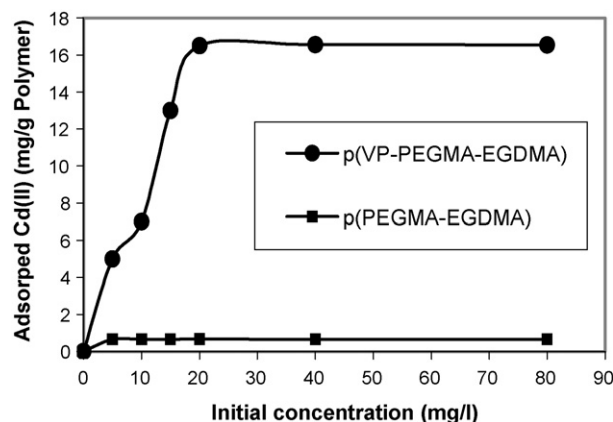


Fig. 4. Adsorption of Cd(II) ions on the poly(VP-PEGMA-EGDMA) and poly(PEGMA-EGDMA) beads; pH 6.0; temperature: 25 °C.

ions. But this low adsorption value of metal ions may be due to diffusion of metal ions into the pores of the swollen matrix of the beads and weak interactions between metal ions and hydroxyl groups on the surface of the poly(PEGMA-EGDMA) beads. However, VP incorporation into the polymeric structure significantly increased the adsorption capacity up to 18.23 mg/g for Pb(II), 16.50 mg/g for Cd(II), 15.81 mg/g for Cr(III) and 18.25 mg/g for Cu(II). The adsorption values increased with increasing initial concentration of metal ions, and a saturation value is achieved around ion concentration of 20 mg/l, which represents saturation of the active binding sites on the poly(VP-PEGMA-EGDMA) beads. The order of these four kinds of metal ion chelation on mass basis for the single component metals is Cu(II) > Pb(II) > Cd(II) > Cr(III). This affinity trend is presented on the mass basis (mg) metal chelation per gram beads and these units are important in quantifying respective metal capacities in real terms.

Adsorbents used in heavy metal removal are in particulate form in most of the cases. In the literature, different affinity sorbents with a wide range of adsorption capacities for heavy metal ions have been reported. Shreedhara-Murthy and Ryan found 5–27 mg/g Cu(II) removal by cellulose-dithiocarbamate resins [31]. Roozmond showed 32 mg/g Cu(II) with pyrazole-containing poly(styrene-divinyl-benzene) sorbents [32]. Say et al. achieved 714.1 mg/g Pb(II), 468.8 mg/g Cr(III) and 639.4 mg/g Cd(II) adsorption capacities with poly(HEMA-MAH) beads [28]. Kara et al. have prepared poly(EGDMA-VIM) beads and found the chelation capacities of these beads were 69.4 mg/g for Cd(II) and 114.8 mg/g for Pb(II) [33].

3.3. Effect of pH on metal binding

The metal ion complexation of polymeric ligands is highly dependent on the equilibrium pH of the medium. In the absence of metal chelating groups, the precipitation of the metal ions is affected by the concentration and form of soluble metal species. The solubility of metal ions is governed by hydroxide or carbonate concentration. Precipitation of metal ions becomes significant at high pHs for all metal ions. The theoretical and

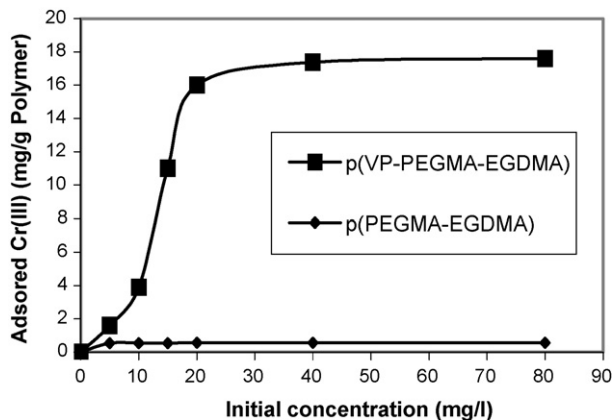


Fig. 5. Adsorption of Cr(III) ions on the poly(VP-PEGMA-EGDMA) and poly(PEGMA-EGDMA) beads; pH 6.0; temperature: 25 °C.

experimental precipitation curves indicate that precipitation begins above these pHs, which also depends on the concentration of metal ions in the medium. Therefore, in our study, in order to establish the effect of pH on the chelation of metal ions onto the chelating beads, we repeated the batch equilibrium studies at different pH in the range of 2.0–10.0. In this group of experiments, the initial concentration of metal ions was 20 mg/l for all metal ions at 100 ml volume. Fig. 7 shows the pH effect. The chelation capacities of the chelating beads are 18.23 mg/g for Pb(II), 16.50 mg/g for Cd(II), 17.38 mg/g for Cr(III) and 18.25 mg/g for Cu(II), respectively. It appears that the newly synthesized chelating beads had the strongest affinity for Cu(II). The affinity order of metal ions at initial concentration of 20 mg/l is Cu(II) > Pb(II) > Cr(III) > Cd(II).

Poly(VP-PEGMA-EGDMA) chelating beads exhibited a low affinity for heavy metal ions in acidic conditions (pH < 4.0), a somewhat higher affinity between pH 6.0 and 8.0. The difference in chelation behaviour of heavy metal ions can be explained by the different affinity of heavy metal ions for the donor atoms (i.e., nitrogen) in the VP. In the case of poly(PEGMA-EGDMA) beads, adsorption is pH independent. But it is indicated that the adsorption of metal ions onto the poly(VP-PEGMA-EGDMA) beads was pH dependent

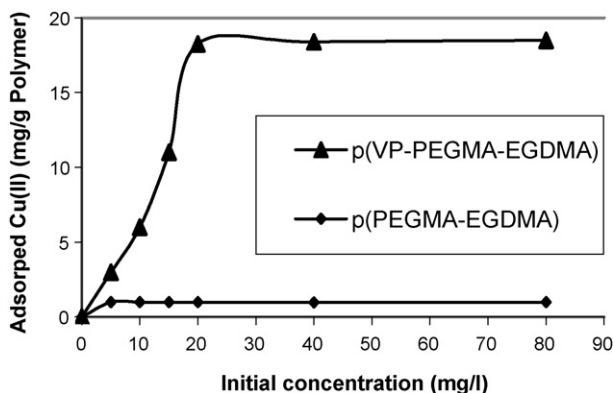


Fig. 6. Adsorption of Cu(II) ions on the poly(VP-PEGMA-EGDMA) and poly(PEGMA-EGDMA) beads; pH 6.0; temperature: 25 °C.

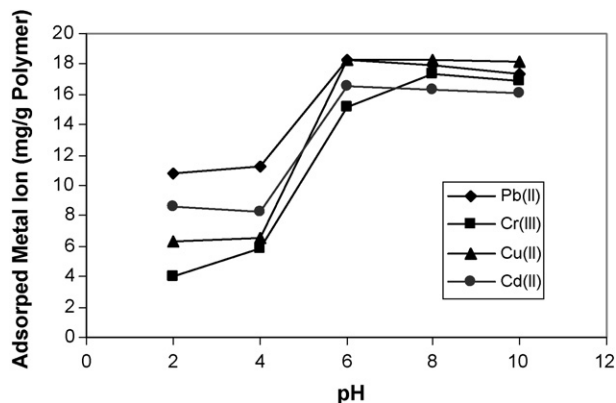


Fig. 7. Effect of pH on the adsorption of metal ions on poly(VP-PEGMA-EGDMA) beads; initial concentration of metal ions: 20 mg/l; temperature: 25 °C. Each data point is the average of three parallel studies.

3.4. Elution and repeated use

The repeated use of the polymer beads is a key factor in improving process economics. Elution of the adsorbed metal ions from the poly(VP-PEGMA-EGDMA) beads was also studied in batch experiments. The poly(VP-PEGMA-EGDMA) beads loading the maximum amounts of the respective metal ions were placed within the elution medium containing 0.1 M HNO₃ and the amount of metal ions desorbed in 1 h was measured. The elution efficiency was then calculated. Elution efficiencies were very high (up to 92%) with the elution agent and conditions used for all metal ions. At the other conditions such as 30 min and 50 ml, the recoveries are not quantitative.

It must be pointed out that in metal chelating systems; chelation (i.e., binding of heavy metal ions with vinyl pyridine) is completely reversible. In order to obtain the reusability of the poly(VP-PEGMA-EGDMA) beads, chelation–elution cycle was repeated 10 times by using the same adsorbent. As shown in Fig. 8, the adsorbents were reused for subsequent chelation–elution cycles with comparable chelation efficiencies over 10 cycles.

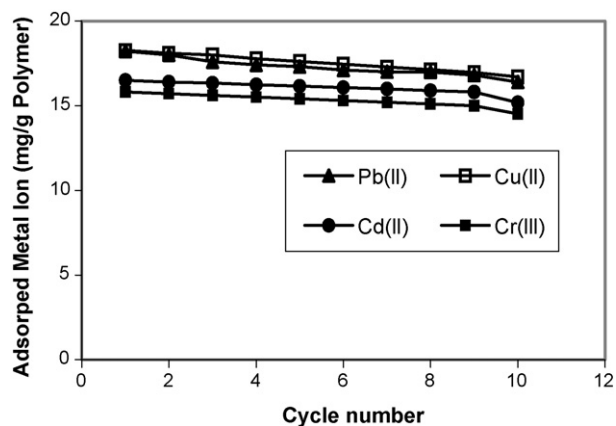


Fig. 8. Heavy metal ions adsorption capacity of poly(VP-PEGMA-EGDMA) beads after repeated adsorption–desorption cycle; initial concentration of metal ions: 20 mg/l; pH 6.0; temperature: 25 °C.

4. Conclusion

Adsorption technology enables the use of polymeric chelating beads for rapid, cost-effective and selective heavy metal removal. In this study, chelating beads were prepared and, was applied to the removal of lead, cadmium, chromium and copper ions from aqueous solutions. In this study, we focused our attention on the development of metal-chelating beads for the assembly of new adsorbents. This approach for the preparation of metal-chelating matrix has many advantages over conventional preparation techniques; those needed the activation of the matrix for metal-chelating ligand immobilization. In this procedure, comonomer VP acted as the metal-chelating ligand, and there is no need to activate the matrix for the chelating-ligand immobilization. Metal-chelating ligand immobilization step was also eliminated. VP was polymerized with EGDMA and PEGMA. There is no leakage of the ligand also. These results suggest that poly(VP-PEGMA-EGDMA) beads may be good heavy metal adsorbents and have great potential applications in environmental protection. The new adsorbent has higher adsorption properties than other adsorbents used in previous works in literature [34–38].

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