

This article was downloaded by:

On: 24 January 2011

Access details: *Access Details: Free Access*

Publisher *Taylor & Francis*

Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Journal of Macromolecular Science, Part A

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713597274>

Heavy Metal Removal from Synthetic Solutions with Magnetic Beads Under Magnetic Field

Serap Senel^a; Lokman Uzun^a; Ali Kara^b; Adil Denizli^a

^a Department of Chemistry, Hacettepe University, Beytepe, Ankara, Turkey ^b Department of Chemistry, Uludag University, Bursa, Turkey

To cite this Article Senel, Serap , Uzun, Lokman , Kara, Ali and Denizli, Adil(2008) 'Heavy Metal Removal from Synthetic Solutions with Magnetic Beads Under Magnetic Field', *Journal of Macromolecular Science, Part A*, 45: 8, 635 – 642

To link to this Article: DOI: 10.1080/10601320802168801

URL: <http://dx.doi.org/10.1080/10601320802168801>

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: <http://www.informaworld.com/terms-and-conditions-of-access.pdf>

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

Heavy Metal Removal from Synthetic Solutions with Magnetic Beads Under Magnetic Field

SERAP SENEL,¹ LOKMAN UZUN,¹ ALI KARA,² and ADIL DENIZLI¹

¹Department of Chemistry, Hacettepe University, Beytepe, Ankara, Turkey

²Department of Chemistry, Uludag University, Bursa, Turkey

Received January, 2008, Accepted February, 2008

The aim of this study is to prepare magnetic beads which can be used for the removal of heavy metal ions from synthetic solutions. Magnetic poly(ethylene glycol dimethacrylate-vinyl imidazole) [m-poly(EGDMA-VIM)] beads were produced by suspension polymerization in the presence of magnetite Fe₃O₄ nano-powder. The specific surface area of the m-poly(EGDMA-VIM) beads was found to be 63.1 m²/g with a size range of 150–200 μm in diameter and the swelling ratio was 85%. The average Fe₃O₄ content of the resulting m-poly(EGDMA-VIM) beads was 12.4%. The maximum binding capacities of the m-poly(EGDMA-VIM) beads were 32.4 mg/g for Cu²⁺, 45.8 mg/g for Zn²⁺, 84.2 mg/g for Cd²⁺ and 134.5 mg/g for Pb²⁺. The affinity order on mass basis is Pb²⁺ > Cd²⁺ > Zn²⁺ > Cu²⁺. Equilibrium data agreed well with the Langmuir model. pH significantly affected the binding capacity of the magnetic beads. Binding of heavy metal ions from synthetic wastewater was also studied. The binding capacities were 26.2 mg/g for Cu²⁺, 33.7 mg/g for Zn²⁺, 54.7 mg/g for Cd²⁺ and 108.4 mg/g for Pb²⁺. The magnetic beads could be regenerated up to about 97% by treating with 0.1 M HNO₃. These features make m-poly(EGDMA-VIM) beads a potential candidate for support of heavy metal removal under magnetic field.

Keywords: heavy metal removal; magnetic beads; affinity binding; n-vinyl imidazole

1 Introduction

Contamination of water by heavy metal ions is a serious hazard to ecology and health, due to the toxic effects of these ions at very low concentrations (1). Heavy metals are metabolic poisons and enzyme inhibitors (2). They can cause mental retardation and semi-permanent brain damage. Heavy metals are classified as persistent environmental toxic substances because they cannot be rendered harmless by chemical or biological remediation processes (3). Heavy metals are released into the environment in a number of different ways. Coal combustion, sewage wastewaters, automobile emissions, battery industry, mining activities, tanneries, alloy industries and the utilization of fossil fuels are just a few examples (4).

Numerous research efforts are being done to develop methods to remove heavy metal ions, particularly in waste streams of hydrometallurgy and related industries, and to subsequently reuse them. The conventional treatments used to remove heavy metals from wastewaters are precipitation, coagulation, solvent extraction, reduction, neutralization,

electrochemical separation through membranes, ion-exchange and adsorption (3–8).

Adsorption is considered to be an effective and economical method for the removal of heavy metal ions. Toxic metal ion removal by using polymers would be of great importance in environmental applications (9–16). Several criteria are important in the design of metal-chelating polymers with substantial stability for the selective removal of metal ions: specific and fast complexation of the metal ions, as well as the reusability of the metal-chelating polymer (17). A large number of polymers incorporating a variety of chelating ligands including polyethylene-imine, amidoxime, acrylamide, dithiocarbamate, triazole and amino acids have been prepared and their adsorption and analytical properties were investigated (18–24). An expensive and critical step in this preparation process is a coupling of a chelating ligand to the support. 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 binding technique which caused a decrease in binding capacity (15–20). The time consuming and high cost of chelating procedure has inspired a search for suitable low-cost supports.

Magnetic beads are currently enjoying a fairly ample range of applications in many fields including among others biotechnology, nanotechnology, biochemistry, colloid sciences

Address correspondence to: Adil Denizli, Department of Chemistry, Hacettepe University, Beytepe, Ankara, Turkey. E-mail: denizli@hacettepe.edu.tr

and medicine (21). The magnetic character implies that they respond to a magnet, making sampling and collection easier and faster, but their magnetization disappears once the magnetic field is removed. Magnetically stabilized fluidized bed promises to solve many of the problems associated with chromatographic separations in packed bed and in conventional fluidized bed systems (22). Magnetic carriers combine some of the best characteristics of fluidized beds (low pressure drop and high feed-stream solid tolerances) and of fixed beds (absence of particle mixing, high mass transfer rates, and good fluid-solid contact). Magnetic beads are more commonly manufactured from polymers since they have a variety of surface functional groups which can be tailored to use in specific applications. Different synthetic and natural polymeric magnetic beads in the size range of 50–300 μm in diameter are used in different applications (23, 24).

For these reasons, we focused our attention on the development of magnetic beads for the assembly of a new class of novel heavy metal support. In this work, we show that *m*-poly(EGDMA-VIM) beads can be used directly for heavy metal removal under magnetic field. This novel approach for the preparation of support has many advantages over conventional supports, those needed the activation of the matrix for metal-chelating ligand immobilization. In this procedure, comonomer VIM acted as the metal-chelating ligand, and there is no need to activate the matrix for the chelating ligand immobilization. Ligand immobilization step was also eliminated. VIM was polymerized with EGDMA and there is no leakage of the ligand also.

2 Experimental

2.1 Materials

Ethylene glycol dimethacrylate (EGDMA) was obtained from Merck (Darmstadt, Germany), purified by passing through active alumina and stored at 4°C until use. *N*-Vinyl imidazole (VIM, Aldrich, Steinheim, Germany) was distilled under vacuum (74–76°C, 10 mm Hg). 2,2'-Azobisisobutyronitrile (AIBN) was obtained from Fluka A.G. (Buchs, Switzerland). Poly(vinyl alcohol) (PVAL; Mw: 100.000, 98% hydrolyzed) was supplied from Aldrich Chem. Co. (USA). Magnetite nanopowder (Fe_3O_4 , diameter: 20–50 nm) was obtained from Sigma. All other chemicals were of reagent grade and were purchased from Merck AG (Darmstadt, Germany). All water used in the binding experiments was purified using a Barnstead (Dubuque, IA) ROpure LP[®] reverse osmosis unit with a high flow cellulose acetate membrane (Barnstead D2731) followed by a Barnstead D3804 NANOpure[®] organic/colloid removal and ion exchange packed-bed system. Buffer and sample solutions were prefiltered through a 0.2 μm membrane (Sartorius, Göttingen, Germany). All glassware was extensively washed with dilute nitric acid before use.

2.2 Preparation of *m*-poly(EGDMA-VIM) Beads

EGDMA and VIM were polymerized in suspension by using AIBN and poly(vinyl alcohol) as the initiator and the stabilizer, respectively. Toluene was included in the polymerization recipe as the diluent (as a pore former). A typical preparation procedure was exemplified below. Continuous medium was prepared by dissolving poly(vinyl alcohol) (200 mg) in the purified water (50 ml). For the preparation of dispersion phase, EGDMA (6 ml; 30 mmol), magnetite Fe_3O_4 nanopowder (1.0 g) and toluene (4 ml) were stirred for 15 min at room temperature. Then, VIM (3 ml; 30 mmol) and AIBN (100 mg) were dissolved in the homogeneous organic phase. The organic phase was dispersed in the aqueous medium by stirring the mixture magnetically (400 rpm), in a sealed-cylindrical pyrex polymerization reactor. The reactor content was heated to polymerization temperature (i.e., 70°C) within 4 h and the polymerization was conducted for 2 h with a 600 rpm stirring rate at 90°C. Final beads were extensively washed with ethanol and water to remove any unreacted monomer or diluent and then dried at 50°C in vacuum oven. The magnetic beads then were sieved to different sizes. Microscopic inspection shows that almost all the magnetic beads are perfectly spherical.

2.3 Characterization Experiments

The porosity of the beads was measured by a N_2 gas sorption technique, performed on Flowsorb II, (Micromeritics Instrument Corporation, Norcross, USA). The specific surface area of beads in a dry state was determined by a multipoint Brunauer-Emmett-Teller (BET) apparatus (Quantachrome, Nova 2200E, USA). 0.5 g of bead was placed in the sample holder of BET and degassed by passing through N_2 gas onto the beads at 150°C for 1 h. The adsorption of the N_2 gas onto the beads was performed at -210°C while its desorption was performed at room temperature. Experimental values obtained from the desorption step was used to calculate the specific surface area of the beads. Pore volumes and average pore diameter for the beads were determined by the BJH (Barrett, Joyner, Halenda) model. The average size and size distribution of the beads were determined by screen analysis performed using standard sieves (Model AS200, Retsch Gmb & Co., KG, Haan, Germany).

The water uptake ratios for the beads were determined using distilled water. The water uptake experiments were conducted as follows: dry beads were carefully weighed out (± 0.0001 g) before being soaked into 50 mL vials containing distilled water. The vials were then placed into an isothermal water bath at 25°C for 2 h after which the wet bead samples were taken out of the vials, wiped out with a filter paper, and weighed out. The water content of the beads was calculated by using the following expression:

$$\text{Water uptake ratio (\%)} = [(W_s - W_o)/W_o] \times 100 \quad (1)$$

where W_o and W_s are the weights of beads before and after water uptake, respectively.

The surface structures of the beads were visualized and examined by scanning electron microscopy (SEM). After the bead samples were dried at 25°C for seven days, tiny fragments of the bead samples were mounted on SEM sample holders on which they were sputter coated for 2 min. The samples were then consecutively mounted in a scanning electron microscope (JEOL, JEM 1200EX, Tokyo, Japan) to visualize the surface structures of each bead sample at desired magnification levels.

The magnetization curve of the bead sample was measured by a vibrating sample magnetometer (VSM, Princeton Applied Research, Model 150A, USA).

The presence of magnetite nano-powders in the bead samples was investigated with an electron spin resonance (ESR) spectrophotometer (EL 9, Varian, USA).

2.4 Removal of Heavy Metal Ions from Aqueous Solutions

The removal tests of heavy metal ions from aqueous solutions were studied for the m-poly(EGDMA-VIM) beads. The heavy metal solutions (Pb^{2+} , Cd^{2+} , Zn^{2+} , Cu^{2+}) were prepared in ultra-pure water by gradually diluting the stock solution (1000 ppm) to desired concentrations. Nitrate salt was used as the source of heavy metal ions. The beads suspended in pure water were degassed under reduced pressure (by using water suction pump) and magnetically stabilized into a column (10 cm × 0.9 cm inside diameter) equipped with a water jacket for temperature control. The magnetic field was generated by DC-powered two modified Helmholtz coils (1.5 cm diameter × 2.5 cm thick) spaced 4 cm apart. At a current of 1.6 A (50 W), each coil produced a magnetic field of 40 Gauss. The heavy metal solution was introduced into the column from underneath the grid using a peristaltic pump, and circulating in the system via the storage tank. The volumetric flow rate of the circulating heavy metal solution was measured by a flow meter incorporated in the flow circuit from which the superficial velocity was calculated. Dynamic binding capacity (DBC) was calculated from metal ions breakthrough curves. It has been noted that the pressure difference across the grid at all the flow conditions that were investigated are negligible (less than 5 Pa). The concentration of the heavy metal ions in the aqueous phase, after the desired treatment periods was measured using a graphite furnace atomic absorption spectrophotometer (GFAAS, Analyst 800/Perkin-Elmer, USA). The instrument response was periodically checked with known metal solution standards. The experiments were performed in replicates of three and the samples were analyzed in replicates of three as well. For each set of data present, standard statistical methods were used to determine the mean values and standard deviations. Confidence intervals of 95% were calculated for each set of samples in order to determine the margin of error. The amount of metal ions binding per unit mass of the beads was evaluated by using the mass balance.

2.5 Removal of Heavy Metal Ions from Synthetic Wastewater

Binding of heavy metal ions from synthetic wastewater was carried out in a continuous system described above. A solution (100 ml) containing 0.5 mmol/L from each metal ions [i.e., Cd^{2+} , Pb^{2+} , Zn^{2+} , Cu^{2+}] was pumped through the column at a pH of 7.0 at room temperature. Synthetic wastewater also contains Ni^{2+} , Fe^{2+} , Co^{2+} , Sn^{2+} and Ag^+ . Concentration of each metal ions in synthetic wastewater is 0.1 mmol/L. In order to adjust salinity, 700 ppm NaCl was added to the synthetic wastewater. After binding, the concentration of the metal ions in the remaining solution was determined by AAS as described above.

2.6 Regeneration and Repeated Use

Metal ions bound to m-poly(EGDMA-VIM) in a column was eluted by circulating a desorbing agent, a solution of 0.1 M HNO_3 , through the magnetically stabilized fluidized bed. 50 ml of the elution agent recirculated through the magnetically stabilized fluidized bed for 1 h at room temperature. The final metal ions concentration in the elution medium was determined by GFAA spectroscopy. The elution ratio was calculated from the amount of metal ions adsorbed on the m-poly(EGDMA-VIM) beads and the final metal ions concentration in the elution medium. In order to evaluate the reusability of the magnetically stabilized fluidized bed, the metal ion binding-elution cycle was repeated ten times for the same magnetically stabilized fluidized bed.

3 Results and Discussion

3.1 Characterization Studies

m-Poly(EGDMA-VIM) beads were prepared in the size range of 10–200 in diameter. Specific surface area, total pore volume and average pore diameter of m-poly(EGDMA-VIM) were found to be 63.1 m²/g, 0.144 ml/g, 40 Å, respectively. This indicated that the magnetic beads contained mainly mesopores. The equilibrium swelling ratio for m-poly(EGDMA-VIM) is 85%. This pore diameter is possibly in the range of diffusion of metal ions.

The surface morphology and bulk structures of the m-poly(EGDMA-VIM) beads were visualized by SEM which are presented in Figure 1. All the beads have a spherical form and rough surface. In the SEM photograph of the bulk structure, a large quantity of well-distributed pores could be observed and they have netlike structure. It is well known that, in order to facilitate diffusion of metal ions, the beads should have large pores. The m-poly(EGDMA-VIM) beads prepared in this study had this characteristics and these mesopores would increase the specific surface area, the binding capacity of beads, as well as the mass transfer rate of binding metal ions.

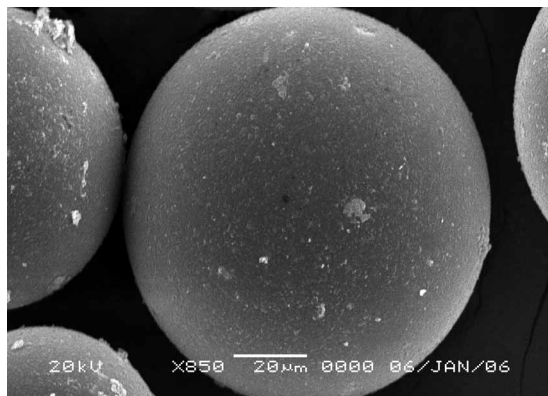


Fig. 1. SEM Photographs of m-poly(EGDMA-VIM) beads.

Magnetic characteristics of magnetic materials are related to their type generally, while those of magnetic materials are usually related to the content of magnetic component inside. So, Fe_3O_4 content is very important to the magnetic responsibility of magnetic materials. In general, the higher Fe_3O_4 content shows the stronger magnetic responsibility (25). For this reason, the average Fe_3O_4 content of the m-poly(EGDMA-VIM) beads was determined by density analysis. The hydrated density of the m-poly(EGDMA-VIM) beads measured at 25°C was 1.19 g/ml. By the same procedure, the density of Fe_3O_4 particles was found to be 1.97 g/ml at 25°C . The density of non-magnetic poly(EGDMA-VIM) beads measured at 25°C was 1.08 g/ml. The magnetic particles volume fraction in the m-poly(EGDMA-VIM) beads can be calculated from the following equation derived from the mass balance:

$$\phi = (\rho_C - \rho_M) / (\rho_C - \rho_A) \quad (2)$$

where, ρ_A , ρ_C and ρ_M are the densities of non-magnetic poly(EGDMA-VIM) beads, Fe_3O_4 nanopowder, and the m-poly(EGDMA-VIM) beads, respectively. Thus, with the density data mentioned above, the m-poly(EGDMA-VIM) beads gel volume fraction in the magnetic beads was estimated to be 87.6%. Therefore, the average Fe_3O_4 content of the resulting m-poly(EGDMA-VIM) beads was 12.4%.

The presence of magnetite nanopowder in the polymer structure was also confirmed by the ESR. The intensity of the magnetite peak against magnetic field (Gauss) is shown in Figure 2. A peak of magnetite was detected in the ESR spectrum. It should be noted that the non-magnetic beads cannot be magnetized under this condition. It reflects response ability of magnetic materials to the change of external magnetic field firstly and it characterizes the ability of magnetic materials to keep magnetic field strength when the external magnetic field is removed. In order to show the magnetic stability, the m-poly(EGDMA-VIM) beads were kept in distilled water and ambient air for 3 months, and the same ESR spectrum was obtained.

With the goal of testing the mechanical stability of the m-poly(EGDMA-VIM) beads, a bead sample was treated in

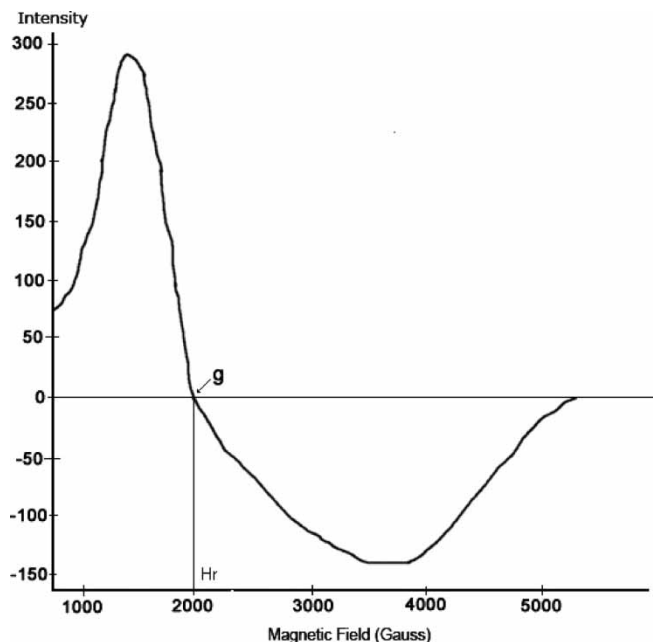


Fig. 2. ESR spectrum of m-poly(EGDMA-VIM) beads.

a ball mill for 12 h. SEM photographs show that a zero percentage of the sample was broken.

The g factor given in Figure 2 can be considered as quantity characteristic of the molecules in which the unpaired electrons are located, and it is calculated from Equation (3.) The measurement of the g factor for an unknown signal can be a valuable aid in the identification of a signal. In the literature, the g factor for Fe^{3+} is determined between 1.4–3.1 for low spin and 2.0–9.7 for high spin complexes (26). The g factor was found to be 3.22 for m-poly(EGDMA-VIM) structure.

$$g = h \cdot \nu / \beta \cdot H_r \quad (3)$$

Here, h is the Planck constant (6.626×10^{-27} erg/s); β is Universal constant (9.274×10^{-21} erg/G); ν is frequency (9.707×10^9 Hz) and H_r is resonance of magnetic field (G).

Magnetic properties of the polymeric structure was also shown using electron mass unit (EMU), showing the behavior of magnetic beads in a magnetic field using a vibrating magnetometer, in Figure 3, and H_r value, is defined as the external magnetic field at resonance. In EMU spectrum and from H_r value, 2250 Gauss magnetic field was found to be sufficient to excite all of the dipole moments present in 1.0 g of the sample. This value will be an important design parameter for a magnetically stabilized fluidized bed or magnetic filtration using the beads. The value of this magnetic field is a function of the flow velocity, bead size and magnetic susceptibility of solids to be removed. In the literature, this value was found to change from 8 kG to 20 kG for various applications, thus magnetic beads presented in this study will need less magnetic intensity in a magnetically stabilized fluidized bed or for a magnetic filter system (27).

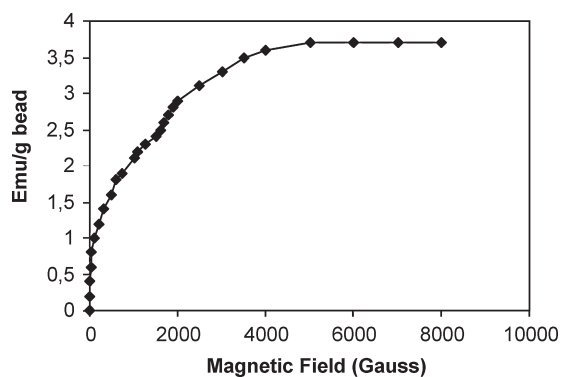


Fig. 3. The magnetic behavior of m-poly(EGDMA-VIM) beads.

3.2 Heavy Metal Removal from Aqueous Solutions

3.2.1 Effect of Flow-rate

Binding capacity of metal ions of the m-poly(EGDMA-VIM) beads at different flow rates is shown in Figure 4. It should be noted that the magnetic beads showed homogenous fluidization over the whole range of flow rates without any agglomeration. The metal ion binding capacity decreased drastically with the increase of the flow rate. When the flow rate decreases, the contact time in the column is longer. Thus, metal ions have more time to diffuse the pores of m-poly(EGDMA-VIM) beads and to bind to the imidazole binding sites, hence a better binding capacity is obtained.

3.2.2 Binding Isotherms

Figure 5 shows the dependence of the equilibrium concentration on the bound amount of the metal ions onto the m-poly(EGDMA-VIM) beads. The amount of metal ions bound per unit mass of the polymer increased first with the concentration of metal ions then reached a plateau value which represents saturation of the active binding sites on the magnetic beads. This is obvious because more efficient utilization of the binding capacities of the beads is expected

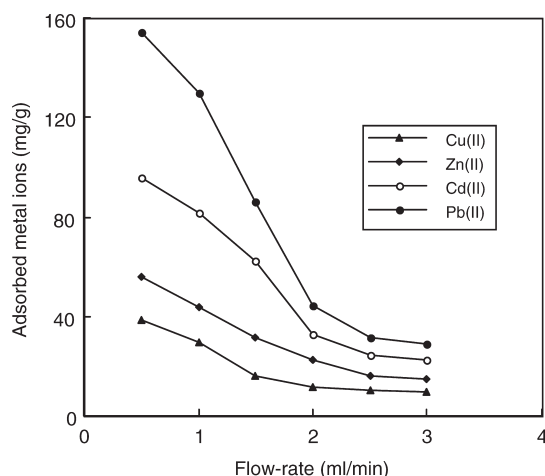


Fig. 4. Effect of flow rate on metal ion binding: Metal ion concentration: 200 mg/L; T: 25°C.

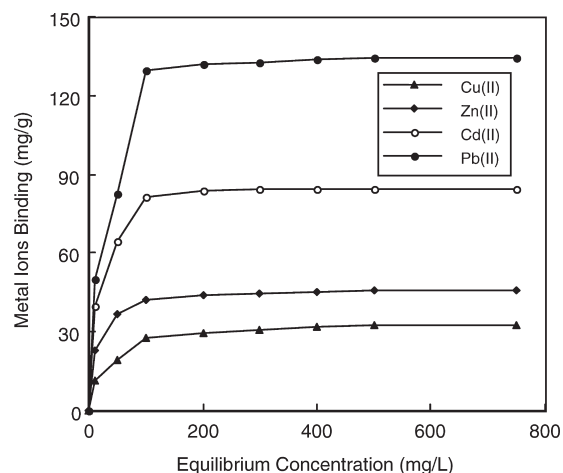


Fig. 5. Binding isotherms of m-poly(EGDMA-VIM) beads: Flow rate: 0.5 ml/min; pH: 5.0; T: 25°C.

due to a greater driving force by a higher concentration gradient. Binding of metal ions reached a saturation level at a bulk concentration, i.e., at about 100 mg/L. Due to the precipitation possibility of heavy metal ions, we did not increase the initial concentration over 750 mg/L. The binding capacities of the magnetic beads are 32.4 mg/g for Cu^{2+} , 45.8 mg/g for Zn^{2+} , 84.2 mg/g for Cd^{2+} and 134.5 mg/g for Pb^{2+} . It appears that the magnetic beads had the strongest affinity for Pb^{2+} ions. The order of these four kinds of metal ion binding on mass basis for the single component metals is $\text{Pb}^{2+} > \text{Cd}^{2+} > \text{Zn}^{2+} > \text{Cu}^{2+}$. The binding trend is presented on the mass basis (mg) metal binding per gram beads and these units are important in quantifying respective metal capacities in real terms. However, a more effective approach, for this work is to compare metal binding on a molar basis; this gives a measure of the total number of metal ions adsorbed, as opposed to total mass, and is an indication of the total number of binding sites available on the support to each metal. Additionally, the molar basis of calculation is the only accurate way of investigating competition in multi-component metal mixtures. Molar basis units are measured as mmol per gram of dry-support. The binding capacities of the magnetic beads on molar basis are 0.51 mmol/g for Cu^{2+} , 0.70 mmol/g for Zn^{2+} , 0.75 mmol/g for Cd^{2+} and 0.65 mmol/g for Pb^{2+} . The order of capacity of the magnetic beads on molar basis for the single component metals is $\text{Cd}^{2+} > \text{Zn}^{2+} > \text{Pb}^{2+} > \text{Cu}^{2+}$. The difference in the behavior of these metal ions may be related to the strength of their coordination complexes with imidazole.

The Langmuir and the Freundlich binding isotherms were constructed to evaluate the binding properties of m-poly(EGDMA-VIM). Equation (4) expresses the Langmuir binding equation used to construct our isotherms,

$$q = q_{\max} \cdot b \cdot C_{\text{eq}} / (1 + bC_{\text{eq}}) \quad (4)$$

where, q is the amount of bound metal ions (mg/g), C_{eq} is the equilibrium metal ion concentration (mg/mL), b is the

Langmuir constant (ml/mg) and q_{\max} is the maximal metal ions adsorption (mg/g).

Compared to the Langmuir isotherm technique, the Freundlich isotherm technique describes reversible binding and is not restricted to the formation of the monolayer. The empirical equation required to plot the Freundlich isotherm is given in Equation (5):

$$q = K_F \cdot C_e^{1/n} \quad (5)$$

where, K_F is the Freundlich constant, and n is the Freundlich exponent. $1/n$ is a measure of the surface heterogeneity ranging between 0 and 1, becoming more heterogeneous as its value gets closer to zero.

Table 1 shows the equilibrium constants of the Langmuir and the Freundlich isotherms. According to the correlation coefficients (R^2) of the isotherms, the Langmuir adsorption model was found to favor the monolayer binding.

3.2.3 Effect of pH on Heavy Metal Ions Binding

Metal ion binding on supports is pH dependent (28). 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 approximately pH 7.0 for all metal ions. The theoretical and 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 binding of metal ions onto the magnetic beads, we repeated the equilibrium studies at different pH in the range of 3.0–7.0. In this group of experiments, the initial concentration of metal ions was 200 mg/L for all metal ions. Figure 6 shows the pH effect. The binding capacities of the magnetic beads are 29.7 mg/g for Cu^{2+} , 43.5 mg/g for Zn^{2+} , 81.4 mg/g for Cd^{2+} and 126.7 mg/g for Pb^{2+} , respectively. It appears that the newly synthesized magnetic beads had the strongest affinity for Pb^{2+} . The affinity order is $\text{Pb}^{2+} > \text{Cd}^{2+} > \text{Zn}^{2+} > \text{Cu}^{2+}$.

m-Poly(EGDMA-VIM) chelating beads exhibited a low affinity for heavy metal ions in acidic conditions ($\text{pH} < 4.0$), a somewhat higher affinity between pH 5.0 and 7.0. The difference in binding behavior of heavy metal ions can be explained by the different affinity of heavy metal ions for the donor atoms

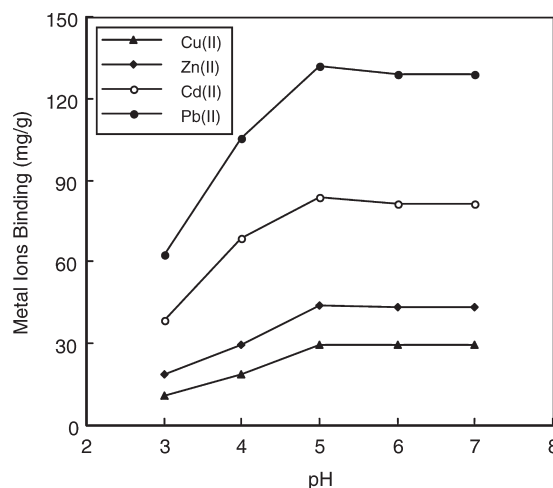


Fig. 6. Effect of pH on binding of metal ions: initial concentration of metal ions: 200 mg/L; Flow rate: 0.5 ml/min; T: 25°C.

(i.e., nitrogen) in the VIM. A difference in coordination behavior is most probably also case for the attached VIM resulting in a relatively high binding of metal ions at high pH under non-competitive binding conditions.

3.2.4 Removal of Heavy Metal Ions From Synthetic Wastewater

Binding capacities of the m-poly(EGDMA-VIM) beads from synthetic wastewater for Cu^{2+} , Zn^{2+} , Cd^{2+} , and Pb^{2+} were also studied. The interactive effects of a metal mixture on a polymer matrix are extremely complex and depend on polymer type, number of metals competing for binding sites, metal combination, levels of metal concentration, residence time and experimental conditions. Three types of responses may occur: (i) The effect of the mixture is greater than that of each of the individual effects of the constituents in the mixture (synergism); (ii) the effect of the mixture is less than that of each of the individual effects of the constituents in the mixture (antagonism); (iii) the effect of the mixture is no more or less than that of each of the individual effects of the constituents in the mixture (non-interaction) (29). It is worth noting that the binding capacities of the m-poly(EGDMA-VIM) beads from synthetic wastewater for all metal ions were much lower than the single solutions. The most logical reason for the antagonistic action is claimed to

Table 1. The Langmuir and the Freundlich binding constants for m-poly(EGDMA-VIM)

Metal ions	Langmuir				Freundlich		
	q_{exp}	q_e	b	R^2	K_F	n	R^2
Cu^{2+}	32.4	33.7	0.040	0.999	7.51	0.242	0.908
Zn^{2+}	45.8	46.5	0.084	1.000	18.01	0.157	0.857
Cd^{2+}	84.2	85.5	0.114	0.999	31.21	0.169	0.823
Pb^{2+}	134.5	138.9	0.061	0.999	33.92	0.233	0.843

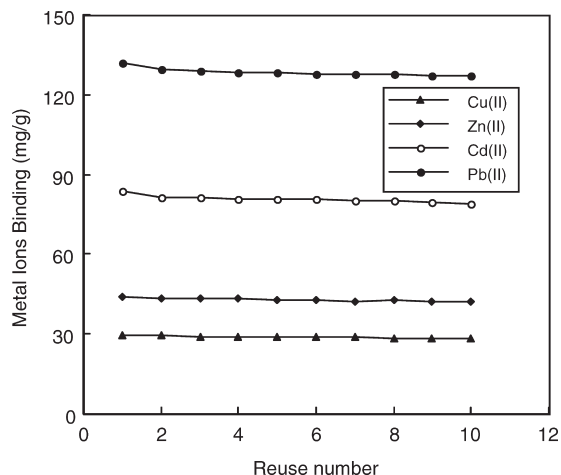


Fig. 7. Binding-elution cycle of m-poly(EGDMA-VIM) beads; Binding conditions: Metal ion concentration: 200 mg/L; Flow-rate: 0.5 ml/min; T: 25°C.

be the competition for the binding sites on the polymer beads and/or a screening effect by the other metal ions. The binding capacities were 26.2 mg/g for Cu^{2+} , 33.7 mg/g for Zn^{2+} , 54.7 mg/g for Cd^{2+} and 108.4 mg/g for Pb^{2+} . The magnetic beads exhibited the following metal ion affinity sequence on mass basis: $\text{Pb}^{2+} > \text{Cd}^{2+} > \text{Zn}^{2+} > \text{Cu}^{2+}$. In this case, magnetic beads adsorbed other metal ions also [i.e., Ni(II), Fe(II), Co(II), Sn(II), and Ag(I)]. The presence of other metal ions in the synthetic wastewater decreased the binding capacities of magnetic beads for Pb^{2+} , Cd^{2+} , Zn^{2+} , and Cu^{2+} ions.

3.2.5 Elution and Repeated Use

The regeneration is one of the most important strongpoint of supports with this capability of supports being considered as having a great influence on their extended application in improving process economics (30). For this reason, the regeneration property of m-poly(EGMDA-VIM) beads is worthy of study. Elution of the metal ions from the magnetic beads was performed in a magnetic column. Various factors are probably involved in determining rates of metal ions elution, such as the extent of hydration of the metal ions and polymer microstructure. However, an important factor appears to be binding strength. In this study, elution ratios are high (up to 95%). In order to obtain the reusability of the magnetic beads, binding-elution cycles were repeated 10 times using the same group of magnetic beads. The binding capacity of the recycled magnetic beads can still be maintained at 97% level at the 10th cycle (Figure 7). These beads can be regenerated and reused, so it provides a potential application.

4 Conclusions

Adsorption chromatography with a packed column of beads as a support material is not easy to scale up because the pressure

drop in packed columns is high, leading to compaction of the bed under pressure and low flow rates (31). Rigid porous beads overcome the compressibility problem, but the bead size employed to prevent high operating pressures may lead to diffusional limitations which degrade performance. Packed-bed columns usually require long elution times. The development of alternative methods is therefore of considerable interest. Magnetically stabilized fluidized beds exhibit a unique combination of packed-bed and fluidized-bed properties (32). Magnetically stabilized fluidized bed enables the use of magnetic processing for rapid and selective removal (33). Magnetically stabilized bed has many advantages such as the low pressure drop and the high mass transfer efficiency. When dealing with highly viscous mediums the magnetically stabilized fluidized bed is desirable because of high convective transport rates (34). This results in a rapid processing, which greatly improves the binding properties. In a previous study, we prepared non-magnetic poly(EGDMA-VIM) beads by suspension polymerization (35). In light of the above information, here we studied and assessed the m-poly(EGDMA-VIM) for its capability to remove metal ions under magnetic field.

5 Acknowledgments

The authors wish to thank Scientific and Technological Research Council of Turkey (Project number: 105T157) for the financial sponsorship of the research work.

6 References

- Vieira, R.S. and Beppu, M.M. (2006) *Water Research*, **40**, 1726.
- Friberg, L., Nordberg, G.F. and Vouk, B. (eds.) *Handbook on the Toxicology of Metals*; Elsevier: North-Holland, Biomedical Press: Amsterdam, 1979.
- Devi, M. and Fingermann, M. (1995) *Bull. Environ. Contam. Toxicol.*, **55**, 746.
- Zhang, F.S., Nriagu, J.O. and Itoh, H. (2005) *Water Research*, **39**, 389.
- Uzun, L., Kara, A., Tuzmen, N., Karabakan, A., Besirli, N. and Denizli, A. (2006) *J. Appl. Polym. Sci.*, **102**, 4276.
- Beuvais, R.A. and Alexandratos, S.D. (1998) *React. Funct. Polym.*, **36**, 113.
- Rivas, B.L., Pooley, S.A., Maturana, H.A. and Villegas, S. (2001) *Macromol. Chem. Phys.*, **202**, 443.
- Zhou, D., Zhang, L., Zhou, J. and Guo, S. (2004) *Water Research*, **38**, 2643.
- Birlik, E., Buyuktiryaki, S., Ersoz, A., Denizli, A. and Say, R. (2006) *Sep. Sci. Technol.*, **41**, 3109.
- George, B., Rajasekharan Pillai, V.N. and Mathew, B. (1999) *J. Appl. Polym. Sci.*, **74**, 3432.
- Beatty, S.T., Fischer, R.J., Hagers, D.L. and Rosenberg, E. (1999) *Ind. Eng. Chem. Res.*, **38**, 4402.
- Chanda, M. and Rempel, G.L. (1997) *React. Funct. Polym.*, **35**, 197.
- Manohar, D.M., Krishnan, K.A. and Anirudhan, T.S. (2002) *Water Research*, **36**, 1609.

14. Li, W., Zhao, H., Teasdale, P.R., John, R. and Zhang, S. (2002) *React. Funct. Polym.*, **52**, 31.
15. Say, R., Birlik, E., Ersöz, A., Yilmaz, F., Gedikbey, T. and Denizli, A. (2003) *Anal. Chim. Acta*, **480**, 251.
16. Wang, C.C., Chang, C.V. and Chen, C.Y. (2001) *Macromol. Chem. Phys.*, **202**, 882.
17. Denizli, A., Say, R., Garipcan, B., Emir, S., Karabakan, A. and Patir, S. (2003) *Sep. Purif. Technol.*, **30**, 3.
18. Gupta, M.N., Jain, S. and Roy, I. (2002) *Biotechnol. Prog.*, **18**, 78.
19. Li, W., Zhao, H., Teasdale, P.R. and John, R. (2002) *Polymer*, **43**, 4803.
20. Kesenci, K., Say, R. and Denizli, A. (2002) *European Polym. J.*, **38**, 1443.
21. Safarik, I. and Safarikova, M. (1999) *J. Chromatogr. B.*, **722**, 33.
22. Ma, Z.Y., Guan, Y.P., Liu, X.Q. and Liu, H.Z. (2005) *Langmuir*, **21**, 6987.
23. Odabasi, M. and Denizli, A. (2001) *J. Chromatogr. B.*, **760**, 137.
24. Akgöl, S. and Denizli, A. (2004) *J. Mol. Catalys. B*, **28**, 7.
25. Lu, S., Cheng, G. and Pang, X. (2006) *J. Appl. Polym. Sci.*, **99**, 2401.
26. Swartz, H.M., Bolton, J.R. and Borg, D.C. *Biological Applications of Electron Spin Resonance*; Wiley: New York, 1972.
27. Özkara, S., Akgöl, S., Çanak, Y. and Denizli, A. (2004) *Biotechnol. Prog.*, **20**, 1169.
28. Denizli, A., Say, R., Garipcan, B. and Patir, S. (2004) *React. Funct. Polym.*, **58**, 123.
29. Sag, Y. (2001) *Sep. Purif. Methods*, **30**, 1.
30. Denizli, A. and Piskin, E. (2001) *J. Biochem. Biophys. Methods*, **49**, 391.
31. Benes, M.J., Horak, D. and Svec, F. (2005) *J. Sep. Sci.*, **28**, 1855.
32. Hausmann, R., Hoffmann, C., Franzreb, M. and Höll, W.H. (2000) *Chem. Eng. Sci.*, **55**, 1477.
33. Odabasi, M., Ozkayar, N., Ozkara, S., Unal, S. and Denizli, A. (2005) *J. Chromatogr. B.*, **826**, 50.
34. Uzun, L. and Denizli, A. (2006) *J. Biomater. Sci. Polym. Ed.*, **17**, 791.
35. Kara, A., Uzun, L., Besirli, N. and Denizli, A. (2004) *J. Hazardous Materials B*, **106B**, 93.