

Reactive Green HE-4BD Functionalized Supramacroporous Poly(hydroxyethyl methacrylate) Cryogel for Heavy Metal Removal

Çiğdem Arpa, Nilay Bereli, Elif Özdil, Sema Bektaş, Adil Denizli

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

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ABSTRACT: The aim of this study was to investigate the heavy metal adsorption performance of supramacroporous poly(hydroxyethyl methacrylate) [PHEMA] cryogel. The PHEMA cryogel was produced by cryo-polymerization. The PHEMA cryogel was characterized by scanning electron microscopy (SEM). The PHEMA cryogel containing 385 μmol Reactive Green HE-4BD/g were used in the adsorption studies. Adsorption capacity of the PHEMA cryogel for the metal ions, i.e., Cu^{2+} , Cd^{2+} , and Pb^{2+} were investigated in aqueous media containing different amounts of the ions (5–600 mg/L) and at different pH values (3.2–6.9). The maximum adsorption capacities of the PHEMA cryogel were 11.6 mg/g (56 μmol /g) for Pb^{2+} , 24.5 mg/g (385 μmol /g) for Cu^{2+} and 29.1 mg/g (256 μmol /g)

for Cd^{2+} . The competitive adsorption capacities were 10.9 mg/g (52 μmol /g) for Pb^{2+} , 22.1 mg/g for Cd^{2+} (196 μmol /g) and 23.2 mg/g (365 μmol /g) for Cu^{2+} . The PHEMA/Reactive Green HE-4BD cryogel exhibited the following metal ion affinity sequence on molar basis: $\text{Cu}^{2+} > \text{Cd}^{2+} > \text{Pb}^{2+}$. The PHEMA/Reactive Green HE-4BD cryogel can be easily regenerated by 50 mM EDTA with higher effectiveness. These features make the PHEMA/Reactive Green HE-4BD cryogel a potential adsorbent for heavy metal removal. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 118: 2208–2215, 2010

Key words: heavy metal removal; dye-affinity adsorbents cryogels; PHEMA

INTRODUCTION

Industrial wastewater is one of the major sources of aquatic pollution. Among the aquatic pollutants, heavy metals have gained relatively more significance in view of their persistence and toxicity.¹ These metal ions are metabolic poisons and enzyme inhibitors.² They can cause mental retardation and semipermanent brain damage. Metals are classified as persistent environmental toxins because they can not be rendered harmless by chemical or biological remediation processes.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 methods of treatment for industrial wastewaters have been reported in the literature, amongst these methods are precipitation, membrane filtration, neutralization, ion-exchange, coprecipitation/adsorption.⁵ Adsorption is generally preferred for the removal of heavy metal ions due to its high efficiency, easy handling,

availability of different adsorbents, and cost effectiveness.⁶ The necessity to reduce the amount of heavy metal ions to acceptable levels in wastewater streams and subsequent possible re-use of these metal ions, has led to an increasing interest in selective polymer adsorbents.^{7–15} Several criteria are important in the design of chelating polymers with substantial stability for the selective removal of heavy metal ions: specific and fast complexation of the metal ions as well as the reusability of the chelating polymeric ligands.¹⁶ A large number of polymers incorporating a variety of chelating-ligands have been prepared and their adsorption and analytical properties investigated.^{17–20} Recently, reactive dyes bearing polymers and their different applications have been reported in a series of recent publications.^{21–26} The idea of using dyes by the scientists stems from the fact that dyes are very reactive with metal ions.^{19–23} The higher structural flexibility and durability of the dyes as well as significantly lower material and manufacturing costs are also very important.²⁷

Monoliths are a new class of chromatographic materials as alternative to traditional packed-bed columns. Supramacroporous monolithic structures have recently been used as efficient adsorbents for diverse applications. The macroporous structure of monoliths allows the overcoming of some of the

Correspondence to: A. Denizli (denizli@hacettepe.edu.tr).

disadvantages of bead-based columns.²⁸ Monoliths have lower mass transfer resistance and pressure drop than conventional packed-bed columns.²⁹ In this case, all liquid phase flows through the pores and mass exchange occurs significantly faster compared conventional packings.³⁰ Because of easy and cheaper preparation, high capacity and performance, and high porosity, the monolithic stationary phases have been applied in diverse applications.^{5,31–34}

According to the above discussion, there is an emerging need for the development of novel solid supports. Therefore, we have focused our attention for the preparation of poly(hydroxy-ethyl methacrylate) based cryogel containing Reactive Green HE-4BD. The results of adsorption/desorption studies with Cu^{2+} , Cd^{2+} , and Pb^{2+} ions were reported here.

EXPERIMENTAL

Materials

Reactive Green HE-4BD (Color index number: Green 19A) was obtained from Polyscience (Warrington) and used without further purification. Hydroxyethyl methacrylate, *N,N'*-methylene-bis(acrylamide) (MBAAm) and ammonium persulfate (APS) were supplied by Sigma (St Louis, MO). *N,N,N',N'*-Tetramethylene diamine (TEMED) was obtained from Fluka A.G. (Buchs, Switzerland). All other chemicals were of reagent grade and were purchased from Merck AG (Darmstadt, Germany). All water used in the adsorption 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. Laboratory glassware was kept overnight in a 5% nitric acid solution. Before use, all the glassware was rinsed with deionised water and dried in a dust-free environment.

Preparation of PHEMA cryogel

Preparation of the poly(hydroxyethyl methacrylate) [PHEMA] cryogel is described below. Briefly, monomers (1.6 mL HEMA and 0.3 g *N,N'*-methylene-bis(acrylamide) (MBAAm) were dissolved in deionized water (5 mL), and the mixture was degassed under vacuum for 5 min to eliminate soluble oxygen. Total concentration of monomers was 12% (w/v). The cryogel was produced by free radical polymerization initiated by TEMED and APS. After adding APS (25 μL , 1% (w/v) of the total monomers), the solution was cooled in an ice bath for 2–3 min. TEMED (20 mg, 1% (w/v) of the total monomers) was added, and the reaction mixture was stirred for 1 min. Then, the reaction mixture was poured

between two glass sheets. The polymerization solution between two glass sheets was frozen at -16°C for 24 h and then thawed at room temperature. After washing with 200 mL of water, the cryogel was cut into disks (1.0 cm in diameter) with a perforator. The cryogel disks were stored in buffer containing 0.02% sodium azide (NaN_3) at 4°C until use.

Characterization of PHEMA cryogel

The swelling degree of the cryogel (S) was determined as follows: cryogel was washed with water until washing water was clear. Then it was sucked dry and then transferred to previously weighed vial and weighed ($m_{\text{wet gel}}$). After drying to constant mass in the oven at 60°C , the mass of dried sample was determined ($m_{\text{dry gel}}$). The swelling degree was calculated as:

$$S = (m_{\text{wet gel}} - m_{\text{dry gel}}) / m_{\text{dry gel}} \quad (1)$$

The morphology of a cross section of the cryogel was investigated by scanning electron microscopy (SEM). The sample was fixed in 2.5% glutaraldehyde in 0.15 M sodium cacodylate buffer overnight, post-fixed in 1% osmium tetroxide for 1 h. Then the sample was dehydrated stepwise in ethanol and transferred to a critical point drier tempered to 10°C , where the ethanol was changed for liquid carbon dioxide as transitional fluid. The temperature was then raised to 40°C and the pressure to ca. 100 bar. Liquid CO_2 was transformed directly to gas uniformly throughout the whole sample without heat of vaporization or surface tension forces causing damage. Release of the pressure at a constant temperature of 40°C resulted in dried cryogel. Finally, it was coated with gold-palladium (40 : 60) and examined using a JEOL JSM 5600 scanning electron microscope.

Fourier transform infrared (FTIR) spectrums of the PHEMA and the PHEMA/ Reactive Green HE-4BD cryogels were obtained by using a FTIR spectrometer (FTIR 8000 Series, Shimadzu, Japan). The dry cryogel (about 0.1 g) was thoroughly mixed with KBr (0.1 g, IR Grade, Merck, Germany), and pressed into a pellet form, and the spectrum was recorded.

Reactive Green HE-4BD attachment

Reactive Green HE-4BD attachment was carried out in a batch system equipped with a water jacket glass column for temperature control. The PHEMA cryogel was washed with 100 mL of water. After washing procedure, the PHEMA cryogel was treated with 50 mL of sodium carbonate (Na_2CO_3 , 50 mM) at 1.0 mL/min for 1 h. Then, the PHEMA cryogel was incubated with 50 mL of Reactive Green HE-4BD

solution (3.0 mg/mL) at 60°C for 2 h. To stimulate the deposition of the Reactive Green HE-4BD on the surface of the cryogel, NaCl (7.0 g) was added into the dye solution. 1.0 g of sodium carbonate (Na_2CO_3) was added to accelerate the reaction between Reactive Green HE-4BD molecules and cryogel. A nucleophilic substitution reaction takes place between the chloride of Reactive Green HE-4BD's triazine ring and the hydroxyl group of the HEMA, with the elimination of NaCl, resulting in the coupling of Reactive Green HE-4BD to the PHEMA cryogel under alkaline conditions.³⁵ Any remaining chlorine atoms in the PHEMA/Reactive Green HE-4BD cryogel due to the dichloro triazinyl dye structure after covalent immobilization were converted to amino groups by treating with 2 M NH_4Cl at pH 8.5 for 24 h at room temperature.

Reactive Green HE-4BD loading was determined by an elemental analysis instrument (Leco, CHNS-932). The amount of Reactive Green HE-4BD loading on the PHEMA cryogel was calculated from these data by considering the sulfur stoichiometry.

Removal of heavy metal ions from aqueous solutions

The removal tests of heavy metal ions from aqueous solutions were studied for the PHEMA/Reactive Green HE-4BD cryogel. In a typical adsorption system, 20 mL of the aqueous solution (in the range of 5–600 mg/L) was incubated with the cryogel (cryogel weight: 25.5 mg). Equilibrium adsorption time was 120 min. Stirring rate was 400 rpm. Nitrate salts were used for the preparation of metal ion solutions. pH was adjusted with HNO_3 or NaOH at the beginning of the experiment and not controlled afterwards. Investigations were made for pH values in the range of 3.2–6.9. The concentration of the heavy metal ions in the aqueous phase, after the desired treatment periods was measured using a flame atomic absorption spectrophotometer (AAS, Analyst 800/Perkin Elmer). The instrument response was periodically checked with known standard solutions. 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 to determine the margin of error. The amount of heavy metal adsorption per unit mass of the PHEMA cryogel was evaluated by using the mass balance.

To determine the reusability of the PHEMA cryogel, consecutive adsorption-desorption cycles were repeated five times by using the same cryogel. Desorption of metal ions was performed using 50 mM

EDTA solution. In a typical desorption system, 25 mL of the EDTA solution was incubated with the PHEMA cryogel for 2 h. The desorption ratio was calculated from the amount of metal ions adsorbed on the PHEMA cryogel and the final metal ions concentration in the desorption medium.

RESULTS AND DISCUSSION

PHEMA cryogel was produced by copolymerization in the frozen state of HEMA with MBAAm in the presence of APS/TEMED. The hydroxyl groups on the PHEMA cryogel allowed modification with Reactive Green HE-4BD. The SEM images of the pore structure of the cryogel is shown in Figure 1. The PHEMA cryogel have non-porous and thin polymer walls, large continuous interconnected pores that provide channels for the mobile phase to flow through. The pore sizes are in the range of about 10–200 μm in diameter. Pore size of the matrix is much larger than the size of the heavy metal ions, allowing them to pass easily. As a result of the convective flow of the mobile phase through the pores, the mass transfer resistance is practically negligible.

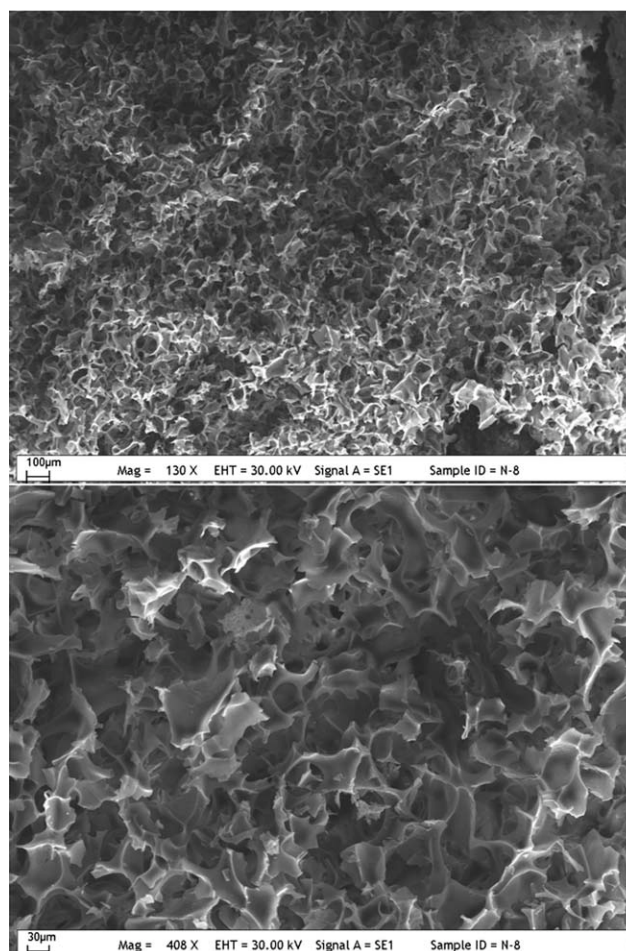


Figure 1 SEM images of the PHEMA cryogel.

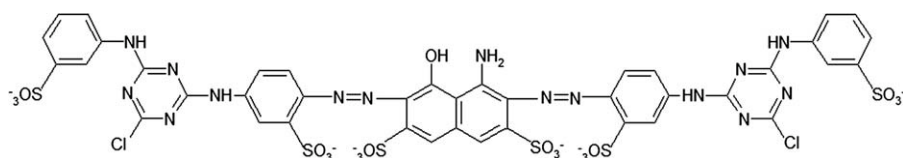


Figure 2 Chemical structure of reactive green HE-4BD.

The equilibrium swelling degree of the PHEMA cryogel was 8.56 g H₂O/g cryogel. PHEMA cryogel is opaque, sponge like, and elastic. This cryogel can be easily compressed by hand to remove water accumulated inside the pores. When the compressed piece of cryogel was submerged in water, it soaked in water and within 1–2 s restored its original size and shape.

Reactive Green HE-4BD is a dichlorotriazine dye (Fig. 2), and it contains six sulfonic acid groups, five basic primary and secondary amino groups. Reactive Green HE-4BD is covalently attached on PHEMA cryogel, via the reaction between the chloride groups of the dye molecules and the hydroxyl groups of the PHEMA. The highest dye loading obtained was 385 μmol Reactive Green HE-4BD/g polymer. The visual

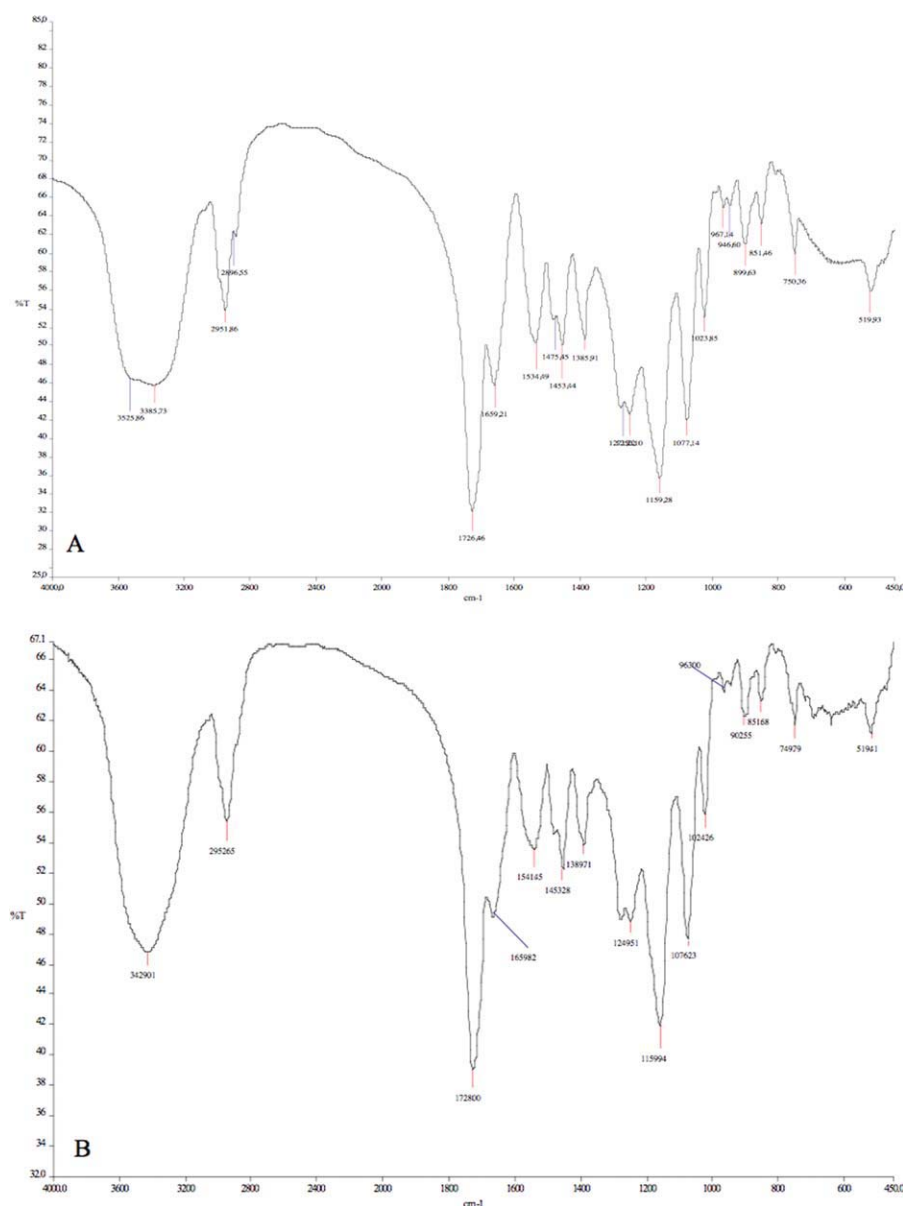


Figure 3 FTIR spectra of (A) PHEMA; (B) PHEMA/reactive green HE-4BD cryogel. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

observations (the color of the cryogel) ensured attachment of dye molecules. The PHEMA/Reactive Green HE-4BD cryogel was extensively washed with methanol until to ensure that there is no dye leakage from any of the cryogel and in any media used at adsorption-desorption steps.

FTIR spectra of the PHEMA and the PHEMA/Reactive Green HE-4BD cryogels are given in Figure 3. FTIR spectra of both PHEMA and PHEMA/Reactive Green HE-4BD have the characteristic stretching vibration band of hydrogen bonded alcohol, O—H, around 3500 cm^{-1} . The FTIR spectrum of PHEMA/Reactive Green HE-4BD has some absorption bands different than those of PHEMA. These are at 3385 cm^{-1} , 1534 cm^{-1} , and 1249 cm^{-1} characteristic N—H stretching, conjugated C=N, and aromatic C—N vibration, respectively, observed also in Reactive Green HE-4BD. PHEMA/Reactive Green HE-4BD has a sharp shoulder absorption band at about 3500 cm^{-1} and interpreted as the N—H absorption. The bands at 1077 cm^{-1} and 1159 cm^{-1} represent symmetric stretching of S=O and asymmetric stretching of S=O, respectively, are due to Reactive Green HE-4BD attached to PHEMA. These bands, however, do not appear, because plain PHEMA also has some absorption bands in the same region. Thus, absorption bands of plain PHEMA overlap with those of the Reactive Green HE-4BD at around these wavenumbers.

Adsorption isotherms

Figure 4 shows the Cu^{2+} , Cd^{2+} , and Pb^{2+} adsorption curves of the PHEMA/Reactive Green HE-4BD cryogel. The amount of metal ions adsorbed per unit

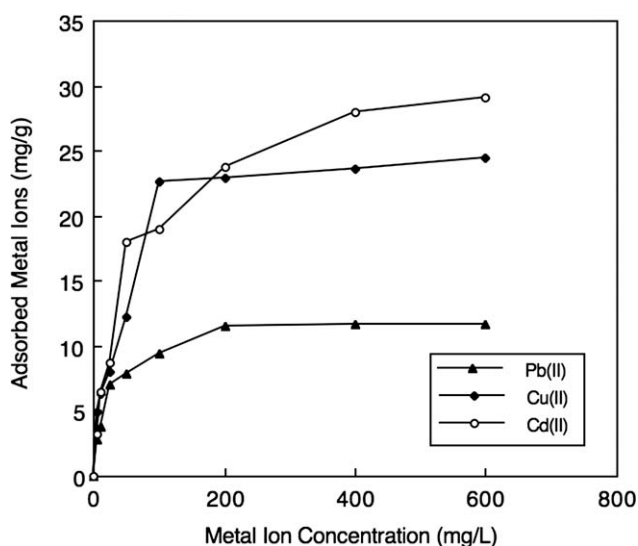


Figure 4 Adsorption capacity of the PHEMA cryogel: Reactive green HE-4BD content: $385\text{ }\mu\text{mol/g}$; pH: 6.0; T : 20°C .

mass of the polymer (i.e., adsorption capacity) increased first with the concentration of metal ions then reached a plateau value, which represents saturation of the active adsorption sites (which are available for metal ions) on the cryogel. Adsorption of heavy metal ions reached a saturation level at a lower bulk concentrations, i.e., at about 200 mg/L . Due to precipitation possibility we did not increase the initial concentration over 600 mg/L . The adsorption capacities of the PHEMA/Reactive Green HE-4BD cryogel are 11.6 mg/g for Pb^{2+} , 24.5 mg/g for Cu^{2+} , and 29.1 mg/g for Cd^{2+} . It appears that the PHEMA/Reactive Green HE-4BD cryogel had the more affinity for Cd^{2+} ions. The observed adsorption order for the single component metals on mass basis is as follows:



This adsorption sequence is given on the basis of mass (mg) metal adsorption per gram cryogel 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 adsorption on a molar basis; this gives a measure of the total number of metal ions adsorbed, as opposed to total weight, and is an indication of the total number of binding sites available on the adsorbent matrix, to each metal. Additionally the molar basis of measurement is the only accurate way of investigating competition in multi-component metal mixtures. Molar basis units are measured as μmol per gram of dry-adsorbent. The adsorption capacities of the PHEMA/Reactive Green HE-4BD cryogel are $56\text{ }\mu\text{mol/g}$ for Pb^{2+} , $256\text{ }\mu\text{mol/g}$ for Cd^{2+} , and $385\text{ }\mu\text{mol/g}$ for Cu^{2+} . It is evident from the results that the adsorption sequence of the PHEMA/Reactive Green HE-4BD cryogel for the single component metals is as follows:



It should be also noted that non-specific adsorption of heavy metal ions onto the PHEMA cryogel without including Reactive Green HE-4BD was also performed under the same experimental conditions. The heavy metal ions adsorption capacities on the PHEMA cryogel are relatively low, about 0.22 mg/g for Cu^{2+} , 0.35 mg/g for Pb^{2+} , and 0.28 mg/g for Cd^{2+} . Note that the PHEMA cryogel is highly porous, which therefore may absorb heavy metal ions within the pores of the cryogel. In addition, the hydroxyl and carbonyl groups of HEMA may interact with heavy metal ions (similar to solvation with water), which may also cause this non-specific-adsorption.

TABLE I
Langmuir and Freundlich Adsorption Isotherm Constants

Metal ions	Langmuir				Freundlich		
	q_{exp}	q_e	b	R^2	K_F	n	R^2
Pb ²⁺	11.6	10.7	0.195	0.992	2.77	0.246	0.889
Cu ²⁺	24.5	25.2	0.942	0.994	4.78	0.264	0.911
Cd ²⁺	29.1	28.9	0.040	0.998	3.93	0.319	0.908

Two important physico-chemical aspects for evaluation of the adsorption process as a unit operation are the kinetics and the equilibria of adsorption. Modeling of the equilibrium data has been done using the Langmuir and Freundlich isotherms. The Langmuir and Freundlich isotherms are represented as follows by eqs. (2) and (3), respectively.

$$q = q_{\text{max}} \cdot b \cdot C_e / (1 + bC_e) \quad (2)$$

$$q = K_F \cdot C_e^{1/n} \quad (3)$$

where, q is the Langmuir adsorption capacity (mg/g), C_e is the equilibrium metal ion concentration (mg/mL), b is the constant related to the affinity binding sites, K_F is the Freundlich constant, and n is the Freundlich exponent.

Table I shows the calculated results. The correlation coefficients (R^2) are high for Langmuir model. Also, the calculated q_{max} values are very close to the experimental value. Equilibrium data fitted very well to the Langmuir model in the entire concentration range (5–600 mg/L), which indicates that the metal ions adsorb on the PHEMA/Reactive Green

HE-4BD cryogel as a monolayer adsorption. The correlation coefficients (R^2) are lower than 0.91 for Freundlich model. These values show poor agreement of Freundlich isotherm with the experimental data.

Effect of pH on metal binding

To establish the effect of pH on the adsorption of metal ions onto the PHEMA cryogel, the adsorption studies were repeated at different pH in the range of 3.2–6.9. In this group of experiments, the initial concentration of metal ions was 10 mg/L for all metal ions. Figure 5 shows the pH effect. The PHEMA/Reactive Green HE-4BD cryogel exhibited a low affinity for heavy metal ions in acidic conditions (pH < 5.0), a somewhat higher affinity between pH 5.0 and 7.0. Metal cations have a strong tendency to be hydrated in aqueous solution. The effective size of the hydrated species depend on the charge of the species. The species with smaller effective hydrated size show high mobility in comparison with larger hydrated species, resulting in increased adsorption during adsorbate/adsorbent interaction. The observed reduced adsorption at low pH value (3.2) may be attributed to (i) higher hydrated species having low mobility and (ii) protonation of the functional sulfhydryl groups as well as the competition between metal ions and H⁺ or H₃O⁺ ions present in the solution. At higher pH values (5.0–6.0), more functional reactive groups are available for metal ion adsorption due to deprotonation, resulting in high adsorption. Therefore pH 6.0 was chosen for subsequent experiments. Same adsorption behavior as a function of pH was reported in literature.^{10,12,34}

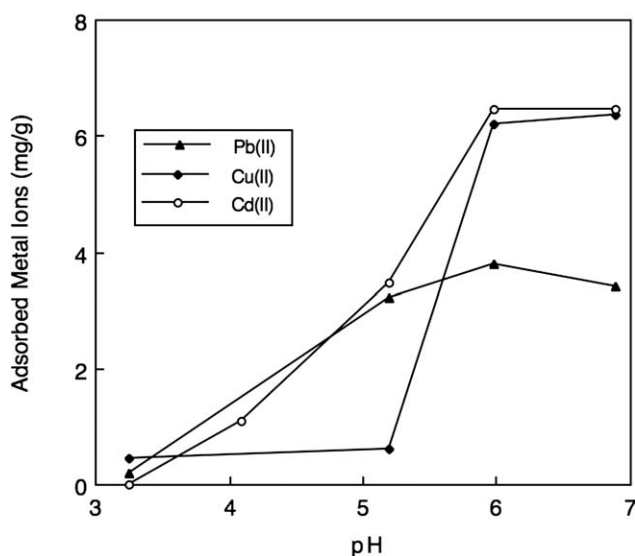


Figure 5 Effect of pH on adsorption of metal ions on PHEMA/reactive green HE-4BD cryogel: Reactive green HE-4BD content: 385 $\mu\text{mol/g}$; concentration: 10 mg/L; T: 20°C.

TABLE II
Competitive Adsorption of Cu²⁺, Cd²⁺, and Pb²⁺ from their Mixture onto the PHEMA/Reactive Green HE-4BD Cryogel: Metal Concentration: 200 mg/L; Reactive Green HE 4BD Content: 385 $\mu\text{mol/g}$; pH: 6.0; T: 20°C

Metal ions	Metal ions adsorbed	
	(mg/g Polymer)	($\mu\text{mol/g}$ Polymer)
Pb ²⁺	10.9	52
Cd ²⁺	22.1	196
Cu ²⁺	23.2	365

TABLE III
Heavy Metal Ions Adsorption Capacity of the PHEMA/Reactive Green HE-4BD Cryogel After Repeated Adsorption–Desorption Cycle: Initial Concentrations of Metal Ions 10 mg/L pH: 6.0; T: 20°C

Cycle No	Pb ²⁺		Cu ²⁺		Cd ²⁺	
	Adsorption (mg/g)	Desorption (%)	Adsorption (mg/g)	Desorption (%)	Adsorption (mg/g)	Desorption (%)
1	3.80	98.5	6.40	97.7	6.48	97.5
2	3.78	98.2	6.35	98.6	6.44	98.0
3	3.77	99.1	6.32	99.1	6.35	98.5
4	3.75	98.5	6.28	99.5	6.33	98.2
5	3.70	99.4	6.22	99.3	6.27	98.1

Competitive adsorption

In competitive adsorption studies from solutions containing all three ions, adsorbed amounts of Cu²⁺ ions are higher than those obtained for Cd²⁺ and Pb²⁺ in molar basis (Table II). The adsorption capacities are 10.9 mg/g for Pb²⁺; 22.1 mg/g for Cd²⁺, and 23.2 mg/g for Cu²⁺. From these results, the order of affinity is Cu²⁺ > Cd²⁺ > Pb²⁺. It is also evident from Table II that the sequence of adsorption capacity of the PHEMA/Reactive Green HE-4BD cryogel is as follows: Cu²⁺ > Cd²⁺ > Pb²⁺. The PHEMA/Reactive Green HE-4BD cryogel showed more affinity to Cu²⁺ ions for both mass and molar basis.

Desorption and repeated use

The repeated use (i.e., regenerability) of the polymeric adsorbents is likely to be a key factor in improving process economics.³⁶ The PHEMA cryogel loading the maximum amounts of the respective metal ions were placed within the desorption medium containing 50 mM EDTA and the amount of metal ions desorbed in 2 h was measured. Desorption ratios were very high (up to 99%) with the desorption agent and conditions used for all metal ions.

To obtain the reusability of the PHEMA/Reactive Green HE-4BD cryogel, adsorption-desorption cycle was repeated five times using the same cryogel. As shown in Table III, adsorption capacity of the PHEMA/Reactive Green HE-4BD cryogel for all metal ions did not significantly changed during the repeated adsorption-desorption operations.

CONCLUSIONS

There is a promising scope for the development of advanced materials including cryogels with high selectivity and enhanced separation capacity in environmental and bioseparation applications.^{37–41} Supermacroporous cryogels are a new class of materials introduced as alternative to traditional supports.^{42–48} This study demonstrated that the PHEMA/Reactive

Green HE-4BD cryogel could be used as an effective adsorbent for the treatment of wastewater containing heavy metal ions. The adsorption process is dependent on several factors such as equilibrium heavy metal concentration and medium pH. The adsorption capacity of the PHEMA/Reactive Green HE-4BD cryogel is 11.6 mg/g for Pb²⁺, 24.5 mg/g for Cu²⁺, and 29.1 mg/g for Cd²⁺. It appears that the PHEMA/Reactive Green HE-4BD cryogel had the strongest affinity for Cu²⁺ ions. The adsorption capacities under competitive conditions are 10.9 mg/g for Pb²⁺; 22.1 mg/g for Cd²⁺, and 23.2 mg/g for Cu²⁺. From these results, the affinity sequence is Cu²⁺ > Cd²⁺ > Pb²⁺. The PHEMA/Reactive Green HE-4BD cryogel can be used repeatedly without changing significantly their adsorption capacities, and there are high desorption percentages for heavy metal ions. The PHEMA/Reactive Green HE-4BD cryogel gave a potential application as a high adsorption capacity and effective reusable adsorbent.

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