Preparation and characterization of polyethyleneglycolmethacrylate (PEGMA)-*co*-vinylimidazole (VI) microspheres to use in heavy metal removal

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ABSTRACT

Polyethyleneglycolmethacrylate (PEGMA) and vinylimidazole (VI) were used in order to obtain microspheres of PEGMA-VI copolymers that can be used in heavy metal removal applications. The obtained copolymers were characterized and their use as sorbents in heavy metal removal was investigated. In the first part of the study, PEGMA-VI microspheres were prepared by suspension polymerization method. The obtained swellable microspheres with 10–50 μm average diameter did not have permanent porosity according to the morphological and physicochemical determinations. The sizes of microspheres became smaller with increasing VI and cross-linker ethyleneglycoldimethacrylate (EGDMA) contents and increasing agitation rate. The VI content, EGDMA ratio, pH and ionic strength were determined as the effective parameters on the swelling behavior of PEGMA-VI microspheres. In the second part of the study, Cu(II) ions were used as a model species in order to investigate the usability of the obtained PEGMA-VI microspheres in heavy metal removal. Adsorption capacities under optimum conditions were determined. The Cu(II) ion adsorption capacity increased by increasing the initial Cu(II) ion concentration, and it reached the maximum value (i.e., 30 mg Cu(II)/g PEGMA-VI microspheres) at 400 mg Cu(II)/L initial Cu(II) ion concentration under the determined optimum conditions. Microspheres were found to be reusable after desorption for several times.

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1. Introduction

Heavy metal contamination exists in aqueous waste streams of many industries such as metal plating facilities, mining operations and tanneries. These toxic heavy metals are cadmium, arsenic, chromium, copper, lead, nickel, selenium, silver, zinc, mercury, etc. They are metabolic poisons and enzyme inhibitors, they are not biodegradable and tend to accumulate in living organisms, causing serious diseases and disorders [1]. In the last decades, many different types of treatment techniques were applied to remove the heavy metals from waste water streams. Some of them are chemical precipitation, filtration, neutralization, ion-exchange, and adsorption [2–8]. Heavy metal removal capacity, easy handling, and cost effectiveness were evaluated as the most effective parameters in these treatment techniques. Adsorption processes seem to be the most attractive among the heavy metal removal methods taking these effective parameters into account. In these processes, effec-

tive alternative technologies and/or sorbents are needed. Sorbent polymers and copolymers have gained an increasing interest in heavy metal removal studies. Specific polymer sorbents consisting of metal chelate forming agents or some copolymers in the form of polymeric microspheres were investigated as useful polymeric adsorbents in removing heavy metals [1,2,5–13]. In recent applications, some specific ligands were used to remove specific metal ions from the stream, but the leakage of the ligand was a very big problem for the reusability of the sorbents [9–11]. The ligand molecules can be bonded covalently on the sorbents or they can be incorporated as comonomeric substances during the formation of sorbents to overcome this problem. Different types of metal chelating agents were investigated as the ligands in this respect [12]. Vinylimidazole (VI) groups are the most favorable species among them [13]. Therefore, VI incorporated polymeric sorbents useful in removing the heavy metals from aqueous media were prepared in this study. For this purpose, polyethleneglycolmethacrylate (PEGMA) was used as the comonomer with VI groups. Thus, the microspheres containing functional groups were obtained by inserting the VI into the PEGMA structure by using the suspension polymerization method. Here, PEGMA is considered as the matrice and VI groups are the ligands

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containing amine groups capable to form metal-chelate complexes. The PEGMA-VI microspheres were also characterized on the basis of their chemical structures, morphologies, size–size distributions and swelling (water uptake) behaviors. The VI content, cross-linker (i.e., ethyleneglycoldimethacrylate, EGDMA) concentration and stirring rate were investigated as the effective parameters on the characteristics of the microspheres. In the last part of the studies, Cu(II) ions were used as a model heavy metal species to be removed by PEGMA-VI microspheres and the adsorption capacities under optimum conditions were determined. PEGMA-VI microspheres were found to be reusable after desorption of the adsorbed Cu(II) ions for several times (i.e., 5 times).

2. Materials and methods

2.1. Chemicals

Poly(ethyleneglycol)methacrylate (PEGMA, M_n: 360, $n \approx 6$, Aldrich Chemical Co., Milwaukee, WI) was used without inhibitor removal. The monomer *N*-vinylimidazole (VI, Aldrich Chemical Co., Milwaukee, WI) was used without further purification. Ethyleneglycoldimethacrylate (EGDMA, Aldrich) was used as cross-linker and cyclohexanol (Cyc-OH, Merck A.G., Germany) was used as diluent. 2-2′-Azobisisobutyronitrile (AIBN; BDH) was crystallized with methanol and used as initiator and poly(vinylpyrrolidone) (PVP-K90, M_r: 360000, K: 80–100, Sigma Chemical Co., St. Louis, MO) was used as stabilizer. Ethyl alcohol used as solvent in the washing procedures of the obtained microspheres was product of Birpa Co., Turkey. In the adsorption studies, copper(II) chloride dihydrate ($CuCl_2 2H_2O$, Merck), sodium diethyldithiocarbamate trihydrate ($C_5H_{10}NNaS_2 3H_2O$, Merck), ammonia (NH_3 25%, Merck), nitric acid (HNO_3 65%, Merck), sulphuric acid (H_2SO_4 96%, Emir Chemistry, Turkey), sodium hydroxide (NaOH, Merck), and hydrochloric acid (HCl 32%, Merck) were used. Distilled water was used in all adsorption and desorption studies.

2.2. Preparation and characterization of PEGMA-VI microspheres

The PEGMA-VI microspheres were prepared by copolymerizing PEGMA with VI at a 1:1 molar ratio in the presence of the initiator AIBN according to the following reaction:

Poly(ethyleneglycol)methacrylate (PEGMA)-Vinylimidazole (VI)   PEGMA-VI
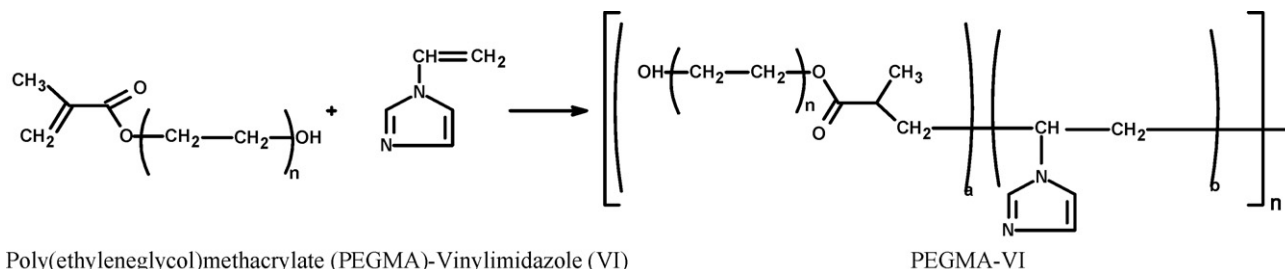
The PEGMA-VI microspheres were prepared by suspension polymerization technique. In a typical procedure, the monomer phase was prepared by dissolution of PEGMA and VI in cyclohexanol. Furthermore, the cross-linker (i.e., ethyleneglycoldimethacrylate, EGDMA) and initiator (i.e., azobisisobutironitrile, AIBN) were also added into this monomer mixture. Continuous phase (dispersion or suspension medium) was prepared by dissolution of polivinylpyrrolidone (PVP-K90) as a stabilizer in distilled water. These two phases were combined in a 100 mL sealed Pyrex reactor, the reactor was exposed to nitrogen purge for 2 min, and then placed in a shaking bath equipped with a temperature controller. The applied temperature program was 85 °C for 4 h and 90 °C for 1 h. Thus the copolymerization was performed. The obtained PEGMA-VI

Table 1
The recipes used in the preparation of the microspheres.

Ingredients and experimental conditions	Recipe 1	Recipe 2	Recipe 3	Recipe 4	Recipe 5
PEGMA (mL)	4	4	4	4	4
VI (mL)	0	0.25	0.5	1	2
EGDMA (mL)	0.8	0.8	0.8	0.8	0.8
AIBN (g)	0.2	0.2	0.2	0.2	0.2
Cyc-OH (mL)	6	6	6	6	6
PVP-K90 (g)	0.5	0.5	0.5	0.5	0.5
Water (mL)	40	40	40	40	40
Stirring rate (rpm)	250	250	250	250	250
Ingredients and experimental conditions	Recipe 6	Recipe 7	Recipe 8	Recipe 9	Recipe 10
PEGMA (mL)	4	4	4.27	4	3.47
VI (mL)	2	2	2.13	2	1.73
EGDMA (mL)	0.8	0.8	0.4	0.8	1.6
AIBN (g)	0.2	0.2	0.2	0.2	0.2
Cyc-OH (mL)	6	6	6	6	6
PVP-K90 (g)	0.5	0.5	0.5	0.5	0.5
Water (mL)	40	40	40	40	40
Stirring rate (rpm)	150	350	250	250	250

microspheres were kept at room temperature for cooling after polymerization and the suspension medium was decanted after cooling. The PEGMA-VI microspheres were washed with distilled water, then with ethyl alcohol and then with distilled water again, and the washing solution was removed by centrifugation at 4500 rpm for 5 min at each step. After washing procedures, PEGMA-VI microspheres were dried at 60 °C and 30 mm Hg down to constant weight. Varying comonomer VI contents, cross-linker EGDMA contents and stirring rates were used in the recipes for preparation of PEGMA-VI microspheres (Table 1). The initial VI amount, cross-linker amount and the stirring rate were selected as the most effective parameters over the characteristics of the obtained microspheres.

2.2.1. Determination of the yield of microspheres

The washed microspheres were dried in a vacuum oven at 60 °C for 48 h before weighing. The microsphere yield was determined by the following expression:

$$\text{Microsphere yield} = \left(\frac{W_p}{W_m} \right) \times 100 \quad (1)$$

where W_p and W_m are the weight of dry microspheres and the total weight of the monomers initially charged in the reactor, respectively.

2.2.2. Determination of the size and the size distribution

The size and the size distribution of PEGMA-VI microspheres were found by using micrographs obtained in an optical microscope (Olympus, Japan). During the imagination, the samples of the microspheres were placed on a glass slide and dried at room temperature. The obtained images of the microspheres were transferred into the computer and evaluated via an image analysis system (Image-Pro Express, Media Cybernetics, USA). The size and the size distribution of the microspheres were calculated with this system and 100–200 microspheres were evaluated for each micrograph during the measurements.

2.2.3. Structural analysis

Chemical structures of PEGMA and PEGMA-VI microspheres were analyzed by FTIR spectra. The FTIR samples were prepared with 2 mg microspheres and 100 mg KBr mixture, and the mixture was pressed in a hydraulic press at $600 \, kg/cm^2$ for 10 min. FTIR spectra of the microspheres were obtained with a FTIR system (Shimadzu 8001, Japan).

Morphological evaluations were made by using a scanning electron microscope (SEM) (JEOL, JEM 1200EX, Japan). For this purpose, the obtained PEGMA-VI microspheres were dried at 40 °C in a vacuum oven and coated with a thin layer of gold (around 110 Å) before the microscopic evaluations.

2.2.4. Swelling behavior of the microspheres

The PEGMA-VI microspheres swell in aqueous media since they have hydrogel structure. Thus, the swelling ratios of all PEGMA-VI microspheres were evaluated according to the preparation conditions – or effective parameters over the size and the size distribution – of the microspheres. Swelling ratios of the microspheres were determined with volumetric method in which certain amounts of well dried microspheres (around 50 mg) were filled into the capillary tube (internal diameter is 2 mm and the height is 100 mm) and top point of the microspheres was pointed (h_0). Then the tube was filled with distilled water and the level of the microspheres was pointed for particular time intervals (i.e., each 5 min). This procedure was followed until reaching constant level (h_f). Reaching the constant level shows that the microspheres reached the saturated swelling ratio. Swelling ratios of the microspheres were calculated by using the following equation.

$$\text{Swelling ratio} = \left(\frac{(h_f - h_0)}{h_0} \right) \times 100 \qquad (2)$$

2.3. Heavy metal removal studies

2.3.1. Adsorption studies

In the adsorption of Cu(II) ions, first of all, the initial VI amount used in the preparation of PEGMA-VI microspheres was changed between 0 and 2 mL as the most effective parameter. Other effective parameters on the adsorption of Cu(II) ions were selected as medium pH, initial Cu(II) concentration and adsorption time. The experiments for the investigation of the effects of these parameters were carried out by using 2 mL of initial VI amount since the maximum adsorption capacity was reached for this value under the determined optimum experimental conditions. During these studies, medium pH was adjusted by using diluted HCl and NaOH solutions. The volume of the adsorption medium and the amount of microspheres were kept as 25 mL and 0.25 g, respectively, in all studies. In the adsorption kinetics studies, the concentration of Cu(II) ions was 80 mg/mL. Adsorption studies were batchwise type and were performed at room temperature. Adsorption capacities of

the microspheres were calculated by using the following equation:

$$Q = \left[\frac{(A_0 - A_f)}{A_0} \right] \left[\frac{(C_0 \times V)}{M_p} \right] \qquad (3)$$

Here Q (mg/g) is the adsorption capacity, A_0 and A_f are the absorbance values of the adsorption medium before and after the adsorption process, respectively, C_0 (mg/mL) is the initial heavy metal concentration, V (mL) is the volume of the adsorption medium and M_p (g) is the amount of the adsorbent PEGMA-VI microspheres.

2.3.2. Adsorption–desorption studies: reusability

Reusability of the adsorbents is one of the most important considerations in the adsorption and removal studies of the heavy metals. In the study, first the microsphere formulation and adsorption conditions were determined for the highest Cu(II) ion adsorption capacity and the determined formulation and conditions were used for adsorption–desorption studies. $0.1 \, M \, HNO_3$ solution was used as desorption medium. The volumes of the adsorption and desorption media were both kept constant as 25 mL. Desorption time was optimized as 2 h. At the end of the adsorption–desorption studies, the microspheres were washed with the $0.1 \, M \, HNO_3$ solution first and then with distilled water for three times for 30 min in all adsorption–desorption steps.

3. Results and discussion

3.1. Structural analysis

In the FTIR studies, PEGMA and PEGMA-VI microspheres were compared with respect to their FTIR spectrums. In the comparison of the FTIR spectra, some typical characteristic peaks were observed indicating that VI groups were attached to the PEGMA structure. These can be summarized as typical imidazole chain (C=C—H/N=C—H) peak at $3120 \, cm^{-1}$, the carbonyl peak at $1720 \, cm^{-1}$, C—C/N—C stretching peak at $1500 \, cm^{-1}$, ring vibration peak at $1220 \, cm^{-1}$ and peak for C—H bent at $1098 \, cm^{-1}$ for VI groups in the case of FTIR spectrum of PEGMA-VI microspheres (Fig. 1).

In the morphological evaluations, some SEM micrographs of the PEGMA-VI microspheres were obtained and given in Fig. 2. This figure represented the surface and the cross section of PEGMA-VI microspheres. Both the surface and cross sectional views of the PEGMA-VI microspheres show that there is not any pore. This
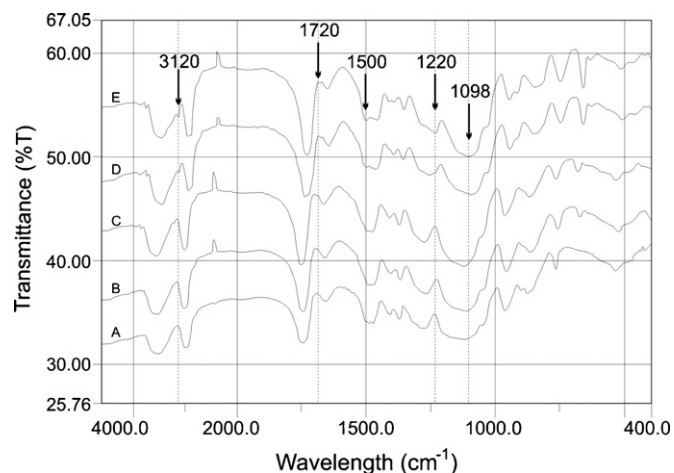

Fig. 1. The FTIR spectra of the PEGMA-VI microspheres for samples obtained by using different initial VI amounts: (A/B/C/D/E:0/0.25/0.5/1/2 mL VI).
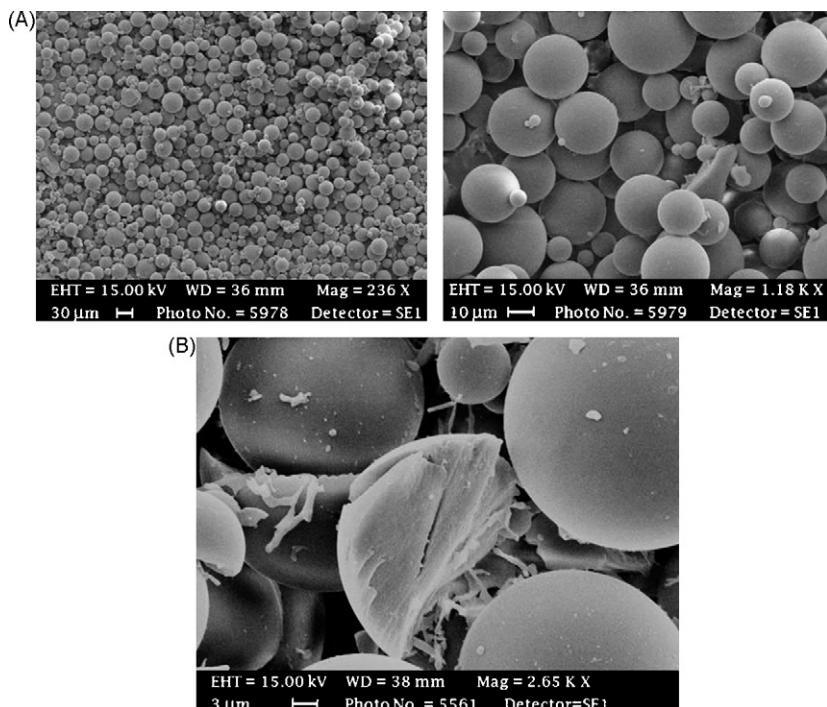
Fig. 2. SEM micrographs of PEGMA-VI microspheres: (A) surface view with different magnifications, (B) cross sectional view.

means that the microspheres have non-porous structure. Thus, it can be concluded that the microspheres are in hydrogel structure and they do not have any permanent porosity, but some molecular spaces can form with water uptake during swelling process. Furthermore, for the permanent porosity, the pores must be larger as macropores. Actually the average size of the final product changes between 50 and 1000 μm in suspension polymerization technique, but here the size range of PEGMA-VI microspheres was changed between 10 and 50 μm. This can be explained by the polarity of VI groups and water insoluble diluent (i.e., cyclohexanol) with lower surface tension.

3.2. Microsphere yields

The microsphere yields slightly decreased as the initial VI concentration in the organic phase was increased. However, the average microsphere yield was generally about 80% (Table 2). It was observed that the agitation rate did not affect the yield of the microspheres significantly. This result is in accordance with previous literature [14]. The microsphere yield increased as the initial concentration of the cross-linker EGDMA in the monomer phase was increased. This is also in accordance with literature since the monomer conversion is expected to be higher when the cross-linker concentration is higher in the formation of the cross-linked polymeric structures [14–15].

3.3. The size and the size distribution

According to the mathematical models which were used widely by different researchers, the average particle size is directly proportional with the container diameter, ratio of droplet phase to the suspension medium, viscosity of droplet phase and the internal tension between two immiscible phases; and it is inversely proportional with the stirrer diameter, stirring rate, viscosity of suspension medium and stabilizer concentration during the suspension polymerization [16]. In this study, a previously determined stabilizer

concentration and temperature program were applied during all the polymerization reactions and the same reactor system was used for all polymerizations. The container and stirrer diameters, stabilizer concentration and viscosity of suspension medium were kept constant throughout the study. Under these constant conditions, the initial comonomer VI concentration, cross-linker EGDMA concentration and stirring rate were changed as shown in Table 1. Thus the effects of the above mentioned parameters on the size and size distribution of the particles were investigated.

Table 2
The effects of VI content, cross-linker concentration and the stirring rate on the microsphere yield and on the size and size distribution of the (PEGMA-VI) microspheres

VI content (mL)	Average microsphere diameter (μm ± S.D.)	Microsphere yield (%, w/w)
The effect of VI content		
0.00	35.97 ± 12.68	85.2
0.25	38.08 ± 11.91	83.2
0.50	26.52 ± 9.41	80.2
1.00	22.36 ± 9.08	71.6
2.00	19.07 ± 7.01	74.3
EGDMA content (mL)	Average microsphere diameter (μm ± S.D.)	Microsphere yield (%, w/w)
The effect of cross-linker concentration		
0.4	26.59 ± 8.33	65
0.8	19.07 ± 7.01	74.3
1.6	17.86 ± 7.94	82.2
Stirring rate (rpm)	Average microsphere diameter (μm ± S.D.)	Microsphere yield (%, w/w)
The effect of stirring rate		
150	45.09 ± 8.91	68.7
250	19.07 ± 7.01	74.3
350	18.59 ± 2.78	67.6

3.3.1. The effect of VI content on the size and size distribution

Table 2 shows the changes in the size and the size distribution of microspheres by changing VI concentration. As shown in the table, the obtained microspheres are not so different from each other for their size distribution. However, by increasing the VI content, a decrease in the microsphere size and size distribution was observed. At high VI content, microsphere diameter decreased approximately to 20 μm. The reason of this may be the decrease in the monomer phase viscosity due to the increase in VI concentration since a decrease in monomer phase viscosity or internal tension requires a decrease in average size according to the general mathematical model of suspension polymerization [17].

3.3.2. The effect of the cross-linker concentration on the size and size distribution

The highest average size was obtained for the lowest cross-linker concentration. This result is related with the equilibrium swelling capacities of microspheres since the average size was determined by the swollen form. Another reason of the decrease in the average size may be the viscosity of the droplet phase. An increase in the feeding concentration of EGDMA may cause a decrease in monomer phase viscosity. This behavior is due to the decrease in microsphere size related to the previous models results for different suspension polymerization systems [16–17].

During the preparation of (PEGMA-VI) microspheres, a decrease in microsphere size was expected due to the different shrinking extents of the microspheres by increasing the cross-linker (EGDMA) content. The effect of EGDMA concentration on the size and the size distribution of microspheres are shown in Table 2. A decrease in the size and the size distribution of (PEGMA-VI) microspheres was observed by increasing the EGDMA content as shown in the table.

3.3.3. The effect of stirring rate on the size and size distribution

Although there are some differences between the methods used for the preparation of polymeric microspheres, there is a common circular movement as shaking or spinning in all of these methods. For the different suspension polymerization systems, one of the important parameters controlling the size and the size distribution of microspheres is the stirring rate. The size and the size distribution of microspheres decrease clearly by increasing the rate of stirring as explained in the related literature [18]. The effect of stirring rate on the size and size distribution was investigated by using different stirring rates and the obtained results are shown in Table 2. As shown in the table, a decrease in the size and size distribution of microspheres was observed by increasing the stirring rate. By a further increase in the stirring rate, almost no difference in microsphere diameter was observed, but an important decrease in the size distribution was observed and the size of the obtained microspheres was started to approach to the average value.

3.4. Swelling behavior of the microspheres

Chemicals used for the preparation of (PEGMA-VI) microspheres were hydrophilic. So, the water uptake occurred when the microspheres were placed into an aqueous medium. It was observed that the microspheres swelled at certain quantities and got larger in size depending on the cross-linking density as a result of the water uptake. Depending on the structural properties of the microspheres and the medium in which they placed, some differences in swelling behaviors were observed. In the related literature, the parameters affecting the swelling behavior of hydrophilic polymers were determined as the ratio of hydrophilic parts, cross-linker ratio, pH and ionic strength of the swelling medium. Thus these parameters were investigated in this study to observe the effects of them on the swelling behaviors of the microspheres prepared according to the

Table 3
The effects of VI content, cross-linker concentration, pH and ionic strength on swelling behavior

VI content	Swelling ratio (%)[a]
The effect of VI content	
PEGMA	185
PEGMA-VI	150
EGDMA content (mL)	**Swelling ratio (%)[a]**
The effect of cross-linker concentration	
0.4	200
0.8	150
1.6	100
pH	**Swelling ratio (%)[a]**
The effect of pH	
5.0	175
7.0	150
9.0	125
Ionic strength (M)	**Swelling ratio (%)[a]**
The effect of ionic strength	
0.0	150
0.1	100
1.0	95

[a] Equilibrium swelling ratios were obtained after approximately 15–20 min.

formulations given in Table 1. The obtained equilibrium swelling ratios were given in Table 3. All of the obtained microspheres reached the equilibrium swelling ratios in about 15–20 min.

3.4.1. The effect of VI content on the swelling behavior

By increasing the VI content, which was used as a comonomer in the preparation of the (PEGMA-VI) microspheres, a decrease in the swelling ratios was observed due to the decrease in hydrophilicity of the structure. The obtained equilibrium swelling ratios are given in Table 3. As shown in the table, the swelling ratio of the microspheres prepared without VI was 185%, but this ratio decreased to 150% in the case of 2 mL VI addition.

3.4.2. The Effect of the cross-linker concentration on the swelling behavior

The most important parameter affecting the swelling behavior of the microspheres is the amount of cross-linker which was added during the polymerization process. As shown in Table 3, by changing the cross-linker (EGDMA) amount, the swelling behavior of the microspheres changed significantly. In the study, the cross-linker amount was changed between 0.4 and 1.6 mL and the swelling ratios were decreased from 200% to 100% due to the increase in the cross-linking density of the polymers by increasing the EGDMA amount. As a result, the swelling ratio of the microspheres can easily be controlled by changing the amount of cross-linker in the preparation of the (PEGMA-VI) microspheres.

3.4.3. The effect of the pH on the swelling behavior

The swelling behavior of the (PEGMA-VI) microspheres was affected significantly by the ambient pH value. The microspheres prepared by using 2 mL of VI were placed into the mediums having different pH values and the swelling behavior was investigated periodically. The observations are shown in Table 3. As shown in the table, by increasing the pH, a decrease in the swelling ratios of the microspheres was observed. Due to the basic structure of VI, the ionization of VI decreased when the medium was more basic and this decrease resulted in a decrease in the swelling ratio.

3.4.4. The effect of ionic strength on the swelling behavior

The effect of the ionic strength was investigated by using the same formulation as used in the above-mentioned studies, and the obtained results are shown in Table 3. As shown in the table, the microspheres containing no salt swelled in the ratio of 150% while this value decreased to 100% and even less in the case of 0.1–1.0 M ionic strength. This decrease was expected theoretically.

3.5. Heavy metal removal studies

3.5.1. Adsorption studies

The adsorption of Cu(II) ions by PEGMA-VI microspheres was evaluated in the adsorption studies. The effects of the pH of the adsorption medium, initial concentration of Cu(II) ions and VI content of PEGMA-VI microspheres were investigated as the effective parameters on the adsorption capacities of the microspheres. Furthermore, the adsorption rate of the microspheres was also investigated for determination of the optimum adsorption time. This represents the required time for maximum adsorption capacity.

3.5.1.1. Adsorption rates.
PEGMA-VI microspheres with the highest VI content (i.e., 2 mL of VI) were used in the determination of adsorption capacities and rates. In this part of the study, certain amounts of PEGMA-VI microspheres were interacted with Cu(II) ions and the adsorptions of Cu(II) ions were determined periodically (i.e., after 10, 20, 40, 80, 120, 160, and 200 min). The obtained results are represented in Fig. 3. Cu(II) ions were adsorbed onto the PEGMA-VI microspheres in a very short time and maximum adsorption capacity was achieved in almost 2 h as shown in Fig. 3. This can be due to the VI content of the microspheres. It is very well known that VI groups are very good chelator agents for heavy metals such as Cu(II) ions as given in related literature [2]. Some of the similar investigations related with this study are summarized as follows. George et al. investigated the adsorptions of Co(II), Ni(II), Cu(II) and Zn(II) ions onto the *N,N′*-methylenebisacrylamide cross-linked polyacrylamide and glycine attached divinylbenzene structures, and they reported that the maximum Cu(II) ion adsorption could be achieved at 2.5 h [19]. Shreedhara-Murthy and Ryan investigated uranium, mercury, copper, cadmium and lead ions adsorption onto the cellulose dithiocarbamate resin and they reported that the maximum adsorption value could be achieved in a very long time [20]. Roozemond et al. investigated copper and cadmium ions adsorption to *p*-aminomethyl attached 3,5-dimethyl-1-hydroxymethylpyrazole and they reported that the adsorption rate is very low and maximum adsorption took two days [21]. Reed and Matsumoto used the activated carbon as the sorbent for cadmium ions and they reported that maximum cadmium
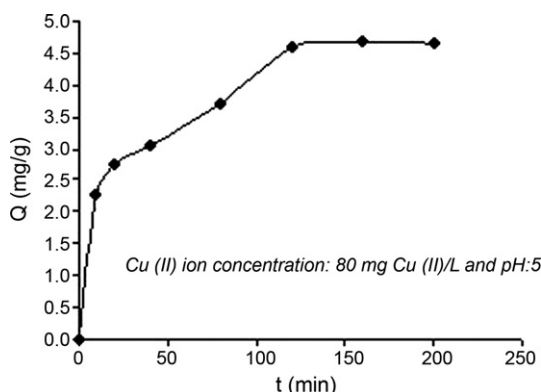
adsorption took around 6 h [22]. Marchese et al. investigated the adsorption of cobalt, nickel and copper ions adsorption by using alanine liquid membranes and they determined the required time as 4–5 h for maximum adsorption [23]. Egawa et al. investigated uranium ion adsorption with amidoxime containing polyacrylonitrile fibers and they reported that the maximum ion adsorption took around 7 h [24]. Ebraheem and Hamdi investigated Ni(II), Cu(II), Zn(II) and Cd(II) ions by poly(salycilaldoxim-3-5-dimethylene) containing phenol formaldehyde polymers, and they reported that maximum ion adsorption took around 10 h [25]. Latha et al. tried to extract Fe(III), Fe(II), Cu(II) and Ni(II) ions with ethylenediamine functionalized polyacrylamide resins, and they reported that the required time for maximum adsorption was 5 h [26]. However, all of the given examples are not reflected the same conditions as used in our studies. Therefore, it is not so convenient to compare these data with the data obtained in our studies although a relatively higher adsorption rate was obtained.

3.5.1.2. Effective parameters on the adsorption capacity. VI content of PEGMA-VI microspheres.
The first effective parameter on the Cu(II) ion adsorption of PEGMA-VI microspheres was selected as VI content of the microspheres due to the chelating characteristics of VI groups with Cu(II) ions. During the preparation of PEGMA-VI microspheres, the VI content was changed between 0 and 2 mL for a typical procedure to prepare different PEGMA-VI microspheres with different VI contents. Adsorption medium pH was adjusted as pH: 5, initial Cu(II) concentration was used as 400 mg Cu(II)/L and adsorption time was fixed as 2 h (this time is the saturation value for Cu(II) ion adsorption onto the PEGMA-VI microspheres). The obtained results are shown in Fig. 4. Cu(II) ion adsorption capacity increased by increasing VI content of the microspheres as shown in this figure. Minimum Cu(II) ion adsorption was obtained with PEGMA microspheres (without VI groups) (i.e., 4 mg Cu(II)/g PEGMA microspheres) and maximum adsorption was achieved using PEGMA-VI microspheres (i.e., 30 mg Cu(II)/g PEGMA-VI microspheres) with the highest VI content (i.e., 2 mL) as expected.

Medium pH. It is very well known that both specific and non-specific heavy metal adsorptions onto the sorbents are affected by any change in the adsorption medium pH [22,27–28]. Therefore in this study the effect of pH of the adsorption medium on the sorption of Cu(II) ions was also investigated and the heavy metal concentration was adjusted as to prevent the precipitation. Adsorption medium pH was changed from 1 to 5 for this purpose by using HCl and NaOH solutions. It is also very well known that the Cu(II) ions can be hydrolyzed after a certain pH value depending on the concentration of Cu(II) ions in the medium. In the study, initial Cu(II) ion concentration was used as 80 mg/L and the saturation time was defined as 2 h. According to these
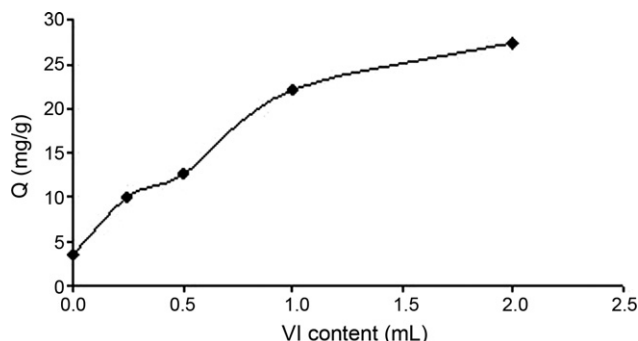

Fig. 3. Cu(II) ions adsorption rates onto the (PEGMA-VI) microspheres.

Fig. 4. The effect of VI content over the Cu(II) ion adsorption.
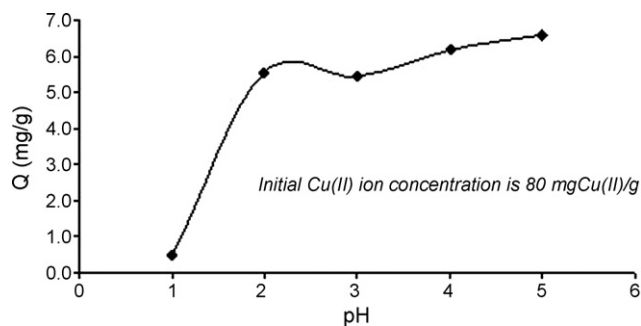
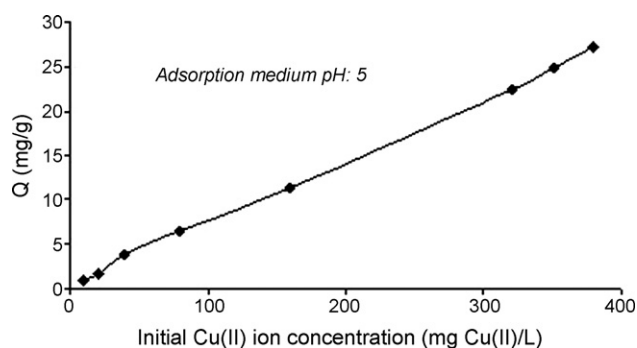Fig. 5. The effect of medium pH over the Cu(II) ion adsorption.

Fig. 6. The effect of initial Cu(II) ion concentration over the Cu(II) ion adsorption.

Fig. 7. Adsorption–desorption values for Cu(II) ions with PEGMA-VI microspheres.

values, Cu(II) ions were hydrolyzed after pH 5 and precipitated as its hydroxides, therefore maximum pH value was used as pH 5 as mentioned before. Cu(II) ion adsorption values are shown in Fig. 5. The adsorption capacity of PEGMA-VI microspheres was very low at the highly acidic medium (i.e., pH 1). This may be due to the protonation of the functional groups in the microsphere structures. On the other hand, the adsorption value increased significantly with increasing pH and it reached the maximum value of approximately 7 mg Cu(II)/g adsorbent at pH 5. At higher pH values than 5, copper hydroxide precipitation was observed as expected. Adsorption capacity of Cu(II) ions was found very low around pH:3.5 in another similar study which was established by poly(HEMA-co-MAH) microspheres. But, adsorption capacity of the microspheres increased by increasing the medium pH up to pH 5 [29].

Initial metal ion concentration. After the determination of the optimum pH value, the effect of initial Cu(II) ion concentration on the Cu(II) ion adsorption with PEGMA-VI microspheres was evaluated. PEGMA-VI microspheres with the highest VI content (i.e., 2 mL) were used in these studies. Cu(II) ions were precipitated as hydroxides after a certain concentration, therefore adsorption
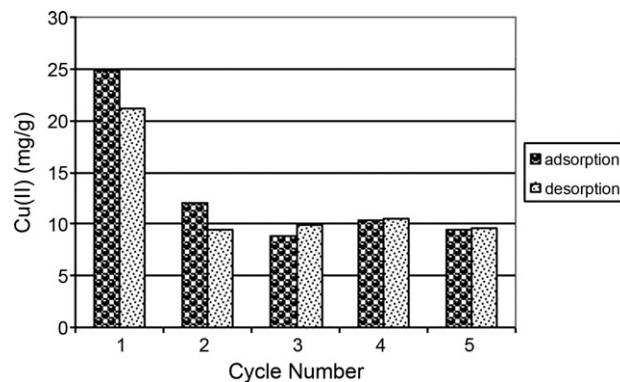
reported in literature. Roozemond et al. reported that 32 mg Cu(II)/g sorbent could be removed by using prisol-containing poly(styrene-divinylbenzene) as sorbent [21]. Liu et al. reached the adsorption capacity of 16.5 mg Cu(II)/g N-hydroxymethylthioamide resin as adsorbent [30]. Maeda and Egawa showed that 88 mg Cu(II)/g could be complexated by methylmethacrylate-divinylbenzene copolymer microspheres containing aminomethylphosphonic acid [31]. Hudson and Matejka investigated the effect of the pendant groups on the heavy metal adsorption on polymeric microspheres. They reported adsorption capacities between 14.4 and 46 mg/g [32]. Sağ and Kutsal used Zoogloea Ramigera microorganisms for heavy metal adsorption. They reached a maximum adsorption capacity of 35 mg Cu(II)/1 g dry microorganism [33]. Shambhu and colleagues immobilized polyamines such as ethylenediamine, diethylenetriamine and triethylenetetraamine onto polystyrene and reached an adsorption of 33 mg Cu(II) per g of polymer [34]. Denizli et al. immobilized ethylenediamine (EDA) and hexamethylenediamine (HMDA) on poly(hydroxymethacrylate) microspheres by glow discharge and they obtained an adsorption capacity of 7 mg Cu(II)/g adsorbent for HMDA-immobilized microspheres [27].

3.5.2. Adsorption–desorption (reusability) studies

In this part of the study, the PEGMA-VI microspheres adsorbed Cu(II) ions were treated with a suitable solution (i.e., 0.1 M HNO$_3$) to remove the adsorbed Cu(II) ions for the investigation of reusability of the PEGMA-VI microspheres in Cu(II) ion adsorption studies. This characteristic is very important for the economical perspective of the PEGMA-VI microspheres as an adsorbent for heavy metal removal. Adsorption medium pH was 5, initial Cu(II) ion concentration was 400 mg Cu(II)/L and VI content of PEGMA-VI microspheres was 2 mL in all experiments of this part of the study. Desorption time was fixed as 2 h throughout the adsorption period. Desorption ratio was calculated by using the following equation:

$$\text{Desorption ratio} = \frac{\text{Amount of desorbed Cu(II) ions into the desorption medium}}{\text{Amount of adsorbed Cu(II) ions onto the PEGMA} - \text{VI microspheres}} \times 100 \qquad (4)$$

studies were completed after this value (i.e., 400 mg Cu(II)/L). The obtained adsorption results are shown in Fig. 6. The Cu(II) ion adsorption capacity was increased by increasing the initial Cu(II) ion concentration and it reached the maximum value (i.e., 30 mg Cu(II)/g PEGMA-VI microspheres) at 400 mg Cu(II)/L initial Cu(II) ion concentration. As can be seen in Fig. 6, the increase in the adsorption capacity is linear for the initial Cu(II) ion concentration values between 40 and 400 mg Cu(II)/L. Various effective adsorbents with a wide range of adsorption capacities were

Adsorption–desorption studies were replicated for five times and desorbed PEGMA-VI microspheres were washed with distilled water before the following adsorption steps. The obtained results are shown in Fig. 7. As can be seen in the figure, while the adsorption capacity for Cu(II) ions was approximately 25 mg/g adsorbent in the first step, this value decreased to approximately 10 mg/g adsorbent in the following steps. In spite of this decrease in the adsorption of Cu(II) ions, no excessive change was observed after the second step. Furthermore, almost all of the Cu(II) ions adsorbed by the microspheres could be removed from the microspheres according to the desorption ratios.

4. Conclusions

Polyethyleneglycolmethacrylate-*co*-vinylimidazole (PEGMA-VI) microspheres were synthesized and characterized as a novel sorbent for heavy metal removal from aqueous media. Suspension polymerization method was used in the preparation of microspheres by various formulations. Adsorption capacities of the microspheres for the sorption of Cu(II) ions from aqueous solutions under optimum conditions were determined. The Cu(II) ion adsorption capacity increased by increasing VI content and by increasing initial Cu(II) ion concentration, and it reached the maximum value (i.e., 30 mg Cu(II)/g PEGMA-VI microspheres) at 400 mg Cu(II)/L initial Cu(II) ion concentration under the determined optimum conditions. Saturation adsorption value was reached in 2 h, a relatively short time, in the adsorption experiments. Microspheres were found to be reusable after desorption for several times. The obtained microspheres may also be useful in the removal of other heavy metal ions from aqueous media. They may also be used in the separation and purification processes of various biomolecules such as proteins in metal-chelate affinity applications.

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