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The use of polyethyleneglycolmethacrylate-co-vinylimidazole (PEGMA-co-VI) microspheres for the removal of nickel(II) and chromium(VI) ions

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ABSTRACT

The polyethyleneglycolmethacrylate-co-vinylimidazole (PEGMA-VI) copolymers, that can be used in heavy metal removal applications, were synthesized and characterized; and their use as sorbents in heavy metal removal was investigated. It was determined that the ligand vinylimidazole was successfully inserted into the polymer structure. Then, chromium (Cr(VI)) and nickel (Ni(II)) ions were used as model species to investigate the usability of the obtained microspheres in heavy metal removal. The effects of pH of the adsorption medium, initial concentration of the metal ions and VI content of PEGMA-VI microspheres were investigated as the effective parameters on the adsorption capacities of the microspheres. The adsorption rate of the microspheres was also investigated for determination of the optimum adsorption time which is the required time for maximum adsorption capacity. The adsorption capacities under optimum conditions were also determined. The order of adsorption affinities of PEGMA-VI microspheres with respect to the used metals was determined by competitive adsorption studies. According to the obtained results, the highest adsorption affinity of the PEGMA-VI microspheres was towards Cr(VI) ions, the adsorption affinity was less for Ni(II) and the least affinity was towards Cu(II) ions. The adsorption–desorption studies showed that the microspheres were reusable without a significant decrease in the ion adsorption capacities.

1. Introduction

Heavy metals are being isolated, purified, modified and used in various industrial processes. Heavy metal contamination therefore is a very great environmental concern since it is very well known that the heavy metal ions such as cadmium, chromium, copper, lead, mercury, nickel, selenium, silver, and zinc are generally toxic in nature. Thus, heavy metal removal is a recent research area attracting a great interest [1–4]. Various removal methods such as membrane processes (dialysis, electrodialysis, reverse osmosis, etc.), neutralization–precipitation, extraction and ion exchange are useful [5–9]. However, in recent years, adsorption becomes an effective and economical alternative technique since the other methods may have some limitations [5,10,11]. Adsorption may be considered as preferable in many cases due to its economical advantages, high efficiency and applicability [5]. Some non-specific adsorbents such as activated carbon, metal oxides, silica and ion exchanger resins are used in adsorption processes [11,12]. On the other hand, the specific sorbents consisting of a ligand (e.g., ion exchanger or chelating agent) and an inorganic (aluminum oxide, activated carbon, silica, etc.) or a polymeric (styrene–divinylbenzene copolymer, glycydilmethacrylate–divinylbenzene copolymer, etc.) carrier matrix became important [13–18]. Chelating polymers have also been produced and used as adsorbents for removal of toxic heavy metal ions in recent years [1,18–36]. These selective polymeric adsorbents have gained a growing interest since they are especially useful in the removal of heavy metal ions from waste water effluents and reuse of the adsorbent polymer and recovery of heavy metals are also possible. Polymers have some significant advantages in the preparation of carrier matrix. For instance, polymers can be readily produced in a wide range of physicochemical properties (size, size distribution, porosity, hydrophobicity, etc.) and they are modifiable by inserting various ligands into the structure in order to make them specific sorbents.

The production and characterization of a novel polymeric sorbent – polyethyleneglycolmethacrylate (PEGMA)-co-vinylimidazole (VI) microspheres and its use in the removal of copper (Cu(II)) ions were performed in the previous study [1]. In the present study, the same way was followed for the production of the PEGMA-VI sorbent and for its use in the removal of nickel (Ni(II)) and chromium (Cr(VI)) ions since chromium and nickel

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produce a general toxic effect on the human organism. Chromium exists in hexavalent and trivalent forms. Hexavalent form of the chromium is more toxic than trivalent and requires more concern. Strong exposure to Cr(VI) causes cancer in the digestive tract and lungs and may cause epigastric pain, nausea, vomiting, severe diarrhea and hemorrhage and nickel can lead to serious problems, including nasopharynx, lung and dermatological diseases and malignant tumors. It is therefore essential to remove Cr(VI) and Ni(II) from waste water before disposal.

In this study, first, the hydrophilic comonomer, N-vinylimidazole (VI), including amine groups capable of forming metal–chelate complexes, was inserted into the PEGMA matrix by suspension polymerization method in the aqueous dispersion medium. By this way, the hydrophilic and cross-linked microspheres, with different VI contents and including functional groups, were produced. Then, the produced microspheres were interacted with aqueous solutions containing heavy metal ions to investigate their heavy metal adsorbent properties. For this purpose, the prepared heavy metal solutions were used in adsorption and desorption studies. It was concluded according to the obtained results that the produced polymeric microspheres were useful for the removal of heavy metals from aqueous media.

2. Materials and methods

2.1. Chemicals

Poly(ethyleneglycolmethacrylate) (PEGMA, M_n: 360, $n \approx 6$, Aldrich Chemical Co., Milwaukee, WI.) was used without inhibitor removal. The monomer 1-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: 360 000, K: 80–100 Sigma Chemical Co., St. Louis, MO) was used as stabilizer. Distilled water was used for all dispersion media. Distilled water and ethanol (Birpa Co., Turkey) were used as the solvents in the washing procedures of the obtained microspheres.

In the adsorption studies, potassium dichromate ($K_2Cr_2O_7$, Merck), sodium diethyldithiocarbamate trihydrate ($C_5H_{10}NNaS_2 3H_2O$, Merck), 1,5-diphenylcarbazide ($C_{13}H_{14}N_4O$, 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.

2.2. Preparation of PEGMA-VI microspheres

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., 2,2′-azobisisobutyronitrile, AIBN) were also added into this monomer mixture. Continuous phase (dispersion or suspension medium) was prepared by dissolution of polyvinylpyrrolidone (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 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 mmHg down to constant weight. In the previous study, varying comonomer VI contents, cross-linker EGDMA contents and stirring rates were used in the recipes for preparation of PEGMA-VI microspheres and 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 [1]. The microspheres with varying VI contents were used for the removal of heavy metals separately.

2.3. Heavy metal removal studies

2.3.1. Adsorption studies

The adsorption of Cu(II) ions by using the produced adsorbent microspheres was studied in the previous study [1]. Similar methods were also applied in this study to investigate the removal of Cr(VI) and Ni(II) ions. In the adsorption of Cr(VI) and Ni(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 the heavy metal ions were selected as medium pH, initial heavy metal ions 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 Ni(II) and Cr(VI) ions was 80 mg/mL. Adsorption studies were batchwise type and were performed at room temperature. The adsorption capacities of the microspheres were calculated by using the following equation:

$$Q = \left[\frac{A_0 - A_f}{A_0}\right]\left[\frac{C_0 V}{M_p}\right] \quad (1)$$

where 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 Ni(II) and Cr(VI) ions adsorption capacity and the determined formulation and conditions were used for adsorption–desorption studies. The 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. Characterization of PEGMA-VI microspheres

Physicochemical nature of the PEGMA and PEGMA-VI microspheres was evaluated with FTIR spectra and the obtained results

were given in the previous study [1]. In these FTIR studies, some typical characteristic peaks were observed indicating that VI groups were introduced into the PEGMA structure.

In the morphological evaluations, SEM micrographs of PEGMA-VI microspheres were obtained as the surface and cross-section of PEGMA-VI microspheres [1]. Both the surface and cross-sectional views of the PEGMA-VI microspheres obviously show that the structure is not porous. This 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 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.

On the other hand, the average microsphere yield in the production of the PEGMA-VI microspheres was generally about 80%. 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 [37,38].

In the size and size distribution studies, VI content in the formulation, cross-linker concentration and stirring rate were evaluated as the most effective parameters [1]. The obtained results showed that increasing the VI content causes a decrease in the microsphere size due to the increase in VI concentration since a decrease in monomer phase viscosity or internal tension requires a decrease in the average size due to the general characteristics of suspension polymerization. Increasing the cross-linker concentration caused a decrease in the average size of the microspheres and this can be speculated from the decrease in the monomer phase viscosity during the cross-linking in accordance with related literatures [39,40]. Stirring rate, as the final effective parameter, caused a decrease in the size and the size distribution clearly as explained in the related literature [41]. 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 started to approach to the average value.

3.2. Heavy metal removal studies

3.2.1. Adsorption studies

The adsorption of Ni(II) and Cr(VI) ions by PEGMA-VI microspheres was evaluated in the adsorption studies. The effects of the pH of the adsorption medium, initial concentration of the metal 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.

3.2.2. 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 the metal ions and the adsorption of the metal ions were determined periodically (i.e., after 10, 20, 40, 80, 120, 160, 200 min). The obtained results were represented in Fig. 1.

The adsorption of Ni(II) and Cr(VI) ions are very fast and the saturation values are just 120 min for Ni(II) and 20 min for Cr(VI) as shown in Fig. 1. This may result from the ion affinity differences of the VI groups in the PEGMA microspheres. On the other hand in some similar studies investigators found very low adsorption rates for different ions to the different adsorbent systems [42–47]. However, all of the given examples are not reflected the same conditions as used in our studies. Even if it is not so convenient to compare these data with the data obtained in our studies, we can conclude that the adsorption time values found in our sudies are rather very short against the others and this is a very big advantage for our PEGMA-VI microspheres.

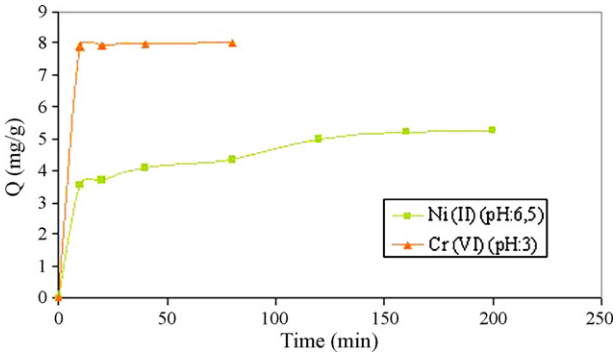

Fig. 1. Adsorption rates of Ni(II) and Cr(VI) ions on PEGMA-VI microspheres (C_0: 80 ppm).

3.3. Effective parameters on adsorption capacity

3.3.1. Medium pH

It was reported in the related literature that the pH of the adsorption medium is one of the most important parameters affecting the adsorption capacities [44,48,49]. Therefore, the pH of the adsorption medium was selected as an effective parameter on the Ni(II) and Cr(VI) ions adsorption onto the PEGMA-VI microspheres in this study. Adsorption medium pH was changed from 2 to 8 for this purpose by using HCl and NaOH solutions. This pH range was selected due to the hydrolysis reaction possibility of the metal ions out of this range. In this part of the study, maximum VI content was used in the formulation of PEGMA-VI microspheres as in all similar studies and the initial Ni(II) or Cr(VI) ion concentration was kept as 80 mg/L. The obtained adsorption rates were shown in Fig. 2 for both Ni(II) and Cr(VI) ions.

In the absence of metal complex formation agents, the metal ion concentration and soluble metal types played a very big role in the hydrolysis and precipitation reactions. The hydrolysis of Ni(II) ion is more clearly seen at the pH values higher than 8.5; and the change in the Ni(II) ion concentration shows that there is a pre-

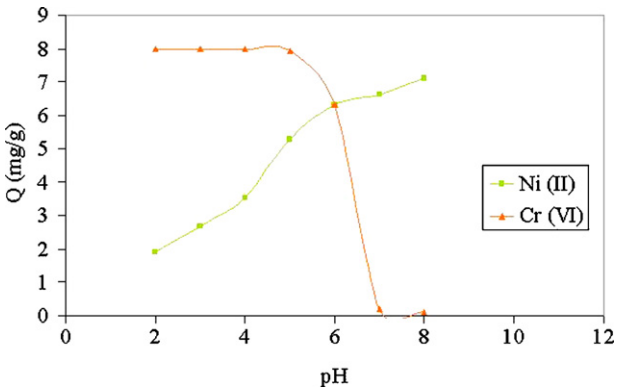

Fig. 2. The effect of medium pH over the Ni(II) and Cr(VI) ions adsorption.

cipitation tendency over pH 5 according to the experimental data. As seen in Fig. 2, Ni(II) ion adsorption ratio increased by increasing the medium pH up to 8 and the adsorption value reached to the plateau value as saturation. On the other hand, the adsorption values are really very low under extremely acidic and basic conditions [50]. This can be explained by the protonizing of larger amount of amine groups in the microsphere structure. After this stage, cationic repulsive forces can be available between the Ni ion species (i.e., Ni (II) and $NiNO_3^+$) and these protonated amine groups. The pH range of 6–8 seems very suitable for the Ni(II) ion removal from aqueous solutions and the maximum adsorption value is 7.5 mg Ni(II)/g PEGMA-VI microspheres at pH 8.

In the case of Cr(VI) ion adsorption studies, Cr(VI) adsorption value reached the saturation value after 120 min. During the investigation of the effects of adsorption medium pH; for the Cr(VI) ion adsorption values, all the Cr(VI) ions were adsorbed at the medium pH between 2 and 5, and the adsorbed Cr(VI) amount was 8.0 mg Cr(VI)/g PEGMA-VI microspheres. The higher adsorption rates for the Cr(VI) ions at lower pH values can be explained by the interactions between the adsorbent surface and the chromium species. The most active chromium species are $Cr_2O_7^{2-}$, $HCrO_4^-$ and CrO_4^{2-} at acidic conditions. Under these conditions, the surface charge of the adsorbent starts protonation and this affects the anionic chromium species, and in the case of higher zeta potential than that of the adsorbent surface, the electrostatic interactions between the adsorbent surface and the chromium species will decrease and hence the adsorption rate will also decrease [51]. As a result, the pH 2 was detected as the maximum Cr(VI) adsorption pH value and very similar results were also found in related literature [52–55].

3.3.2. Metal ion concentration

In this part of the study, the initial metal ion concentrations were changed to investigate the effects of the ion concentrations on their adsorption and removal with PEGMA-VI microparticles. Adsorption medium pH values were kept constant at pH 7 and pH 3 for the Ni(II) and Cr(VI) ions, respectively, as the maximum adsorption medium pH values, as expressed before. The initial metal ion concentration was increased up to certain values since at higher concentrations than these values the metal ions precipitated as their hydroxide forms. The obtained results for the effects of initial metal ion concentration on the adsorption rates were given in Figs. 3 and 4 for the Ni(II) and Cr(VI), respectively.

Fig. 3 represents the effects of initial Ni(II) ion concentration over the Ni(II) adsorption by PEGMA-VI microparticles. Actually the adsorption rate of Ni(II) ions increased and when the initial Ni(II) ion concentration reached to 800 mg/L then the Ni(II) ion adsorption value reached 45 mg/g adsorbent as a maximum rate as seen in Fig. 3. After this point the Ni(II) ions precipitated as its hydroxides.

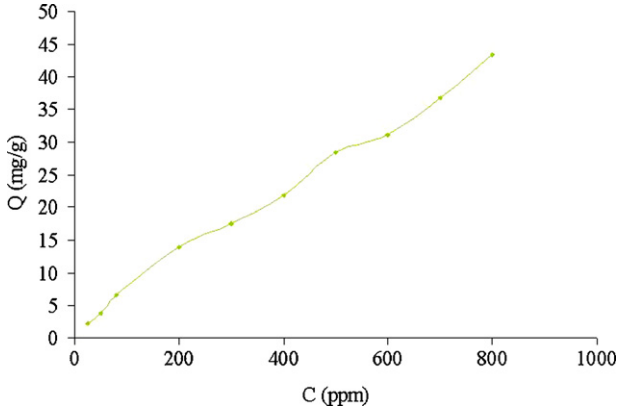

Fig. 3. The effect of initial metal ion concentration over the Ni(II) ions adsorption.

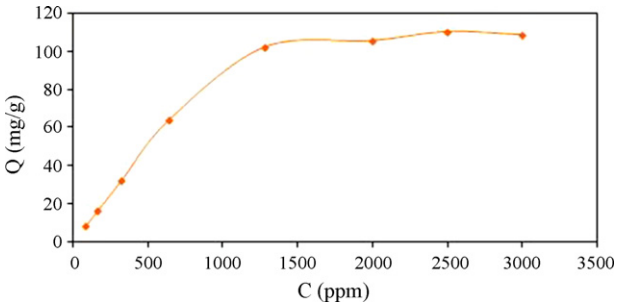

Fig. 4. The effect of initial metal ion concentration over the Cr(VI) ions adsorption.

Fig. 4 shows the effect of initial Cr(VI) ion concentration over the Cr(VI) adsorption by PEGMA-VI microparticles. Initially Cr(VI) adsorption rate increased by increasing the Cr(VI) ion concentration in the medium as expected and the adsorption rate reached to the constant value at an initial Cr(VI) ion concentration of 1280 mg/L. This can be speculated with the bonding site capacities of the PEGMA-VI microparticles for the Cr(VI) ions. This means that these sites were fully occupied with Cr(VI) ions at concentrations higher than 1280 mg/L. The adsorption capacity of the PEGMA-VI microparticles at this condition was found as 102.2 mg Cr(VI)/g PEGMA-VI microparticles and it was measured as 108.7 mg Cr(VI)/g PEGMA-VI microparticles when the initial Cr(VI) concentration increased up to the 3000 mg/L maximum adsorption capacity. On the other hand any hydrolysis reaction of Cr(VI) ions does not occur even in the case of very high Cr(VI) ion concentrations and this may be originated from the acidic adsorption conditions (i.e., pH 3).

In comparison of the obtained results with the related literature, it is also possible to find some other very active adsorbent systems prepared with different polymers for the removal of Ni(II) and Cr(VI) [41,56–61]. PEGMA-VI microspheres may be an additional new polymer, in this context, for the removal of Cu(II) ions, according to the results obtained in the previous study [1], and for the removal of Ni(II) and Cr(VI) ions, as found in the present study.

3.3.3. VI content of PEGMA-VI microspheres

Another effective parameter on the Ni(II) and Cr(VI) ions adsorption of PEGMA-VI microspheres was selected as the VI content of the microspheres due to the chelating characteristics of VI groups with metal ions. During the preparation of PEGMA-VI microspheres, 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 7, initial Ni(II) concentration was used as 800 mg Ni(II)/L for Ni(II) ions removal, and the conditions of pH 3 and initial Cr(VI) concentration of 1280 mg Cr(VI)/L were used for Cr(VI) ions removal. The obtained results were shown in Fig. 5. Both Ni(II) and Cr(VI) ions adsorption capacities increased by increasing the VI content of the microspheres as shown in this figure. Minimum adsorption was obtained with PEGMA microspheres (without VI groups) (i.e., 10 mg Ni(II)/g PEGMA microspheres and 2 mg Cr(VI)/g PEGMA microspheres) and maximum adsorption was achieved with PEGMA-VI microspheres (i.e., 45 mg Ni(II)/g PEGMA-VI microspheres and 108.7 mg Cr(VI)/g PEGMA-VI microspheres) with the highest VI content (i.e., 2 mL) as expected. These results showed that the VI content in PEGMA-VI microspheres is really very important for the adsorption of heavy metal ions for the removal studies and VI is a very good candidate as a ligand for this purpose.

3.4. Adsorption–desorption (reusability) studies

The production cost and reusability of the adsorbents are the most effective parameters for the sorbents in the waste

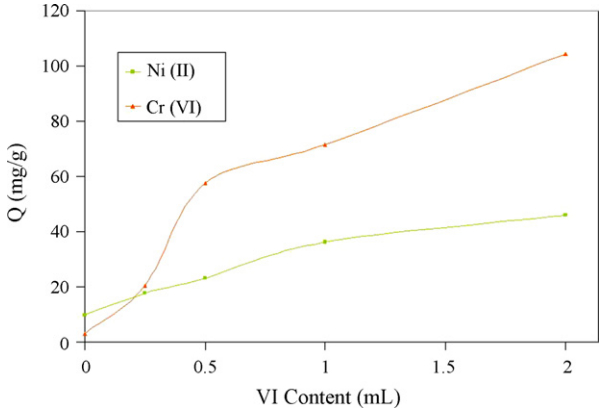

Fig. 5. The effect of VI content over the Ni(II) and Cr(VI) ions adsorption.

water treatment systems. Therefore reusability of the PEGMA-VI microparticles were also evaluated for the Ni(II) and Cr(VI) ions removal studies. During these studies, the optimized PEGMA-VI microparticle formulation and adsorption conditions (i.e., VI content, medium pH, initial ion concentration) which can provide maximum ions removal were used.

In this part of the study, the PEGMA-VI microspheres, adsorbed Ni(II) and Cr(VI) ions, were treated with a suitable solution (i.e., for Ni(II) ions with 0.1 M HNO_3 and for Cr(VI) ions with 0.2 M NaOH solutions) to remove the adsorbed Ni(II) and Cr(VI) ions for the investigation of reusability of the PEGMA-VI microspheres in these ions adsorption studies. This characteristic is very important for the economical perspective of the use of PEGMA-VI microspheres as an adsorbent for heavy metal removal. The adsorption medium pH was 7 and initial Ni(II) ion concentration was 800 mg Ni(II)/L for the Ni(II) ion studies while the pH was 3 and initial Cr(VI) ion concentration was 1280 mg Cr(VI)/L for the Cr(VI) ion studies; and the VI content of PEGMA-VI microspheres was 2 mL in all experiments in 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:

$$\text{desorption ratio} = \frac{\text{amount of desorbed Cu(II) ions into the desorption medium}}{\text{amount of adsorbed Cu(II) ions onto the PEGMA-VI microspheres}} \times 100 \quad (2)$$

Adsorption–desorption studies were replicated for five times and desorbed PEGMA-VI microspheres were washed with distilled

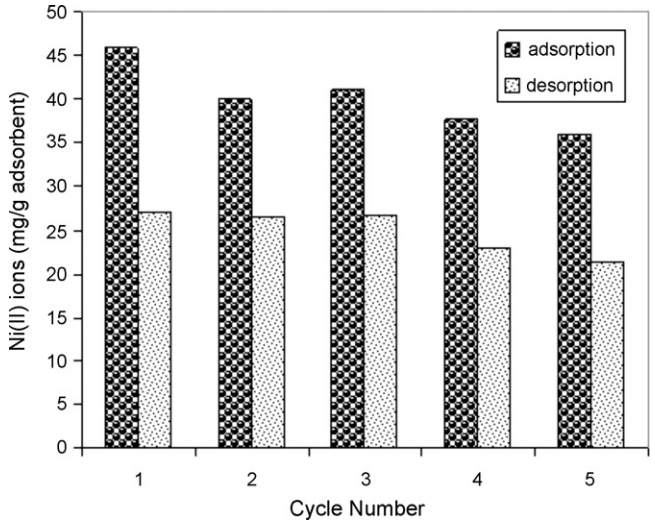

Fig. 6. Adsorption–desorption values for Ni(II) ions with PEGMA-VI microspheres.

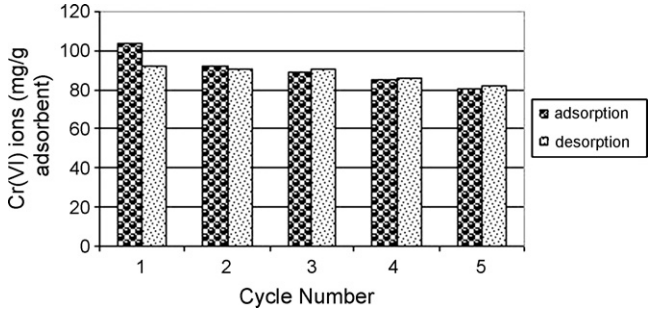

Fig. 7. Adsorption–desorption values for Cr(VI) ions with PEGMA-VI microspheres.

water before applying the following adsorption steps. The obtained results were shown in Figs. 6 and 7. As can be seen in both the figures, while the adsorption capacity for Ni(II) ions was approximately 45 mg/g adsorbent in the first step for the Ni(II) ions and 105 mg/g adsorbent for the Cr(VI) ions, these values decreased to approximately 36 mg/g adsorbent for the Ni(II) ions and 80 mg/g adsorbent for the Cr(VI) ions in the following steps. In spite of these decreases in the adsorption of both Ni(II) and Cr(VI) ions, no excessive changes were observed after the second step. Furthermore, almost all of the adsorbed Ni(II) and Cr(VI) ions could be removed from the microspheres according to the found desorption ratios.

3.5. Competitive adsorption studies for Cu(II), Ni(II) and Cr(VI) ions

In order to prepare mediums containing heavy metals all together, in other words, to simulate the real conditions, the adsorption studies for Cu(II), Ni(II) and Cr(VI) ions in the same medium were performed. In this part of the study, the concentrations of heavy metal ions and the pH of adsorption medium were kept constant as 80 mg/L and 5, respectively. The reason of the selection of this pH for adsorption studies is that 5 is the pH for maximum adsorption of Cu(II) and Cr(VI) while pH 8 is the optimum pH value for maximum adsorption of Ni(II) as discussed earlier. Because Ni(II) adsorption is not so different for pH 5 and 8, pH 5 was chosen as the pH of the adsorption medium. The volume of the adsorption medium, the amount of PEGMA-VI microspheres which were used as adsorbents and the adsorption duration were chosen as 25 mL, 0.25 g and 2 h, respectively. The stirring rate at which the earlier studies were performed was also applied for this part of the study. On the other hand, for the detection of the maximum metal ion adsorption of PEGMA-VI microspheres, the complexing agent specific to each metal ion and the wave length specific to these complexing agents were used. According to the obtained results, 7.90 mg of Cr(VI), 6.89 mg of Ni(II) and 4.71 mg of Cu(II) ions were adsorbed per gram of PEGMA-VI microspheres. PEGMA-VI microspheres were found to have the highest affinity for Cr(VI) ions and lower affinities for Ni(II) and Cu(II) ions, respectively.

4. Conclusions

Polyethyleneglycolmethacrylate-co-vinylimidazole (PEGMA-VI) microspheres were synthesized and characterized as a novel sorbent for heavy metal removal from aqueous media and Cu(II) ions were used as a model heavy metal to be removed in the previous study [1]. On the other hand, chromium (Cr(VI)) and nickel (Ni(II)) ions also have serious toxic effects [62,63]. Thus, PEGMA-VI microspheres were evaluated for the removal of

chromium, Cr(VI) and nickel, Ni(II) metal ions in the present study. The effects of the adsorption medium pH, initial concentration of the metal ions and VI content of PEGMA-VI microspheres were investigated as the effective parameters on the adsorption capacities of the PEGMA-VI microspheres. Increasing the pH value caused an increase in Ni(II) ion adsorption while it caused a decrease in Cr(VI) ion adsorption capacity. In the investigation of initial ion concentration and VI content as the effective parameters, it was found that the increase in both of them increased the adsorption of the metal ions. The maximum initial ion concentrations were 800 ppm and 1280 ppm for Ni(II) and Cr(VI), respectively, since the metal ions precipitated as their hydroxides in the case of higher concentrations. The maximum metal ion adsorption capacities (i.e., 45 mg Ni(II)/g PEGMA-VI microspheres and 108.7 mg Cr(VI)/g PEGMA-VI microspheres) were achieved with PEGMA-VI microspheres including the highest VI content (i.e., 2 mL), as expected. The minimum adsorption was obtained with PEGMA microspheres (without VI groups) (i.e., 10 mg Ni(II)/g PEGMA microspheres and 2 mg Cr(VI)/g PEGMA microspheres). These results showed that VI is a very good candidate as a ligand for the removal of toxic Cr(VI) and Ni(II) metal ions as Cu(II) ions. The PEGMA-VI microspheres have the highest affinity for Cr(VI) ions and lower affinities for Ni(II) and Cu(II) ions, respectively, according to the competitive adsorption studies. The reusability data of the PEGMA-VI microspheres seem quite well and promising for their use again and again many times in heavy metal removal with a high performance and removal capacity.

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