



Synthesis of Cr(VI)-imprinted poly(4-vinyl pyridine-co-hydroxyethyl methacrylate) particles: Its adsorption propensity to Cr(VI)

Gulay Bayramoglu*, M. Yakup Arica

Biochemical Processing and Biomaterial Research Laboratory, Faculty of Arts and Sciences, Gazi University, 06500 Ankara, Turkey

ARTICLE INFO

Article history:

Received 24 March 2010
Received in revised form 7 December 2010
Accepted 5 January 2011
Available online 13 January 2011

Keywords:

4-Vinyl pyridine
Ion-imprinted
Chromium anions
Selectivity coefficient
Heavy metal removal

ABSTRACT

The aim of this study is to prepare ion-imprinted polymers, which can be used for the selective removal of Cr(VI) anions from aqueous media. 4-Vinyl pyridine (4-VP) was used as functional monomer. The Cr(VI)-imprinted poly(4-vinyl pyridine-co-2-hydroxyethyl methacrylate), poly(VP-HEMA), particles were prepared by bulk polymerization. The Cr(VI)-imprinted polymer particles were gained from the bulk polymer, and the template ions (i.e., Cr(VI)) were removed using thiourea (0.5%, v/v) in 0.5 M HCl. The Cr(VI)-imprinted polymer contained 21.4 μmol 4-VP/g polymers. The specific surface area of the IIP2 particles was found to be 34.5 m^2/g (size range of 75–150 μm), and the swelling ratio was about to 108%. The effect of initial concentration of Cr(VI) anions, the adsorption rate and the pH of the medium on adsorption capacity of Cr(VI)-imprinting polymer were studied. The maximum experimental adsorption capacity was 3.31 mmol Cr(VI)/g polymer. Under competitive condition, the adsorption capacity of Cr(VI)-imprinted particles for Cr(VI) is 13.8 and 11.7 folds greater than that of the Cr(III) and Ni(II) ions, respectively. The first- and second order kinetics models were estimated on the basis of comparative analysis of the corresponding rate parameters, equilibrium capacity and correlation coefficients. The Langmuir adsorption isotherm model was well described the Cr(VI)-imprinted system and the maximum adsorption capacity (Q_{max}) was found to be 3.42 mmol/g. Moreover, the reusability of the poly(VP-HEMA) particles was tested for several times and no significant loss in adsorption capacity was observed.

© 2011 Elsevier B.V. All rights reserved.

1. Introduction

Molecular imprinting (MIP) technology is a strategy for producing chemically selective binding cavities on adsorbent surface, which recognize a particular molecule. In the process of molecular imprinting, a molecular template (print molecule) is used to direct the arrangement of the functional monomers around the template molecules, which are then chemically fixed by co-polymerization with a cross-linking monomer [1]. The molecular imprinting technique has been widely used in the separation and purification of various fine chemical and biological molecules [2–7]. Molecular recognition-based separation techniques have received much attention in environmental technology for removal of toxic heavy metal ions, because MIP adsorbents have high selectivity to their target metal ions. Ion-imprinted polymers (IIP) are similar to MIP, but they recognize metal ions after imprinting and retain all virtues of MIP [5,8,9]. In ion-imprinted polymer system, the selectivity of a polymeric adsorbent is based on the coordination geometry,

coordination number of the ions, on their charges and sizes [5,10,11].

Chromium has a wide range (–2 to +6, in rare cases –4 and –3 are reported) of possible oxidation states [12,13]. Two of them are stable (i.e., trivalent Cr(III) and hexavalent Cr(VI)) in the majority of terrestrial surface and aqueous environments [14–18]. All Cr(VI) species are highly soluble oxides (i.e., chromate (CrO_4^{2-}), hydrochromate (HCrO_4^-) and dichromate ($\text{Cr}_2\text{O}_7^{2-}$) anions) [19–23]. Cr(VI) anions species are strong oxidants, which act as carcinogens, mutagens and teratogens in biological systems [14,24]. The structural similarity of chromium Cr(VI) anions to biologically important inorganic anions, such as SO_4^{2-} and PO_4^{3-} , is likely responsible for their ability to readily transverse cell membranes, via the sulfate transport system. The incorporated Cr(VI) anion into cell can be oxidize biological molecules [25]. In contrast, the water-soluble Cr(III) species do not occur naturally and are unstable in the environment. Cr(III) exhibits solubility (around 10 μM) under very acidic ($\text{pH} \leq 5$) or very basic ($14 \geq \text{pH}$) conditions [26,27]. Therefore, Cr(III) ions have low toxicity due to their limited bio-availability and solubility. In contrast, the high solubility and bio-availability of Cr(VI) anions make it a particular environmental concern [28–35].

* Corresponding author. Tel.: +90 312 202 1142; fax: +90 312 212 2279.
E-mail address: g.bayramoglu@hotmail.com (G. Bayramoglu).

To date some studies have been done on complexing of 4-vinyl pyridine with various metal ions for ion imprinting technology [1,11,36–38] however, according to our knowledge, there is no reports about on Cr(VI) anions imprinted-polymer using 4-vinyl pyridine monomer. Herein, we aimed to prepare a Cr(VI) imprinted co-polymer from 4-vinyl pyridine (complexing monomer) and 2-hydroxyethyl methacrylate (co-monomer) to develop a product with high adsorption capacity and selectivity to Cr(VI) anions. The adsorption studies were carried out under different experimental conditions. The Langmuir isotherm model and thermodynamic parameters were used for the evaluation of binding parameters and elucidation of the nature and type of bonding exist between Cr(VI)-imprinted polymers and Cr(VI) anions.

2. Experimental

2.1. Materials

4-Vinyl pyridine (4-VP), 2-hydroxyethyl methacrylate (HEMA), ethyleneglycol dimethacrylate (EGDMA) and α - α' -azoisobisbutyronitrile (AIBN) were obtained from Fluka AG (Switzerland), and the monomers distilled under reduced pressure in the presence of hydroquinone and stored at 4 °C until use. All other chemicals were of analytical grade and were purchased from Merck AG (Darmstadt, Germany). The water (Milli-Q water) used in the following experiments was obtained from a Milli-Q system (Barnstead D2731 and D3804 units, Dubuque, IA, USA).

2.2. Preparation of Cr(VI)-anion imprinted polymers

4-Vinyl pyridine in water and isopropyl alcohol (1.0:1.0 ratio, v/v) solution was treated with Cr(VI) anions (1.0 M, 100 μ L) solution for 1.0 h at room temperature forming metal–monomer complex 4-VP–Cr(VI). After this period, it was slowly dropped into 2-HEMA and EGDMA monomers mixture containing 50 mg AIBN. Two different 4-VP:HEMA:EGDMA ratios were used for preparation of Cr(VI) imprinted-polymers [i.e., (0.1:1.9:1.0 (IIP1) and 0.3:1.7:1.0 (IIP2) (v/v/v)], respectively. The resulting polymerization mixture was equilibrated in a waterbath at 25 °C for 15 min, and was purged with nitrogen for 10 min. This mixture was distributed into cylindrical moulds and sealed which were exposed to a long-wave UV radiation for 2 h. After polymerization, the cylindrical rods with imprinted-polymer were washed with Milli-Q water several times. Ion-imprinted polymers were grained from the bulk polymers in a mortar. In order to remove unreacted monomers and other ingredients, the grained imprinted particles were extensively washed with ethanol/water mixture (70/30, v/v) for 6 h at room temperature. After cleaning, the template metal ions were removed from the polymer particles in acidified thiourea solution (0.5% thiourea in 0.5 M HCl) for 24 h at 25 °C under magnetic stirring. The non-imprinted poly(4-VP-HEMA) compositions were synthesized in a similar way but in absence of template molecule (i.e., Cr(VI)). The poly(4-VP-HEMA) particles were stored at 4 °C until use. The IIP2 composition has a high adsorption capacity and more sensitive to Cr(VI) anions compared to IIP1 polymer formulation, therefore, the rest of the study was carried out with IIP2 formulation.

2.3. Characterization of poly(VP-HEMA) particles

The average size and size distribution of the Cr(VI)-imprinted particles were determined by using molecular sieves, and 75–150 μ m mesh size was used. The specific surface area of the particles was measured by a surface area apparatus and calculated using the BET (Brunauer, Emmett and Teller) method.

The swelling ratios of both imprinted and non-imprinted polymeric particles were determined in Milli-Q water by using a gravimetric method. The water ratio was defined as the weight ratio of water contained within swollen to dry particles. The swelling ratio of the particles was calculated by using the following expression:

$$\text{Swelling ratio (\%)} = \frac{(W_s - W_d)}{W_d} 100 \quad (1)$$

where W_d and W_s are the dry and swollen weights of particles, respectively.

The surface morphology of the particles was examined using scanning electron microscope (SEM/EDX) (JEOL, JMS 5600, Tokyo, Japan) after coating with thin layer gold under reduced pressure. The samples were scanned at a desired magnification to study the morphology of the imprinted and non-imprinted particles. The Cr(VI) unleached and leached particles were analyzed using a SEM/electron diffraction X-rays (EDX) analyzer. To evaluate the degree of 4-VP incorporation in imprinted and non-imprinted polymer particles, they were subjected to elemental analysis using a Leco Elemental Analyzer (Model CHNS-932). The FTIR spectra of imprinted and non-imprinted polymer particles were obtained using a FTIR spectrophotometer (Shimadzu, FTIR 8000 Series, Japan).

2.4. Adsorption/desorption/reuse

2.4.1. Adsorption studies

The adsorption of Cr(VI) anions from aqueous solution on the imprinted and non-imprinted polymeric particles was investigated in a batch system. A stock solution (1000 mg/L) of chromate anions was obtained by dissolving dried potassium dichromate in Milli-Q water. The different concentrations of Cr(VI) anions were prepared from stock solution. To determine the effect of initial concentration of Cr(VI) anions on the adsorption rate and capacity on the adsorbent, the initial concentrations of Cr(VI) anions were varied between 20 and 400 mg/L in the medium. Diphenylcarbazide (DiPC) method, a colorimetric method was used for determination of chromium anions. This colorimetric method can be used for the determination of Cr(VI) anions in natural and industrial water in the range of 100–1000 μ g/L. In this method for the determination of total chromium content, all the chromium was converted in to hexavalent state by oxidation with potassium permanganate. Effects of the medium pH, adsorbent dosage and the initial Cr(VI) anions concentrations on the adsorption capacities of the tested adsorbents were studied. The effect of the medium pH on the adsorption capacity of the Cr(VI)-imprinted and non-imprinted particles was investigated in the pH range 2.0–8.0 (which was adjusted with H₂SO₄ or NaOH at the beginning of the experiment and not controlled afterwards) at 25 °C. In a typical adsorption experiment, a 100 mg particle was transferred into the adsorption medium containing Cr(VI) anions (200 mg/L) and agitated magnetically at 200 rpm. The concentration of remaining Cr(VI) anions in the adsorption medium was determined at 540 nm using a double beam UV–vis spectrophotometer (PG Instrument Ltd., Model T80+; PRC) after complexation with 1,5 diphenyl carbazide [39]. Before determination of the total quantity of Cr(VI) in the adsorption medium, Cr(III) and Cr(II) were converted to Cr(VI) using KMnO₄ [14,34]. For each set of data present, standard statistical methods were used to determine the mean values and standard deviations. To ensure the accuracy, reliability, and reproducibility of the collected data, all the batch experiments were carried out in duplicate and the mean values of two data sets are presented. The Cr(VI) removal efficiency for all types of adsorbents was within the range of \pm 2.0%. When the relative error exceeded this criterion, the data were disregarded and a third experiment

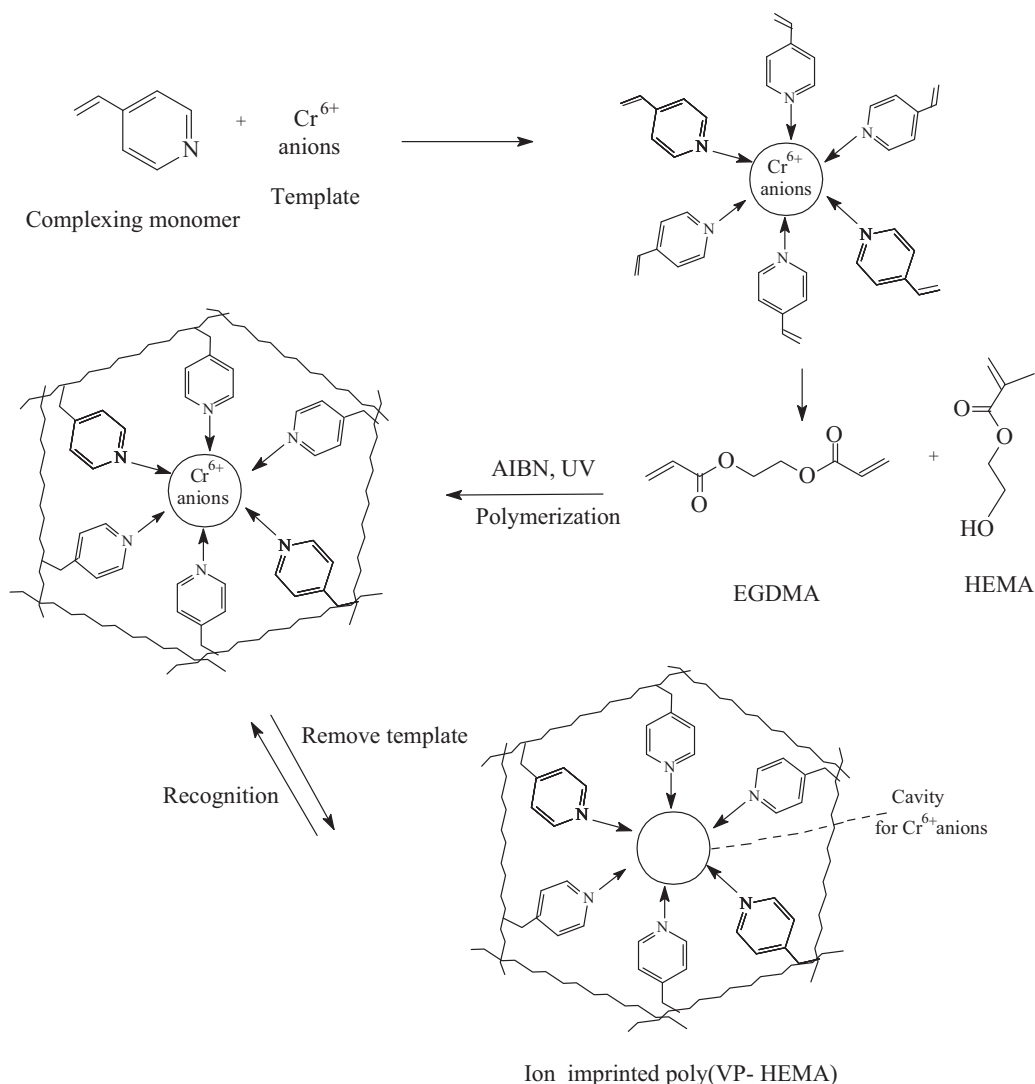


Fig. 1. Schematic representation of complexation of polymer with Cr(VI) anions.

was conducted until the relative error fell within an acceptable range.

The amount of adsorbed Cr(VI) anions per unit ion-imprinted and non-imprinted polymers (mmol metal ions/g dry polymer) was obtained by using the following expression:

$$Q = \frac{[(C_0 - C)V]}{m} \quad (2)$$

where Q is the amount of Cr(VI) anions adsorbed onto the polymeric particles (mmol/g); C_0 and C are the concentrations of the Cr(VI) anions in the initial solution (mmol/L) and after adsorption, respectively; V is the volume of the aqueous phase (L) and m is the amount of polymer (g). Each experiment was repeated three times and results given are the average values.

The selectivity of the poly(VP-HEMA)-Cr(VI) particles towards Cr(VI) ions (ionic radius: 44 pm) in the presence of competitive ions Cr(III) (ionic radius: 75.5 pm) and/or Ni(II) (ionic radius: 69 pm) was evaluated in a batch system. A solution (100 mL) containing 200 mg/L Cr(VI) anions and 50 mg/L Cr(III) or Ni(II) ions was contacted with IIP2 and non-imprinted particles at pH 4.0 and at 25 °C. The adsorption medium was stirred magnetically at 400 rpm. After adsorption equilibrium, the concentration of chromium ions in the remaining solution was measured as described above. The concentration of Ni(II) ions in the remaining solution was also measured by flame atomic absorption spectrophotometer.

2.4.2. Desorption and reuse

Adsorbed Cr(VI) anions were desorbed from adsorbent by treatment with 0.1 M formic acid solution. IIP2 polymeric particles were placed in the desorption medium and stirred continuously at 400 rpm at 25 °C for 2 h. The final Cr(VI) anions concentration in aqueous phase was determined as described above. In order to determine the reusability of IIP2 polymer consecutive adsorption-desorption cycles were repeated six times by using the same particles. The desorption ratio was calculated from the amount of Cr(VI) ions adsorbed on the imprinted-polymer particles and the final Cr(VI) anions concentration in the adsorption medium. Desorption ratio was calculated from the following equation:

$$\text{Desorption ratio (\%)} = \frac{(\text{Cr(VI)desorbed}) \times 100}{(\text{Cr(VI)adsorbed})} \quad (3)$$

3. Result and discussion

3.1. Characterization studies

The 4-vinyl pyridine monomer was used as complexing monomer due to the presence of pyridine group, which has a high affinity to metal ions. The 4-VP-Cr(VI) monomer complex was copolymerized with HEMA (co-monomer) and EGDMA (cross-linker) via UV induced radical polymerization. The molecular formula of

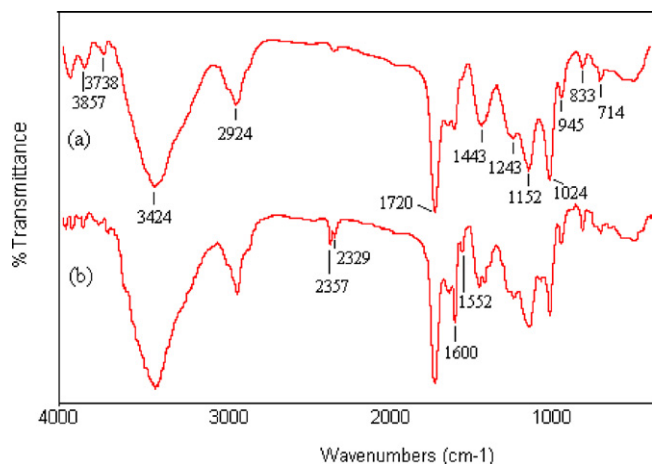


Fig. 2. The FTIR spectra of (A) non-imprinted poly(VP-HEMA) and (B) imprinted poly(VP-HEMA)-Cr(VI) particles.

Cr(VI)-imprinted polymer is schematically presented in Fig. 1. In order to confirm complex formation between Cr(VI) anions and 4-pyridine groups of the polymer, FTIR spectroscopy was performed (Fig. 2). The broad band at 3300–3500 cm^{-1} ranges indicates –OH stretching vibrations in the structure of the acrylic polymers (i.e., HEMA and EGDMA). Two peaks at $\sim 2924\text{ cm}^{-1}$ and 1720 cm^{-1} belong to characteristic group frequencies for methylene vibration and ester configurations in HEMA/EGDMA, respectively. The adsorption bands at 2357 cm^{-1} representing vibration of aromatic rings (i.e., 4-VP) after Cr(VI) anions complexation (Fig. 2B). The peaks at 1552 cm^{-1} are belong to pyridine ring of both Cr(VI)-imprinted and non-imprinted polymers. In the IR spectra of the Cr(VI) imprinted polymer, a new band was observed at 1600 cm^{-1} and this band was assigned the characteristic stretching vibration of pyridine groups absorption after complexation of Cr(VI) anions. As seen in these spectra Cr(VI) anions were complexed with 4-vinyl pyridine (the main complexing groups in the polymer structure).

The synthesized Cr(VI)-imprinted and non-imprinted particles were characterized using scanning electron microscopy (SEM) in order to know the surface morphological image of Cr(VI)-imprinted and non-imprinted particles (Fig. 3 A–C). The general appearance of Cr(VI)-imprinted particle at $100\times$ is presented in Fig. 3A. The surface SEM images of Cr(VI)-imprinted and non-imprinted particles were also obtained at $5000\times$ magnification to compare of surface properties of Cr(VI)-IIP and non-imprinted. The SEM images are presented in Fig. 3B and C, respectively. From figures, the polymer with chromium metal ions (Fig. 3B) is found to be entirely different than that of non-imprinted polymer (Fig. 3C), the Cr(VI)-imprinted polymer is exhibiting patterned surface with pores that may be due to the presence of Cr(VI) ions in the polymer structure. On the other hand, the SEM image of non-imprinted polymer has a rough surface with no pores (Fig. 3C). As reported earlier, the addition of salt of metals to the polymerization medium results in a multi-phase separation during polymerization that produces porous in the matrices [40–46]. Thus, a porous polymer with patterned surface is obtained by addition of Cr(VI) ions compared to polymer contains no metal ions.

The electron diffraction X-rays (EDX) spectra of Cr(VI) unleached and leached IIP2 particles are presented in Fig. 4 confirms the presence of chromium in both unleached and leached polymer particles. During extraction, the template molecule (i.e., Cr(VI) ions on and close to the polymer surface were easily extracted, but those in the bulk were inaccessible. Approximately 20% of the Cr(VI) template was not leached from the Cr(VI) ions imprinted polymer particles.

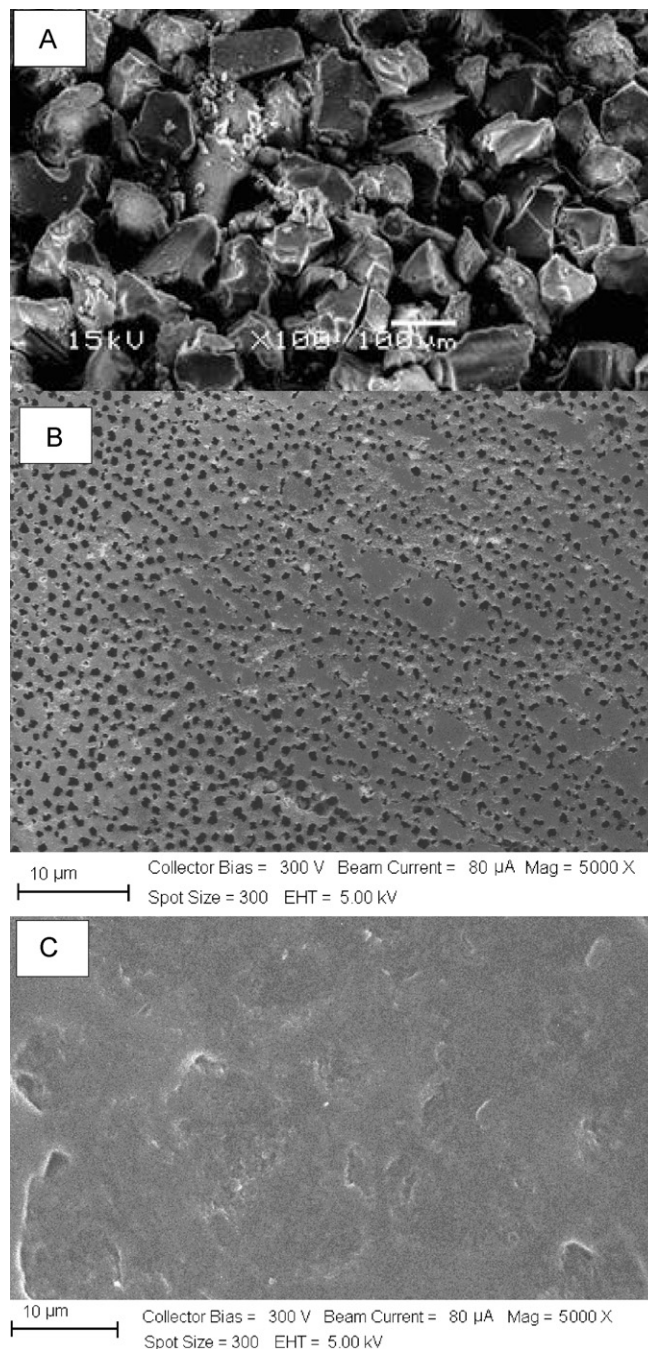


Fig. 3. SEM photographs of (A) Cr(VI)-imprinted particles at $100\times$ magnification and (B) poly(VP-HEMA)-Cr(VI) particles at $5000\times$ magnification; (C) non-imprinted particles at $5000\times$ magnification.

The 4-VP content of Cr(VI)-imprinted and non-imprinted particles were found to be $21.4\ \mu\text{mol g}^{-1}$ and $18.3\ \mu\text{mol g}^{-1}$ polymers, respectively, by using nitrogen stoichiometry. The swelling ratio was about 108% for Cr(VI)-imprinted particles, which swell more, compared to non-imprinted particles (89%). It can be due to the presence of Cr(VI) micro-cavities in the Cr(VI)-imprinted polymer particles formed during polymerization with Cr(VI) anions. The specific surface area ($34.5\ \text{m}^2\ \text{g}^{-1}$) of the Cr(VI)-imprinted polymer particles was higher than that of the non-imprinted particles ($21.7\ \text{m}^2\ \text{g}^{-1}$), which can also indicate the presence of microporous on the surface of the Cr(VI)-imprinted particles.

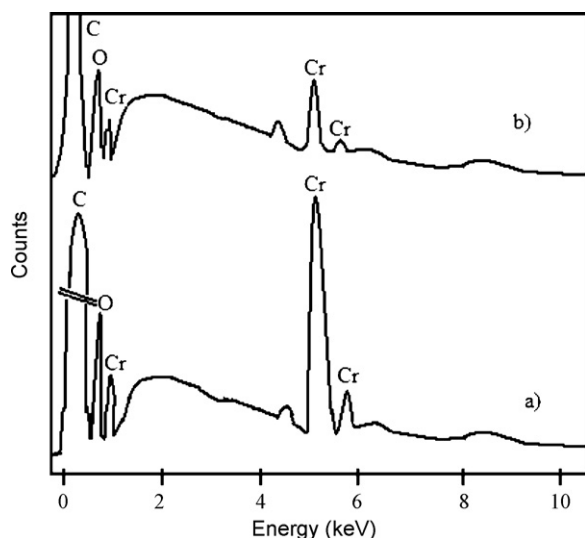


Fig. 4. EDX spectra of IIP2 particle: (a) Cr(VI) unleached and (b) Cr(VI) leached.

3.2. Adsorption of Cr(VI) anions on the polymer preparations

3.2.1. Effect of pH

The binding affinity of poly(4-VP-HEMA) particles is highly dependent on pH of the medium, thus, the polymer pH of the solution is another important parameter for the adsorption process [29,43,44]. The effect of pH on Cr(VI) adsorption was determined on the Cr(VI)-imprinted and non-imprinted particles for different pH values ranging from 2.0 to 8.0, using a 200 mg/L Cr(VI) solution (Fig. 5). As can be seen in this figure the Cr(VI) binding capacity decreased with increasing pH for all the tested adsorbent. At high acidic pH 2.0–4.0, adsorption was very high and decreased rapidly after pH 5.0 for IIP1, IIP2 and non-imprinted polymer particles. This can be due to protonation of the functional pyridine groups on the adsorbents whereas the ion-imprinted adsorbents were more sensitive to medium pH change for binding Cr(VI) anions than that of the non-imprinted counterpart.

The variation in equilibrium pH with IIP2 and non-imprinted particles were measured with 400 mg/L Cr(VI) concentration at pH 4.0. The equilibrium pH was found to increase from 4.00 to 4.08 after 48 h contact time. This indicates that there is no significant change in the final value of solution pH.

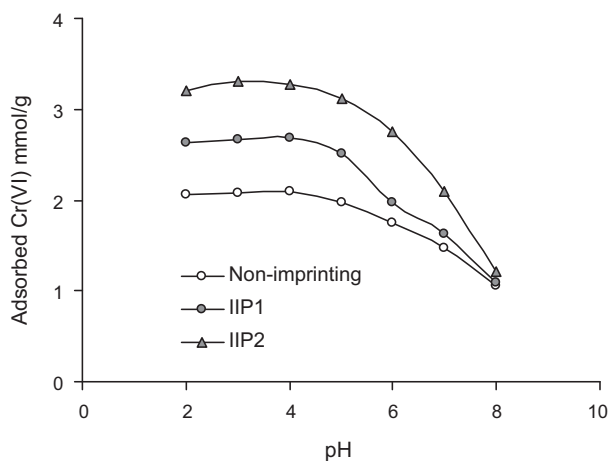


Fig. 5. Effect of pH on Cr(VI) anions adsorption using IIP1, IIP2 and non-imprinting particles. Experimental conditions: initial concentration of Cr(VI) anions: 200 mg/L; temperature: 25 °C.

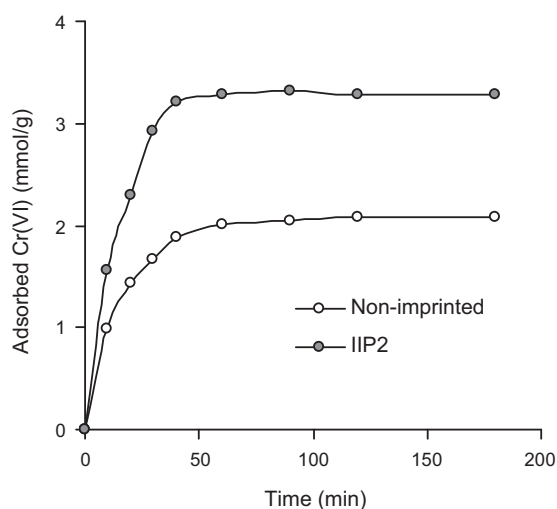


Fig. 6. Experimental adsorption rates of Cr(VI) anions on the IIP2 and non-imprinting particles; pH: 4.0, T: 25 °C.

3.2.2. Adsorption rate

Time dependence of Cr(VI) adsorption from aqueous solutions onto the Cr(VI)-imprinted and non-imprinted particles from aqueous solutions was studied. Fig. 6 shows adsorption rates of Cr(VI) anions onto both Cr(VI)-imprinted and non-imprinted particles from aqueous solutions containing 200 mg/L of Cr(VI) anions at a constant pH of 4.0. High adsorption rate was observed at the beginning of adsorption process, and then saturation value (i.e., adsorption equilibrium) was gradually reached within first 40 min. Adsorption of Cr(VI) was quite fast, and this fast adsorption equilibrium time was most probably due to high complexation rate (i.e., high affinity) between Cr(VI) anions and template groups on the polymer structure. As seen from Fig. 6, the experimental Cr(VI) anions adsorption curve was very steep compared to non-imprinted counterpart. This equilibrium can most probably be due to geometric shape memory between Cr(VI) anions and imprinted polymer structure [3,37]. Several experimental data on the adsorption of various ions by molecularly imprinted polymers have shown a wide range of adsorption rates. For example, Hoai et al., have investigated adsorption of copper ions on the copper(II) ion-imprinted porous particles, which were prepared two functional monomers, methacrylic acid and vinyl pyridine and found 120 min equilibrium adsorption time [10]. Singh and Mishra used a novel ion-imprinted polymer, phenol-formaldehyde-Cd(II)-2-(p-sulphophenyl azo)-1,8-dihydroxy naphthalene-3,6-disulphonate for selective solid phase extraction of Cd(II) from aqueous solutions. They reported that the adsorption equilibrium was gradually reached within 50 min [9]. Liu et al. used methylmercury-imprinted polymers for determination of methylmercury, and equilibrium time was 40 min [11]. Dakova et al., have studied adsorption of mercury via the ion-imprinted polymethacrylic acid microbeads for preconcentration and speciation of mercury and reported 10 min equilibrium adsorption time [3].

3.2.3. Adsorption capacity

Fig. 7 shows the effects of initial concentration of metal ions onto the adsorption capacity of the Cr(VI) anions both imprinted (i.e., IIP1 and IIP2) and non-imprinted poly(4-VP-HEMA) particles at pH 4.0. The amount of Cr(VI) anions adsorbed per unit mass of the Cr(VI)-imprinted polymers (i.e., adsorption capacities) increased with the initial concentration of Cr(VI) ions. The maximum experimental adsorption (corresponding to a 200 ppm Cr(VI) anions), which represents saturation of binding sides on both ion-imprinted (i.e., IIP1 and IIP2) and non-imprinted polymers were 2.69, 3.31

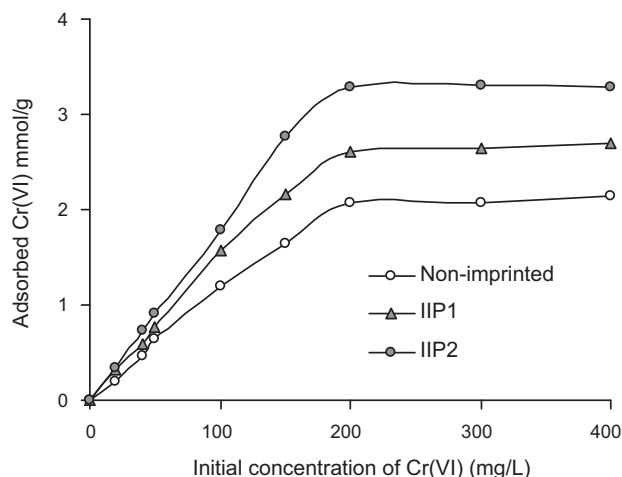


Fig. 7. Experimental adsorption capacity of Cr(VI) anions on the IIP1, IIP2 and non-imprinting particles. Experimental conditions: initial concentration of Cr(VI) anions: 200 mg/L; pH: 4.0, T : 25 °C.

and 2.14 mmol Cr(VI)/g polymer, respectively. The high adsorption equilibrium capacity for imprinted particles is most probably due to high complexation and geometric affinity between Cr(VI) ions and specific Cr(VI) binding cavities on the polymer structure.

A number of attempts have been made to modify different natural and synthetic polymers to increase their adsorption capacity for Cr(VI) ions. To justify viability of the presented study for removal of Cr(VI) ions as an effective adsorbent, the adsorption capacity of IIP2 particles need to be compared to that of other adsorbents. Comparative studies can be made in terms of Cr(VI) removal capacity (mmol/g polymer), optimum pH, and the initial concentration of Cr(VI) used (mg/L). The adsorption capacity some of these modified adsorbents is presented in Table 1. The Cr(VI)-imprinted significantly enhances its Cr-loading capacity compared to other adsorbents. Like other adsorbents, the optimum pH range of Cr(VI)-imprinted particle for effective Cr(VI) adsorption lies in acidic pH range between 2.0 and 4.0

Adsorption isotherm was used to evaluate adsorption properties of the system. The Langmuir model was found to be applicable in interpreting Cr(VI) ions adsorption on both imprinted and non-imprinted adsorbents. Fig. 8 shows the dependence of the equilibrium concentration on the adsorbed amount of Cr(VI) anions onto both imprinted and non-imprinted poly(4-VP-HEMA) particles. The Langmuir adsorption isotherm is expressed by Eq. (4). Langmuir adsorption model assumes that the molecules are adsorbed at a fixed number of well-defined sites, each of which can only hold one molecule [34,45]. The corresponding transformations of the equilibrium data for Cr(VI) anions on the tested adsorbents gave rise to a linear plot, indicating that the Langmuir model could

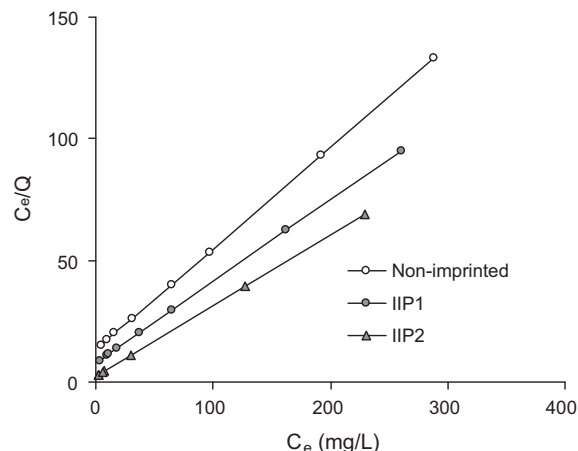


Fig. 8. Langmuir isotherm for adsorption of Cr(VI) anions on the IIP1, IIP2 and non-imprinting particles.

Table 2

Langmuir constants and correlation coefficients for adsorption of Cr(VI) anions adsorption using the non-imprinted and ion-imprinted poly(4-VP-HEMA) particles.

	Q_{exp} (mmol/g)	Q_{max} (mmol/g)	b (L/mmol)	R^2
Non-imprinted	2.14	2.39	1.66	0.994
IIP1	2.69	2.94	2.26	0.996
IIP2	3.31	3.42	6.72	0.998

be applied in these systems and described by the equation:

$$Q = \frac{(Q_{\text{max}} b C_e)}{(1 + b C_e)} \quad (4)$$

where Q is the amount of adsorbed Cr(VI) ions on the adsorbents (mmol/g), C_e the equilibrium Cr(VI) anions concentration in solution (mmol/L), b the Langmuir constant (L/mmol) and Q_{max} is the maximum adsorption capacity (mmol/g). Fig. 8 and Table 2 show the equilibrium isotherm plots and isotherm model parameters determined with the Langmuir isotherm model, respectively. It was observed that the Langmuir model can be applied all the tested particles for adsorption of Cr(VI) anions with high correlation coefficients. The Langmuir adsorption capacities (Q_{max} values) for Cr(VI)-imprinted (i.e., IIP1 and IIP2) and non-imprinted particles were 2.94, 3.42 and 2.39 mmol/g, respectively) those are closest to the experimental values (Q_{exp} , 2.69, 3.31 and 2.14 mmol/g for Cr(VI)-imprinted IIP1, IIP2 and non-imprinted particles, respectively) as presented in Table 2.

Eq. (5) was used to fit the experimental data and change in standard free energy of adsorption (ΔG°) was then determined by:

$$\Delta G^\circ = -RT \ln K_a \quad (5)$$

Table 1

Adsorption capacities of different adsorbents for Cr(VI) ions from batch studies.

Adsorbent	Q_{max} (mmol/g)	pH	Initial Cr(VI) concentration (mg/L)	Reference
Poly(ethyleneglycol methacrylate/vinyl imidazole)	2.09	3.0	1280	[18]
Ethylenediamine grafted poly(GMA/MMA)	0.44	2.0	600	[21]
Ethylene diamine modified starch	0.18	4.0	24	[22]
Amino-functionalized GMA	2.11	1.8	2600	[29]
PEI immobilized acrylate based magnetic beads	2.0	2.64	600	[30]
IIP imprinted chitosan cross-linked with epichlorohydrin	0.98	5.5	1000	[31]
IIP chitosan	0.98	5.5	1000	[31]
Ethylene diamine functionalized magnetic polymer	1.19	2.5	150	[32]
Aniline formaldehyde coated silica gel	1.25	2.0	200	[33]
Chitosan coated on perlite	2.95	4.0	5000	[34]
IIP 4-VP/HEMA	3.31	4.0	200	Present study

Table 3

The first and second order kinetics constants of the experimental data for Cr(VI) anions adsorption on the non-imprinted and ion-imprinted poly(VP-HEMA) particles.

	Experimental		First order kinetic		Second order kinetic		
	$Q_{eq, ex}$ (mmol/g)	$k_1 \times 10^2$ (min ⁻¹)	Q_{eq} (mmol/g)	R^2	$k_2 \times 10^1$ (g/mmol min)	Q_{eq} (mmol/g)	R^2
Non-imprinting	2.14	3.71	0.80	0.963	1.42	2.27	0.996
Cr(VI)-imprinting	3.31	4.08	0.87	0.906	1.72	3.53	0.990

the values of ΔG° calculated from K_a ($K_a = b$) by using Eq. (5). The negative values of ΔG° -18.37 and -21.83 kJ/mol indicate that the adsorption of Cr(VI) anions on the Cr(VI)-imprinted and non-imprinted are feasible and spontaneous, respectively [46]. The free energy of the interactions demonstrated that the processes are favorable for the formation of electrostatic interaction. In general, up to -20 kJ/mol are consistent with electrostatic interaction between charged molecules and surface indicative of physical adsorption while more negative than -40 kJ/mol involve chemical adsorption. The order of magnitude of the values indicates a strong physical adsorption mechanism for the Cr(VI) ions on both particles.

In order to examine the controlling mechanism of adsorption process, pseudo-first- and second-order kinetic models were used to test experimental data [46–48]. As seen in Table 3, the theoretical Q values estimated from second-order kinetic model are closer to the experimental values for both adsorbents with high correlation coefficients. So, the results suggested that the second-order adsorption mechanism is predominant for both IIP2 and non-imprinted particles (Fig. 9).

3.3. Selectivity studies

Adsorption capacities of Cr(VI)-imprinted and non-imprinted particles in the presence of competitive ions such as Cr(VI)/Cr(III) and Cr(VI)/Ni(II) was studied in a batch system and the results are presented in Table 4. The Cr(VI) adsorption capacity of the Cr(VI)-imprinted particles was much higher than that of Cr(III) ions. When they exist in the same medium, a competition will start for the same attachment sites. It should be noted that the ion-imprinted particles showed excellent selectivity for the target molecule (i.e., Cr(VI) anions) due to the presence of specific cavities on imprinted particles. The adsorption capacity of IIP2 particles for Cr(VI) anions is 13.8 and 11.7 fold greater than those of the Cr(III) and Ni(II) ions, respectively.

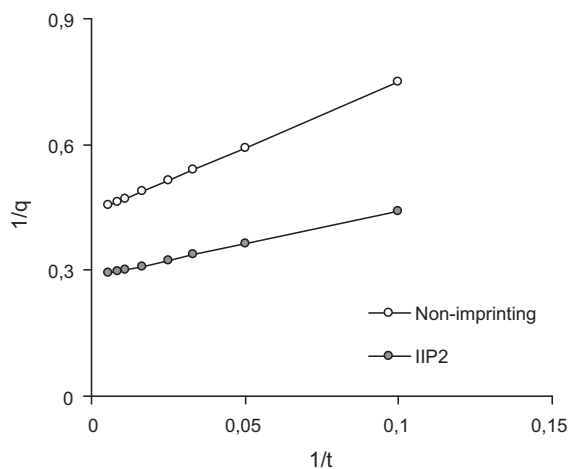


Fig. 9. The pseudo-second order plot for adsorption of Cr(VI) anions on the IIP2 and non-imprinting particles.

Table 4

Competitive adsorption of Cr(VI)/Cr(III) and Cr(VI)/Ni(II) ions on the Cr(VI)-imprinted and non-imprinted particles.

Ions	Adsorption capacity (mmol/g)	
	Cr(VI)-imprinted particles	Non-imprinted particles
Cr(VI)	3.31	2.14
Cr(III)	0.24	0.87
Cr(VI)	3.15	1.90
Ni(II)	0.27	0.79

Distribution and selectivity coefficients of Cr(VI) with respect to Cr(III) were calculated as explained below [49]:

$$K_d = \frac{C_i - C_f}{C_f} (V/m) \quad (6)$$

where K_d , C_i and C_f represent the distribution coefficient, initial and final solution concentrations (mg/L), respectively, V and m are the volume of the solution (L) and the mass of the particles (g). The selectivity coefficient for the binding of an ion in the presence of competitor species can be obtained from equilibrium data according to Eq. (7):

$$k = \frac{K_d (\text{template metal})}{K_d (\text{interferent metal})} \quad (7)$$

where k is the selectivity coefficient of interfering metal (i.e., Cr(III) ions). A comparison of the k values of the imprinted polymer with those of metal ions allows an estimation of the effect of imprinting on selectivity. In order to evaluate an imprinting effect, a relative selectivity coefficient k' was defined as follows [8,49]:

$$k' = \frac{k_{\text{imprinted}}}{k_{\text{non-imprinted}}} \quad (8)$$

The relative selectivity coefficient (k') resulting from the comparison of the k values of the anions imprinted particles with non-imprinted particles allows an estimation of the effect of imprinting on selectivity. The K_d and k values of ion-imprinted particles are significantly larger in comparison to the Cr(VI)-imprinted particles. The relative selectivity coefficients of imprinted poly(VP-HEMA) particles for Cr(VI)/Cr(III) and Cr(VI)/Ni(II) were almost 21.4 and 14.0 times greater than that of non-imprinted (poly(VP-HEMA)) particles, respectively (Table 5). This means that Cr(VI) anions can be selectively removed from aqueous medium even in the presence of Cr(III) and/or Ni(II) ions.

Table 5

The selectivity coefficient (k) and the relative selectivity coefficient (k') values for the particles.

Ions	Cr(VI)-imprinted particles		Non imprinted particles		k'
	K_d (L/g)	k	K_d (L/g)	k	
Cr(VI)	6.170	–	1.25	–	–
Cr(III)	0.067	92.09	0.29	4.31	21.37
Cr(VI)	4.532	–	0.98	–	–
Ni(II)	0.086	52.69	0.26	3.77	13.98

3.4. Desorption and repeated use

Desorption of the adsorbed Cr(VI) anions from the imprinted particles was also studied in a batch experimental system. Various factors are probably involved in determining rates of Cr(VI) desorption, such as the extent of hydration of the metal ions and polymer microstructure. However, an important factor appears to be binding strength. When formic acid was used as a desorption agent, the coordination sphere of chelated Cr(VI) anions is disrupted and subsequently Cr(VI) anions are released from the Cr(VI)-templates into desorption medium. In order to show the reusability of the ion-imprinted particles, adsorption–desorption cycle was repeated 6 times by using the same imprinted particles. The results showed that the Cr(VI) imprinted particles could be used many times without significant decrease in their adsorption capacity to Cr(VI) anions.

3.5. Removal of Cr(VI) from artificial waste-water

The effectiveness of IIP2 particles for removal of Cr(VI) from synthetic waste water was examined. Cr(VI) concentration was 10 mg/L were prepared by diluting appropriate amounts from the stock solution. The measurements were repeated for three times. It was found that the recovered Cr(VI) from artificial waste-water was about to 9.33 ± 0.26 mg/L. The presence of 5 fold excess of Cr(III), Ni(II) and Cd(II) over Cr(VI) does not affect the adsorption capacity of the IIP2 particles. It was found that removal of Cr(VI) from artificial wastewater was effectively performed without any significant interferences from other metal ions commonly present in waste-water.

4. Conclusions

Molecular imprinting is a rapidly evolving technique to prepare synthetic receptors. They are easy to prepare, stable, inexpensive and capable of molecular recognition. In this study, Cr(VI)-imprinted polymer was prepared using 4-vinyl pyridine as a complexing monomer, and it was used for the selective removal of Cr(VI) anions from aqueous solutions under different experimental conditions. The results show that the poly(4-VP-HEMA) particles in the size range of 75–150 μm have bulky rough surface and macropores within the bulk structure. The adsorption rate was found to be relatively fast. The time required to reach equilibrium conditions was around 40 min, suggesting that the fast adsorption equilibrium reached is most probably due to a high binding affinity between Cr(VI) and its binding sites on the polymer structure. The adsorption values increased with increasing initial concentration of Cr(VI) anions, and a saturation value is achieved at ions concentration of 200 mg/L, which represents saturation of the active binding cavities on the poly(4-VP-HEMA) polymers. It can be used in the presence of competitive ions such as Cr(III) and Ni(II) with a high selectivity. Also, it was observed that Cr(VI)-imprinted particles can be used several times without loss in adsorption capacity. Finally, the results showed that MIP particles designed for Cr(VI) removal have high selectivity to its target metal ion.

[40,41].

References

- [1] L. Ye, K. Mosbach, The technique of molecular imprinting – principle, state of the art, and future aspects, *J. Inclusion Phenom. Macromol.* 41 (2001) 107–113.
- [2] X. Li, S.M. Husson, Adsorption of dansylated amino acids on molecularly imprinted surfaces: a surface plasmon resonance study, *Biosens. Bioelectron.* 22 (2006) 336–348.
- [3] I. Dakova, I. Karadjova, V. Georgieva, G. Georgiev, Ion-imprinted poly-methacrylic microbeads as new sorbent for preconcentration and speciation of mercury, *Talanta* 78 (2009) 523–529.
- [4] X. Chen, Z. Yang, S. Si, Potentiometric urea biosensor based on immobilization of urease onto molecularly imprinted TiO₂ film, *J. Electroanal. Chem.* 635 (2009) 1–6.
- [5] H. Su, J. Li, T. Tan, Adsorption mechanism for imprinted ion (Ni²⁺) of the surface molecular imprinting adsorbent (SMIA), *Biochem. Eng. J.* 39 (2008) 503–509.
- [6] S. Muk Ng, R. Narayanaswamy, Fluorescence sensor using a molecularly imprinted polymer as a recognition receptor for the detection of aluminum ions in aqueous media, *Anal. Bioanal. Chem.* 386 (2006) 1235–1244.
- [7] Y. Lu, C.-L. Yan, S.-Y. Gao, Preparation and recognition of surface molecularly imprinted core-shell microbeads for protein in aqueous solutions, *Appl. Surf. Sci.* 255 (2009) 6061–6066.
- [8] K. Araki, T. Maruyama, N. Kamiya, M. Goto, Metal ion-selective membrane prepared by surface molecular imprinting, *J. Chromatogr. B* 818 (2005) 141–145.
- [9] D.K. Singh, S. Mishra, Synthesis, characterization and removal of Cd(II) using Cd(II)-ion imprinted polymer, *J. Hazard. Mater.* 164 (2009) 1547–1551.
- [10] N.T. Hoai, D.-K. Yoo, D. Kim, Batch and column separation characteristics of copper-imprinted porous polymer micro-beads synthesized by a direct imprinting method, *J. Hazard. Mater.* 173 (2010) 462–467.
- [11] Y. Liu, Y. Zai, X. Chang, Y. Guo, S. Meng, F. Feng, Highly selective determination of methylmercury with methylmercury-imprinted polymers, *Anal. Chim. Acta* 575 (2006) 159–165.
- [12] N.N. Greenwood, A. Earnshaw, *Chemistry of the Elements*, Butterworth Heinemann, Oxford, 1998, pp. 1002–1039.
- [13] K. Srividya, K. Mohanty, Biosorption of hexavalent chromium from aqueous solutions by *Catla catla* scales: equilibrium and kinetics studies, *Chem. Eng. J.* 155 (2009) 666–673.
- [14] M.Y. Arica, G. Bayramoglu, Cr(VI) biosorption from aqueous solution using free and immobilized biomass of *Lentinus sajor-caju*: preparation and kinetic characterization, *Colloids Surf. A* 253 (2005) 203–211.
- [15] I. Narin, Y. Surme, M. Soylak, M. Dogan, Speciation of Cr(III) and Cr(VI) in environmental samples by solid phase extraction on Amberorb 563 resin, *J. Hazard. Mater.* 136 (2006) 579–584.
- [16] Y. Khambhaty, K. Mody, S. Basha, B. Jha, Kinetics, equilibrium and thermodynamic studies on biosorption of hexavalent chromium by dead fungal biomass of marine *Aspergillus niger*, *Chem. Eng. J.* 145 (2009) 489–495.
- [17] Z. Aksu, S. Ertugrul, G. Donmez, Single and binary chromium(VI) and Remazol Black B biosorption properties of *Phormidium* sp., *J. Hazard. Mater.* 168 (2009) 310–318.
- [18] E. Uğuzdoğan, E.B. Denkbaş, O.S. Kabasakal, The use of polyethyleneglycol-methacrylate-co-vinylimidazole (PEGMA-co-VI) microspheres for the removal of nickel(II) and chromium(VI) ions, *J. Hazard. Mater.* 177 (2010) 119–125.
- [19] I. Narin, A. Kars, M. Soylak, A novel solid phase extraction procedure on Amberlite XAD-1180 for speciation of Cr(III), Cr(VI) and total chromium in environmental and pharmaceutical samples, *J. Hazard. Mater.* 150 (2008) 453–458.
- [20] S. Bellu, S. Garcia, J.C. Gonzalez, A.M. Atria, L.F. Sala, S. Signorella, Removal of chromium(VI) and chromium(III) from aqueous solution by grainless stalk of corn, *Sep. Sci. Technol.* 43 (2008) 3200–3220.
- [21] G. Bayramoglu, M.Y. Arica, Ethylenediamine grafted poly(glycidylmethacrylate-co-methylmethacrylate) adsorbent for removal of chromate anions, *Sep. Purif. Technol.* 45 (2005) 192–199.
- [22] R.M. Cheng, S.J. Ou, B. Xiang, Y.J. Li, Q.Q. Liao, Adsorption behavior of hexavalent chromium on synthesized ethylenediamine modified starch, *J. Polym. Res.* 16 (2009) 703–708.
- [23] D. Park, Y.-S. Yun, H.W. Lee, J.M. Park, Advanced kinetic model of the Cr(VI) removal by biomaterials, at various pHs and temperatures, *Bioresour. Technol.* 99 (2008) 1141–1147.
- [24] G. Bayramoglu, G. Celik, E. Yalcin, M. Yilmaz, M.Y. Arica, Modification of surface properties of *Lentinus sajor-caju* mycelia by physical and chemical methods: evaluation of their Cr⁶⁺ removal efficiencies from aqueous medium, *J. Hazard. Mater.* 119 (2005) 219–229.
- [25] R. Codd, C.T. Dillon, A. Levina, P.A. Lay, Studies on the genotoxicity of chromium: from the test tube to the cell, *Coord. Chem. Rev.* 537 (2001) 216–217.
- [26] D.E. Kimbrough, Y. Cohen, A.M. Winer, L. Creelman, C. Mabuni, A critical assessment of chromium in the environment, *Crit. Rev. Environ. Sci. Technol.* 29 (1999) 1–46.
- [27] D. Rai, L.E. Eary, J.M. Zachara, Environmental chemistry of chromium, *Sci. Total Environ.* 86 (1989) 15–23.
- [28] B. Kiran, A. Kaushik, C.P. Kaushik, Response surface methodological approach for optimizing removal of Cr(VI) from aqueous solution using immobilized cyanobacterium, *Chem. Eng. J.* 126 (2007) 147–153.
- [29] A. Nastasovic, Z. Sandic, Lj. Surucic, D. Maksin, D. Jakovljevic, A. Onjia, Kinetics of hexavalent chromium sorption on amino-functionalized macroporous glycidyl methacrylate copolymer, *J. Hazard. Mater.* 171 (2009) 153–159.
- [30] G. Bayramoglu, M.Y. Arica, Adsorption of Cr(VI) onto PEI immobilized acrylate based magnetic beads: isotherms, kinetics and thermodynamics study, *Chem. Eng. J.* 139 (2008) 20–28.
- [31] T. Tan, X. He, W. Du, Adsorption behavior of metal ions on imprinted chitosan resins, *J. Chem. Technol. Biotechnol.* 76 (2001) 191–195.
- [32] Y.-G. Zhao, H.-Y. Shen, S.-D. Pan, M.-Q. Hu, Synthesis, characterization and properties of ethylenediamine-functionalized Fe₃O₄ magnetic polymers for removal of Cr(VI) in wastewater, *J. Hazard. Mater.* 182 (2010) 295–302.

- [33] P.A. Kumar, M. Ray, S. Chakraborty, Hexavalent chromium removal from wastewater using aniline formaldehyde condensate coated silica gel, *J. Hazard. Mater.* 143 (2007) 24–32.
- [34] S. Hasan, A. Krishnaiah, T.K. Ghosh, D.S. Viswanath, V.M. Boddu, E.D. Smith, Adsorption of chromium(VI) on chitosan-coated perlite, *Sep. Sci. Technol.* 38 (2003) 3775–3793.
- [35] Y.B. Xu, X.J. Duan, J.N. Yan, S.Y. Sun, Influence of magnetic field on Cr(VI) adsorption capability of given anaerobic sludge, *Biodegradation* 21 (2010) 1–10.
- [36] H. Bessbousse, T. Rhlalou, J.F. Verchere, L. Lebrun, Novel metal-complexing membrane containing poly(4-vinylpyridine) for removal of Hg(II) from aqueous solution, *J. Phys. Chem. B* 113 (2009) 8588–8598.
- [37] M. Khajeh, Y. Yamini, E. Ghasemi, J. Fasihi, M. Shamsipur, Imprinted polymer particles for selenium uptake: synthesis, characterization and analytical applications, *Anal. Chim. Acta* 581 (2007) 208–213.
- [38] A. Duran, M. Soylak, S.A. Tuncel, Poly(vinyl pyridine-ethylene glycol methacrylate-ethylene glycol dimethacrylate) beads for heavy metal removal, *J. Hazard. Mater.* 155 (2008) 114–120.
- [39] Standard Methods for the Examination of Water, in: APHA, AWA, WEF, 20th edition, 1998.
- [40] A. Baghel, M. Boopathi, B. Singh, P. Pandey, T.H. Mahato, P.K. Gutch, K. Sekhar, Synthesis and characterization of metal ion imprinted nano-porous polymer for the selective recognition of copper, *Biosens. Bioelectron.* 22 (2007) 3326–3334.
- [41] Q. Liu, E.L. Hedberg, Z. Liu, R. Bahulekar, R.K. Meszlenyi, A.G. Mikos, Preparation of macroporous poly(2-hydroxyethyl methacrylate) hydrogels by enhanced phase separation, *Biomaterials* 21 (2000) 2163–2169.
- [42] M.Y. Arica, V. Hasirc, Permeability of pHEMA membranes prepared by photoinitiation, *Polym. Int.* 32 (1993) 177–182.
- [43] S. Tunali Akar, A. Gorgulu, B. Anilan, Z. Kaynak, T. Akar, Investigation of the biosorption characteristics of lead(II) ions onto *Symphoricarpus albus*: batch and dynamic flow studies, *J. Hazard. Mater.* 165 (2009) 126–133.
- [44] G. Bayramoglu, M.Y. Arica, Removal of heavy mercury(II), cadmium(II) and zinc(II) metal ions by live and heat inactivated *Lentinus edodes* pellets, *Chem. Eng. J.* 143 (2008) 133–140.
- [45] I. Langmuir, The adsorption of gases on plane surfaces of glass, mica and platinum, *J. Am. Chem. Soc.* 40 (1918) 1361–1403.
- [46] G. Bayramoglu, B. Altintas, M.Y. Arica, Adsorption kinetics and thermodynamic parameters of cationic dyes from aqueous solutions by using a new strong cation-exchange resin, *Chem. Eng. J.* 152 (2009) 339–346.
- [47] S. Lagergren, Zur theorie der sogenannten adsorption gelöster stoffe, *Kungliga Svenska Vetenskapsakademiens Handlingar* 24 (1898) 1–39.
- [48] A.G. Ritchie, Alternative to the Elovich equation for kinetic of adsorption of gases on solids, *J. Chem. Soc., Faraday Trans.* 73 (1977) 1650–1657.
- [49] W. Kuchen, J. Schram, Metal-ion selective exchange resins by matrix imprint with methacrylates, *Angew. Chem. Int. Ed. Engl.* 27 (1988) 1695–1697.