J Incl Phenom Macrocycl Chem (2012) 73:449–458
DOI 10.1007/s10847-011-0083-7

ORIGINAL ARTICLE

Immobilization of novel the semicarbazone derivatives of calix[4]arene onto magnetite nanoparticles for removal of Cr(VI) ion

Enise Akoz · Serkan Erdemir · Mustafa Yilmaz

Received: 13 January 2011 / Accepted: 1 November 2011 / Published online: 22 November 2011

Abstract A series of novel the semicarbazone derivatives of calix[4]arene have been synthesized and then immobilized onto amino functionalized magnetic nanoparticles. Magnetic Fe_3O_4 nanoparticles were prepared by the chemical co-precipitation of Fe(III) and Fe(II) ions and the nanoparticles were modified directly by 3-aminopropyltriethoxy silane (APTES) to introduce reactive amine groups onto the particles' surface. The characterization of the prepared compounds was made by FT-IR, elemental analysis, TGA/DTG and NMR techniques. The sorption properties of the new calix[4]arene based magnetic sorbents toward Cr(VI) ion were also studied. The results showed that the prepared magnetic nanoparticles were effective sorbents for the removal of Cr(VI) ion. Also, Langmuir and Freundlich isotherm models were applied for Cr(VI) ion sorption by using MN-C2 and it was found that the experimental data confirmed to Langmiur isotherm model.

Keywords Calix[4]arene · Nanoparticle · Semicarbazone · Extraction · Anion

Introduction

Anions play a number of fundamental roles in biological and chemical processes and the development of selective synthetic anion receptors is an area of current importance. The use of anions as nucleophiles, bases, redox-active agents and phase-transfer catalysts has led to a desire for receptors which enable stabilisation and separation through co-ordination. The increasing problem of environmental anion pollutants, such as phosphate, chromate and nitrate, which lead to eutrophication, and radioactive pertechnetate, a product of the nuclear fuel cycle, is also an area of concern [1]. Chromate and dichromate anions are important because of their high toxicity and because of their presence in soils and waters. In designing complexants for these particular guest anions a number of structural features can be incorporated into the host molecule that may be important in achieving selective binding. For such a molecule to be effective as a host it is necessary that its structural features are compatible with those of the guest anion. The chromate and dichromate (CrO_4^{2-} and $Cr_2O_7^{2-}$) ions are dianions with oxide functionalities at their periphery. Since the metal center does not bind to additional ligands there is no advantage in designing a host that can act as a complexant to it. Nevertheless, since the periphery of the anions has oxide moieties; these are potential sites for hydrogen bonding to the host molecule [2–4]. Conventional techniques for removing metal ions from wastewater include chemical precipitation, membrane separation, reverse osmosis, evaporation and electrochemical treatment, and solvent extraction. Among them, solvent extraction is one of the most commonly used treatment methods and employs a selective complexant especially for ions in aqueous solution. Although there are numerous examples of molecules that act as hosts and complexants for cations, relatively fewer molecules have been reported as hosts for anions [5, 6] Thus, the development of efficient extractants for anions has received considerable attention in recent years [7].

Calixarenes have generated considerable interest as useful building blocks for the synthesis of receptors for cations, anions and neutral molecules. A variety of calix[4]arene-based receptors that possess unusually shaped cavities have been prepared via ''upper'' and ''lower'' rim

E. Akoz · S. Erdemir · M. Yilmaz (✉)
Department of Chemistry, Selcuk University, 42031 Konya, Turkey
e-mail: myilmaz42@yahoo.com

functionalization [8]. The complexation properties of these molecules appear to be highly dependent upon the nature, number of donor groups, and the conformation of the calix[4]arene moiety [9]. It is known that calix[4]arenes can exist in the conformations cone, partial cone, 1,2-alternate, and 1,3-alternate [10]. The available sites on these macrocyclic compounds can be easily modified to tailor them for many applications such as ionophores in catalysis, as carriers in liquid membrane technology, heavy metal adsorption agents, as alkali metal complexation agents, as extractants for chromium (VI) and as chemical sensors [11–13]. Generally two strategies have been adopted to enhance the affinity of calixarenes toward metal ions and anions. Either different ionophoric groups including carbonyl, amide, nitrile and other suitable functionalities have been incorporated onto the calix-platform, or the calixarene units have been fixed in a polymeric matrix [14–19].

In recent years, superparamagnetic nanoparticles of iron oxides have shown great potential applications in many biological fields, including bioseparation [20, 21], tumor hyperthermia [22], magnetic resonance imaging (MRI) diagnostic contrast agents [23], magnetically guided site-specific drug delivery agents [24], and biomolecules immobilization [25, 26]. The application for biomolecules immobilization is mainly based on the solid-phase magnetic feature which is able to achieve a rapidly easy separation and recovery from the reaction medium in an external magnetic field. Recently, we have synthesized various derivatives of calix[4]arene and immobilized upon magnetic nanoparticles and investigated to their extraction abilities towards Cr(VI) ion [27–29]. In present study, we have been synthesized to a series of novel the semicarbazone derivatives of calix[4]arene and then immobilized onto amino functionalized magnetic nanoparticles. The prepared new calix[4]aren based magnetic nanoparticles were used as sorbent in removing of Cr(VI) ion from waters.

Experimental

Materials and methods

Analytical TLC was performed on precoated silica gel plates (SiO_2, Merck PF254), while silica gel 60 (Merck, particle size 0.040–0.063 mm, 230–240 mesh) was used for preparative column chromatography. Generally, solvents were dried by storage over molecular sieves (Aldrich; 4 Å, 8–12 Mesh). Dichloromethane was distilled from $CaCl_2$. MeOH was distilled from Mg and stored over molecular sieves. All chemicals were purchased from Merck and Fluka and employed without further purification. All aqueous solutions were prepared with deionized water that had been passed through a Millipore Milli-Q Plus water purification system. ^{1}H-NMR and ^{13}C-NMR spectra were recorded on a Varian 400 MHz spectrometer in $CDCl_3$ and FT-IR spectra were recorded on a Perkin Elmer Spectrum 100. UV–vis spectra were obtained on a Shimadzu 160A UV–visible recording. Melting points were determined on an Electrothermal 9100 apparatus in a sealed capillary and are uncorrected. Thermal gravimetric analysis (TGA) was carried out with Seteram thermogravimetric analyzer. The sample weight was 15–17 mg. Analysis was performed from room temperature to 900 °C at heating rate of 10 °C/min in argon atmosphere with a gas flow rate of 20 mL/min.

Synthesis

Preparation of Fe_3O_4 and APTES modified Fe_3O_4 nanoparticles

Magnetic Fe_3O_4 nanoparticles were prepared by the chemical co-precipitation of Fe(III) and Fe(II) ions and the nanoparticles were modified directly by 3-aminopropyltriethoxy silane (APTES) to introduce reactive amine groups onto the particles' surface according to literature [27].

Synthesis of calix[4]arene semicarbazone derivatives

Compounds **1** (*p*-*tert*-butylcalix[4]arene), **2** and **3** were prepared according to known previous procedures [30–32]. The syntheses of compounds **4**, **5** and **6** and their immobilization onto magnetic nanoparticles as illustrated in Figs. 1 and 2 have been carried out as follows.

To a solution of **3** (0.7 g, 0.95 mmol) in $CHCl_3$ (50 mL) was added a solution of appropriate semicarbazide (1.20 mmol) in MeOH (20 mL) and refluxed for 24 h. The reaction mixture was allowed to cool to room temperature and filtered. Evaporation of the solvent and subsequent purification of the mixture by recrystallization from $CHCl_3$/MeOH afforded pure **4–6**.

Compound **4**: Yield 58% (0.55 g); mp: 261–272 °C; FT-IR: 1760 (C=O) cm^{-1}, 1670 (NC=O) cm^{-1}, 1644 (C=N) cm^{-1}; ^{1}H NMR ($CDCl_3$): δ 0.98 (s, 18H, $C(CH_3)_3$), 3.42 (d, 4H, $J = 13.1$ Hz, $ArCH_2Ar$), 3.86 (s, 6H, OCH_3), 4.41 (d, 4H, $J = 13.1$ Hz, $ArCH_2Ar$), 4.72 (s, 4H, OCH_2), 6.84 (s, 4H, ArH), 7.45–7.55 (m, 10H, ArH), 7.67 (s, 2H, Ar-OH), 7.84 (s, 4H, ArH), 8.14 (s, 2H, CHN), 8.97 (s, 2H, NHCO). Anal. Calcd for $C_{58}H_{60}N_4O_{10}$: C, 71.6%; H, 6.17%; N, 5.76. Found: C, 71.44%; H, 6.02%; N, 5.62%.

Compound **5**: Yield 47% (0.45 g); mp: 198–205 °C; FT-IR: 1760 (C=O) cm^{-1}, 1675 (NC=O) cm^{-1}, 1645 (C=N) cm^{-1}; ^{1}H NMR ($CDCl_3$): δ 1.02 (s, 18H, $C(CH_3)_3$), 3.38 (d, 4H, $J = 13.3$ Hz, $ArCH_2Ar$), 3.78 (s, 6H, OCH_3), 4.36 (d, 4H, $J = 13.3$ Hz, $ArCH_2Ar$), 4.75 (s, 4H, OCH_2), 6.94 (t, 2H, $J = 8.0$ Hz, ArH), 6.96 (s, 4H, ArH), 7.18 (t, 4H, $J = 8.0$ Hz, ArH), 7.31(s, 4H, ArH), 7.47 (d, 4H,

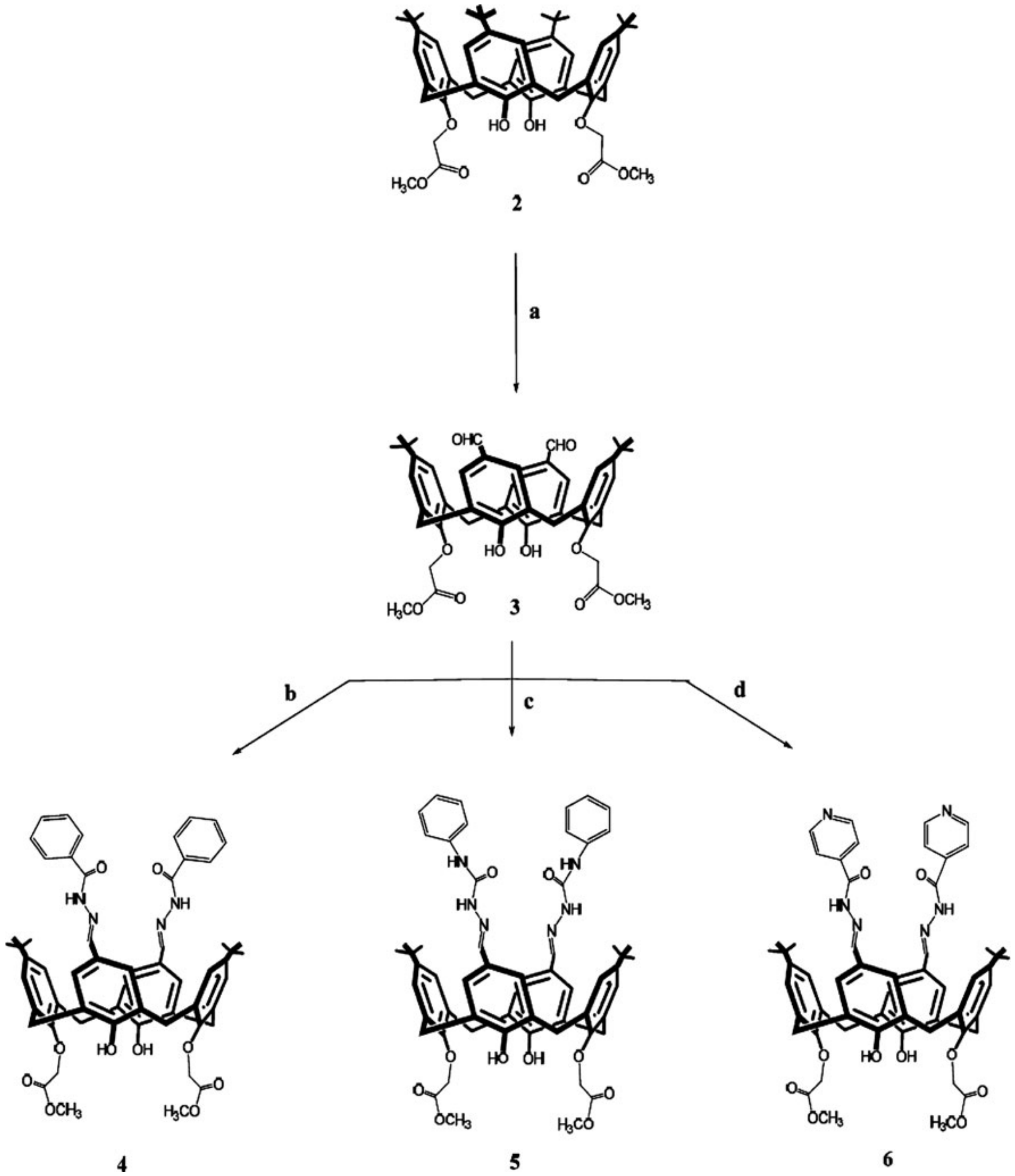


Fig. 1 Synthesis of the semicarbazone derivatives of calix[4]arene; (*a*) TFA, HMTA (hexamethylenetetramine), reflux, 24 h, yield 82%; (*b*) benzhydrazide; (*c*) 4-phenylsemicarbazide; (*d*) isoniazide

$J = 8.0$ Hz, ArH), 7.68 (s, 2H, Ar-OH), 7.97 (s, 2H, CHN), 8.25 (s, 2H, Ar*NH*CO), 10.14 (s, 2H, CO*NH*N). Anal. Calcd for $C_{58}H_{62}N_6O_{10}$: C, 69.46%; H, 6.18%; N, 8.38. Found: C, 69.38%; H, 6.22%; N, 8.26%.

Compound **6**: Yield 47% (0.45 g); mp: 198–205 °C; FT-IR: 1760 (C=O) cm^{-1}, 1675 (NC=O) cm^{-1}, 1645 (C=N) cm^{-1}; ^{1}H NMR ($CDCl_3$): δ 0.91 (s, 18H, $C(CH_3)_3$), 3.37 (d, 4H, $J = 13.3$ Hz, ArCH_2Ar), 3.77 (s, 6H, OCH_3), 4.32 (d, 4H, $J = 13.3$ Hz, ArCH_2Ar), 4.66 (s, 4H, OCH_2), 6.78 (s, 4H, ArH), 7.46 (s, 4H, ArH), 7.74–7.77 (m, 6H, ArH, Ar-OH), 8.23 (s, 2H, CHN), 8.05 (m, 4H, ArH), 11.50 (s, 2H, Ar NHCO). Anal. Calcd for $C_{56}H_{58}N_6O_{10}$: C, 68.98%; H, 6.00%; N, 8.62. Found: C, 69.02%; H, 5.88%; N, 8.30%.

*Immobilization of compounds **4**, **5** and **6** onto magnetic nanoparticles*

Compound **4**, **5** or **6** (0.3 g) was dissolved in 1:1 toluene/MeOH mixture (60 mL) and 0.6 g of amino functionalized magnetic nanoparticles (APTES-MN) was added to the

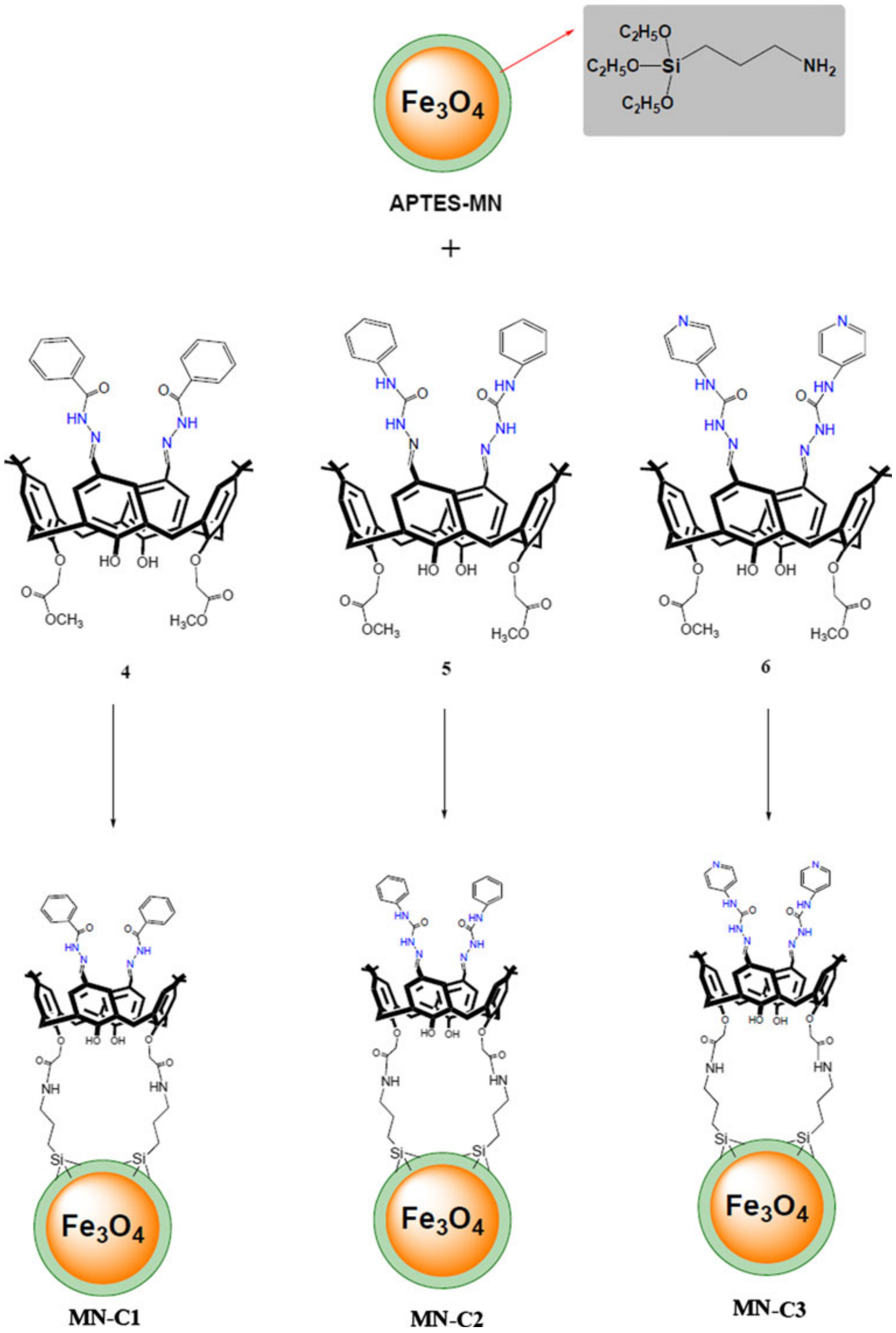


Fig. 2 Immobilization of the semicarbazone derivatives of calix[4]arene onto magnetic nanoparticles

solution. The mixture was refluxed with continuous stirring for about 72 h. After magnetic separation, the resulting compounds (MN-C1, MN-C2 and MN-C3) was washed three times with toluene, dichloromethane, and methanol in turn and dried at 80 °C under vacuum.

Sorption procedure

The sorption capacities of the synthesized calix[4]arene-grafted nanoparticles for Cr(VI) ion were determined by the following techniques [27, 33]:

Cr(VI) ion sorption

25 mg of the sorbent was mixed with 10 mL of an aqueous solution of the sodium dichromate (concentration 1×10^{-4} M) in a stopped flask that was shaken at 175 rpm, 30 °C. The sorbent was removed by magnetic separation before measurements. The residual concentration of aqueous solute was determined spectrophotometrically by UV–vis analyses. The experiments were performed in triplicate. The effect of pH was studied by adjusting the pH of dichromate solutions using diluted HCl and NaOH solutions at 30 °C.

$$(E\%) = \frac{A_o - A}{A_o}$$

The percentage sorption (E %) was calculated [34] from the absorbance (A) of the aqueous phases according to the above equation.

Results and discussion

Preparation and characterization of new calix[4]arene-grafted magnetic nanoparticles

The main focus of this work is the design of new semicarbazone derivatives of calix[4]arene grafted magnetic nanoparticles and evaluation of its extraction properties towards Cr(VI) ion. Firstly, the syntheses of compounds **2** and **3** were carried out according to the previously published procedures [31, 32]. Then, the prepared aldehyde pointed calix[4]arene derivative (**3**) was converted to the semicarbazone derivatives of calix[4]arene (**4**, **5** and **6**) by using 4-phenylsemicarbazide, benzhydrazide and isoniazide in CH_3Cl/MeOH media and the synthetic route is presented in Fig. 1. The ^{1}H-NMR analyses confirmed to the syntheses of compound **4**, **5** and **6** by the appearance of imine protons (CH=N) at 8.14, 7.97 and 8.23, respectively and the disappearance of aldehyde protons belong to compound **3**. In addition, compound **4**, **5** and **6** were characterized as being in the cone conformation at room temperature by the presence of two doublets ($J = 13.1$–13.3 Hz) in their ^{1}H-NMR spectra for the bridging methylenes at ~3.39 and 4.36 ppm. Magnetic Fe_3O_4 nanoparticles were prepared by the chemical co-precipitation of Fe(III) and Fe(II) ions. Then, the nanoparticles were modified directly by 3-aminopropyltriethoxysilane (APTES) to introduce reactive groups onto the particles' surface and semicarbazone derivatives of calix[4]arene (**4**, **5** and **6**) were grafted onto modified nanoparticles by surface (Fig. 2). The characterization of the prepared calix[4]arene based magnetic nanoparticles was made by FT-IR and thermal analysis.

Thermal properties of APTES-modified Fe_3O_4 (APTES-MN) and immobilized calix[4]arene magnetite nanoparticles (MN-C1, MN-C2 and MN-C3) were analyzed by thermogravimetric method. The indication of the coating formation on the magnetic nanoparticles' surface can be obtained from TGA measurement. Figure 3 shows TGA curves of APTES-MN, MN-C1, MN-C2 and MN-C3 magnetic nanoparticles. The total losses temperature range of 25–900 °C are 4.7, 15.1, 21.5 and 13.2% for APTES-

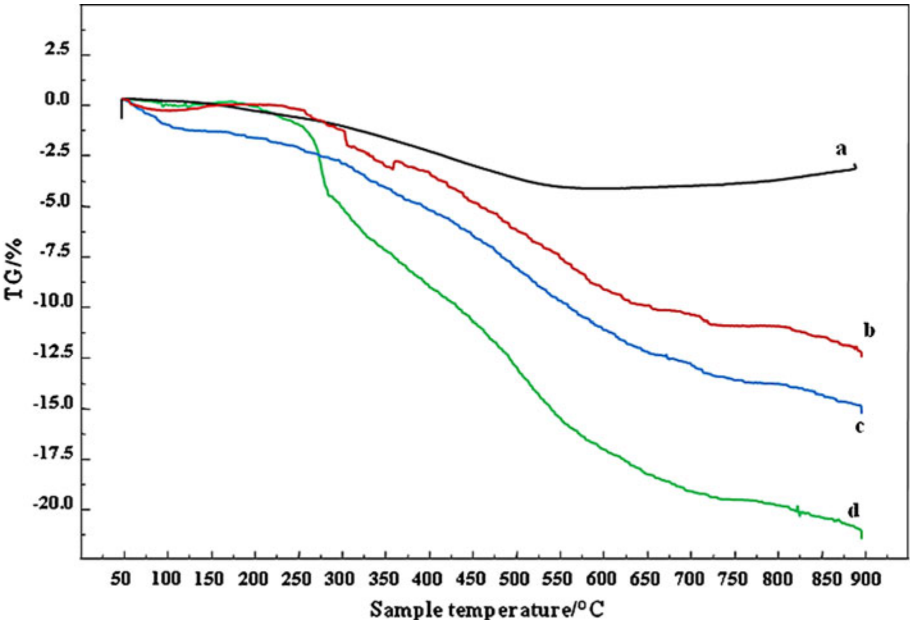


Fig. 3 Thermogravimetric curves of APTES-MN (*a*) MN-C1 (*c*), MN-C3 (*b*) and MN-C2 (*d*) magnetic nanoparticles

MN, MN-C1, MN-C2 and MN-C3, respectively. Thermogravimetric results showed a direct relationship of the loss of mass to the amount of the calixarene molecules anchored on the nanoparticle surfaces. Also, the immobilization of compound **4**, **5** and **6** onto APTES-MN magnetic nanoparticles was confirmed by the appearance of the characteristic amide bands at about 1643, 1697 and 1651 cm^{-1} for MN-C1, MN-C2 and MN-C3, respectively and by the disappearance of ester carbonyl band at 1760 cm^{-1} belong to compounds **4**, **5** and **6** in the FT-IR spectra (Fig. 4). Additional peaks centered at 1123, 1061 and 792 cm^{-1} were most probably due to the symmetric and asymmetric stretching vibration of framework and terminal Si–O– groups.

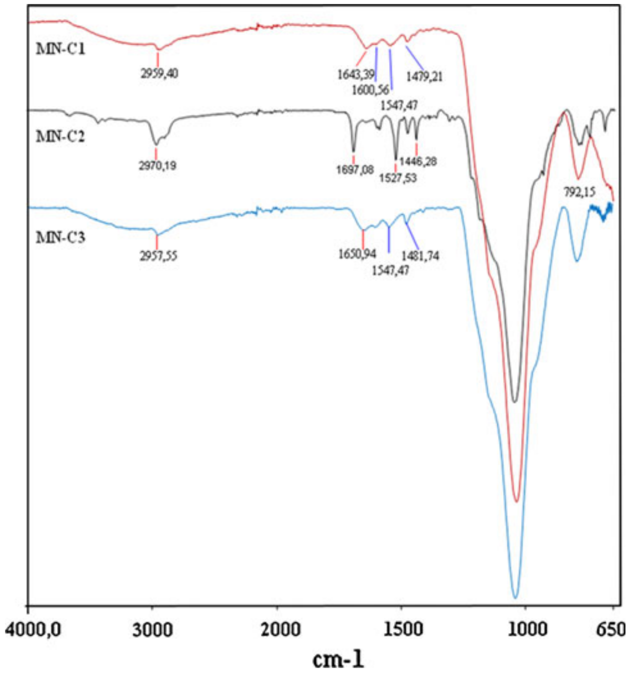


Fig. 4 FT-IR spectra of *MN-C1*, *MN-C2* and *MN-C3* magnetic nanoparticles

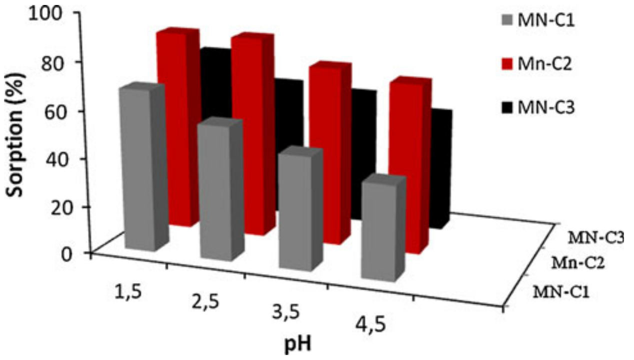


Fig. 5 Sorption percentages of Cr(VI) with *MN-C1*, *MN-C2* and *MN-C3* at pH 1.5–4.5

Sorption of Cr(VI) with MN-C1, MN-C2 and MN-C3

The anions are important because of their high toxicities and because of their widespread presence in soil and water. The dichromate ions ($Cr_2O_7^{2-}/HCr_2O_7^{-}$) are anions where the periphery of the anion has oxide moieties. It is known that calix[4]arenes with a nitrogen functionality for oxoanions [35–37]. For this purpose we have designed receptors having semicarbazone derivatives of calix[4]arene-based magnetic nanoparticles and performed some preliminary evaluations to investigate binding efficiencies of the extractants MN-C1, MN-C2 and MN-C3 for $Na_2Cr_2O_7$ by solid-phase extraction at different pHs. The results are summarized in Fig. 5. it is clear that MN-C1, MN-C2 and MN-C3 magnetic nanoparticles are more effective for the sorption of Cr(VI) at low pH as compared to compound APTES-MN which does not contain calix[4]arene units (the sorption results of APTES-MN for $Na_2Cr_2O_7$ were presented in Ref. 27). The prepared magnetic nanoparticles provide suitable binding sites for dichromate anions at low pH due to the presence of protonable Schiff base moieties. The extraction efficiency of MN-Cn sorbents decreases with increasing pH of the solution, due to the fact that protonation decreases, especially at pH 4.5 (Fig. 6a). It is well known that at more acidic conditions $Na_2Cr_2O_7$ is converted into $H_2Cr_2O_7$ and after ionization in an aqueous solution it exists in the $HCr_2O_7^{-}/Cr_2O_7^{2-}$ form. At higher acidic conditions $HCr_2O_7^{-}$ and $Cr_2O_7^{2-}$ dimers become the dominant Cr^{6+} form and pKa_1 and pKa_2 values of these equations are 0.74 and 6.49, respectively. It is apparent to

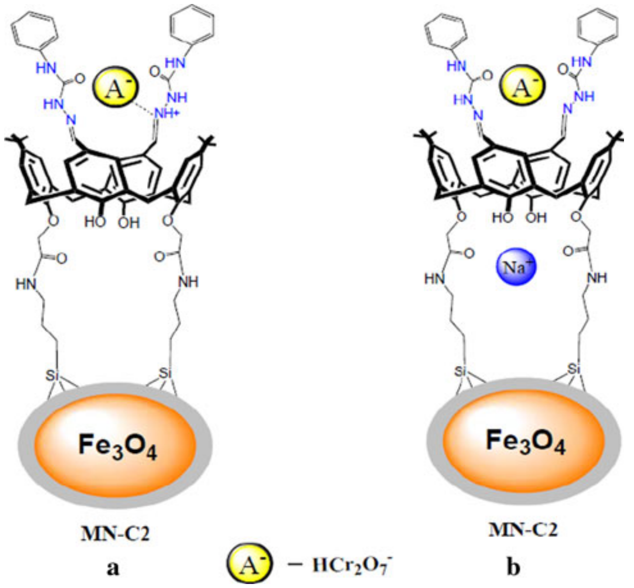


Fig. 6 The proposed interaction of MN-C2 with Cr(VI) at low pH (**a**) and high pH (**b**)

us that the ligands **4–6** form complex mostly with $HCr_2O_7^-$ [35, 36].

Also, the much higher levels of Cr(VI) removal by calix[4]arene based magnetic nanoparticles suggest a role of Na^+ complexation by the calix[4]arene units [38]. To probe this possibility, the levels of residual Na^+ in the aqueous phases following solid–liquid extraction of the Cr(VI) were determined by atomic absorption spectroscopy. The results given in Table 1 showed that the pronounced Na^+ removal suggests an ion-pair extraction mechanism in which Na^+ coordinates with the calix[4]arene moiety, while the dichromate anion interacts with amide hydrogens (Fig. 6b).

From the results in Fig. 5, it was clearly understood that MN-C2 is better sorbents than MN-C1 and MN-C3 for dichromate anions.

Sorption isotherms for Cr(VI)

Effect of initial Cr(VI) concentration

The effect of initial concentrations on dichromate sorption was investigated by varying the initial concentrations of dichromate using 0.025 g sorbent (MN-C2) at pH 2.5 and 1 h of equilibration time and obtained results was presented in Fig. 7. These results show that the removal of Cr(VI) is concentration dependent. Experimental data obtained from the effect of initial concentration on sorption capacity were fitted to Langmuir and Freundlich sorption isotherms.

Langmuir and Freundlich models

In order to optimize the design of a sorption system, it is important to establish the most appropriate correlation for the equilibrium curves. Sorption isotherm is a functional expression that correlate the amount of solute adsorbed per unit amount of sorbent and the concentration of sorbate in bulk solution at given temperature under equilibrium conditions. The most common and frequently used models are Langmuir and Freundlich model.

Table 1 Removal of Na^+ from the aqueous layer by extraction with MN-Cn at pH 1.5 (%)

Compound	MN-C1	MN-C2	MN-C3
Sorption (%)	60	73	65

Solid phase, sorbent = 25 mg MN-Cn; aqueous phase, $Na_2Cr_2O_7$ = 1.0×10^{-4} M at 30 °C for 1 h

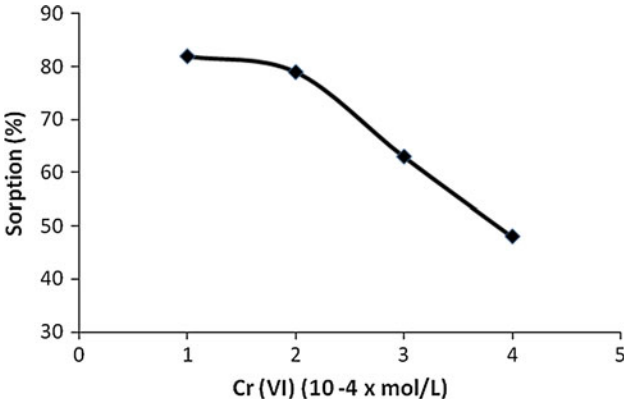


Fig. 7 Effect of initial Cr(VI) concentration on the removal of Cr(VI) (at pH 2.5, 30 °C)

The Langmuir model assumes uniform energies of sorption on the surface and no transmigration of sorbate in the plane of the surface. Langmuir isotherm is represented by the following equation [39]:

$$\frac{C_e}{q_e} = \frac{1}{q_o^b} + \frac{C_e}{q_o}$$

where the constants q_0 is the sorption capacity (mg g^{-1}) and b is related to the surface energy of sorption. A plot of C_e/q_e versus C_e as shown in Fig. 8 exhibits favorable sorption. Where q_0 (15.5 mg g^{-1}) and b (0.13) represent the intercept and slope, respectively. From the value of C_0 and b, dimensionless factor R_L was estimated by using the relationship:

$$R_L = \frac{1}{1 + bC_o}$$

where R_L is the separation factor and b is the Langmuir constant L mg^{-1}. Separation factor shows the nature of sorption process and its value indicate that the sorption process could be favorable, linear, unfavorable, when $0 < R_L < 1$, $R_L = 1$, $R_L > 1$, respectively. The value of

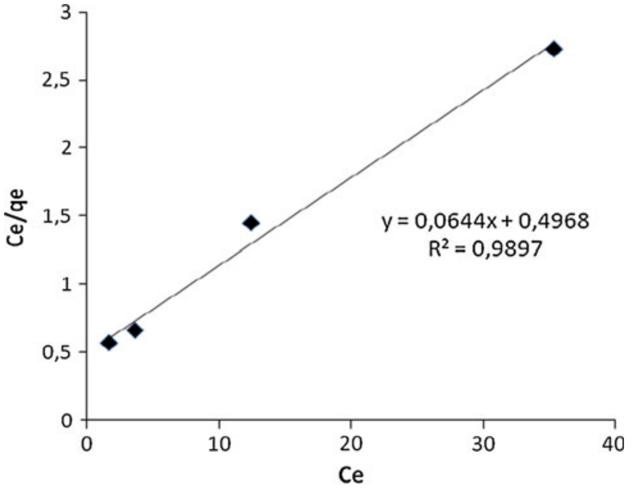


Fig. 8 Langmuir plot for the removal of Cr(VI) (at pH 2.5)

$R_L = 0.263$ showing that sorption of Cr(VI) on MN-C2 is favorable at pH 2.5. The model seems to be more agreeable with respect to the correlation coefficient $R^2 = 0.9897$, resulting monolayer sorption.

The Freundlich isotherm model is in empirical expression describing the exponential distribution of active centers, characteristic of heterogeneous surface and infinite surface coverage:

$$\log q_e = \log K + \frac{1}{n} \log C_e$$

where qe is the amount of the sorbed analyte per unit weight of the solid phase at equilibrium concentration C_e, K is the Freundlich constant related to the sorption capacity, while $1/n$ shows the sorption intensity.

A plot of log qe versus log Ce would exhibit in straight line with slope of $1/n$ and intercept of log K (Fig. 9). If the value of $1/n$ is less than unity, it indicates that significant adsorption is taking place at low concentration. The situation $1/n < 1$ is the most common and corresponds to a normal L-type Langmuir isotherm [40], while $1/n>1$ is indicative of a cooperative sorption [41], which involves strong interactions between the molecules of adsorbate. For $1/n = 1$ indicates that the partition between two phases is independent of concentration. The value of $1/n$ and K are 2.15 and 2.60, respectively. Investigating the figure, Freundlich isotherm seems to be agreeable with respect to the correlation coefficient ($R^2 = 0.9675$). This is an expected result due to the adoption of an excellent strategy by anchoring sophisticated functional groups onto the upper rim and lower rim of calix moiety followed by its immobilization onto the magnetic nanoparticles. On the comparison of the R^2 values given Freundlich and Langmuir, we can conclude that in all cases for the sorption of Cr(VI) ion to the MN-C2. Langmuir equation represents a better fit to the experimental data than the Freundlich equation. This reflects the satisfaction of the Langmuir isotherm model for the adsorption of Cr(VI) ion.

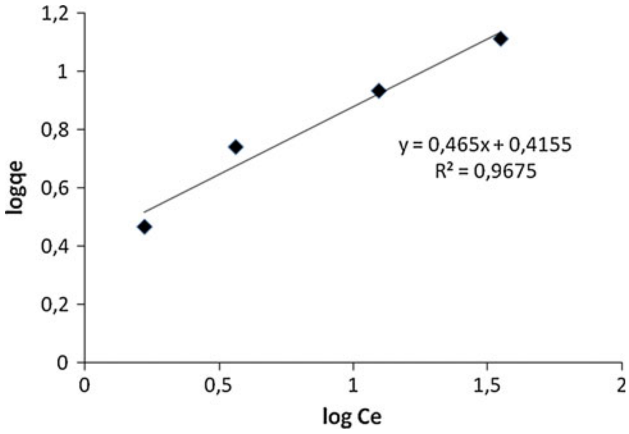
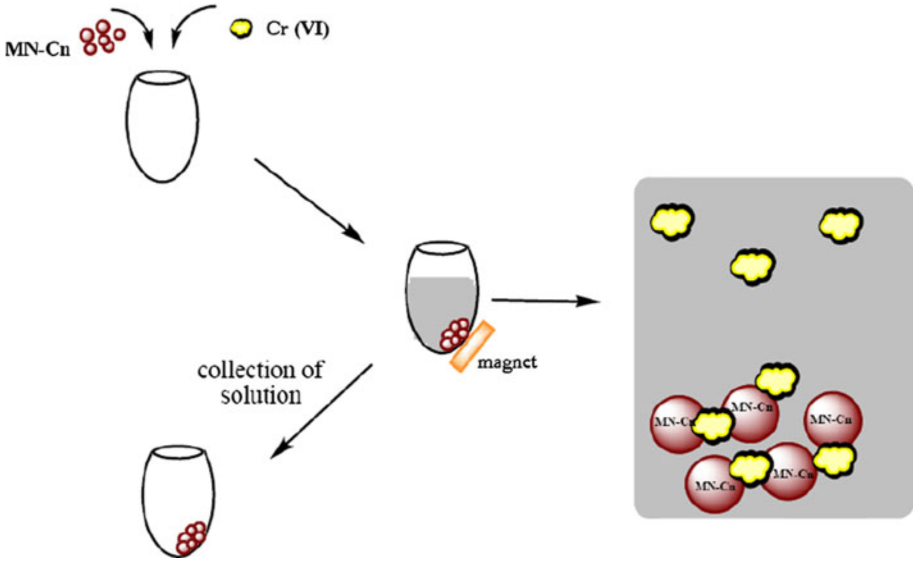


Fig. 9 Freundlich plot for the removal of Cr(VI) (at pH 2.5)

Conclusion

In summary, we have synthesized a series of novel the semicarbazone derivatives of calix[4]arene and immobilized on the prepared amino functionalized magnetic nanoparticles. The prepared new magnetic nanoparticles (MN-Cn) were used in removal of toxic Cr(VI) ion. According to the results obtained in the study, it can be concluded that MN-Cn nanoparticles are effective sorbents towards Cr(VI) ion. Moreover, the maximum Cr(VI) removal in MN-Cn was obtained at pH 1.5–2.5, depending on the surface of sorbents.

Fig. 10 Schematic illustration of magnetic separation of Cr(VI) ion from aqueous solution



The characteristics of the sorption process of Cr(VI) ion on the MN-C2 were evaluated by using the Langmuir and Freundlich adsorption isotherms. In the isotherm studies, it was determined that the experimental data follow better Langmuir isotherm model than that Freundlich.

The experimental studies show that MN-Cn magnetic nanoparticles could be used as an effective and low-risk sorbent material to remove toxic Cr(VI) ion from wastewaters. Also, these new calixarene based magnetic nanoparticles provides a rapidly easy separation and recovery from the reaction medium in an external magnetic field (Fig. 10).

Acknowledgment We thank the Scientific Research Projects Foundation of Selcuk University (SUBAP Grant Number 2009-09201148) for financial support of this work produced from a part of E. Akoz's M.Sc. Thesis.

References

1. Matthews, S.E., Beer, P.D.: Calixarene-based anion receptors. Supramol. Chem. **17**(6), 411–435 (2005)
2. Yilmaz, M., Memon, S., Tabakci, M., Bartsch, R.A.: In: Bregg, R.K. (ed.) New Frontiers in Polymer Research, p. 125. Nova Science Publishers, Hauppauge NY (2006)
3. Tabakci, M., Ersoz, M., Yilmaz, M.: A calix[4]arene-containing polysiloxane resin for removal of heavy metals and dichromate anion. J Macromol Sci Pure Appl Chem **43**, 57–64 (2006)
4. Memon, S., Tabakci, M., Roundhill, D.M., Yilmaz, M.: Synthesis and evaluation of the Cr(VI) extraction ability of amino/nitrile calix[4]arenes immobilized onto a polymeric backbone. React. Funct. Polym. **66**, 1342–1349 (2006)
5. Gokel, G.: Crown ethers, cryptands. In: Stoddart, J.F. (ed.) Monographs in Supramolecular Chemistry. Royal Society of Chemistry, London (1991)
6. Van Veggel, F.C.J.M., Verboom, W., Reinhoudt, D.N.: Metallomacrocycles: supramolecular chemistry with hard and soft metal cations in action. Chem. Rev. **94**, 279–299 (1994)
7. Hamdi, A., Nam, K.C., Ryu, B.J., Kim, J.S., Vicens, J.: Anion complexation. A ditriphenylphosphonium calix[4]arene derivative as a novel receptor for anions. Tetrahedron Lett. **45**, 4689–4962 (2004)
8. Gutsche, C.D.: Calixarenes Revisited. The Royal Society of Chemistry, Cambridge (1998)
9. Asfari, Z., Bohmer, V., Harrowfield, Mc.B., Vincens, J.: Calixarenes. Kluwer Academic Publishers, Dordrecht (2001)
10. Vicens, J., Bohmer, V.: Calixarenes: A Versatile Class of Macrocyclic Compounds. Topics in Inclusion Science, pp. 149–172. Kluwer Academic Publishers, Dordrecht (1991)
11. Memon, S., Roundhill, D.M., Yilmaz, M.: Remediation and Liquid–Liquid Phase Transfer Extraction of Chromium(VI). A Review. Collect Czech Chem. Commun. **69**, 1231–1250 (2004)
12. Dozol, J.F., Rouquette, H., Ungaro, R., Casnati, A.: Chem. Abs. 122, 239730n, (CEA) International Patent WO 94/24138 (1995)
13. Demirel, A., Dogan, A., Canel, E., Memon, S., Yilmaz, M., Kilic, E.: Hydrogen ion-selective poly(vinyl chloride) membrane electrode based on a *p-tert*-butylcalix[4]arene-oxacrown-4. Talanta **62**, 123 (2004)
14. Ertul, S., Bugdayci, M., Yilmaz, M.: Removal of chromate and phosphate anion from aqueous solutions using calix[4]aren receptors containing proton switchable units. J. Hazard. Mater. **181**, 1059–1065 (2010)
15. Memon, S., Yilmaz, A., Roundhill, D.M., Yilmaz, M.: Synthesis of polymeric calix[4]arene dinitrile and diamino-derivatives: exploration of their extraction properties towards dichromate anion. J. Macromol. Sci. Pure. **41**, 433–447 (2004)
16. Tabakci, M., Memon, S., Yilmaz, M., Roundhill, D.M.: Synthesis and extraction studies of a versatile calix[4]arene-based 'proton-switchable extractant' for toxic metals and dichromate anions. J. Incl. Phenom. Macrocycl. Chem. **45**, 267–270 (2003)
17. Ediz, O., Tabakci, M., Memon, S., Yilmaz, M., Roundhill, D.M.: A convenient approach towards the synthesis of a "proton switchable" chromium(VI) extractant based on calix[4]arene. Supramol. Chem. **16**, 199–204 (2004)
18. Bayrakci, M., Ertul, S., Sahin, O., Yilmaz, M.: Synthesis of two new *p-tert*-butylcalix[4]arene β-ketoimin derivatives for extraction of dichromate anion. J. Incl. Phenom. Macrocycl. Chem. **63**, 241–247 (2009)
19. Gungor, O., Memon, S., Yilmaz, M., Roundhill, D.M.: Synthesis of alkyl nitrile and alkyl benzonitrile derivatives of calix[4]arene and their polymer supported analogues: a comparative study in two-phase extraction systems. React. Funct. Polym. **63**, 1–9 (2005)
20. Gupta, A.K., Gupta, M.: Synthesis and surface engineering of iron oxide nanoparticles for biomedical applications. Biomaterials **26**, 3995–4021 (2005)
21. Krizzova, J., Spanova, A., Rittich, B., Horak, D.: Magnetic hydrophilic methacrylate-based polymer microspheres for genomic DNA isolation. J. Chromatogr. A **1064**, 247–253 (2005)
22. Ito, A., Shinkai, M., Honda, H., Kobayashi, T.: Medical application of functionalized magnetic nanoparticles. J. Biosci. Bioeng. **100**, 1 (2005)
23. Mornet, S., Vasseur, S., Grasset, F., Goglio, G., Demourgues, A., Portier, J., Pollert, E., Duguet, E.: Magnetic nanoparticle design for medical applications. Prog. Solid State Chem. **34**, 237–247 (2006)
24. Neuberger, T., Schopf, B., Hofmann, H., Hofmann, M., von Rechenberg, B.: Superparamagnetic nanoparticles for biomedical applications: possibilities and limitations of a new drug delivery system. J. Magn. Magn. Mater. **293**, 483 (2005)
25. del Campo, A., Sen, T., Lellouche, J.P., Bruce, I.J.: Multifunctional magnetite and silica–magnetite nanoparticles: synthesis, surface activation and applications in life sciences. J. Magn. Magn. Mater. **293**, 33–40 (2005)
26. Saiyed, Z.M., Sharma, S., Godawat, R., Telang, S.D., Ramchand, C.N.: Activity and stability of alkaline phosphatase (ALP) immobilized onto magnetic nanoparticles (Fe_3O_4). J. Biotechnol. **131**, 240–244 (2007)
27. Ozcan, F., Ersoz, M., Yilmaz, M.: Preparation and application of calix[4]arene-grafted magnetite nanoparticles for removal of dichromate anions. Mater. Sci. Eng. C **29**, 2378–2383 (2009)
28. Sayin, S., Ozcan, F., Yilmaz, M.: Synthesis and evaluation of chromate and arsenate anions extraction ability of a N-methylglucamine derivative of calix[4]arene immobilized onto magnetic nanoparticles. J. Hazard. Mater. **178**, 312–319 (2010)
29. Sayin, S., Ozcan, F., Yilmaz, M., Tor, A., Memon, S., Cengeloglu, Y.: Synthesis of calix[4]arene-grafted magnetite nanoparticles and evaluation of their arsenate as well as dichromate removal efficiency. Clean-soil Air Water **38**, 639–648 (2010)
30. Gutsche, C.D., Iqbal, M., Stewart, D.: Calixarenes. 19. Syntheses procedures for p-*tert*-butylcalix[4]arene. J. Org. Chem. **51**, 742–745 (1986)
31. Collins, M., McKervey, M.A., Madigan, E., Moran, M.B., Owens, M., Ferguson, G., Harris, S.J.: Chemically modified calix[4]arenes. Regioselective synthesis of 1,3-(distal) derivatives

and related compounds. X-Ray crystal structure of a diphenol-dinitrile. J. Chem. Soc. Perkin. Trans. **1**, 3137–3142 (1991)

32. Chawla, H.M., Pant, N., Srivastava, B., Upreti, S.: Convenient direct synthesis of bisformylated calix[4]arenes via ipso substitution. Org. Lett. **8**, 2237–2240 (2006)
33. Niazi, A., Ghasemi, N., Goodarzi, M., Ebadi, A.: Simultaneous spectrophotometric determination of uranium and thorium using arsenazo III by H-point standard addition method and partial least squares regression. J. Chin. Chem. Soc. **54**, 411–418 (2007)
34. Pedersen, C.J.: Ionic complexes of macrocyclic polyethers. Fed. Proc. Am. Soc. Exp. Biol. **27**, 1305 (1968)
35. Bozkurt, S., Karakucuk, A., Sirit, A., Yilmaz, M.: Synthesis of two calix[4]arene diamide derivatives for extraction of chromium(VI). Tetrahedron **61**, 10443–10448 (2005)
36. Bayrakci, M., Ertul, S., Yilmaz, M.: Synthesis of di-substituted calix[4]arene-based receptors for extraction of chromate and arsenate anions. Tetrahedron **65**, 7963–7968 (2009)
37. Tabakci, M., Memon, S., Yilmaz, M.: Synthesis and extraction properties of new 'proton-switchable' tri- and tetra-substituted calix[4]arene derivatives bearing pyridinium units. Tetrahedron **63**, 6861–6865 (2007)
38. Bozkurt, S., Kocabas, E., Durmaz, M., Yilmaz, M., Sirit, A.: Synthesis and dichromate anion sorption of silica gel-immobilized calix[4]arenas. J. Hazard. Mater. **165**, 974–979 (2009)
39. Memon, G.Z., Bhanger, M.I., Akhtar, M.: The removal efficiency of chestnut shells for selected pesticides from aqueous solutions. J. Colloid Interface Sci. **315**, 33–40 (2007)
40. Selvi, K., Pattabhi, S., Kadirvelu, K.: Removal of Cr(VI) from aqueous solution by adsorption onto activated carbon. Bioresour. Technol. **80**, 87–89 (2001)
41. Garg, V.K., Gupta, R., Kumar, R., Gupta, R.K.: Adsorption of chromium from aqueous solution on treated sawdust. Bioresour. Technol. **92**, 79–81 (2004)