Dichromate and Phosphate Sorption Capacity of *Bis* Formyl Calix[4]arene on Superparamagnetic Iron Oxide Nanoparticles in Aqueous Phase

F. Ozcan[1], A. Aygun[2,*], U.A. Sevil[3] and S. Ertul[1]

[1]Advanced Technology Research and Application Center, 42075 Konya, Turkey
[2]Department of Environmental Engineering, Bursa Technical University, 16109 Bursa, Turkey
[3]Department of Chemical Engineering, Hitit University, 19030 Corum, Turkey

*Corresponding author: Fax: +90 224 3003419; Tel: +90 224 3003590; E-mail: ahmet.aygun@btu.edu.tr

Calix[4]arene derivatives were added into aqueous phase phosphate and dichromate solutions in order to investigate sorption capacity at pH of 1.5 to 5.5. A 25 mg of polymers magnetic calix[4]arenes derivatives was added into the flask shaking at 180 rpm for 1 h at room temperature. pH controls ionic forms of phosphate and dichromate, resulting in their binding capacity to the polymers. Maximum sorption capacity was 96.6 % at pH 2.5 for phosphate and 90.1 % for chromium at pH 3.5. Different polymers may be selective for ions due to their versatility and special characteristics. As a result, magnetic nanoparticle polymers showed both super-paramagnetic behaviour and high sorption capability across dichromate and phosphate ions.

Keywords: Calixarenes, Dichromate, Magnetic nanoparticles, Phosphate, Sorption.

INTRODUCTION

Calix[4]arene is used as main building block for cone formation and its ease of organic functionalization [1]. Calix[4]arene derivatives are highly selective to bind some ions and molecular species [2]. Calix[4]arene-based conjugates were commonly studied due to their versatility and special characteristics [3]. Applications of calix[4]arene derivatives varied in different fields such as molecular recognition [4,5], host-guest chemistry [6,7], catalysis [8], enzyme mimics [9], ion extraction [10,11] and selective ion transport [12]. Calix[4]arenes are formed in different molecular structure such as double calix[4]arenes and calix[4]arene-based tubes. Therefore, receptors for anion recognition based on molecular system were synthesized by chemist in recent years.

Phosphorus commonly existing as phosphate in environment is a key element for biochemical processes and stimulates eutrophication phenomenon in surface water [13,14].

The removal efficiency of phosphate from aqueous phase by conventional methods is not enough to reach desired value. Thus, new methods need to be developed for removal of phosphate. Most receptor organic molecules developed for phosphate anions works only in non-aqueous phase by hydrogen bonding interaction [15].

Chromium is toxic element commonly found in the forms of Cr(III) and Cr(VI) [16]. The wastewater having chromium needs to be treated in order to reach strictly discharge limits set by EPA, WHO and other national authorities [17]. At that point, calixarenes as ionic receptors are important due to their functionalization properties.

Superparamagnetic iron oxide nanoparticles (Fe_3O_4) having multifunctional properties such as small size, superparamagnetism and low toxicity widely used in physics, medicine, biology, *etc*. [18,19].

The architecture of calix[n]arenes and the chelating behaviour of amide have been reported in literature. The sorption capacity of magnetic calix[4]arene derivatives polymers **1, 2a, 2b** and **3** were presented in this study. Novel products which is magnetic polymers were used in solid-liquid extraction process to investigate phosphate and dichromate ions binding capability.

EXPERIMENTAL

All chemicals used without further purification in our experiments were bought from Merck and Aldrich. All commercial grade solvents were distilled and then stored over molecular sieves. All reactions were performed under nitrogen.

Previously synthesized polymers **1, 2a, 2b** and **3** magnetic calix[4]arene published in elsewhere [20] were used for sorption of phosphate and dichromate from aqueous solution.

Solid-liquid sorption studies: The sorption capacity of the synthesized calix[4]arene grafted nanoparticles were

conducted to investigate for phosphate and dichromate ions. A 10 mL of solution containing sodium dichromate and/or disodium hydrogen phosphate at a concentration of 1×10^{-4} M was transferred into a vial and a few drops of 0.01 M KOH/HCl solution were added in order to adjust pH. A 25 mg of polymers **1, 2a, 2b** and **3** magnetic calix[4]arenes was added into the flask shaking at 180 rpm for 1 h at room temperature. And then flask was left on the bench without shaking at additional of 0.5 h.

Aqueous phase dichromate or phosphate concentrations were monitored over the time using spectrophotometric method described as in SM 3500-Cr B and SM 4500-P, E respectively. Based upon our blank experiments showed that no dichromate or phosphate extraction occurred in the absence of the calix[4]arene. The per cent sorption (S %) of dichromate at 346 nm and phosphate at 880 nm for pH of 1.5-4.5 was calculated the following equation:

$$\text{Sorption (\%)} = \frac{(C_0 - C)}{C_0} \times 100$$

where, C_0 is initial concentration, C is concentration at end of the experiment.

RESULTS AND DISCUSSION

Phosphate sorption: Dihydrogen phosphate is one of the most basic anionic guest species; thus, dihydrogen phosphate strongly interacts with the amide protons of the receptor. Phosphate sorption capacity of magnetic calix[4]arene nanoparticle receptors containing amide, crown amide and ethyl ester were performed using solvent extraction.

From Table-1, it is clear that the maximum extraction of 96.61 % for polymer **1**, 84.44 % for polymer **2a**, 95.43 % for polymer **2b** and 93.57 % for polymer **3** occur, respectively, at pH 2.5. There is no sorption data were obtained at pH 1.5
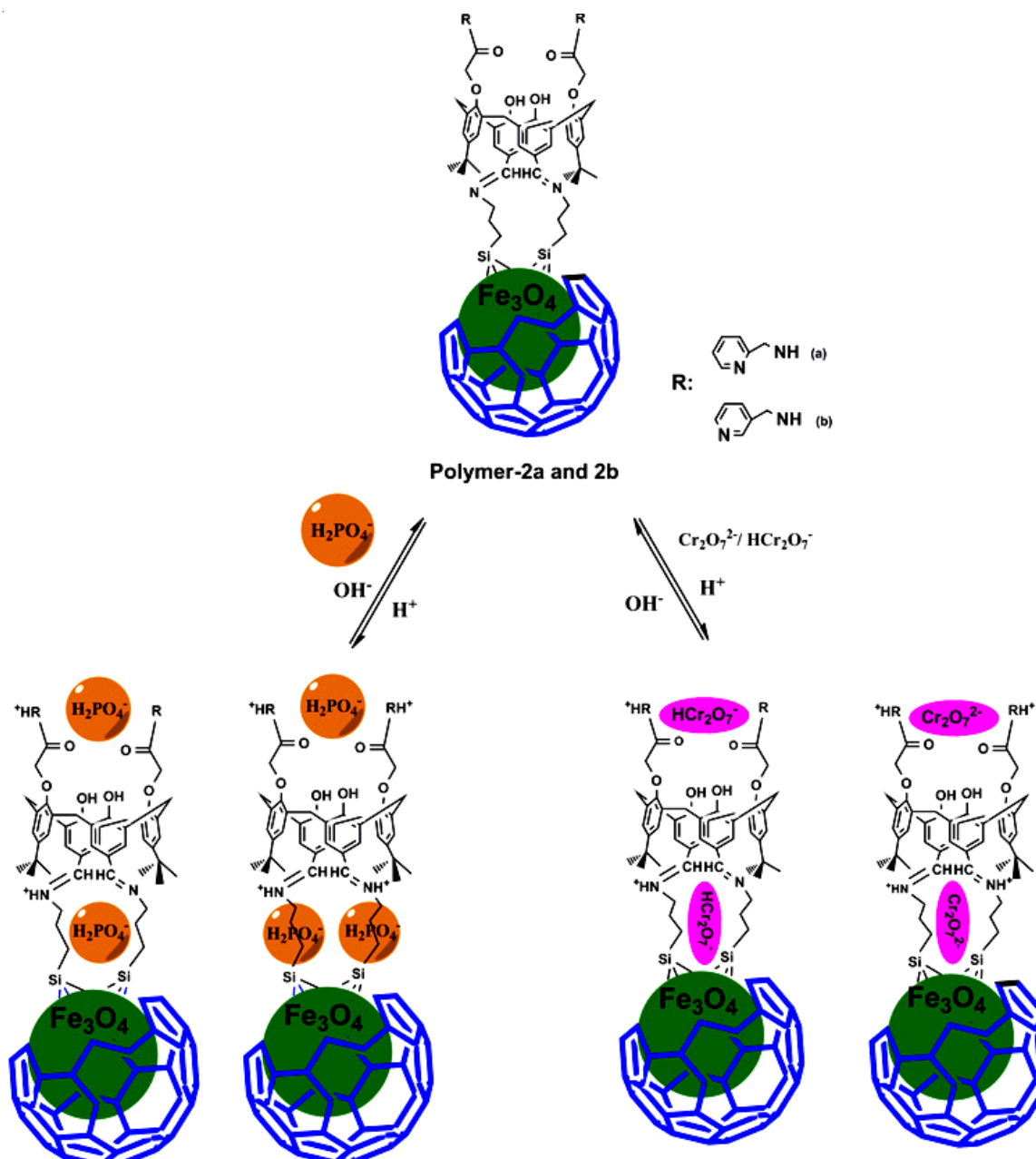

Fig. 1. Suggested complexation phenomenon of phosphate and the dichromate ion with polymer **2a** and **2b**

since nanoparticles on the polymers can be dissolved. This case may attribute to the binding of hydrogen and electrostatic interaction between pyridine amide, crown amide or ethyl ester groups of receptors and the oxygen of phosphate ions. The proposed interaction between the phosphate and the ligands polymers **1, 2a, 2b** and **3** are shown in Figs. 1-3. It is clearly seen in following equation (eqns. 1-3) that phosphate speciation in the solution affected by pH.

$$H_3PO_4 \longrightarrow H_2PO_4^- + H^+ \quad pKa_1 = 2.1 \qquad (1)$$

$$H_2PO_4^- \longrightarrow HPO_4^{2-} + H^+ \quad pKa_2 = 7.2 \qquad (2)$$

$$HPO_4^{2-} \longrightarrow PO_4^{3-} + H^+ \quad pKa_3 = 12.6 \qquad (3)$$

While dominant phosphate species is $H_2PO_4^-$ at pH value between 2 to 4, HPO_4^{2-} dominates at higher pH values. The monoanion ($H_2PO_4^-$) has lower free energy of hydration than that of HPO_4^{2-}, resulting in more $H_2PO_4^-$ extractable amount from aqueous phase. Since $H_2PO_4^-$ extracted two sodium anions in order to loss hydration energy, it may have additional advantage comparing to HPO_4^{2-}.

Upon the addition of NaOH to the aqueous layer, deprotonated calixarene in the aqueous solution is no longer an effective host. It is well known that at more acidic conditions, Na_2HPO_4 is converted into H_3PO_4 and after ionization in an aqueous solution, it exits in the $H_2PO_4^-/HPO_4^{2-}$ form. At higher
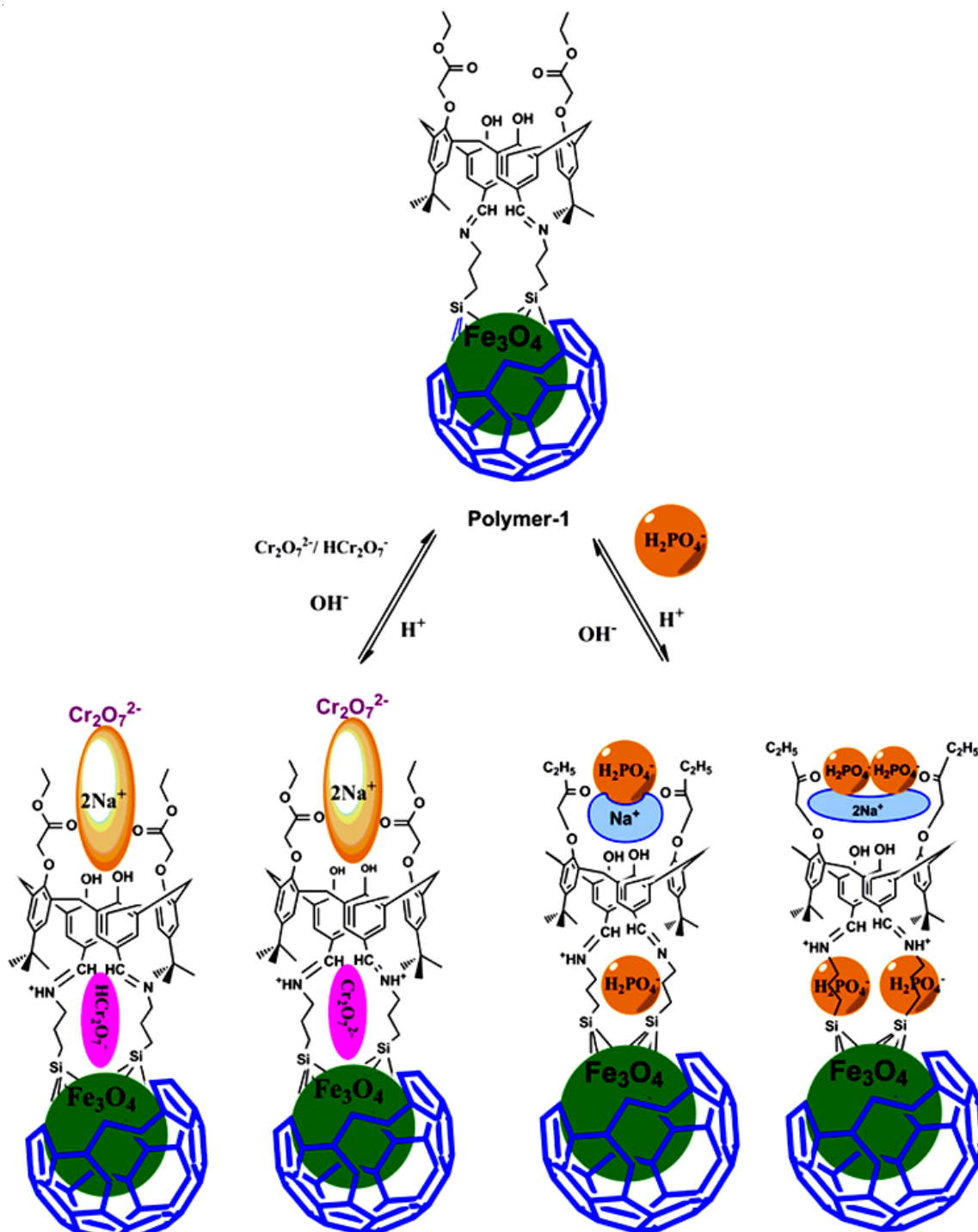

Fig. 2. Suggested complexation phenomenon of phosphate and the dichromate ion with polymer **1**

TABLE-1
PER CENT EXTRACTION OF PHOSPHATE BY
POLYMERS **1, 2a, 2b, 3** AT DIFFERENT pH VALUES

Compound	pH				
	1.5	2.5	3.5	4.5	5.5
Polymer **1**	–	96.61	86.47	79.86	72.80
Polymer **2a**	–	84.44	80.13	73.13	60.85
Polymer **2b**	–	95.43	90.27	83.45	71.76
Polymer **3**		93.57	88.24	77.17	59.82
Fe_3O_4-APTMS	–	43.27	39.60	27.53	19.62

*Aqueous phase, [phasphate] = 1×10^{-4} M; solid phase, 25 mg [ligand] at 25 °C, for 1 h.

acidic conditions, pKa_1 and pKa_2 values of these equations $H_2PO_4^-$ and HPO_4^{2-} dimers are 2.1 and 7.2, respectively.

Polymers **2a** and **2b** receptors provided suitable sites to bind phosphate anions at low pH values due to the presence of protonable amine moieties. Higher sorption property of these ionophores polymers **2a** and **2b** are due to the presence of the protonable pyridinium binding site on the lower rim of the calixarene skeleton (Fig. 1). Furthermore, this situation is explainable because the pKa of protonated amides (Py-NH+) is approximately –1, the protonated form of calix[4]arene diamide derivatives Polymers **2a** and **2b** are not expected to
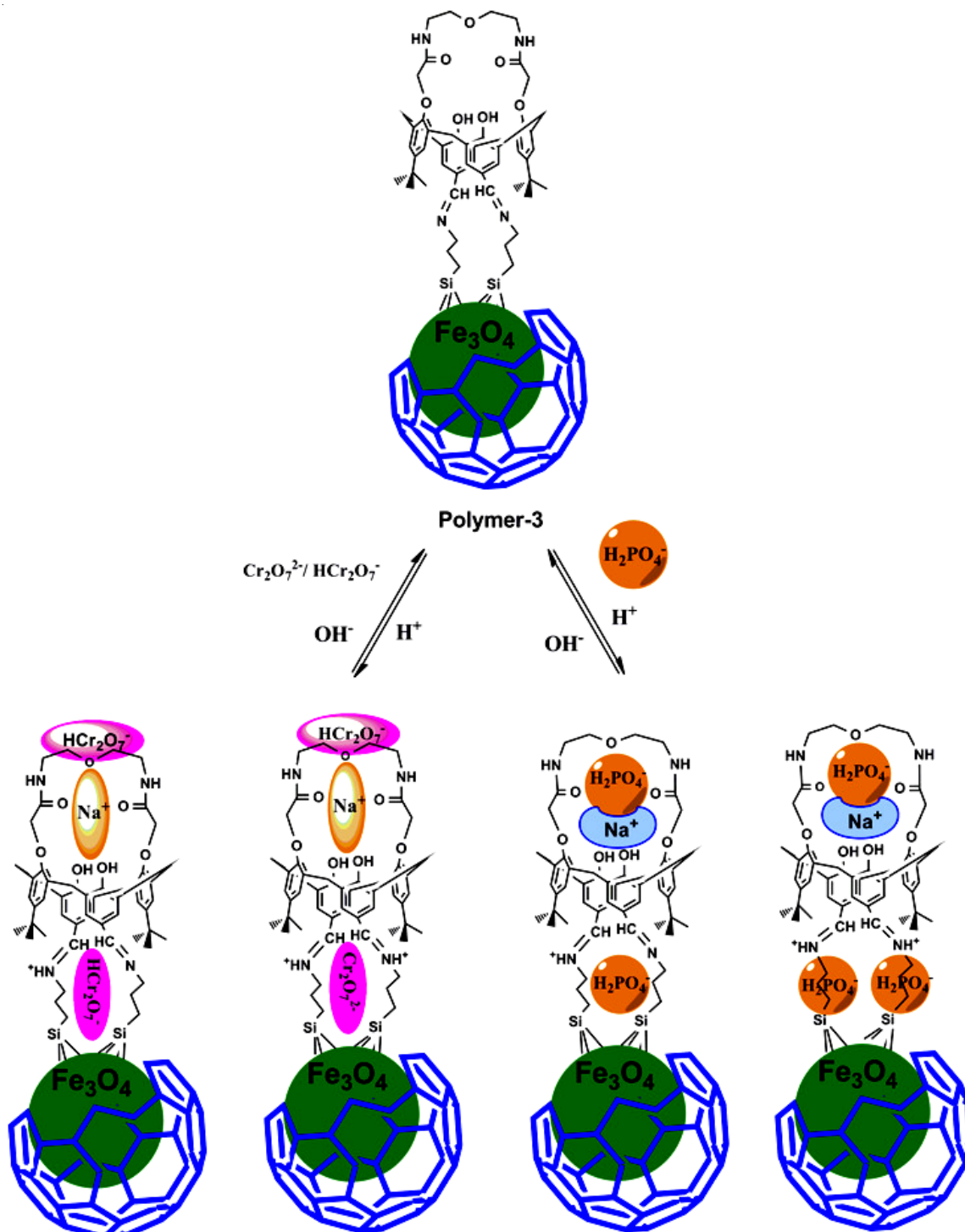

Fig. 3. Suggested complexation phenomenon of phosphate and the dichromate ion with polymer **3**

be present in significant concentration in aqueous solutions having pH values in the 1.5-4.5 range. At the lower pH values, the formation of $H_2PO_4^-$ and the protonation of the pyridinium nitrogens favour sorption surface magnetic nanoparticles. Hence, an anion-switchable complex is formed by the solid-liquid extraction system.

Chromate sorption: Sodium dichromate ($Na_2Cr_2O_7$) is converted into $H_2Cr_2O_7$ at lower pHs, it exists in the $HCr_2O_7^-$/$Cr_2O_7^{2-}$ form. At the low pHs, $HCr_2O_7^-$ and $Cr_2O_7^{2-}$ are dominant form of chromium form and the pKa_1 and pKa_2 values are 0.74 and 6.49, respectively. pH value lower than 6, the oxyanions' structure changes from the monomeric CrO_4^{2-} and the dimeric $HCr_2O_7^-$, resulting in a source of potential sites for hydrogen bonding to the host molecule. Calix[4]arenes with a nitrogen functionality such as pyridine, crown amide and ethyl ester on their lower rim are the efficient extractants for oxoanions. Therefore, sorbent polymers **2a** and **2b** were tested in our experiments which is known as proton-switchable binding lobes for dichromate anions (Fig. 1) and dichromate anions have been removed from the aqueous Na^+ by using other polymers **1** and **3** as an ion pair (Figs. 2 and 3).

Preliminary evaluations tests were conducted in order to investigate sorption capacity of polymers **1, 2a, 2b, 3** for $Na_2Cr_2O_7$ in aqueous phase. Based on the aqueous phase pH values, sorption capacity ranged from 20 to 90 % given in Table-2.

TABLE-2
PER CENT EXTRACTION OF DICHROMATE BY POLYMERS
1, 2a, 2b, 3 AND APTMS Fe_3O_4 AT DIFFERENT pH VALUES

Compound	pH				
	1.5	2.5	3.5	4.5	5.5
Polymer **1**	-	49.48	90.10	86.64	80.69
Polymer **2a**	-	32.47	63.06	25.62	20.10
Polymer **2b**	-	48.74	80.15	45.37	35.20
Polymer **3**		53.37	86.21	67.23	49.37
Fe_3O_4-APTMS	-	30.62	35.23	20.14	-

*Aqueous phase, [dichromate] = 1×10^{-4} M; solid phase, 25 mg [ligand] at 25 °C, for 1 h.

For polymers **1** and **3** the maximum extracted dichromate ions were 90.10 % and 86.21 %, respectively at pH value of 3.5. Conversely, extracted values were 49.48 % for polymer **1** at pH 2.5 and 49.37 % for polymer **3** at pH 5.5. On the other hand, the percentage of dichromate ions extracted was 63.06 % for polymer **2a** and 80.15 % for polymer **2b** at the pH of 3.5.

Better sorption results were obtained by polymers **1** and **3**, which extracted the dichromate anions more efficiently when compared with polymers **2a** and **2b**. This situation showed that magnetic calixarene nanoparticles polymers **1** and **3** are

more effective than extractants polymers **2a** and **2b** (Table-2) containing a protonable prydinium binding site. Magnetic calixarene nanoparticles, that have a rigid structure, have notably increased the anion extraction ability.

Conclusion

Four new magnetic calixarene derivatives immobilized onto the silica based magnetic nanoparticles surface (APTMS-MN) to impact both more rigid structural features and prevent solubility of the compounds. Immobilization improve the separation capability of the calixarene composite silica carriers due to their magnetic properties. Magnetic calixarene derivatives can be used effectively to remove phosphate and dichromate ions from aqueous phase. The complexation of the phosphate and dichromate ions depends on the structural properties of the receptors, such as stability or rigidity and hydrogen binding ability.

REFERENCES

1. K. Iwamoto and S.J. Shinkai, *J. Org. Chem.*, **57**, 7066 (1992).
2. B.S. Creaven, D.F. Donlon and J. McGinley, *Coord. Chem. Rev.*, **253**, 893 (2009).
3. V. Bohmer, *Angew. Chem. Int. Ed. Engl.*, **34**, 713 (1995).
4. I. Leray and B. Valeur, *Eur. J. Inorg. Chem.*, 3525 (2009).
5. M. Durmaz, S. Bozkurt, H.N. Naziroglu, M. Yilmaz and A. Sirit, *Tetrahedron Asym.*, **22**, 791 (2011).
6. S. Bozkurt, E. Kocabas, M. Durmaz, M. Yilmaz and A. Sirit, *J. Hazard. Mater.*, **165**, 974 (2009).
7. M. Bayrakci, S. Ertul and M. Yilmaz, *Tetrahedron*, **65**, 7963 (2009).
8. D.M. Homden and C. Redshaw, *Chem. Rev.*, **108**, 5086 (2008).
9. P. Molenveld, F.J. Engbersen and D.N. Reinhoudt, *Chem. Soc. Rev.*, **29**, 75 (2000).
10. S. Bozkurt, M. Durmaz, A. Sirit and M. Yilmaz, *J. Macromol. Sci. A*, **44**, 159 (2007).
11. H. Luo, S. Dai, P.V. Bonnesen, A.C. Buchanan, J.D. Holbrey, N.J. Bridges and R.D. Rogers, *Anal. Chem.*, **76**, 3078 (2004).
12. K.S.J. Iqbal and P.J. Cragg, *Dalton Trans.*, **1**, 26 (2007).
13. S. Ertul, M. Bayrakci and M. Yilmaz, *J. Hazard. Mater.*, **181**, 1059 (2010).
14. K. Mahadevaiah, M.S.Y. Kumar, M.S.A. Galil, M.S. Suresha, M.A. Sathish and G. Nagendrappa, *E.-J. Chem.*, **4**, 467 (2007).
15. J. Yoon, S.K. Kim, N.J. Singh, J.W. Lee, Y.J. Yang, K. Chellappan and K.S. Kim, *J. Org. Chem.*, **69**, 581 (2004).
16. D.M. Stearns, L.J. Kennedy, K.D. Courtney, P.H. Giangrande, L.S. Phieffer and K.E. Wetterhahn, *Biochemistry*, **34**, 910 (1995).
17. T. Ertugrul, A. Berktay and B. Nas, *Environ. Eng. Sci.*, **23**, 1055 (2006).
18. M. Mikhaylova, D.K. Kim, C.C. Berry, A. Zagorodni, M. Toprak, A.S.G. Curtis and M. Muhammed, *Chem. Mater.*, **16**, 2344 (2004).
19. C.E. Sjögren, C. Johansson, A. Naevestad, P.C. Sontum, K. Briley-Sæbø and A.K. Fahlvik, *Magn. Reson. Imaging*, **15**, 55 (1997).
20. F. Ozcan, M. Bayrakci and S. Ertul, *J. Macromol. Sci. Pure Appl. Chem.*, **52**, 559 (2015).