Journal of Scientific & Industrial Research
Vol. 69, October 2010, pp. 767-772

Synthesis and characterization of Fe(III)-ion imprinted polymer for recovery of Fe(III) from water samples

D K Singh* and Shraddha Mishra

Analytical Research Laboratory, Department of Chemistry, Harcourt Butler Technological Institute, Kanpur 208 002, India

Received 08 February 2010; revised 15 July 2010; accepted 30 July 2010

Ion imprinted polymer (IIP) was prepared by formation of binary complex of iron (imprint ion) with acrylic acid (functional monomer) in cyclohexanol and thermally copolymerizing with styrene (monomer) and divinylbenzene (crosslinker) in presence of 2, 2'-azobisisobutyronitrile (AIBN) as initiator. Imprinted Fe(III) was completely removed by leaching IIP with 1 M HNO_3 and characterized by FTIR and surface area measurement. Cation exchange capacity (H^+/Na^+) of IIP was 0.249 mmol g^{-1}. Adsorption equilibrium time was found to be 60 min. Maximum adsorption (62.4 mg g^{-1}) of Fe(III) ions on to IIP was at pH 6. Distribution studies showed selectivity order as: Fe(III) > Zn(II) > Co(II) > Ni(II). Fe(III)-IIP was used to study preconcentration and recovery of Fe(III) from water samples

Keywords: Binary complex, Imprint ion, Ion imprinted polymer, Solid phase extraction

Introduction

Hemochromatosis results from significant iron overload[1].Typical manifestations are cirrhosis of liver, diabetes and cardiomyopathy. Pituitary failure is common and may be the cause of frequently observed testicular atrophy and loss of libido. Excess iron in tissues, which builds up during normal aging, can promote coronary artery disease and foster growth of latent cancers and infectious organisms[2]. Using polymer imprinting, materials prepared are capable of ion recognition[3-5]. Numerous studies on ion imprinted polymer(IIP) and its use for selective preconcentration and separation of metal ions include UO_2(II)[6], Pd(II)[7], Cd(II)[8], Fe(III)[9], Hg(II)[10], Ni(II)[11], Cr(III)[12] and Zn(II)[13].

In this study, a new Fe(III)- IIP has been synthesized and characterized. Adsorption capacity of developed IIP (62.4 mg g^{-1}) is found higher than that of reported[9] IIP (0.086 mg g^{-1}). Application of IIP in recovery of Fe(III) ions from river water and tap water samples was also studied.

Experimental Section

Reagents and Apparatus

Acrylic acid, cyclohexanol (BDH, India), styrene, divinylbenzene (Merck, Germany) and AIBN (Alfa Aesar, UK) were used. pH was adjusted using HCl / KCl for pH 1 and 2, and CH_3COOH / CH_3COONa for pH 4 and 6. All other reagents were of AR grade. Rotary shaking machine (IEC-56), Systronics digital pH meter, Systronics double beam spectrophotometer 2203, magnetic stirrer with hot plate, vacuum oven, Shimadzu 8201 PC FTIR spectrophotometer were used for shaking, pH measurements, spectrophotometric measurements, stirring, drying and FTIR studies, respectively.

Preparation of Fe(III)-Ion Imprinted Polymer (IIP)

IIP (Fig. 1) was prepared by thermal polymerization. Imprint ion (1 mmol) was complexed with acrylic acid (14.4 mmol) in cyclohexanol (10 ml). This binary complex solution was then mixed with styrene (30 mmol) and divinylbenzene (30 mmol) and 2, 2-azobisisobutyronitrile (50 mg). Polymerization mixture was cooled to 0°C and purged with N_2 for 10 min, sealed and thermally polymerized in an oil bath at 80°C while stirring for 3 h. Resultant IIP was washed with demineralized water (DMW) and dried in a vacuum oven at 50 ±1°C, ground and sieved to 60-100 mesh. Selected particles were treated with 1 M HNO_3 to remove Fe(III) linked to IIP. Non imprinted polymer (NIP) was also prepared under similar experimental conditions without adding imprint ion.

*Author for correspondence
Tel: +919450333734; fax: 91-512-2533812
E-mail: dhruvks123@rediffmail.com

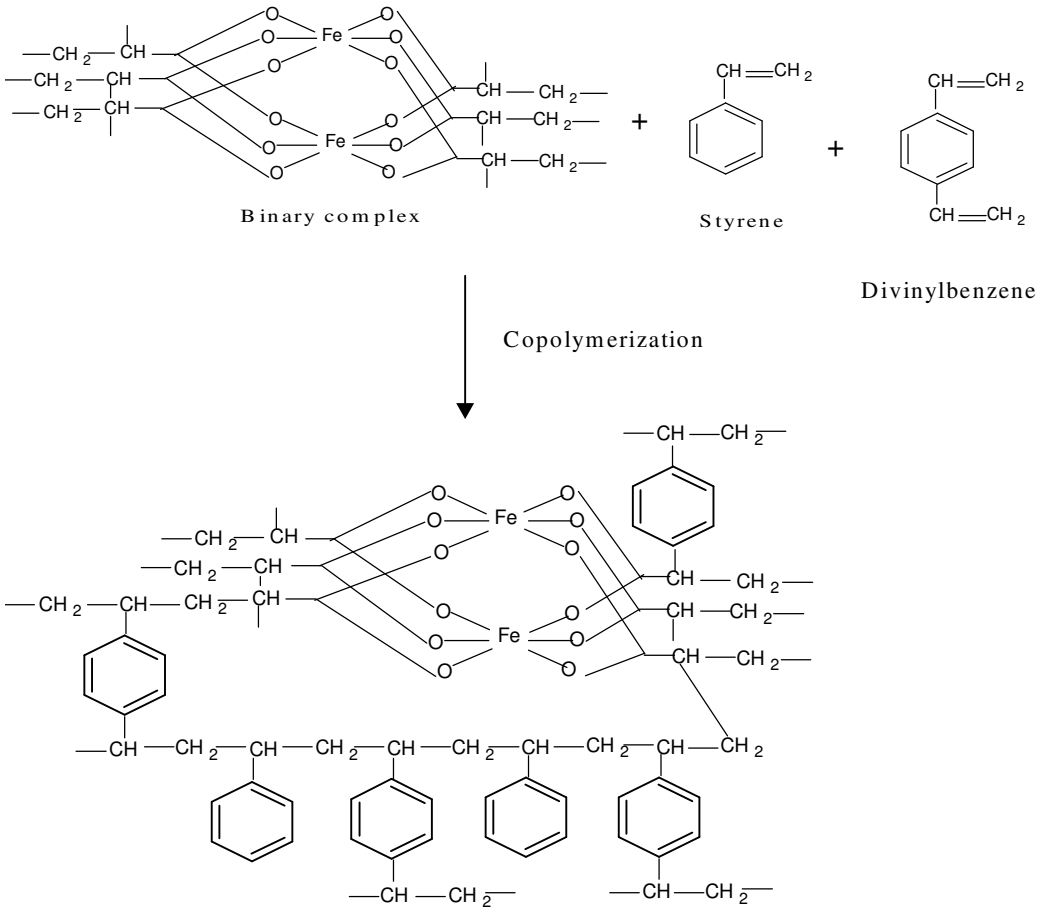

Fig. 1—Scheme for preperation of Fe(III)-ion imprinted polymer

Surface Area Measurement

Surface areas of leached IIP and NIP were measured by methylene blue (MB) adsorption[14]. A standard solution of MB (0.0178 g l^{-1}) was calibrated at λ 600 nm. To calculate surface area, 0.1 g of Fe(III)-IIP was treated with 25 ml of MB (conc., 0.0178 g l^{-1}). Treatment lasted until there was no further decrease in absorbance. Amount of MB adsorbed was calculated based on concentration difference between initial and equilibrium values, measured by spectrophotometry.

Cation Exchange Capacity (CEC)

Leached IIP and NIP (1 g each) were taken in a glass column (i. d. 4 mm) and H^+ ions were eluted by percolating 1 M sodium chloride (NaOH) solution through column at a flow rate of ~0.5 ml min^{-1}. Feed was passed until its pH became equal to that of eluent collected. H^+ ions so eluted were titrated against standardized 0.01 M NaOH solution.

Batch Experiments

Adsorption studies of Fe(III), Zn(II), Co(II), and Ni(II) ions on IIP were carried out by batch experiments. Aliquots (20 ml) of metal ion solutions (100 mg l^{-1}) and 5 ml of buffer solution (pH 1-6) were treated with IIP (50 mg) in 100 ml stoppard conical flasks. Suspensions were shaken for 6 h at 25°C. After centrifugation, supernatant solution was analyzed for metal ions using EDTA titration and standard spectrophotometric method[15]. Adsorption capacities were calculated as difference in metal ion concentration of pre and post adsorption solutions divided by weight of dried IIP. Adsorption capacity was also cross checked by eluting adsorbed Fe(III) on IIP with 1 M HNO_3. Distribution coefficients (ml g^{-1}) of metal ions between IIP particles and aqueous solution were also determined as $D = (C_i-C_f)/C_f.V/m$, where, C_i and C_f represent initial and equilibrium solution concentrations, respectively. V is volume of solution and m is weight of adsorbent used for extraction.

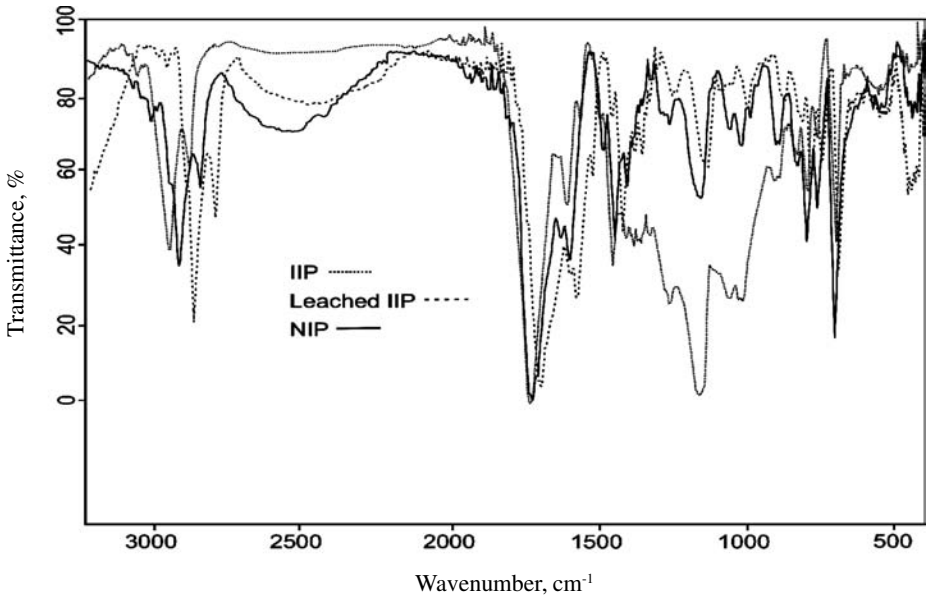

Fig. 2—FTIR spectra of IIP, leached IIP and NIP

Column Experiments

IIP (1 g) was slurred in DMW and then poured into Pyrex glass column (i. d. 4 mm). A small amount of glass wool was placed on disc to prevent loss of IIP during sample loading. Column was preconditioned by passing DMW and then a solution of metal ion was passed through column at a controlled flow rate (0.5 ml min^{-1}) after adjusting pH. For quantitative separations, mixture of metal ions was introduced into column. Adsorbed metal ions were eluted separately.

Results and Discussions

FTIR Characterization

FTIR spectra (Fig. 2) of IIP (leached and unleached) and NIP shows that these polymers have a similar backbone. Broad absorption bands due to –OH stretching of –COOH group expected at 2576 and 2574 cm^{-1} observed in leached IIP and NIP, respectively and disappeared in IIP, indicate formation of carboxylate anion, which takes part in bonding with Fe(III). Carboxylate anion stretching frequency typically observed at 1381 and 1575 cm^{-1} in IIP and disappeared in leached IIP and NIP.

Surface Area Measurement

Surface areas of leached IIP and NIP were calculated as

$$A_s = \frac{GN_{AV}Ø\ 10^{-20}}{MM_W} \quad \ldots(1)$$

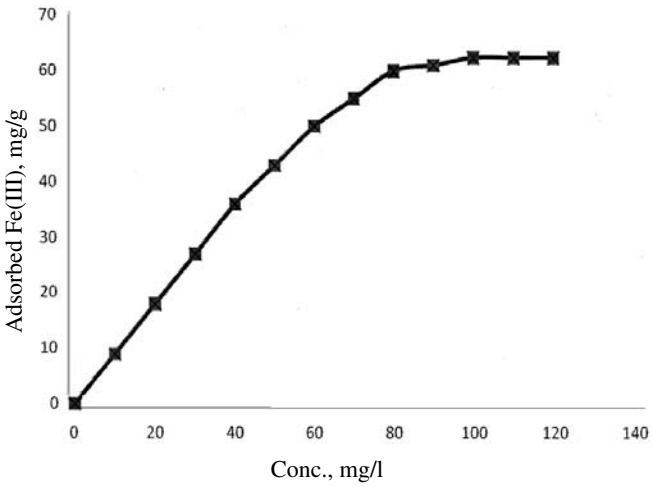

Fig. 3—Effect of concentration on adsorption of Fe(III) on Fe(III)-IIP [Fe(III), 10-100 mg l^{-1}; pH, 6.0; T, 25°C]

where A_s, surface area ($m^2\ g^{-1}$); G, MB adsorbed (g); N_{AV}, Avogadro's number ($6.02x10^{23}\ mol^{-1}$); Ø, MB molecular cross section (197.2 $Å^2$); M_W, mol wt of MB (373.9 g mol^{-1}); and M, adsorbent mass (g). Surface areas of leached IIP and NIP were found as 87.68 and 53.41 $m^2\ g^{-1}$, respectively.

Cation Exchange Capacity (CEC) and Adsorption Capacity

Cation exchange (H^+/Na^+) capacity of leached IIP (0.249 mmol g^{-1}) and NIP (0.252 mmol g^{-1}) seems due to replaceable H^+ ions of –COOH groups by Na^+ ions.

Under adsorption study (Fig. 3) of Fe(III) on Fe(III)-IIP from aqueous solutions (conc. range,

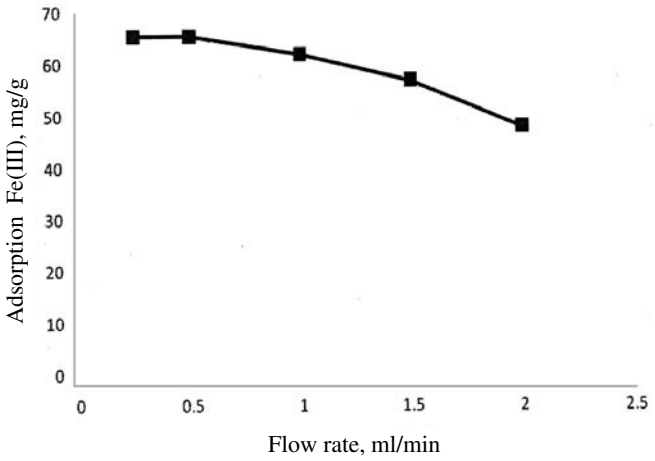

Fig. 4—Effect of flow rate on adsorption of Fe(III) on Fe(III)-IIP [IIP, 1g; Fe(III), 100 mg l^{-1}; pH, 6.0; T, 25°C]

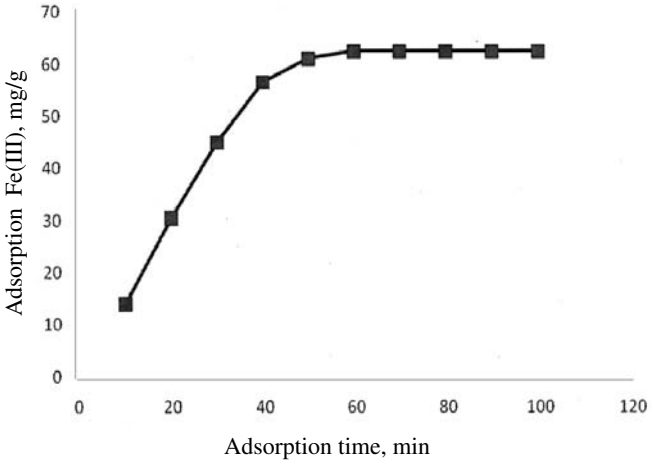

Fig. 5—Adsorption rates of Fe(III) on Fe(III)-IIP [Fe(III), 100 mg l^{-1}; pH, 6.0; T, 25°C]

Table1—Adsorption of Fe(III) and metal ions on Fe(III)-ion imprinted and non-imprinted polymers

Metal Ion	Adsorbed metal ions* (mg g^{-1})	
	Imprinted polymer	Non-imprinted polymer
Fe(III)	62.40	32.42
Zn(II)	14.62	12.51
Co(II)	11.44	11.60
Ni(II)	7.63	7.54

*Five replicate determinations

Table 2—Effect of imprinting and pH on distribution coefficients (D)

Metal Ion	D*, mlg^{-1}				
	Imprinted polymer				Non-imprinted polymer
	pH 6	pH 4	pH 2	pH 1	pH 6
Fe(III)	829.8	714.3	623.9	502.9	239.9
Zn(II)	85.6	67.6	56.5	45.8	71.5
Co(II)	64.6	27.2	19.7	19.7	65.6
Ni(II)	41.3	19.2	9.8	9.7	40.8

*Five replicate determinations

10-100 mg l^{-1}), amount of Fe(III) ions adsorbed per unit mass of IIP was found to increases with increase in initial concentration of Fe(III) up to 100 mg l^{-1}. In order to reach saturation, initial Fe(III) increased concentration till plateau values (adsorption capacity values) were obtained. Maximum Fe(III) adsorption capacity of IIP was 62.4 mg g^{-1} for three replicate measurements.

Effect of Flow Rate

Fe(III) can be adsorbed quantitatively on Fe(III)-IIP at flow rate of $\leq$ 1.0 ml min^{-1}, above which recovery was less than 95% (Fig. 4), may be due to decrease in contact time of Fe(III) with adsorbent. Flow rate (0.5 ml min^{-1}) was chosen as optimum for column procedures.

Equilibrium Adsorption Time

Higher adsorption rates of Cu(II) on to IIP from aqueous solution are observed at beginning of adsorption process, and then adsorption equilibrium gradually reached within 60 min (Fig. 5), seems due to complexation between Fe(III) ions and template group in IIP.

Adsorption and Distribution Studies

Adsorption capacity of Fe(III)-IIP for Fe(III) ion is higher (52%) than that of NIP. However, for Zn(II), Co(II) and Ni(II), there is no significant difference in adsorption capacities of IIP and NIP (Table 1). Higher capacity of IIP for Fe(III) seems due to cavities created after removal of template which is complementary to imprint ion in size and shape.

Distribution coefficient (D) of Fe(III)-IIP in buffer solutions (pH 1, 2, 4 and 6) and NIP at pH 6 for Fe(III) ions (Table 2) shows that IIP has excellent selectivity for Fe(III), probably due to coordination geometry. IIP shows following affinity order: Fe(III) > Zn(II) > Co(II) > Ni(II).

Separation of Metal Ions

To separate pairs of metal ions, separation factor is $D_A/D_B \geq 9$ (Table 3). Experiments required only small

Table 3—Quantitative separation of metal ions on Fe(III)-ion imprinted polymer column

Metal ion	Eluent	Amount loaded µg	Amount found µg	Error* %
Zn(II)	0.05 M HNO3 (25 ml)	321	319	0.62
Fe(III)	1 M HNO3 (20 ml)	280	283	+0.11
Co(II)	0.01 M HNO3 (25 ml)	285	284	0.35
Fe(III)	1 M HNO3 (20 ml)	280	281	+0.36
Ni(II)	0.01 M HNO3 (25 ml)	289	286	-1.04
Fe(III)	1 M HNO3 (20 ml)	280	280	0.00

*Five replicate determinations

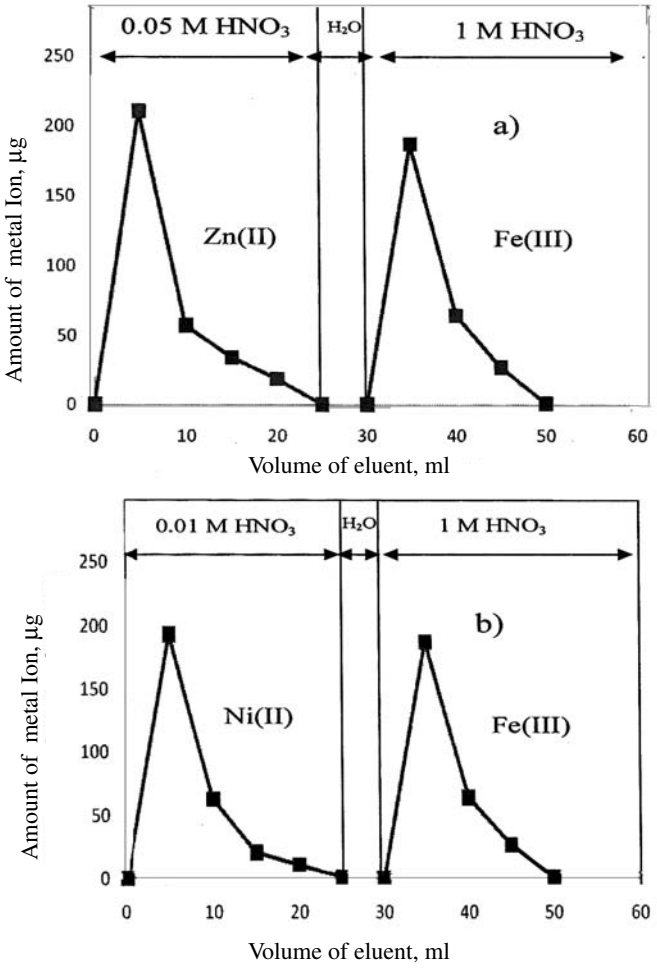

Fig. 6—Separation of: a) Zn(II)-Fe(III); and b) Ni(II)-Fe(III)

eluent volumes and resulted compact chromatograms (Fig. 6).

Recovery of Fe(III) Ions

River water and tap water samples were filtered through Whatman no. 4 filter paper, and spiked with Fe(III) (30-50 mg). Water samples were passed through column (i. d. 4 mm) packed with (1 g) IIP at flow rate of 0.5 ml min^{-1}. Adsorbed Fe(III) was eluted with 1 M HNO_3 and determined by spectrophotometry. Average recovery for five determinations was 97.4-99 % (Table 4).

Table 4—Recovery of Fe(III) from 1 l water samples

Sample	Fe(III) added mg	Fe(III) found mg	Recovery* %
River water	30	29.7	99.0
	40	39.4	98.5
	50	48.7	98.4
Tap water	30	29.5	98.3
	50	48.8	97.6

*Five replicate determinations

Conclusions

Fe(III)-IIP adsorbed corresponding guest Fe(III) ions more effectively than did NIP. Fe(III)-IIP shows good selectivity for Fe(III) ions even in presence of river water and tap water. Preconcentration and recovery of Fe(III) is simple, reproducible and less susceptible to contamination.

Acknowledgement

Authors thank Director, HBTI, Kanpur for providing necessary research facilities.

References

1 Pietrangelo A, Hereditary hemochromatosis - a new look at an old disease, *N Engl J Med,* **350** (2004) 2383-2387.

2 Andrews N C, Disorders of iron metabolism, *N Engl J Med,* **341** (1999) 1986-1995.

3 Wulff G, Molecular imprinting in cross-linked materials with the aid of molecular templates - a way towards artificial antibodies, *Angew Chem Ed Engl,* **34** (1995) 1812-1832.

4 Kempe M & Masbach K, Molecular imprinting used for chiral separations, *J chromatogr, A* **694** (1995) 3-13.

5 Steinke J, Sherrington D C & Dunkin I R, Imprinting of synthetic polymers using molecular templates, *Adv Polym Sci,* **123** (1995) 81-125.

6 Singh D K & Mishra S, Synthesis and characterization of UO_2(II)-ion imprinted polymer for selective extraction of UO_2(II), *Anal Chim Acta,* **644** (2009) 42-47.

7 Daniel S, Praveen R S & Rao T P, Ternary ion-association complexed based ion imprinted polymers (IIPs) for trace determination of palladium(II) in environmental samples, *Anal Chim Acta,* **570** (2006) 79-87.

8 Singh D K & Mishra S, Synthesis, characterization and removal of Cd(II)-ion imprinted polymer, *J Hazard Mater,* **164** (2009) 1547-1551.

9 Owens G S, Southard G E, Houten K A V & Murray G M, Molecularly imprinted ion-exchange resin for Fe(III), *Sep Sci Technol,* **40** (2005) 2205-2005.

10 Dakova I, Karadjova I, Georgieva V & Georgiev G, Ion-imprinted polymethacrylic microbeads as new sorbent for preconcentration and separation of mercury, *Talanta,* **78** (2009) 523-529.

11 Otero-Romani J, Moreda-Pineiro A, Bermejo-Barrera P & Martin-Esteban A, Synthesis, characterization and evaluation of ionic-imprinted polymers for solid-phase extraction of nickel from seawater, *Anal Chim Acta,* **630** (2008) 1-9.

12 Birlik E, Ersoz A, Acikkalp E, Denizli A & Say R, Cr(III)-imprinted polymeric beads: sorption and preconcentration studies, *J Hazard Mater,* **140** (2007) 110-116.

13 Zhao J, Han B, Zhang Y & Wang D, Synthesis of Zn(II) ion-imprinted solid-phase extraction material and its analytical applications, *Anal Chim Acta,* **603** (2007) 87-92.

14 Kaewprasit C, Hequet E, Abidi N & Gourlot J P, Application of methylene blue adsorption to cotton fiber specific surface area measurement: part I. methodology, *J Cotton Sci,* **2** (1998) 164-173.

15 Sandell E B, *Colorimetric Determination of Traces of Metals,* **3rd edn** (Interscience Publishers, Academic press, New York) 1959.