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Extraction of Polystyrene from Styrofoam Waste: Synthesis of Novel Chelating Resin for the Enrichment and Speciation of Cr(III)/Cr(VI) Ions in Industrial Effluents

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Abstract**—**Polystyrene (PS) was extracted from Styrofoam (expanded polystyrene foam) waste, so called white pollutant. The PS was functionalized with *N,N*- Bis(2-aminobenzylidene)benzene-1,2-diamine (ABA) ligand through an azo spacer. The resin was characterized by FT-IR spectroscopy and elemental analysis. The PS-N=N-ABA resin was used for the enrichment and speciation of Cr(III)/Cr(VI) ions and total Cr determination in aqueous samples by flame atomic absorption spectrometry (FAAS). The separation of Cr(III)/Cr(VI) ions was achieved at pH 2. The recovery of Cr(VI) ions was achieved ≥ 95.0% at optimum parameters: pH 2; resin amount 300mg; flow rates 2.0mL min^{-1} of solution and 2.0mL min^{-1} of eluent (2.0mol L^{-1} HNO_3). Total Cr was determined by oxidation of Cr(III) to Cr(VI) ions using H_2O_2. The limit of detection (LOD) and quantification (LOQ) of Cr(VI) were found to be 0.40 and 1.20µg L^{-1}, respectively with preconcentration factor of 250. Total saturation and breakthrough capacitates of the resin for Cr(IV) ions were found to be 0.181 and 0.531mmol g^{-1}, respectively. The proposed method was successfully applied for the preconcentration/speciation of Cr(III)/Cr(VI) ions and determination of total Cr in industrial effluents.

Keywords**—**Styrofoam waste, Polymeric resin, Preconcentration, Speciation, Cr(III)/Cr(VI) ions, FAAS.

I. Introduction

THE different metallic species such as Sb(III)/Sb(V), As(III)/As(V), Se(VI)/Se(IV), Cr(III)/Cr(VI), Co(II)/Co(III), Hg(I)/Hg(II), Mn(II)/Mn(VI) ions, etc. co-exist in environmental and biological samples. These species are differentiated by their physico-chemical forms and toxic activities [1]. In speciation analysis, the separation of different metallic species and their concentrations have been determined in given samples [2]. Chromium has been widely used in electroplating, metallurgy, leather tanning, oxidative dyeing, and manufacturing of ceramics, steel, photographic materials, wood preservatives, fungicides, inks and rubber for years [3], [4]. The chromium contaminated water discharges to environment and contaminated the environmental aquatic bodies due to its non-biodegradable nature. The wastewater contains Cr(III) as $Cr(OH)_4^-$ and $Cr(OH)_2^+$and Cr(VI) as $Cr_2O_7^{2-}$ (dichromate), $HCrO_4^{2-}$ (bichromate) and CrO_4^{2-} (chromate) anions depending on pH [5]. Structurally, Cr(VI) ion is similar to PO_4^{3-} and SO_4^{2-} anions which can be easily enter the cell membranes via sulfate transport system**.** The maximum allowable concentration of Cr(VI) ions in potable water has been fixed as 0.05mg L^{-1}.The chromium contaminated water, discharges to environment and contaminated the environmental aquatic bodies due to its non-biodegradable nature. The maximum allowable concentration of Cr(VI) ions in potable water has been fixed as 0.05mg L^{-1}. Long exposure to Cr(VI) ions cause acute health problems such as cancer in breast, lungs and digestive tract, sperms death, epigastric pain, vomiting, nausea, asthma, hemorrhage, severe diarrhea, and defects in urinary system [4], [6]. Cr(III) is an essential nutrient, maintains the normal glucose level in human [7], [8]. For good health, 50-500mg of Cr(III) ions per day is required [9].

The toxicity of metals strongly depends on their oxidation states rather than their total concentrations [10]. Therefore, metallic species has been becoming a prime task for analytical chemists for years [2].

In present study, PS was extracted from Styrofoam waste and coupled with ABA ligand for the synthesis of PS-N=N-ABA resin. The synthesized resin was used as efficient sold phase for solid phase extractive enrichment and speciation of Cr(III)/Cr(VI) ions in aqueous samples.

II. Experimental

A. Apparatus and Chemicals

The determinations of studied metals were performed by PerkinElmer FAAS (Analyst 800, USA). PerkinElmer FT-IR spectrometer (SN-92417, UK) was used to record the FT-IR spectra. PerkinElmer Series II CHNSO Analyzer 2400 was used for elemental analysis. Digital pH meter (Hanna 211, Germany) was used for the pH measurements. Reverse osmosis system was used to obtaining ultrapure (UP) quality water. UP quality water and analytical reagent-grade reagents were used throughout the experiments. The standards and working solutions were prepared daily by dilution of commercial stock solutions (1000±4.0mg L^{-1}) of Cr(III) and Cr(VI) ions. The buffer solutions, H_3PO_4/NaH_2PO_4,

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CH_3COOH/CH_3COONa and NH_4OH/NH_4Cl were used to adjust pH 2, 4-6 and 8-10, respectively. The Styrofoam was collected from local market of Hyderabad, Sindh-Pakistan.

B. Extraction of PS from Styrofoam Waste

Styrofoam is composed of 5.0% of PS and 95.0% air [11]-[13]. Pre-cleaned 5.0g of Styrofoam foam was dissolved in 50mL of acetone with mechanically stirred. The air was liberated as effervescence and PS was settled down as a white colored gummy material. The gummy material was air-dried for 24h, grinded and sieved to 150-200µm. The PS extracted from Styrofoam foam waste was used as polymer matrix for the synthesis of PS-N=N-ABA resin.

C. Synthesis of PS-N=N-ABA Resin

Fig.1 illustrates the reaction scheme for the synthesis of PS-N=N-ABA resin. 5.0g of PS was modified to diazonium derivative by reported procedure [14]. The $PS\text{-}N_2Cl$ was coupled with 13.6g of *N,N*-Bis(2-aminobenzylidene)benzene-1,2-diamine (ABA) ligand at 0-5°C for 24h. The synthesized resin was filtered, washed and air-dried.

D. Preconcentration Procedure

Glass column (10cm x 1.0cm) with stopcock and porous disc was packed with 300mg of PS-N=N-ABA resin (grounded and sieved to 150-200µm) and 25mL of 0.8µg mL^{-1} Cr(III)/Cr(VI) ions solution was adjusted to pH 2 and passed through the column by gravitationally at the flow rate of 3.0mL min^{-1}. The retained metal ions were desorbed by with 2.0mL of 2.0mol L^{-1} HNO_3 at the flow rate of 2.0mL min^{-1} and determined by FAAS.

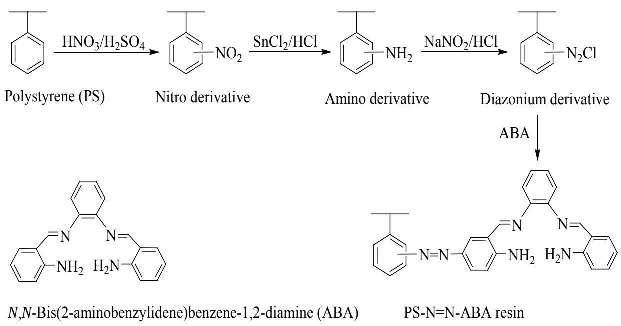

Fig. 1 Reaction scheme for the synthesis of PS-N=N-ABAresin

III. Result and Discussions

A. Characterization

The synthesized resin was characterized by FT-IR spectroscopy, the characteristic peaks in FT-IR spectrum at 3350, 1674, 1551 and 1253cm^{-1}, correspond to the stretching vibrations of N-H, N=N, N=N and HN-C, respectively, indicated the coupling of ABA ligand with PS through –N=N- spacer.

The synthesized resin was also characterized by elemental analysis. The experimental values were found to be C, 75.16; H, 5.81; N, 18.03% and theoretical values calculated for single repeating unit ($C_{29}H_{26}N_6$) of the resin are C, 75.96; H, 5.71; N, 18.33%. A close agreement between experimental and theoretical values confirmed the successful coupling of ABA ligand with each of repeating units of PS through an azo spacer.

B. Effect of pH

pH is an important parameter which strongly influences surface activity of resin toward the metal ions Thus, the effect of pH on the retention of Cr(III) and Cr(VI) ions on the column was investigated separately. For this purpose, 25mL of model solutions was adjusted to 2-9. The retained ions were eluted with 5.0mL of 3.0mol L^{-1} HNO_3 and determined by FAAS. The recoveries of Cr(VI) and Cr(III) ions were achieved 96.0±4.0% and 1.5±2.0%, respectively at pH 2.0 as shown in Fig. 2. Therefore, pH 2.0 was chosen as best point for the separation of Cr(VI) and Cr(III) ions.

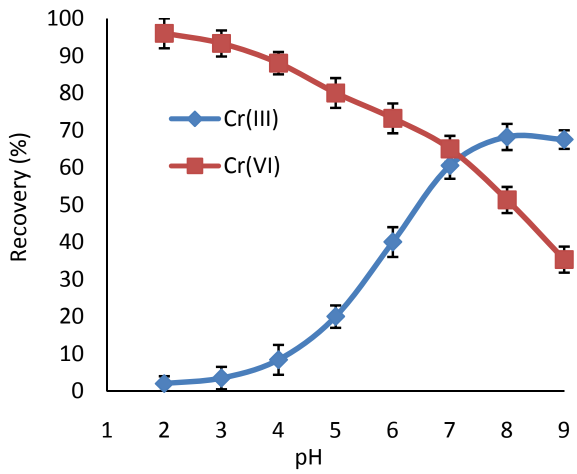

Fig. 2 Effect of pH on the recovery of Cr(VI) ions

C. Effect of Eluent

Different eluent such as HCl and HNO_3 with different concentration and different volume were screened for the desorption of Cr(VI) ions. The recovery of Cr(VI) ions was achieved 96.0±3.5% with 2.0mL of 2.0mol L^{-1} HNO_3. Therefore, 2.0mL of 2.0mol L^{-1} HNO_3 was chosen as best eluent.

D. Effect of Flow Rate

The effects of flow rates of sample solution and eluent were investigated. For this, 25mL of model solution was passed through the column at the flow rate of 1-5.0mL min^{-1}. The retained metal ions were eluted with 2.0mL of 3.0mol L^{-1} HNO_3 at the flow rate of 1-5.0mL min^{-1}. The recovery of Cr(VI) ions was achieved 96.0±2.5% at the flow rate of 3.0 and 2.0mL min^{-1} of sample solution and eluent, respectively. Therefore, 3.0 and 2.0mL min^{-1} were chosen as optimum flow rates of sample solution and eluent, respectively.

E. Effect of Resin Amount

The column was packed with 100-500mg of the resin and model solution was passed at the flow rate of 3.0mL min^{-1}.

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The recoveries of Cr(VI) ions were achieved ≥95.5 with RSD ≤4.0% using 300-500mg of the resin. Therefore, 300mg was chosen as optimum resin amount for the further experiments.

F. Effect of Sample Volume

The model solution (2.0mg L^{-1}) of Cr(VI) ions was diluted to 25-800mL and adjusted to pH 2. The diluted sample solution was passed through the column. The recoveries of Cr(VI) ions from the diluted sample solutions were achieved ≥95.0% with RSD ≤3.5 until 500mL of sample solution as shown in Fig. 3. Therefore, the preconcentration factor calculated was 250 as 2.0mL of final solution was subjected to FAAS.

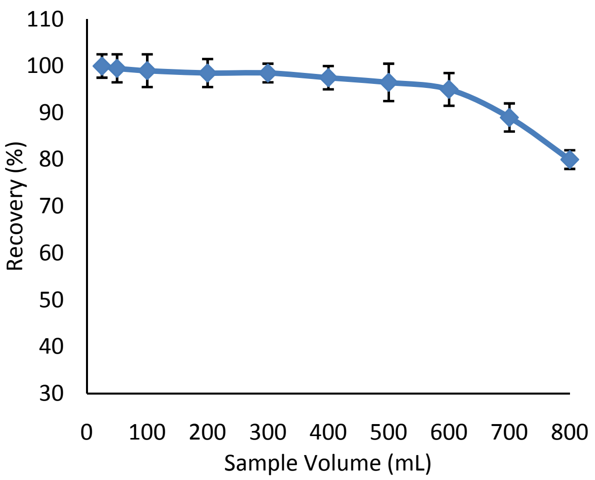

Fig. 3 Effect of sample volume on the recovery of Cr(VI) ions

G. Effect of Matrix Ions

The matrix ions influence the selectivity and sensitivity of method. Thus, the effects of different matrix ions at the different levels on the recovery of Cr(VI) ions were investigated. The recovery of Cr(VI) ions was achieved ≥95.0% with RSD ≤4.5% (volume 25mL, n = 3) in presence of significant level of matrix ions as shown in Table I. Therefore, the synthesized resin possessed high tolerance limit for the matrix ions.

H. LOD and LOQ

According to IUPAC, LOD and LOQ are defined as blank + 3σ and blank + 10 σ, respectively (where σ is standard deviation of blank analysis for 15 replicates) [15], [16]. The LOD and LOQ were found to be 0.40 and 1.22μg L^{-1}, respectively.

I. Sorption Capacity

The efficiency of PS-N=N-ABA resinfor the retention of Cr(VI) ions was obtained by determining sorption capacity using column procedure.The resin amount, flow rate (of sample solution) and the initial concentration ofCr(VI) ions were fixed as 300mg, 3.0mL min^{-1} and 10mg L^{-1}, respectively.

The breakthrough point occurs when the final concentration (C_f) becomes 5.0% of the initial concentration (C_o) and the column attains complete saturation when C_f approaches to C_o. The breakthrough curve was plotted to obtain the capacities of the resin for Cr(VI) ions. Therefore, total saturation and breakthrough capacitates of the PS-N=N-ABA resin for Cr(IV) ions were found to be 0.181 and 0.531mmol g^{-1}, respectively.

TABLE I
EFFECT OF MATRIX IONS ON THE RECOVERY OF CHROMIUM (VI) ION

Ions	Added salts	Conc. (mg L^{-1})	R±RSD (%)
Na^{+}	$NaNO_3$	14000	95.0±4.5
K^{+}	KCl	14000	97.7±3.5
Mg^{2+}	$MgCl_2$	10000	96.6±3.0
Ca^{2+}	$CaCl_2$	8000	97.5±2.5
Ba^{2+}	$BaCO_3$	8000	97.5±3.5
Cl^{-}	NaCl	18500	96.5±3.0
F^{-}	NaF	18000	98.0±2.0
HCO_3^{-}	$NaHCO_3$	10000	95.5±3.5
CO_3^{2-}	Na_2CO_3	10000	98.0±4.0
SO_4^{2-}	$(NH_4)_2SO_4$	8000	97.5±2.0
PO_4^{3-}	Na_3PO_4	5000	98.0±3.5
NO_3^{-}	KNO_3	5000	96.5±3.5
CH_3COO^{-}	CH_3COONa	12000	97.0±2.0

R: Recovery (%), RSD: Relative standard deviation, nd: Not detected

J. Determination of Total Cr

The model solution contained different amount of Cr(VI) and Cr(III) ions was prepared. The Cr(III) ions in the model solution was oxidized to Cr(VI) ions using H_2O_2 in basic media according to reported procedure [17]. Thereafter, the model solutions contained total chromium as Cr(VI) ions was adjusted to pH 2 and passed through the column according to the proposed method. The results (Table II) showed that the proposed method could be successfully applied for the determination of total chromium.

TABLE II
DETERMINATION OF TOTAL CHROMIUM IN TEST-SOLUTIONS

Added (μg)		Found (μg)			R±RSD (%)		
Cr^{3+}	Cr^{6+}	Cr^{3+}	Cr^{6+}	Cr	Cr^{3+}	Cr^{6+}	Cr
0.0	20	nd	19.0	19.5	-	97.5±2.0	97.5±2.0
5	15	4.9	14.5	19.4	98.0±2.0	96.7±2.0	97.0±4.0
10	10	9.8	9.9	19.7	98.0±1.5	99.0±2.0	98.5±3.5
15	5	14.7	4.9	19.6	98.0±2.0	98.0±2.0	98.0±4.0
20	0	19.8	nd	19.8	-	99.0±3.0	99.0±3.0

R: Recovery (%), RSD: Relative standard deviation, nd: Not detected

IV. APPLICATIONS OF DEVELOPED METHOD

The proposed method was applied for the preconcentration and speciation of Cr(III)/Cr(VI) ions in industrial effluents collected from industrial site area in Karachi-Pakistan. The samples were analyzed (volume 500mL, n = 3) with and without standard addition method. A good agreement was obtained between added and determined values as shown in Table III.

TABLE III
APPLICATION OF THE METHOD FOR DETERMINATIONS OF TOTAL CR IN SPIKED WATER SAMPLES

Sample	Added (μg)		R±RSD (%)		
	Cr^{3+}	Cr^{6+}	Cr^{3+}	Cr^{6+}	Cr
waste water-1	0.0	0.0	-	-	-
	5.0	5.0	100±2.0	98.0±2.5	99.0±4.0
	10	10	98.0±1.5	99.0±2.0	98.5±3.5
waste water-2	0.0	0.0	-	-	-
	5.0	5.0	98.0±1.5	100±2.0	99.0±3.5
	10	10	99.0±2.0	99.0±2.0	99.0±2.0

R: Recovery (%), RSD: Relative standard deviation, nd: Not detected

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