

Chemical Speciation of Chromium(III) and (VI) Using Phosphonium Cation Impregnated Polyurethane Foams Prior to Their Spectrometric Determination

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Fast and selective sorptions of Cr(VI) species from aqueous media onto tetraphenylphosphonium bromide (TPP⁺·Br⁻) physically immobilized polyurethane foams (PUFs) sorbent were achieved. Based on the Scatchard model of binding sites of the PUFs and Langmuir and Dubinin–Radushkevich (D-R) adsorption models of Cr(VI) retention onto TPP⁺·Br⁻ immobilized PUFs, a dual retention mechanism involving absorption related to “weak-base anion ion exchange” and an added component for “surface adsorption” was proposed. Thus, the TPP⁺·Br⁻ loaded PUFs were successfully packed in column mode for preconcentration of trace and ultra trace concentrations of Cr(VI) as halochromates [CrO₃C]⁻_{aq} from aqueous HCl media. The retained [CrOCl₃]⁻_{aq} species were recovered with NaOH (1.0 mol L⁻¹) and analyzed by flame atomic absorption spectrometry. Cr(III) species after oxidation to Cr(VI) with H₂O₂ in aqueous KOH (1.0 mol L⁻¹) were also retained and could be recovered by the proposed method. The limits of detection (LOD) and quantification (LOQ) of Cr(VI) were 0.04 and 0.13 μg L⁻¹, respectively. The chemical speciation of Cr(III, VI) species in various water samples at trace and ultra trace levels were carried out by TPP⁺·Br⁻ loaded PUFs packed column. The enhancement factor and sensitivity factor of [CrO₃C]⁻_{aq} sorption were 80.0 and 30.0, respectively.

(Received February 22, 2011; Accepted May 10, 2011; Published July 10, 2011)

Introduction

Chromium is a metallic element usually found in aquatic systems in two oxidation states, Cr(III) and Cr(VI). Cr(III) appears to be an essential trace element species since it plays an important role in some metabolic processes and it is responsible for reducing blood glucose in addition to insulin,¹ while Cr(VI) is highly toxic and potentially responsible for carcinogenic effects in humans.² Thus, chemical speciation is one of the most interesting areas of research in the fields of environmental science, toxicology, nutritional sciences, environmental and occupational medicine and analytical sciences.^{1–3} Cr(III) and Cr(VI) species interact differently with living organisms. The guideline values set by World Health Organization (WHO) for Cr(VI) in ground and drinking water is 0.05 mg L⁻¹ for drinking water.^{4,5} Thus, the developing of effective, precise and accurate analytical methods for preconcentration and chemical speciation of Cr(III) and Cr(VI) species at trace level is extremely important.⁵

The two predominant forms of chromium in water *i.e.* Cr(III) and Cr(VI) have very different properties. The solution chemistry of chromium containing water plays an important role in the efficient removal of chromium by sorption/ion exchange.²

Thus, preconcentration of chromium could be carried either as Cr(III) ions or as Cr(VI) ions.

Liquid-liquid^{6,7} and solid phase extraction (SPE) *e.g.* clay minerals, gelatin, biosorbent, and active carbon, synthetic polymers, C18-bonded silica, silica gel immobilized with Zr(IV) and Zr(VI) phosphate have been used for preconcentration and/or separation of trace and ultra trace amounts of toxic metal ions from complex matrices.^{8–15} Determination and chemical speciation of Cr(III) and Cr(VI) at trace levels in welding fumes and in drinking water samples using strong anion ion-exchange,¹⁶ neutral alumina,¹⁷ mini-columns packed with resin immobilized with 8-hydroxyquinoline,¹⁸ activated carbon,¹⁹ leaching procedure with sodium carbonate⁵ and drawn and modified lingo cellulosic materials^{20,21} have been reported. However, some of these SPE methods^{10–15} are too expensive or unselective; they require careful experimental conditions, are time consuming and are not compatible with the detection limit of Cr(VI) in various matrices.

In the last three decades, polyurethane foam (PUF) sorbent has been used in extraction chromatography and in gas-solid and gas-liquid partition chromatography.^{22–24} The cellular structures of the PUFs in foamed and micro spherical forms make it a suitable and excellent filling material with good capacity for firmly retaining various extracting agents.^{25,26} Based on the resilience characters of the PUFs, El-Shahawi *et al.*²⁷ have used tetraphenylphosphonium bromide (TPP⁺·Br⁻) treated PUFs in medical syringes in pulse column for speciation of Cr(III) and Cr(VI) species in wastewater. The reagent TPP⁺·Br⁻ loaded PUFs sorbent survived the extraction and stripping process, its recycle ability was fine, it is safe as long as

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its storage and its disposal are undertaken in a safe manner. Thus, the present article reports the sorption mechanism of the halochromate species from the aqueous media onto the TPP⁺·Br⁻ loaded PUFs sorbent, the randomly distribution sites of energy in the PUFs sorbent and finally application of the treated PUFs column for preconcentration and subsequent speciation of Cr(III) and Cr(VI) species in wastewater.

Experimental

Reagents and materials

All chemicals used were of analytical reagent grade. Doubly deionized water was used throughout. BDH (BDH, Poole, England) diphenylcarbazide, DPC solution (0.1% w/v) was prepared by dissolving the required weight of the reagent in acetone-H₂SO₄ (0.01 mol L⁻¹). Stock solutions of BDH reagents TPP⁺·Br⁻, tetraphenylarsonium chloride (TPAs⁺·Cl⁻) (0.1% w/v), and K₂Cr₂O₇ (1 mg mL⁻¹) were prepared in deionized water. Foam cubes (10 – 15 mm edges) of commercial white sheets of polyether-type based PUFs were cut from the foam sheets, purified and finally dried.²³ Some immobilized reagent TPAs⁺·Cl⁻ or TPP⁺·Br⁻ immobilized PUFs foam cubes were prepared and homogeneously packed in the glass columns as reported.²⁵

Apparatus

A Varian Model AA-875 flame atomic absorption spectrometer (FAAS) was used at the optimum conditions of chromium determination at the optimum operational parameters for chromium. A single beam Digital Spectro UV-VIS RS Labomed, spectrophotometer (USA) with quartz cell (10 mm path length) was used for recording the absorbance of Cr(VI) species before and after extraction following the method reported by Sano.²⁸ A Lab-line mechanical Shaker (Corporation Precision Scientific, Chicago, USA) with a shaking rate in the range of 10 – 250 rpm and a glass column (18 × 10 mm i.d.) were used in batch and column experiments for chromatographic separation of Cr(VI), respectively. Deionized water was obtained from Milli-Q Plus system (Milford, MA). A Thermo Orion pH Meter Model 720 (Thermo Fisher Scientific, MA) was used for the pH measurements with absolute accuracy limits of pH defined by NIST buffers. A glass column of 18 mm length and 10 mm inner diameter was used in flow experiments.

Reagent foam preparation

The reagent foams were prepared by mixing the dried foam cubes with an aqueous solution containing TPP⁺·Br⁻ at 0.02% w/v (50 mL/g dry foam) with efficient stirring for 30 min. The immobilized reagent foam cubes were then squeezed and dried as reported earlier.²⁴

Batch experiment

An accurate weight (0.2 ± 0.01 g) of the reagent TPP⁺·Br⁻ or TPAs⁺·Cl⁻ treated PUFs was shaken with an aqueous solution (50.0 mL) containing Cr(VI) ions (10 µg mL⁻¹) and HCl (1.0 mol L⁻¹) at 25 ± 0.1 °C in a low density polyethylene bottle for 2 h on a mechanical shaker. After phase separation, the aliquot solution was separated out and assayed by direct spectrophotometry at 545 nm²⁶ or by FAAS. At Cr(VI) concentrations lower than the lower limit of detection (LOD) of DPC,²⁷ AAS was used at the optimum operational conditions. The amount of Cr(VI) retained at equilibrium q_e on the PUFs cubes was determined from the differences between the absorbance of Cr(VI) solutions before (A_b) and after (A_a) shaking

with the reagent PUFs cubes. The extraction percentage (%*E*) and the distribution ratio (*D*) of the Cr(VI) sorption onto the reagent loaded foam were then calculated as reported earlier.^{23,24}

Following these procedures, the influence of HCl concentration, polarity of the extraction medium, sample volume, cation size of mono valence ions and Cr(VI) concentration (0.05 – 80 µg mL⁻¹) on the retention step from the aqueous solutions onto the reagent loaded PUFs were examined. All experiments were performed in triplicate at ambient temperature (25 ± 0.1 °C). The results of %*E* and *D* are the average of three measurements and the precision in most cases was ±2%.

Chromatographic separation of Cr(VI)

An aqueous solution (1.0 L) containing Cr(VI) at a total concentration in the range 0.05 – 5 µg mL⁻¹ in HCl (1.0 mol L⁻¹) was percolated through the TPP⁺·Br⁻ immobilized PUFs packed (4.0 ± 0.01 g) column at 10 mL min⁻¹ flow rate. The sample and the blank foam packed columns were then washed with an aqueous solution containing HCl (100 mL; 1.0 mol L⁻¹) at the same flow rate. Cr(VI) sorption took place on the PUFs as indicated from the analysis of Cr(VI) in the effluent solution. The sorbed Cr(VI) species were recovered from the foam column with NaOH (10 mL; 1.0 mol L⁻¹) at 3 mL min⁻¹ flow rate.

Retention of Cr(III)

An aliquot of the aqueous solution (100.0 mL) containing Cr(III) ions at a concentration in the range 0.05 – 50 µg mL⁻¹ was transferred to a conical flask (250 mL). The solution was oxidized to Cr(VI) in alkaline media (KOH, 1.0 mol L⁻¹) after boiling for 10 min with H₂O₂ (2 mL, 10.0% w/v). The solution was adjusted to the required acidity with HCl (1.0 mol L⁻¹) after cooling and was finally percolated through the reagent TPP⁺·Br⁻ loaded PUFs packed columns at 10 mL min⁻¹ flow rate as described for Cr(VI). The retained Cr(VI) species were then recovered from the foam column with NaOH (10 mL, 1.0 mol L⁻¹) at 3 mL min⁻¹ flow rate and determined *via* its standard curve.²⁹ Blank experiments were carried out under the same experimental conditions.

Chemical speciation of inorganic Cr(III) and Cr(VI)

An aqueous solution (0.5 L) containing the binary mixture of Cr(III) and Cr(VI) species at a total concentration of chromium species ≤15 µg mL⁻¹ was percolated through the TPP⁺·Br⁻ immobilized foam packed column at 5 mL min⁻¹ and analyzed according to the described procedure for Cr(VI) recovery. Another aliquot sample (0.5 L) was first oxidized to Cr(VI) and then analyzed as mentioned for Cr(III) retention. The absorbance of the recovered species of the first aliquot (A_1) will thus be a measure of Cr(VI) ions in the mixture, while the absorbance of the eluted species of the second aliquot (A_2) is a measure of the sum of Cr(III) and Cr(VI) ions. Therefore, the absorbance ($A_2 - A_1$) is a measure of the Cr(III) ions in the binary mixture.

Application

Fresh- or industrial wastewater samples (1.0 L) were first filtered through a piece of filter paper of Milpore type of 0.45 µm porosity. An aliquot (100 mL) of the sample that was adjusted with HCl of concentration 1.0 mol L⁻¹ and spiked with Cr(III) and/or Cr(VI) at a total concentration level ≤15.0 µg L⁻¹ was percolated through TPP⁺·Br⁻ immobilized PUFs packed column at 10 mL min⁻¹ flow rate as described for Cr(VI). The column was washed with an aqueous solution containing HCl (10 mL; 1.0 mol L⁻¹) at the same flow rate. The sorbed Cr(VI) species were recovered with NaOH solution (10 mL, 2 mol L⁻¹) at 3.0 mL min⁻¹ flow rate. The recovered Cr(VI) species was

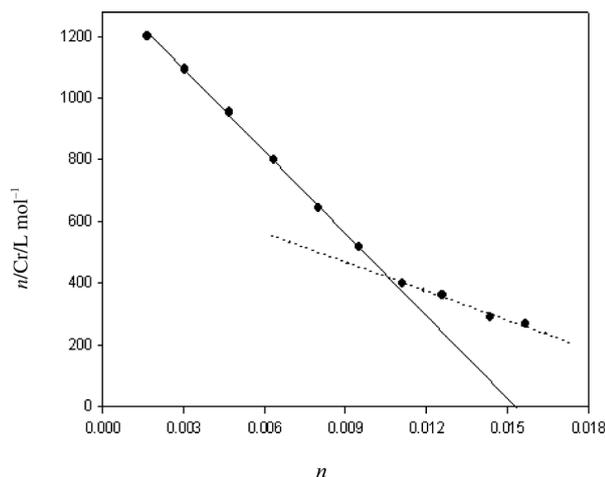


Fig. 1 Scatchard plot for the $[\text{CrO}_3\text{Cl}]^-$ retention from the aqueous solution onto PUFs in the presence of HCl (3.0 mol L^{-1}).

then analyzed with the aid of standard curve. Another aliquot sample (100 mL) was treated as described earlier for Cr(III) retention. The concentrations of Cr(VI) and total Cr(III, VI) were then determined from their standard curves constructed by FAAS.

Results and Discussion

Retention profile of Cr(VI) towards immobilized PUFs

A recent study²⁷ has revealed that, Cr(VI) sorption from aqueous solution by TPAs⁺-Cl⁻ or TPP⁺-Br⁻ loaded PUFs reached a maximum from HCl (3.0 mol L^{-1}) medium. These results and the data reported earlier²⁸ suggest that extraction of Cr(VI) by solvent extraction mechanism and the uptake will most likely proceed as follows:



Here, X = As or P.

The protonation of the ether oxygen $(-\text{CH}_2-\text{O}-\text{CH}_2-)_{\text{foam}}$ and/or amide nitrogen $(-\text{NH}-\text{COO}-)_{\text{foam}}$ linkages available in the PUFs sorbent membrane are -3 and -6 , respectively.²⁹ Thus, in HCl extraction medium, the retention of the $[\text{CrO}_3\text{Cl}]^-_{\text{aq}}$ species that proceeded *via* the formation of ternary ion associates $[\text{CrO}_3\text{Cl}]^-_{\text{aq}} \cdot \text{PQ}^+ \cdot \text{Cl}^-$ on/in the PUFs membrane was enhanced. The stability constants of the binding sites of the PUFs with $[\text{CrO}_3\text{Cl}]^-_{\text{aq}}$ were calculated using the Scatchard equation:

$$\frac{n}{[\text{Cr}]} = K(n_t - n) \quad (3)$$

$$n = \frac{\text{Weight of chromium bound to foam (g)}}{\text{Weight of foam (g)}} \quad (4)$$

Here, K is stability constant of $[\text{CrO}_3\text{Cl}]^-_{\text{aq}}$ sorbed onto PUF, n_t the maximum concentration of $[\text{CrO}_3\text{Cl}]^-_{\text{aq}}$ sorbed onto the available sites of PUFs, and $[\text{Cr}]$ the equilibrium concentration of Cr(VI) in solution (mol L^{-1}). The plot of $n/[\text{Cr}]$ versus n is shown in Fig. 1. It revealed formation of more than one class of complex species where each complex has its own unique

formation constant. The stability constants ($\log K_1$ and $\log K_2$) of the sorption step of $[\text{CrO}_3\text{Cl}]^-_{\text{aq}}$ species onto PUFs took place readily on site K_1 belong to the ether group. This group has a greater stability than the amide group (site K_2) as reported.²⁹ The stability constants $\log K_1$ and $\log K_2$ for the sorbed species derived from the respective slopes were 4.95 ± 0.07 and 4.48 ± 0.09 , respectively. The calculated values of n_1 and n_2 were 0.015 ± 0.005 and $0.024 \pm 0.001 \text{ mol g}^{-1}$, respectively. The values of the stability constants ($\log K_1$ and $\log K_2$) indicated that the sorption of species took place readily on site K_1 or most likely belongs to the ether group because this group has a greater stability than the amide group (site K_2) as reported earlier.³⁰ The high values of K_1 and K_2 indicated that, both bonding sites of PUF are highly active towards $[\text{CrO}_3\text{Cl}]^-_{\text{aq}}$ species. The results are in good agreement with the data reported earlier involving the extraction of the bulky anion $[\text{CrO}_3\text{Cl}]^-_{\text{aq}}$ by methyl isobutyl ketone and other solvents that possess ether linkages in their structures *e.g.* diethyl ether and isopropyl ether.³¹ Based on these data and the results reported on the retention of AuCl_4^- and CdI_4^- by PUFs,^{25,30} a sorption mechanism involving a weak base anion ion exchange and solvent extraction of $[\text{BiI}_4]^-_{\text{aq}}$ by the protonated ether $(-\text{CH}_2-\text{HO}^+-\text{CH}_2-)$ oxygen or urethane $(-\text{N}^+\text{H}_2\text{COO}-)$ nitrogen linkages of the PUFs as a ternary complex ion associate will most likely proceed as follows.

The effect of ethanol content (1 - 15% v/v) *i.e.* solvent polarity upon Cr(VI) sorption by the reagent treated PUFs was investigated. The retention percentage ($\%E$) of Cr(VI) species onto PUFs increased linearly on raising the ethanol content from 0.0% ($E = 62\%$) and reached maximum at 2% ($E = 78.3\%$), followed by a plateau. The change of the environment around the Cr(VI) ions makes the available binding sites of the PUFs more hydrophilic which further diminished the need for solvating water molecules and reduces the Cr(VI) uptake onto the reagent immobilized PUFs to the added ethanol in the medium.³⁰

The effects of cation (Li^+ , Na^+ , K^+ and NH_4^+) size and concentrations (0.05 - 1% w/v) on the Cr(VI) uptake onto PUFs were studied. On increasing the salt concentration, one finds a slight increase ($\sim 5 - 9\%$) in the extraction percentage of Cr(VI) in the presence of LiCl, NaCl, KCl and NH_4Cl . The order of extraction followed the sequence: Li^+ ($\log D = 3.1$) > Na^+ ($\log D = 2.95$) \sim NH_4^+ ($\log D = 2.96$) > K^+ ($\log D = 2.7$).

This effect is most likely attributed to the reduction of the repulsive forces between adjacent sorbed species of $[\text{CrO}_3\text{Cl} \cdot \text{TPX}^+]_{\text{foam}}$.^{31,32} Thus, the ion-dipole interaction of NH_4^+ with the oxygen sites of the PUFs are not the predominating factors in the retention step of $[\text{CrO}_3\text{Cl}]^-_{\text{aq}}$ species and "solvent extraction" mechanism with the salt acting as salting-out agent participates on Cr(VI) uptake onto PUFs. The added ions (Li^+ , Na^+ , K^+ or NH_4^+) reduce the water molecules available to solvate the $[\text{CrO}_3\text{Cl}]^-_{\text{aq}}$ species which would be forced out of the solvent phase onto the PUFs. The free water molecules are preferentially used to solvate the added cations.³³

The influences of surfactant type and concentrations (0.0 - 2% m/v) *e.g.* tetraethyl ammonium chloride, sodium dodecyl sulfate (SDS) or Triton-X 100 on Cr(VI) uptake were investigated. The sorption percentage ($E = 62\%$) of Cr(VI) increased in the presence of SDS or Triton-X100 ($E = 86.7\%$) up to 0.1% (w/v) and leveled off at higher surfactant concentrations. The added surfactant increases the solution viscosity leading to a progressive change in the physical properties of the microenvironment of the associate ($\text{CrO}_3\text{Cl} \cdot \text{TPX}^+$) onto PUFs. It enhances the aggregation of the associate and also lowers the diffusion rate of the analyte within the PUFs membranes.³⁴ The competition between the excess

surfactant and the ion pair reagent towards Cr(VI) may also predominate in the sorption step. Anionic surfactant may also interact directly with the ion pair reagent resulting in minimizing the retention of $[\text{CrO}_3\text{Cl}]_{\text{aq}}$ onto PUFs during the extraction process.

Sorption isotherms

The sorption profile of Cr(VI) from the bulk aqueous solution onto the reagent loaded foam over a wide range of concentrations ($0.05 - 80 \mu\text{g mL}^{-1}$) was determined. The amount of Cr(VI) retained onto the PUFs sorbent varies linearly at low or moderate analyte concentration in the aqueous test solution suggesting a first order behavior. On raising the Cr(VI), the values of D decreased rapidly and the most favorable D values were achieved for dilute solutions. Thus, film diffusion and intraparticle transport are the two steps that controlling the molecular diffusion at the macro pore of the PUFs.³⁵ Thus, the uptake of the analyte from the solution was subjected to Langmuir³⁶ and Dubinin-Radushkevich (D-R)³⁵ sorption models. The Langmuir sorption isotherm is expressed in the following linear form:³⁶

$$\frac{C_e}{C_{\text{ads}}} = \frac{1}{Q_b} + \frac{C_e}{Q} \quad (5)$$

where, C_e the equilibrium concentration (mol L^{-1}) of Cr(VI) in solution and C_{ads} the retained Cr(VI) concentration onto the loaded PUFs per unit mass of sorbent at equilibrium (mol g^{-1}). The Langmuir parameters Q and b are related to the maximum sorption capacity and to the binding energy of the solute sorption. Plots of C_e/C_{ads} versus C_e were linear over the entire concentration range of the analyte. The values of Q and b calculated from the slopes and intercepts of the linear plots were found 0.148 ± 0.05 , $0.153 \pm 0.03 \text{ mmol g}^{-1}$ and 12.2 ± 0.07 , $11.12 \pm 0.06 \text{ L mol}^{-1}$ for Cr(VI) sorption onto TPAs⁺-Cl⁻ and TPP⁺-Br⁻ loaded foams, respectively.

The D-R isotherm model³⁶ was postulated within the adsorption space close to the adsorbent surface. The linear form of D-R isotherm can be expressed as follows:

$$\ln C_{\text{ads}} = \ln K_{\text{DR}} - \beta \varepsilon^2 \quad (6)$$

where, K_{DR} , β and ε are constants related to the maximum amount of Cr(VI) retained onto the solid sorbent to the energy of transfer of the solute from the bulk solution to the solid sorbent, and the Polanyi potential, respectively. The value of ε is given by the equation:

$$\varepsilon = RT \ln \left(1 + \frac{1}{C_e} \right) \quad (7)$$

where, R the gas constant ($\text{kJ mol}^{-1} \text{K}^{-1}$) and T the absolute temperature in Kelvin. The plots of $\ln C_{\text{ads}}$ versus ε^2 are linear (Fig. 2) indicating that the D-R isotherm is applied for Cr(VI) sorption onto TPAs⁺-Cl⁻ or TPP⁺-Br⁻ loaded PUFs over the entire concentration. The K_{DR} and β values calculated from the intercepts and slopes are in the range $99 - 120 \text{ mmol g}^{-1}$ and $0.002 - 0.003 \text{ mol}^2 \text{kJ}^{-2}$, respectively, indicating that the surface adsorption of the analyte by the solid sorbent participates in the retention step. Based on these results and the data reported,^{25,34} a dual retention mechanism model is proposed and can be expressed by the equation:

$$C_r = C_{\text{abs}} + C_{\text{ads}} = DC_{\text{aq}} + \frac{SK_L C_{\text{aq}}}{1 + K_L C_{\text{aq}}} \quad (8)$$

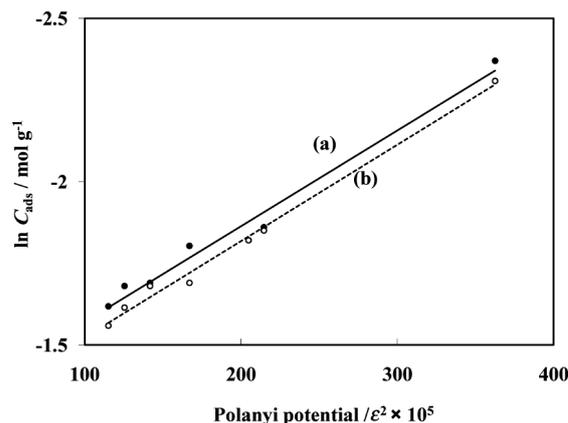


Fig. 2 Dubinin-Radushkevich (D-R) plots of Cr(VI) sorption ($0.05 - 80 \mu\text{g mL}^{-1}$) onto TPAs⁺-Cl⁻ (a) and TPP⁺-Br⁻ (b) immobilized foams ($0.2 \pm 0.01 \text{ g}$) at pH 0 and 298 K.

where C_r and C_{aq} are the equilibrium concentrations of Cr(VI) ions onto the solid sorbent and in aqueous solution, respectively. C_{abs} and C_{ads} are the equilibrium concentrations of analyte retained onto the used solid sorbents as an absorbed species and adsorbed species, respectively and S and K_L are the saturation values for the Langmuir adsorption model.^{24,36}

Chromatographic separation of Cr(VI)

The membrane like structures and the excellent hydrodynamic and aerodynamic properties of PUFs sorbent³⁷ enhanced Cr(VI) uptake onto the TPP⁺-Br⁻ treated PUFs packed columns. The kinetics and the sorption characteristics of TPP⁺-Br⁻ PUFs towards Cr(VI)²⁷ also suggested the use of the TPP⁺-Br⁻ treated PUFs in columns for the chromatographic separation of chromium. The sorption characteristics of Cr(VI) onto TPP⁺-Br⁻ immobilized PUFs suggested the use of reagent TPP⁺-Br⁻ loaded PUFs in column mode for the quantitative extraction, recovery and subsequent chemical speciation of Cr(III) and Cr(VI) from large sample volumes. Thus, distilled and/or tap water samples (1.0 L) containing HCl (1.0 mol L^{-1}) and various concentrations ($0.2 - 5.0 \mu\text{g mL}^{-1}$) of Cr(VI) were percolated through the PUFs packed column at the optimum experimental conditions and at various flow rates ($5 - 20 \text{ mL min}^{-1}$). Analysis of the effluent solutions against the reagent blank have revealed complete ($96 - 98 \pm 1.6\%$) retention of Cr(VI) at $5 - 10 \text{ mL min}^{-1}$. The sorbed Cr(VI) species were then recovered quantitatively ($97 \pm 2.6\%$) from the PUFs packed column with NaOH (10 mL , 1.0 mol L^{-1}) at 3 mL min^{-1} flow rate. The TPP⁺-Br⁻ packed column was also tested for the collection and recovery of Cr(III) ions. Aqueous solutions (0.1 L) containing Cr(III) at various concentrations ($0.05 - 50 \mu\text{g mL}^{-1}$) were oxidized to Cr(VI) using H_2O_2 in alkaline KOH (1.0 mol L^{-1}).²² They were then percolated through TPP⁺-Br⁻ PUFs packed column at 5 mL min^{-1} flow rate against reagent blank at the optimum conditions of Cr(VI) retention. The resultant Cr(VI) solutions were percolated through TPP⁺-Br⁻ PUFs packed column at 5 mL min^{-1} flow rate against reagent blank. The retained Cr(VI) species were then recovered with NaOH (10 mL , 1.0 mol L^{-1}) at 5 mL min^{-1} flow rate. A satisfactory recovery percentage ($96 \pm 2.7 - 102 \pm 1.9\%$, $n = 5$) of Cr(III) species was achieved.

The TPP⁺-Br⁻ packed PUFs column was also used for the preconcentration and recovery of the binary mixture solution (0.5 L) containing Cr(III) and Cr(VI) at a total concentration $\leq 15.0 \mu\text{g mL}^{-1}$ in HCl (1.0 mol L^{-1}). The test solution was first

Table 1 Recovery data of total inorganic Cr(III) and Cr(VI) in their binary mixture in the aqueous media by the developed PUFs packed column

Added/ $\mu\text{g L}^{-1}$		Average total chromium found/ $\mu\text{g L}^{-1}$	Recovery, % ^a
Cr ³⁺	Cr ⁶⁺		
10.0	5.0	15.9	106.0 \pm 3.3
5.0	5.0	9.7	97.0 \pm 3.2
5.0	10.0	14.9	98.7 \pm 4.5

a. Average recovery ($n = 5$) \pm relative standard deviation.

percolated and recovered through the TPP⁺·Br⁻ packed PUFs column at 2–3 mL min⁻¹ flow rate against a reagent blank. It was then analyzed as described for Cr(VI). Another aliquot sample was analyzed following the recommended procedures for Cr(III) retention and recovery. Cr(III) ions were then determined from the difference ($A_2 - A_1$) between the absorbance of the first (A_1) and second (A_2) aliquots. Satisfactory recovery percentage of the total Cr(III) and Cr(VI) species was obtained in the range 97.0 \pm 3.2 – 106.0 \pm 3.3% (Table 1). The effect of flow rate (5–25 mL min⁻¹) on the retention of Cr(VI) by the TPP⁺·Br⁻ treated PUFs-packed columns was examined by percolating 0.5 L of distilled water spiked with 20 μg of Cr(VI) ions. Complete sorption of Cr(VI) ions from the test solutions was achieved quantitatively (\sim 98.6 \pm 2%) at a flow rate \leq 15 mL min⁻¹.

Performance of the developed TPP⁺·Br⁻ PUFs packed column

The performance of the proposed TPP⁺·Br⁻ loaded PUFs packed columns for the Cr(VI) uptake at 10 mL min⁻¹ was determined from the elution curves of Cr(VI) with NaOH. Complete sorption of Cr(VI) onto the packed column took place at 5 mL min⁻¹. The retained Cr(VI) species were then recovered with NaOH (10 mL, 1.0 mol L⁻¹) and analyzed. The results are demonstrated in Fig. 3. The height equivalent (HETP) and the number (N) of the theoretical plates calculated from the elution curves³⁷ (Fig. 3) were 0.95–0.98 \pm 0.1 mm and 138–141 \pm 5, respectively. The HETP and N values computed from the breakthrough capacity curves (Fig. 4) were 0.97 \pm 0.1; 131 \pm 3 and 0.92 \pm 0.13; 129 \pm 4 ($n = 5$), respectively. The critical capacity of Cr(VI) ion sorption onto TPAs⁺·Cl⁻ and TPP⁺·Br⁻ loaded PUFs packed column calculated from Fig. 4 were 14.8 \pm 1.2 and 15 \pm 1 mg/g PUFs, respectively at 5 mL min⁻¹ flow rate. The breakthrough capacities³⁸ of Cr(VI) uptake onto the reagent TPAs⁺·Cl⁻ or TPP⁺·Br⁻ PUFs calculated from Fig. 4 were 19.0 \pm 1.5 and 19.8 \pm 1 mg g⁻¹, respectively. These values are quite good by comparison with other solid support such as Voltalef, silica gel and solid ion exchange in column modes.³⁷

Figure of merits of TPP⁺·Br⁻ treated PUFs packed method

Under the established conditions for the retention and recovery of various concentrations of Cr(VI) species from the test aqueous solutions (100 mL) onto TPP⁺·Br⁻ treated PUFs packed column, a linear calibration curve was obtained with the following regression equation:

$$A = 0.52C + 0.034 \quad (n = 5; R^2 = 0.98) \quad (9)$$

Here, C represents the analyte concentration (0–15 $\mu\text{g L}^{-1}$). According to the IUPAC,³⁹ the lower limits of detection ($\text{LOD} = 3S_{y/x}/b$) and quantification ($\text{LOQ} = 10S_{y/x}/b$) were found to be equal 0.04 and 0.13 $\mu\text{g L}^{-1}$, respectively where $S_{y/x}$ is the

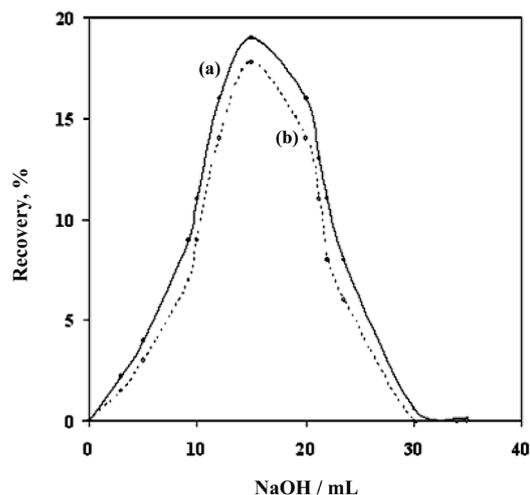


Fig. 3 Elution curves of Cr(VI) from immobilized TPAs⁺·Cl⁻ (a) and TPP⁺·Br⁻ (b) PUFs packed column (4 \pm 0.01 g) at 3 mL min⁻¹ employing NaOH (1.0 mol L⁻¹) as an eluting agent.

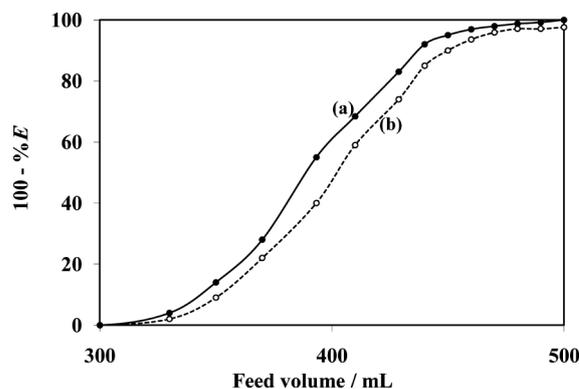


Fig. 4 Breakthrough curves for Cr(VI) at 10 $\mu\text{g mL}^{-1}$ sorption onto TPAs⁺·Cl⁻ (a) and TPP⁺·Br⁻ (b) impregnated PUFs (4 \pm 0.01 g) packed column at 5 mL min⁻¹ flow rate.

standard deviation of y -residual and b the slope of the calibration plot.³⁷ The LOD is far below the permissible limit of chromium by most of the reported methods^{10–17} and the values of Cr(VI) at 0.05 and 0.2 ng mL⁻¹ in fresh and marine water samples, respectively. The LOD is sufficiently low as compared to those attained by AAS (9.0 $\mu\text{g L}^{-1}$) and ICP-OES (1.0 $\mu\text{g L}^{-1}$). Moreover, the LOD and LOQ could be improved to lower values by prior collection of ultra trace concentrations of chromium species from large sample volumes at the optimum conditions. An enrichment factor of 50 was obtained ($V_{\text{sample}} = 1000$ and $V_{\text{eluent}} = 20$ mL). The sensitivity factor calculated from the ratio of slopes of the calibration plots with and without pre-concentration step was close to 30. A relative standard deviation (RSD) of \pm 3.4% was achieved at a Cr(VI) concentration of 0.1 $\mu\text{g mL}^{-1}$, $n = 5$, confirming the precision of the method. The analytical features of the proposed method were showed excellent performance compared with most of the reported methods.^{10,16} Some of these methods exhibited high detection limits in the range of 0.01–7.5 $\mu\text{g L}^{-1}$.²³ Hence, the developed method is simple and less toxic, and provides an effective approach for the chemical speciation of Cr(III) and Cr(VI).

Table 2 Analysis of Cr(III) and Cr(VI) ions in industrial wastewater (1.0 L) by the proposed TPP⁺-Br⁻ foam packed column (A) and AAS (B) methods^a

Cr(III) added/ μg mL ⁻¹	Cr(VI) added/ μg mL ⁻¹	Cr found/μg mL ⁻¹		
		A		B total chromium
		Cr ³⁺	Cr ⁶⁺	
10	—	10.4 ± 0.12	2.4 ± 0.11	12.9 ± 0.1
5	10	5.43 ± 0.14	13.05 ± 0.26	17.9 ± 0.05
5	5	5.54 ± 0.17	7.56 ± 0.14	12.9 ± 0.2
10	5	10.57 ± 0.16	7.33 ± 0.20	18.1 ± 0.2

a. Average ($n = 5$) ± standard deviation.

Tolerance of electrolytes and diverse ions

The selectivity of the developed TPP⁺-Cl⁻ immobilized PUFs packed column for the preconcentration of Cr(VI) at 5 μg mL⁻¹ concentration level from aqueous media (50 mL) was examined in the presence of a relatively high excess (1 mg) of the ions relevant to waste water *e.g.* alkali and alkaline earth metals, Cu²⁺, Al³⁺, Ni²⁺, Co²⁺, Cd²⁺, Hg²⁺, Fe³⁺, VO₃⁻, AsO₂⁻, SO₄²⁻, PO₄³⁻ and MnO₄⁻ ions which are often accompanying Cr(VI) ion. The tolerance less than ±2% change in the uptake of Cr(VI) is considered free from interference. The limit was set as the amount of foreign ion:analyte ratio (w/w) causing an error of ±2%. Good extraction efficiency (>98 ± 2%) for the Cr(VI) ions was achieved in the presence of the investigated ions except Fe³⁺, VO₃⁻, MnO₄⁻, N₃⁻. The interference of Fe³⁺ and VO₃⁻ at 1:100 analyte to interfering ion was eliminated by adding 2 mL of NaF (1.0 mol L⁻¹) solution to the aqueous solution to obtain unambiguous and selective preconcentration and recovery of Cr(VI). In case of MnO₄⁻ ions, NaN₃ (1.0 mL, 0.1 % w/v) was added to the test solution to reduce Mn⁷⁺ to Mn²⁺ and an acceptable retention percentage of Cr(VI) of 98.02 ± 2.12% was achieved.

Applications

The TPP⁺-Cl⁻ treated PUFs packed column was applied for the determination of nanomolar concentrations of Cr(III) and/or Cr(VI) and total inorganic chromium in tap and/or industrial wastewater samples. A first aliquot (1 L) of tap water spiked (or without) with and/or Cr(VI) was percolated through the PUFs packed column at 3–5 mL min⁻¹ as described for Cr(VI) uptake. Cr(VI) was retained quantitatively, while Cr(III) species were passed through the column without sorption. The retained Cr(VI) species were then recovered by NaOH (10.0 mL, 1.0 mol L⁻¹) at a 2 mL min⁻¹ flow rate and analyzed by AAS. The results revealed the absence (not detectable) of Cr(III) and/or Cr(VI) in tap water; good extraction and recovery (98 ± 2%) of the spiked Cr(III) and/or Cr(VI) species were achieved. The chemical speciation of Cr(III) and Cr(VI) ions in industrial wastewater samples of an electroplating plant was carried by the standard addition. The results are given in Table 2. As it is seen, the results of the developed packed column and the data obtained by AAS are quite close. Cr(VI) sorption at concentration ≤0.01 μg L⁻¹ was also tested for tap and wastewater samples (100 mL) and analyzed by FAAS as described.

Conclusion

The developed method allows continuous monitoring of Cr(VI)

and total Cr(III) and Cr(VI) species content in electroplating industry. The PUFs packed column was reused three times without decrease in its efficiency. The method could be applied even at ultra trace Cr(III) and/or Cr(VI) in the aqueous media. Work is still continuing for the speciation and sequential determination of organic and inorganic chromium species in environmental samples by on-site analysis.

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