



# Retention profile and subsequent chemical speciation of chromium (III) and (VI) in industrial wastewater samples employing some onium cations loaded polyurethane foams

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## Abstract

The retention of chromium (VI) from aqueous media onto tetraphenylarsonium chloride (TPAs<sup>+</sup>Cl<sup>-</sup>) or tetraphenylphosphonium bromide (TPP<sup>+</sup>Br<sup>-</sup>) immobilized polyurethane foams (PUFs) was fast and followed first order reaction. The kinetic data of the retention step were subjected to Weber-Morris, Lagergren, Bhattacharya and Venkobachar and Bt kinetic models. The results revealed that, film and intraparticle transport might be the two steps controlling the rate of chromium (VI) sorption from the aqueous acid solutions of pH ~ zero. The positive values of the  $\Delta H$  of chromium (VI) retention by the reagents loaded PUFs were interpreted as an endothermic process. Under the optimum pH (pH ~ zero) of the aqueous solution, the proposed TPAs<sup>+</sup>Cl<sup>-</sup> or TPP<sup>+</sup>Br<sup>-</sup> immobilized PUFs was successfully used in a series of medical syringe (30, 50 mL capacity) as pulse columns for complete collection of chromium (VI) species present in fresh and industrial wastewater samples at ultra trace low level of chromium (VI) ( $\leq 0.05 \mu\text{g mL}^{-1}$ ). The collected chromium (VI) species onto TPAs<sup>+</sup>Cl<sup>-</sup> or TPP<sup>+</sup>Br<sup>-</sup>-PUFs was then stripped quantitatively (98–102 ± 2.6%) from the pulse columns with NaOH (2.0 mol L<sup>-1</sup>) and subsequently analyzed photometrically. The chromium (VI) ions could be pre concentrated up to 100-fold from large volume of water samples. The proposed pulse foam columns were applied successfully for complete collection, recovery (97.5 ± 2.6%,  $n=5$ ) and subsequent chemical speciation of chromium (III) and (VI) in wastewater samples. The results are in good agreement with the reported and standard methods at 95% confidence.

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## 1. Introduction

Chromium (III) is an essential element having an important role in the normal glucose tolerance factor, lipid, protein and fat metabolism in humans with a daily recommended intake of 50–200  $\mu\text{g/day}$  for the adult [1,2]. Chromium (VI) has a definitely adverse impact on living organism. Chromium (VI) can easily penetrate the cell wall and exert its noxious influence in the cell itself, being a source of cancer disease [3,4]. The reference dose

(RD) for chromium (VI) and chromium (III) are 0.005 mg/kg and 1.0 mg kg<sup>-1</sup> per day for body weight [3,4], respectively. Thus, chemical speciation of chromium in environmental samples is necessary to accurately assess pollution levels [5–8]. The concentration of chromium in natural water is very low [9–12], in order of a few 5  $\mu\text{g L}^{-1}$ . Therefore, powerful techniques with sufficient detection power e.g. inert organic solvents are required. Inert solvents e.g. chloroform, benzene and dichloromethane have been successfully used for the extraction of the ion associates of chromium (VI) with a series of high molecular weight amines from aqueous acid media [12–15].

The low level of chromium in drinking water is not compatible with the detection limit of most spectrochemical

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techniques. Thus, preconcentration and separation steps are frequently required in order to improve the detection capability of the employed techniques. Various preconcentration procedures e.g. solvent extraction, strong anion-exchange, activated neutral alumina, chelating resin immobilized with 8-hydroxyquinoline, co-precipitation, precipitation; saltbush biomass and activated carbon have been reported for the chemical speciation of chromium [16–24].

Recent years have seen an upsurge of interest in the applications of PUFs as an excellent support in reversed phase extraction chromatography, gas–solid and gas–liquid partition chromatography [25–32]. The cellular structures, the resilient characteristics and the available surface area of the PUF in both foamed and micro spherical forms make it suitable as an excellent sorbent and as a column filing material with good capacity for firmly retaining various loading and extracting agents [33,34]. This class of sorbent can easily be packed in glass medical syringes of various adequate capacities (30–50.0 mL), compressed and released by moving the plunger of the syringe PUFs [34]. Therefore, in the present manuscript we have tried to use pulse columns packed PUFs sorbent in an attempt to develop a simple, convenient and low cost extraction procedure for the preconcentration, recovery and subsequent chemical speciation of chromium (III) and (VI) species in wastewater. Application of the developed method for the analysis of chromium (VI) in wastewater is also critically considered.

## 2. Experimental

### 2.1. Reagents and materials

All chemicals used were of analytical reagent grade. Doubly de-ionized water was used throughout. The reagent diphenylcarbazide, DPC (BDH) solution (0.1%w/v) was prepared by dissolving the required weight in acetone containing sulfuric acid (0.01 mol L<sup>-1</sup>). Stock solutions of TPAs<sup>+</sup>Cl<sup>-</sup> (1% w/v), TPP<sup>+</sup>Br<sup>-</sup> (1% w/v) and K<sub>2</sub>CrO<sub>4</sub> (1 mg mL<sup>-1</sup>) were prepared in water and adjusted to pH zero with HCl (1.0 mol L<sup>-1</sup>). Foam cubes (10–15 mm edge) of commercial white sheets of polyether-type based PUFs were cut from the foam sheets, purified and finally dried at 80 °C in an oven for 2 h as reported earlier [34] and were used as solid sorbents. The immobilized reagent PUFs cubes were prepared by mixing the dried foam cubes with an aqueous solution (0.02%w/v) containing TPAs<sup>+</sup>Cl<sup>-</sup> or TPP<sup>+</sup>Br<sup>-</sup> (50 mL g<sup>-1</sup> dry foam) with efficient stirring for 30 min, squeezed and finally dried [31]. The reagent TPAs<sup>+</sup>Cl<sup>-</sup> or TPP<sup>+</sup>Br<sup>-</sup> immobilized PUFs was partially packed (0.3 g) in a series of medical syringe (30 or 50 mL adequate capacity) as pulse columns by applying gentle pressure as reported [34]. All containers used were pre-cleaned by soaking in nitric acid (20% w/v) and rinsed with de-ionized water before use. Low density polyethylene (LDPE) bottles, Nalgene were used for the collection of the different water samples. LDPE bottles were carefully cleaned first with hot detergent, soaked in 50% HCl (Analar), HNO<sub>3</sub> (2.0 mol L<sup>-1</sup>), subsequently washed with dilute HCl (0.5 mol L<sup>-1</sup>) and finally

rinsed with water. Wastewater samples were collected from the industrial liquid waste of electroplating company, Cairo City in LDPE bottles, Nalgene and stored at –20 °C in a refrigerator. Tap- and marine sea water samples were also collected from the boundary side of Ras-El Bar area in the Mediterranean Sea in LDPE bottles. For the chemical speciation measurements of chromium (III) and (VI) in the water samples, the aliquot samples were acidified with HCl (1.0 mol L<sup>-1</sup>), stored in LDPE sampling bottles at 4 °C until analysis and finally irradiated with UV for 4 h using 100 W mercury vapor lamp.

### 2.2. Apparatus

A Varian model AA-875 atomic absorption spectrometer (AAS) was used at the optimum conditions of chromium determination. A series of medical syringe (30 or 50 mL) was used as pulse columns. A Soxhlet extractor and a lab-line Orbital mechanical shaker SO1 (UK) were used for the purification of PUFs cubes and in batch experiments, respectively. The absorbance of the test solutions were measured with a single beam Digital Spectro UV–VIS RS Labomed, spectrophotometer (USA) with quartz cell (10 mm path length). A pH meter model 3305 (JENWAY) was also used for the pH measurements.

### 2.3. Recommended procedures

#### 2.3.1. Batch experiments

In a dry 100 mL polyethylene bottle, an accurate weight (0.2±0.01 g) of the reagent TPAs<sup>+</sup>Cl<sup>-</sup> or TPP<sup>+</sup>Br<sup>-</sup> loaded foam cubes was shaken for 2 h on a mechanical shaker with 50 mL of an aqueous solution containing chromium (VI) ions at 10 µg mL<sup>-1</sup> concentration level at 25±0.1 °C at the required pH adjusted by diluted HCl and/or NaOH. After phase separation, a 5 mL of the aliquot solution was transferred to a 10 mL standard flask containing 1 mL of dipenylcarbazide, DPC. The solution was then diluted with water to the mark, mixed thoroughly and assayed by direct spectrophotometry at 545 nm [19]. Alternatively, the reagent TPAs<sup>+</sup>Cl<sup>-</sup> were used for the analysis of chromium (VI) at 355 nm in the test solution after extraction into chloroform [20]. At concentrations of chromium (VI) lower than the lower limit of detection (LOD) of DPC [19] or TPAs<sup>+</sup>Cl<sup>-</sup> [20] method, AAS was used. The amount of chromium (VI) retained at equilibrium,  $q_e$  on the foam cubes was then determined from the difference between the absorbance of chromium (VI) solutions before ( $A_b$ ) and after ( $A_a$ ) extraction with the reagent foam cubes employing the equation:

$$q_e = (A_b - A_a) \cdot v/w \quad (1)$$

where,  $v$  and  $w$  are the volume (mL) of the aqueous solution and the weight (g) of the foam cubes, respectively. The extraction percentage (%E) and the distribution ratio ( $D$ ) of the chromium (VI) sorption onto the reagent-loaded foam were then calculated as reported earlier [33,34]. Following these procedures, the influence of temperature (298–348 K) on the sorption step of chromium (VI) by the loaded PUFs sorbents was fully studied. All

experiments were performed in triplicate at ambient temperature ( $25 \pm 0.1$  °C). The results of %E and *D* are the average of three independent measurements and the precision in most cases was  $\pm 2\%$ .

### 2.3.2. Pulse column-filling operation for chromium (VI)

The extraction efficiency was studied using spiked water samples for the recovery of traces of chromium (VI) species at the optimum acidity of the analyte sorption onto the PUFs. Doubly distilled water and/or industrial wastewater samples (200.0–500.0 mL) were spiked with known chromium (VI) concentrations ( $0.03\text{--}5$   $\mu\text{g mL}^{-1}$ ). The concentrations of chromium (VI) in the spiked water samples were determined as follows: immobilized  $\text{TPP}^+\text{Br}^-$  PUFs cubes ( $0.3 \pm 0.01$  g) were partially packed in a medical syringe (30 and 50 mL) under gentle pressure employing a glass rod. In each medical syringe separation was performed in a manner that allowed the external chromium (VI) solution to enter or leave the syringe at  $20\text{--}25$   $\text{mL min}^{-1}$  by releasing and/or pressing the plunger of the syringe. In this case, separation is performed by repeating the inflow/outflow cycle and each cycle constitutes one pulse. In this arrangement, the %E is related to the distribution ratio, number of pulses (*n*) and the maximum volume concentration (*P*) ( $P = w_t/v_p$ , where  $w_t$  is the total sample volume and  $v_p$  is the compressed foam volume) by the equation [34]:

$$E_{n,\text{op}} = D/P[1 - (nD/p + nD)^n] \quad (2)$$

The retained chromium (VI) species onto the PUFs sorbents were then stripped from the foam with NaOH (20 mL,  $1.0$   $\text{mol L}^{-1}$ ) by releasing or pressing (pulsing) the glass plunger of the syringe several times (25–30) with the glass tip of the syringe in NaOH solution. The recovery percentage of the retained chromium (VI) onto the  $\text{TPP}^+\text{Br}^-$  immobilized PUFs was then calculated from the original quantity of chromium (VI) species and that determined by AAS after stripping with NaOH from the PUFs sorbents.

### 2.3.3. Retention and sequential determination of chromium (III)

An aliquot (200 mL) of the aqueous solution containing  $0.01\text{--}5$   $\mu\text{g mL}^{-1}$  of chromium (III) was transferred to a conical flask (50 mL). The test solutions were then oxidized to chromium (VI) in alkaline media (NaOH,  $1.0$   $\text{mol L}^{-1}$ ) after boiling for 10 min with hydrogen peroxide (2 mL, 10% w/v). The test solutions were then cooled adjusted to pH  $\sim$  zero by HCl ( $1.0\text{--}2.0$   $\text{mol L}^{-1}$ ) and treated as described for chromium (VI) retention using the pulse column. The retained species were then recovered from the PUFs and quantified as described [20,35] or by AAS standard curve prepared under the same experimental conditions.

### 2.3.4. Separation and chemical speciation of inorganic chromium (III) and (VI)

Transfer an aliquot portion (200 mL) containing the binary mixture of chromium (III) and (VI) species at a total concentration of chromium species  $\leq 0.5$   $\mu\text{g mL}^{-1}$  to a conical flask. The test

solution was adjusted to pH zero with HCl ( $1.0$   $\text{mol L}^{-1}$ ), treated as described for chromium (VI) retention and stripping as described using the pulse column mode and finally analyzed as reported [30,36] or with AAS. Another aliquot mixture (200 mL) was transferred to the conical flask and treated as described for chromium (III) species before. On the bases of these procedures, the absorbance of the first aliquot ( $A_1$ ) will be a measure of chromium (VI) ions in the mixture, while the absorbance of the second aliquot ( $A_2$ ) is a measure of the sum of chromium (III) and (VI) ions. Therefore, the absorbance ( $A_2 - A_1$ ) is a measure of the chromium (III) ions in the binary mixture. At chromium (VI) concentrations lower than the LOD [35,36] AAS was used under the optimum conditions of chromium determination with the aid of standard curve.

### 2.4. Analytical applications

Industrial wastewater samples (100–500 mL) of electroplating industry were filtered through  $0.4$   $\mu\text{m}$  cellulose acetate membrane filters immediately upon collection and stored in LDPE bottles. The sample solutions were then adjusted to pH zero with HCl ( $1.0$   $\text{mol L}^{-1}$ ) in the laboratory. The water samples were then spiked with chromium (VI) at total concentration level  $\leq 0.05\text{--}5$   $\mu\text{g mL}^{-1}$  chromium (VI) ions. The sample solutions were then retained, stripped and recovered from  $\text{TPP}^+\text{Br}^-$  immobilized PUFs ( $0.2 \pm 0.01$  g) using immobilized PUFs packed medical syringes (50 mL) as described for chromium (VI) ions. The recovered chromium (VI) species was then analyzed with AAS and the chromium (VI) present in the wastewater sample was then calculated from the curve of standard addition method using the AAS after stripping from the solid phase with NaOH. The preconcentration procedure was optimized using model solutions containing chromium (VI) ions.

## 3. Results and discussion

### 3.1. Retention profile of chromium (VI) onto the PUFs

Screening tests on the application of the PUFs for the retention of chromium (VI) from the aqueous solution have shown that, the amount of the analyte ions extracted from the aqueous solution by the  $\text{TPAs}^+\text{Cl}^-$  or  $\text{TPP}^+\text{Br}^-$  loaded foam depends on the solution pH. Therefore, the sorption profile of an aqueous solution (100 mL,  $10$   $\mu\text{g mL}^{-1}$ ) containing chromium (VI) ions at different pH by  $\text{TPAs}^+\text{Cl}^-$  or  $\text{TPP}^+\text{Br}^-$  loaded foams was critically studied after shaking for 1 h at room temperature. The amount of chromium (VI) remaining in the aqueous solution at equilibrium was determined as reported [35,36]. The % E and the *D* of the chromium (VI) sorption from the aqueous solutions onto the  $\text{TPAs}^+\text{Cl}^-$  or  $\text{TPP}^+\text{Br}^-$  loaded PUFs decreased markedly on increasing the solution pH and maximum uptake was achieved at pH  $\sim$  zero. Representative data are shown in Fig. 1. At high pH, the observed decrease in the chromium (VI) uptake onto the reagent PUFs is most likely attributed to the instability, hydrolysis or the incomplete extraction of the produced complex ion associate of chromium

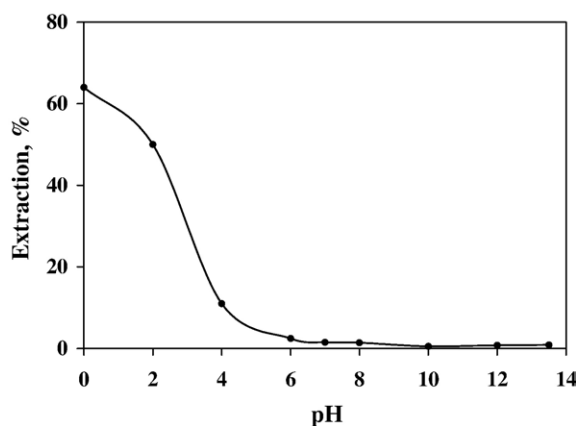


Fig. 1. Effect of pH on the sorption percentage of chromium (VI) from aqueous solution onto TPP<sup>+</sup>Br<sup>-</sup> immobilized foams at 25 ± 1 °C.

(VI)-TPAs<sup>+</sup>Cl<sup>-</sup> or chromium (VI)-TPP<sup>+</sup>Br<sup>-</sup> [37]. Thus, in the subsequent work, the solution was selected at pH zero.

The influence of the nature of the mineral acid (HCl, HNO<sub>3</sub> and H<sub>2</sub>SO<sub>4</sub> at 1 M concentration) on the chromium (VI) retention onto the PUFs was also investigated. Of these, HCl was proved satisfactory as the extraction medium of the produced complex ion associate between the halo chromate (CrO<sub>3</sub>Cl<sup>-</sup>)<sub>aq</sub> ions and TPAs<sup>+</sup> or TPP<sup>+</sup> immobilized PUFs. The influence of HCl concentration (1–5 mol L<sup>-1</sup>) was also examined. A sharp increase in the extraction of chromium (VI) was observed on increasing HCl concentration up to 3.0 mol L<sup>-1</sup>. Thus, in the subsequent work, HCl (3 M) was selected as a proper extraction medium on the chromium (VI) sorption from the aqueous solution onto TPAs<sup>+</sup>Cl<sup>-</sup> or TPP<sup>+</sup>Br<sup>-</sup> loaded PUFs. At HCl concentrations >3 mol L<sup>-1</sup>, the foam cubes were degraded and a progressive decrease in the chromium (VI) uptake onto the reagent loaded foams was observed in good agreement with the data reported earlier [33,34]. On the bases of these results and the data reported earlier [37,38], a possible “weak base ion exchange” extraction mechanism involving formation of complex ion associate of the general formula CrO<sub>3</sub>Cl<sup>-</sup>TPX<sup>+</sup> was retained onto the PUFs, where, X=As<sup>+</sup> or P<sup>+</sup>.

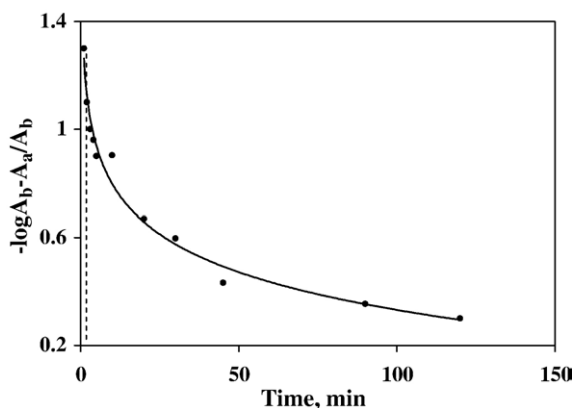


Fig. 2. Rate of chromium (VI) sorption from aqueous solution at 25 ± 1 °C onto TPP<sup>+</sup>Br<sup>-</sup> immobilized foams.

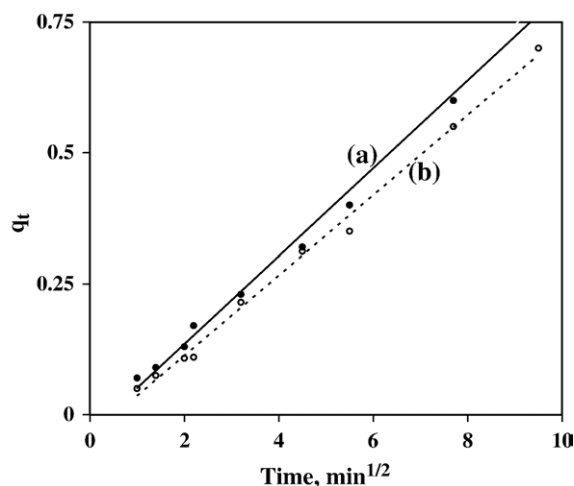


Fig. 3. The sorbed concentration of chromium (VI) at 5 µg/mL from aqueous solutions (50 mL) at pH zero and 25 ± 0.1 °C onto TPP<sup>+</sup>Br<sup>-</sup> immobilized PUFs (0.2 ± 0.01 g) as a function of square root of time.

### 3.2. Kinetic behavior of chromium (VI) uptake onto the PUFs

The chromium (VI) sorption onto the reagent TPAs<sup>+</sup>Cl<sup>-</sup> or TPP<sup>+</sup>Br<sup>-</sup> treated PUFs from the aqueous media containing HCl (3.0 mol L<sup>-1</sup>) at different time intervals was critically studied. The chromium (VI) ions uptake was found fast and reached equilibrium within ~30 min contact time. The half-life time ( $t_{1/2}$ ) of the equilibrium sorption to reach 50% saturation of the sorption capacity is calculated as 2 min (Fig. 2), consequently, 45 min shaking time was adopted in the subsequent experiments.

The sorbed chromium (VI) concentration  $q_t$  (mmol g<sup>-1</sup>) at time  $t$  was plotted against time to test the applicability of the Weber-Morris equation [39,40]:

$$q_t = R_d(t)^{1/2}, \quad (3)$$

where  $R_d$  is the rate constant of intraparticle transport in mmol g<sup>-1</sup> min<sup>-1/2</sup>. The diffusion rate is rapid in the initial stages and slows down with passage of time (Fig. 3). The data indicates that, for up to 8 min, the relationship fits well and starts to deviate as the shaking time increases. The values of  $R_d$  computed from slopes of the Weber-Morris plot (Fig. 3). in the initial stage up to 8 min were estimated to be 54 and 64 mmol g<sup>-1</sup> min<sup>-1/2</sup> for TPAs<sup>+</sup>Cl<sup>-</sup> and TPP<sup>+</sup>Br<sup>-</sup>, respectively [40,41].

The kinetic data of the chromium (VI) retention onto the reagent immobilized PUFs were also determined employing Lagergren model [42] over the entire range of agitation time explored using the equation:

$$\log(q_e - q_t) = \log q_e - (kt/2.303) \quad (4)$$

where,  $q_e$  is the sorbed chromium (VI) concentration onto the PUFs at equilibrium (mmol g<sup>-1</sup>) and  $k$  is the overall first order rate constant. The plots were linear. The values  $k$  calculated from the linear plots of  $\log(q_e - q_t)$  versus time up to 60 min (Fig. 4) were found equal 0.0076 ± 0.001 and 0.007 ± 0.0013 min<sup>-1</sup> for TPAs<sup>+</sup>Cl<sup>-</sup> and TPP<sup>+</sup>Br<sup>-</sup>, respectively. The results obtained in the light of Lagergren were further confirmed



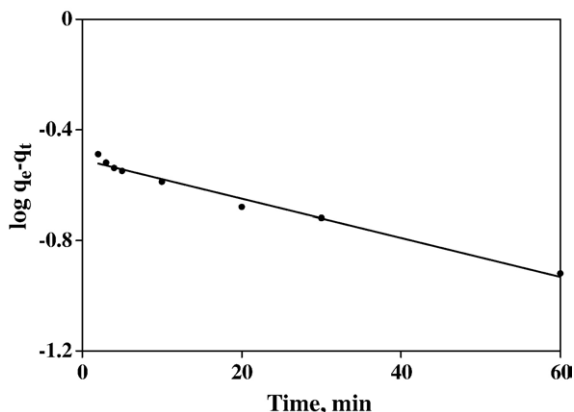


Fig. 4. Lagergren plots of the kinetics of chromium (VI) uptake from aqueous solution at pH zero at  $25 \pm 1$  °C onto TPAs<sup>+</sup>Cl<sup>-</sup> (a) and TPP<sup>+</sup>Br<sup>-</sup> (b) immobilized foams.

by Bhattacharya and Venkobachar model [43] confirming the formation of monomolecular layer of chromium (VI) species onto the surface of the adsorbent.

The value of Bt, which is a mathematical function ( $F$ ) of the ratio of the fraction sorbed ( $q_t$ ) in mol/g at time  $t$  and at equilibrium ( $q_e$ ) in mol/g i.e.  $q_t/q_e$  was calculated for each value of  $F$  employing Reichenburg equation [44]:

$$Bt = -0.4977 - 2.303 \log (1 - F) \quad (5)$$

Plots of Bt versus time at  $25 \pm 1$  °C were linear for up to 60 min shaking for chromium (VI) sorption onto TPAs<sup>+</sup>Cl<sup>-</sup> and TPP<sup>+</sup>Br<sup>-</sup> loaded foams, respectively. These data confirmed the observed behavior of the Weber-Morris equation test [39,40], where the straight lines (Fig. 3) does not pass through the origin. Thus, particle diffusion is the most probable operating mechanism and does not control the kinetics of chromium (VI) ions sorption onto the TPAs<sup>+</sup>Cl<sup>-</sup> and TPP<sup>+</sup>Br<sup>-</sup> immobilized foams. Therefore, the retention of chromium (VI) onto PUF cubes probably involves three steps: bulk transport of chromium (VI) in solution, film transfer involving diffusion of chromium (VI) species within the pore volume of PUF and/or along the pore wall surface to an active sorption site [33] and finally formation of  $[\text{CrO}_3\text{Cl TPX}^+]_{\text{foam}}$ . The actual sorption of the solute on the interior surface site is very fast, and hence it is not the rate-determining step therefore, film and intraparticle transport might be the two steps controlling the rate of sorption from acid solutions (pH ~ zero).

### 3.3. Thermodynamic characteristics of chromium (VI) uptake

The thermodynamic parameters ( $\Delta H$ ,  $\Delta S$ , and  $\Delta G$ ) of chromium (VI) uptake onto TPAs<sup>+</sup>Cl<sup>-</sup> or TPP<sup>+</sup>Br<sup>-</sup> immobilized foams have been evaluated [40]. The equilibrium constant  $K_c$  of the sorption process of chromium (VI) onto PUFs was calculated employing the equation:

$$K_c = \frac{F_e}{1 - F_e} \quad (6)$$

where  $F_e$  is the fractional attainment of the sorption step by the TPAs<sup>+</sup>Cl<sup>-</sup> or TPP<sup>+</sup>Br<sup>-</sup> loaded PUFs. The plots of  $\log D$  or  $\log K_c$  versus  $1/T$  (Fig. 5) were found linear over the investigated temperature range (300–353 K). The values of  $\Delta H$ ,  $\Delta S$  and  $\Delta G$  calculated from the slopes and intercepts of Fig. 5 were found equal  $5.67 \pm 0.1$  kJ mol<sup>-1</sup>,  $17.97 \pm 0.3$  J/(mol K) and  $0.31 \pm 0.04$  kJ mol<sup>-1</sup> (at 298 K), respectively for chromium (VI) sorption onto TPAs<sup>+</sup>Cl<sup>-</sup> immobilized foam. The values of  $\Delta H$ ,  $\Delta S$  and  $\Delta G$  for the chromium (VI) sorption onto the TPP<sup>+</sup>Br<sup>-</sup> loaded foams are  $13.4 \pm 1.6$  kJ mol<sup>-1</sup>,  $43.2 \pm 2.1$  J/(mol K) and  $0.6$  kJ mol<sup>-1</sup>, respectively with a correlation factor of 0.998.

The values of  $\Delta H$  and  $K_c$  indicated that, the chromium (VI) sorption onto the TPAs<sup>+</sup>Cl<sup>-</sup> or TPP<sup>+</sup>Br<sup>-</sup> loaded PUFs is an endothermic process. The energy of the urethane nitrogen and/or ether-oxygen sites of the PUFs provided by raising the temperature enhanced the possible interaction between the active sites of the PUFs and the complex ion associates of chromium (VI) ions and TPAs<sup>+</sup>Cl<sup>-</sup> or TPP<sup>+</sup>Br<sup>-</sup> resulting a higher sorption percentage. Thus, a dual-mode sorption mechanism involves absorption related to “solvent extraction” and an added component for “surface adsorption” seems a more probable model for chromium (VI) uptake. These results suggest the possible use of the reagent loaded foam in flow and pulsating modes for quantitative collection, chemical speciation, sequential determination of chromium (VI) and total inorganic chromium (III).

### 3.4. Chemical speciation of inorganic chromium (III) species on pulse PUFs column

The analytical utility of the foam pulse column depends mainly on: i—the flexibility of the PUFs; ii—the rate of the reaction between the chromium (VI) ions in the test solution and the reagent TPP<sup>+</sup>Cl<sup>-</sup> immobilized PUFs and finally iii—the reaction between the eluting agent (NaOH, 1 mol L<sup>-1</sup>) and the retained chromium (VI) species onto the loaded PUF cubes. Thus, the tip of the syringe packed with the reagent loaded PUFs ( $0.2 \pm 0.01$  g) was allowed to pulse with the test solution

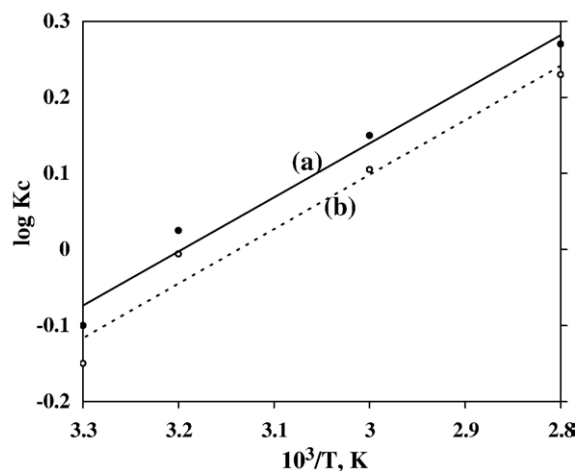


Fig. 5. Variation of  $\log K_c$  versus  $1000/T$  ( $\text{K}^{-1}$ ) for chromium (VI) uptake at 5  $\mu\text{g/mL}$  concentration level from aqueous solution at pH zero onto TPAs<sup>+</sup>Cl<sup>-</sup> (a) and TPP<sup>+</sup>Br<sup>-</sup> (b) immobilized PUFs ( $0.2 \pm 0.01$  g).

Table 1  
Chemical speciation of chromium (III and VI) ions in distilled water (100 mL) by the proposed TPP<sup>+</sup>Cl<sup>-</sup> pulse foam partially packed syringe (A) and reference AAS (B) methods

Cr(III) added, μg mL <sup>-1</sup>	Cr(VI) added, μg mL <sup>-1</sup>	Total chromium (III and VI), μg mL <sup>-1</sup>	
		A	B
10	–	10.2±0.2	10.1±0.1
5	10	14.8±0.2	15.3±0.2
5	5	9.9±0.3	10.2±0.2

Average ( $n=5$ )±standard deviation.

(100 mL, 0.05–5 μg mL<sup>-1</sup> chromium ions) at pH 3.2 which will go into the pulse column and the PUFs cubes will return back to its original volume. On repeating this process, for several times (30–35), complete (97.4±2.9%) retention of chromium (VI) was only achieved, while chromium (III) does not as detected from AAS measurement of the test solution. The retained chromium (VI) species was then recovered with NaOH by allowing the tip of the syringe packed with the TPP<sup>+</sup>Cl<sup>-</sup> PUFs to pulse with the stripping agent (25 mL, 2 mol L<sup>-1</sup>). The stripping agent will go into the column, and the PUF cubes will return to its original volume. Similarly, on repeating this process for several times the NaOH solution will be exposed to the retained chromium (VI) species on the PUFs. This will result in a reaction between the sorbed chromium (VI) and NaOH. Complete recovery (98.2±3.1%) of the retained chromium (VI) species was achieved after 30–35 pulses (Table 1). These data recommended the use of the pulse column for the separation, recovery and chemical speciation of chromium (III and VI) species from large sample volumes.

### 3.5. Effect of diverse ions on the retention and recovery of chromium (VI) species

The proposed TPP<sup>+</sup>Cl<sup>-</sup> immobilized PUFs in pulse mode was investigated for the separation of chromium (VI) (5 μg/mL Cr<sup>6+</sup>) from aqueous media (50 mL) in the presence of a series of diverse ions under the optimal experimental conditions. A relatively high excess (1 mg) of some diverse ions e.g. Cu<sup>2+</sup>, Al<sup>3+</sup>, Ni<sup>2+</sup>, Co<sup>2+</sup>, Cd<sup>2+</sup>, SO<sub>4</sub><sup>2-</sup>, PO<sub>4</sub><sup>3-</sup>, alkali and alkaline earth metals relevant to waste water and are often accompanying chromium (VI) ions was examined. The amount of foreign ion causing an error ±2% in the uptake of chromium (VI) is considered free from interference ratios (w/w) limit. Good extraction and recovery efficiency (>96.9±2%) for the chromium (VI) ions was achieved successfully in the presence of these diverse ions. In the presence of some other ions e.g. MnO<sub>4</sub><sup>-</sup>, Fe<sup>3+</sup> and VO<sub>3</sub><sup>-</sup>, 2 mL of NaN<sub>3</sub> (0.1%) and NaF (0.1%) solutions were introduced to the aqueous solution, respectively to obtain unambiguous and selective preconcentration and recovery. The reagent NaN<sub>3</sub> was added to eliminate the interference of permanganate ions via reduction of manganese (VII) to manganese (II) ions. The tolerance limit of these interfering ions was improved to acceptable limit (97.6±2.2%) after employing these modifications. These results and the resilient characteristics of the PUFs also extend the use of the

proposed reagent immobilized PUFs for the separation and sequential speciation of chromium (III) and (VI).

### 3.6. Analytical performance of the developed foams packed columns

The performance of the TPP<sup>+</sup>Cl<sup>-</sup> immobilized PUFs partially packed in the medical syringe (50.0 mL capacity) towards chromium (VI) solution (0.05–5 μg Cr/mL) in the test solution (200.0 mL) was determined. The capacity of the pulse column partially packed with TPP<sup>+</sup>Cl<sup>-</sup> immobilized PUFs towards chromium (VI) sorption was found 5.2±0.34 mg g<sup>-1</sup>. The aliquot solution was allowed to enter or leave the syringe by releasing and/or pressing the plunger of the syringe at 25 mL min<sup>-1</sup> as described before. Complete sorption of chromium (VI) took place as indicated from the AAS analysis of chromium in the effluent solution. The sorbed chromium (VI) species in the column were then stripped quantitatively (98.2–101.5±1.8%) with NaOH (20.0 mL, 2. mol L<sup>-1</sup>, 30 pulses). The lower limits of detection (LOD) and quantification (LOQ) of chromium (VI) sorption under the optimal conditions was computed using the equations [45]:

$$\text{LOD} = 3\text{SD}/b \quad (7)$$

$$\text{LOQ} = 10\text{SD}/b \quad (8)$$

where SD is the standard deviation ( $n=3$ ) of the blank and  $b$  is the slope of the calibration plot. The LOD and LOQ of 0.4 and 1.2 μg L<sup>-1</sup> were achieved, respectively. For sample volume of 200 mL at pH 3–4, the enrichment factors calculated as the ratio between calibrations graphs with and without preconcentration were up 100 for unloaded and PAR treated PUFs using pulse columns of 50 mL of adequate capacity. The precision of the unloaded and PAR treated PUFs pulse columns for standard solutions containing 0.5 μg mL<sup>-1</sup> of chromium (VI) were 1.8 and 2.3% ( $n=5$ ), respectively, expressed as relative standard deviation

### 3.7. Analytical applications

The retention characteristics of the developed PUFs pulse column suggest its use for the separation and subsequent determination of chromium species at low level (nanomolar) of inorganic chromium (III) and/or (VI) in tap and/or industrial wastewater samples. A first aliquot (100 mL) of water samples

Table 2  
Analysis of chromium (III) and (VI) in industrial wastewater (100 mL) by the developed TPP<sup>+</sup>Cl<sup>-</sup> foam partially packed syringe (A) and reference AAS (B) methods

Cr(III) added μg mL <sup>-1</sup>	Cr (VI) added μg mL <sup>-1</sup>	Total chromium (III&VI) μg mL <sup>-1</sup>	
		A	B
10	–	13.1±0.2	12.9±0.1
5	10	18.1±0.16	17.9±0.05
5	5	12.9±0.2	12.9±0.2

Average ( $n=5$ )±standard deviation.

of an electroplating spiked with (or without) chromium (III) and (VI) at concentration 0.05–5  $\mu\text{g mL}^{-1}$  was treated as described for chromium (VI) in the experimental section. Chromium (VI) species were only retained quantitatively after 30–35 pulse while chromium (III) remained in solution. The retained chromium (VI) species were then recovered with NaOH (25, 2.0 mol  $\text{L}^{-1}$ ) after 30–35 pulse. Another aliquot (100 mL) of the spiked sample solution was then oxidized to chromate ions with  $\text{H}_2\text{O}_2$  and treated as described for chromium (VI). The chromium (VI) content before extraction and after recovery in the stripped solutions was finally determined with AAS. The results are summarized in Table 2 using the standard addition methods. The data are in good agreement with the values obtained using direct AAS. On these bases, the amount of chromium in the first aliquot will be equivalent to chromium (VI) in the analyzed sample, while the amount of chromium in the second aliquot will be equivalent to total inorganic chromium (III) and (VI). The concentration of chromium (VI) species present in the industrial wastewater obtained by the developed method is in good agreement with the value obtained by AAS. The retention of chromium (IV) at concentration  $\leq 0.01 \mu\text{g mL}^{-1}$  was also tested for one liter of wastewater samples under the optimum experimental conditions was achieved successfully with good extraction and recovery (98  $\pm$  2%) were achieved.

#### 4. Conclusion

This article demonstrates the utility of PUFs sorbent in pulse mode as a simple, convenient, and low cost solid extractor for the separation, chemical speciation and sequential photometric determination of inorganic chromium (III) and (VI) ions in industrial wastewater. The PUFs packed columns can be re used many times without decrease in its performance. The developed method allows continuous monitoring of chromium (VI) and total inorganic chromium (III and VI) species present in wastewater samples of electroplating industry. The proposed pulse mode of separation does not require transport bulky water samples into the laboratory for analysis, since pre-concentration can easily be made on the spot. The developed method can be optimized for the preconcentration of the analyte for the flow analysis measurements. Future work is continuing for the chemical speciation of organic and inorganic chromium species and some other toxic metal ions in the environmental samples.

#### References

- [1] E. Merian, *Metals and Their Compounds in The Environment, Occurrence, Analysis and Biological References*, VCH, 1980.
- [2] W. Mertz, *Trace Elements in Human and Animal Nutrition*, Academic Press, London, 1986.
- [3] J.R. Holum, *Elements of General, Organic and Biological Chemistry*, 9th edn., John Wiley and Sons, 1995.
- [4] J.O. Nriagu, E. Nieboer, *Chromium in Natural and Human Environment*, Wiley, New York, 1988 edn.
- [5] J. Threeprom, R. Meelapsom, W. Som-aun, J.M. Lin, *Talanta* 71 (2007) 103.
- [6] Y. Xiang, L. Mei, N. Li, A. Tong, *Anal. Chim. Acta* 581 (2007) 132.
- [7] A. Beni, R. Karosi, J. Posta, *Microchem. J.* 85 (2007) 103.
- [8] V. Comez, M.P. Callao, *Trac* 25 (2006) 1006.
- [9] S. Matsuoka, Y. Tennichi, K. Takehara, K. Yoshimura, *Analyst* 124 (1999) 787.
- [10] M.J. Marques, A. Salvador, A.M. Rubio, M. de la Guardia, *Fresenius J. Anal. Chem.* 367 (2003) 1386.
- [11] Y. Luo, S. Nakano, D.A. Holman, J. Ruzicka, G.D. Christian, *Talanta* 44 (1977) 1563.
- [12] V.M. Shinde, S.M. Khopkar, *Fresenius Z. Anal. Chem.* 249 (1970) 239.
- [13] J. Adam, *Talanta* 18 (1971) 91.
- [14] M.N. Sastri, D.S. Sundar, *Anal. Chim. Acta* 33 (1965) 340.
- [15] M.S. El-Shahawi, S.S. Hassan, A.M. Othman, M.A. Zyada, M.A. El-Sonbati, *Anal. Chim. Acta* 534 (1–2) (2005) 319.
- [16] R. Milacic, J. Scancar, J. Tusek, *Anal. Bioanal. Chem.* 372 (2002) 549.
- [17] A.C. Sahayan, *Anal. Bioanal. Chem.* 372 (2002) 840.
- [18] C.G.B. Bruhn, F.E. Pino, V.H. Campos, J.A. Nobrega, *Anal. Bioanal. Chem.* 374 (2002) 131.
- [19] D.M. Adria Cerezo, M. Lilobat-Esteles, A.R. Mauuri-Aucejo, *Talanta* 51 (2000) 531.
- [20] G.M. Wuilloud, R.G. Wuilloud, J.C.A. de Wuilloud, R.A. Olsina, L.D. Martinez, *J. Pharm. Biomed. Anal.* 31 (2003) 117.
- [21] R.A. Gil, S. Cerutti, J.A. Gasquez, R.A. Olsina, L.D. Martinez, *Talanta* 68 (2006) 1065.
- [22] R. Karosi, V. Andruch, J. Posta, J. Balogh, *Microchem. J.* 82 (2006) 61.
- [23] V. Gomez, A. Pasamontes, M.P. Callao, *Microchem. J.* 83 (2006) 98.
- [24] M.F. Sawalha, J.L. Gardea-Torresedey, G. Parso, J.R. Peralta-Videa, *Microchem. J.* 81 (2005) 122.
- [25] M.S. El-Shahawi, A.M. Othman, H.M. Nassef, M.A. Abdelfadeel, *Anal. Chim. Acta* 536 (1–2) (2005) 227.
- [26] V.A. Lemos, M.S. Santos, E.S. Santos, M.J.S. Santos, W.N.L. dos Santos, A.S. Souza, D.S. de Jesus, C.F. das Virgens, M.S. Carvalho, N. Oleszczuk, M.G.R. Vale, B. Welz, S.L.C. Ferreira, *Spectrochim. Acta B* 62 (2007) 4.
- [27] M.S. El-Shahawi, H.A. Nassif, *Anal. Chim. Acta* 481 (2003) 29.
- [28] M.M. Saeed, M. Ahemd, *Anal. Chim. Acta* 525 (2004) 289.
- [29] S.M. Hasany, M.M. Saeed, M. Ahmed, *Sep. Sci. Technol.* 35 (2000) 379.
- [30] P.F. Marchisio, A. Sales, S. Cerutti, E. Marchevski, L.D. Martinez, *J. Hazard. Mater. B* 124 (2005) 113.
- [31] A.N. Anthemidis, G.A. Zachariadis, J. Stratis, *Talanta* 58 (2002) 831.
- [32] S.L. Ferreira, W.N. dos Santos, M.A. Bezerra, V.A. Lemos, J.M. Bosques-Sendra, *Anal. Bioanal. Chem.* 375 (2003) 443.
- [33] T. Braun, J.D. Navratil, A.B. Farag, *Polyurethane Foam Sorbents in Separation Science*, CRC Press, Inc, FL, Boca Raton, 1985.
- [34] S. Palagyi, T. Braun, *Separation and Preconcentration of Trace Elements and Inorganic Species on Solid Polyurethane Foam Sorbents*, in: Z.B. Alfassi, C.M. Wai (Eds.), *Pre-concentration Techniques for Trace Elements*, CRC Press, Boca Raton, FL, 1992.
- [35] H. Sano, *Anal. Chim. Acta* 27 (1962) 398.
- [36] S. Lacroix, M. Labalade, *Anal. Chim. Acta* 3 (1949) 262.
- [37] I.I. Stewart, A. Chow, *Talanta* 40 (1993) 1345.
- [38] M.N. Sastri, T.S.R. Prasada Rao, *J. Inorg. Nucl. Chem.* 30 (1968) 1727.
- [39] W.J. Weber Jr., J.C. Morris, *J. Sanit. Eng. Div. Am. Soc. Civ. Eng.* 90 (SA3) (1964) 70.
- [40] M. Saeed, S.M. Hasany, M. Ahmed, *Talanta* 50 (1999) 625.
- [41] M. Hasany, M.M. Saeed, M. Ahmed, *Talanta* 54 (2001) 89.
- [42] S. Lagergren, B.K. Sven, *Vatenskapsakad. Handl.* (1898) 24.
- [43] A.K. Bhattacharya, C. Venkobachar, *J. Environ. Eng.* 110 (1984) 110.
- [44] D. Reichenburg, *J. Am. Chem. Soc.* 75 (1972) 589.
- [45] J.C. Miller, J.N. Miller, *Statistics for Analytical Chemistry*, 4th edn., Ellis-Horwood, New York, 1994, p. 115.