Research Article

Penka Vasileva, Ivanka Dakova, Tanya Yordanova*, Irina Karadjova

New composite sorbent for speciation analysis of soluble chromium in textiles

<https://doi.org/10.1515/chem-2019-0115>

received January 8, 2019; accepted April 15, 2019.

Abstract: Micrometer-sized silica spheres coated with a layer of Cr(VI) imprinted methylimidazolium ionic liquid were synthesized and applied for fast and selective determination of leachable Cr(VI) in fabrics. The silica cores were synthesized via original seeded growth procedure. Formation of ionic liquid layer onto their surface was simultaneously combined with CrO_4^{2-} imprinting. The sorbent characterization was accomplished by SEM/EDS, elemental microanalysis, and thermogravimetry. Excellent separation of Cr(VI) from Cr(III) was achieved at pH 3 for 10 minutes in a batch mode. A mixture of ascorbic and nitric acids was found to be the most efficient eluent. The adsorption equilibrium data were best represented by the Langmuir isotherm model. The sorbent was applied for quantification of Cr(VI) in textile extracts in accordance with international standard ISO105-E04. The analytical procedure developed (LOD 0.015 $\mu\text{g/g}$ (measured by ETAAS), RSD 3–8% for concentration levels of Cr(VI) 0.015–0.5 $\mu\text{g/g}$) completely meets the requirements of the international textile regulations.

Keywords: ionic liquid layer; silica microspheres; leachable Cr(VI); speciation; textiles.

1 Introduction

Chromium is a chemical element that can naturally exist under various forms but its predominantly occurring oxidation states are Cr(III) and Cr(VI). It is well known that these Cr species have totally contrasting physiological

effects – Cr(III) is identified as an essential nutrient for humans, required for glucose and fats metabolism [1], while Cr(VI) and its compounds are definitely recognized as carcinogenic and mutagenic substances [2]. In spite of that, Cr(VI) containing chemicals still find numerous industrial applications such as pigments production, plating, metal finishing, anticorrosive coatings, wood preservatives, cement production [3,4]. Furthermore, chromium compounds are widely used in the manufacture of dyes and in textile dyeing process [5–7]. The extremely toxic potassium dichromate (commercially known as Chrome) is additionally utilized as a mordant agent providing permanent fixing of synthetic or natural colourful dyes on fabrics [7,8]. Chromate based dyestuffs may be quite hazardous for human health since Cr(VI) is a strong dermal irritant, which can be released from fabrics, when the clothes are in direct contact with the human skin. As a result of perspiration, the soluble Cr(VI) species are able to migrate from textiles onto the skin, which is a dangerous route of absorption, promoting allergic contact dermatitis and skin ulcers [9]. The European legislation established the ecological criteria for the award of the EU Ecolabel for textile products: Chrome mordant dyes shall not be used, while metal complex dyes based on copper, chrome and nickel shall only be permitted for dyeing of wool, polyamide fibres and blends of wool and/or polyamide with man-made cellulose fibres [10]. The international Oeko-Tex standard 100 defines the limit value for total Cr content in textiles in direct skin contact as 2.0 mg/kg, while leachable Cr(VI) must not exceed 0.5 mg/kg [11]. In this regard, quality control of textiles requires development of analytical methods for selective quantification of Cr(VI) in artificial sweat solutions more sensitive than standard UV-VIS method (diphenylcarbazide) [9,12] or less expensive than ion-chromatography [13].

A large variety of non-chromatographic systems for separation and preconcentration of Cr(VI), mainly in natural and waste water samples have been described [14–16]. During the recent years ionic liquids tend to be one of the most promising green extractants and due to

*Corresponding author: Tanya Yordanova, Faculty of Chemistry and Pharmacy, University of Sofia “St. Kliment Ohridski”, 1 James Bourchier Blvd., Sofia 1164, Bulgaria, E-mail: t.yordanova@chem.uni-sofia.bg

Penka Vasileva, Ivanka Dakova, Irina Karadjova, Faculty of Chemistry and Pharmacy, University of Sofia “St. Kliment Ohridski”, 1 James Bourchier Blvd., Sofia 1164, Bulgaria

their unique properties, they reasonably find numerous analytical applications in different extraction procedures [17,18]. Furthermore, ionic liquids have been successfully applied in speciation analysis of trace elements as effective solvents for liquid-liquid extraction procedures [19,20], as well as layer coatings supported on appropriate carriers, e.g. chitosan [21], polyvinyl chloride [22], silica coated magnetic nanoparticles [23]. Effective “green” sorbents for Cr(VI) separation and enrichment have been recently introduced based on ionic liquids with high separation efficiency and selectivity supported on silica gel with high surface area, chemical activity and mechanical stability [24–29].

The present work is focused on the synthesis of a versatile sorbent material for separation and determination of extractable Cr(VI) in textile samples. In order to combine the main advantages of ionic liquids and ion imprinting, the sorbent particles of core-shell type were prepared by grafting of 3-methyl-1-trimethoxysilylpropylimidazole, preliminarily coordinated to CrO_4^{2-} as a template ion, onto the surface of micrometer-sized silica spheres. Micron-sized silica particles with perfect spherical morphology compared to silica gel as cores ensure faster diffusion mass transfer and more efficient access of the analyte to the active sites on the surface of core-shell sorbent. The synthesized composite material was characterized by scanning electron microscopy (SEM) and energy-dispersive X-ray spectroscopy (EDS) analysis, elemental microanalysis, N_2 adsorption–desorption isotherm measurements and thermogravimetry. The optimal extraction conditions for selective separation of Cr(VI) were defined and analytical procedure for Cr(VI) determination in textiles according to the ISO105-E04 was developed and applied for different types of fabrics.

2 Experimental

2.1 Reagents

All reagents used were of analytical-reagent grade and all aqueous solutions were prepared in high-purity water (Millipore Corp., USA). The stock standard solutions for Cr(VI) and Cr(III) (1000 $\mu\text{g/mL}$) were Titrisol (Merck, Germany) in 2% HNO_3 . Tetraethylorthosilicate (TEOS, 99%, Fluka, Germany), ammonia solution (25% NH_3 , Merck, Germany) and absolute ethanol (EtOH, 99.8%, Sigma-Aldrich, USA) were used for preparation of silica spheres. Methanol (Labscan, Ireland), 1-methylimidazole (MIA), (3-chloropropyl)trimethoxysilane (CPTMS), and

ammonium chromate (Sigma-Aldrich, Germany) were used for the second stage of the sorbent synthesis, i.e. coating of silica spheres with 1-methylimidazolium ionic liquid layer. Sodium chloride, sodium dihydrogen phosphatemonobasic dihydrate ($\text{NaH}_2\text{PO}_4 \cdot 2\text{H}_2\text{O}$, Sigma-Aldrich, Germany), L-histidine monohydrochloride monohydrate ($\text{C}_6\text{H}_9\text{O}_2\text{N}_3\text{HCl} \cdot \text{H}_2\text{O}$) and sodium hydroxide (Merck, Germany) were used for the preparation of the artificial sweat solutions required for the lixiviation study.

2.2 Apparatus

The morphological characterization of the synthesized bare μSiO_2 spheres and $\mu\text{SiO}_2@\text{Cr(VI)-IIL}$ was carried out by SEM observation using a JEOL JSM-5510 apparatus. Particle size distribution histograms and average particle diameters were determined by counting at least 250 particles from the different SEM micrographs of each sample using Image J software.

Qualitative elemental composition was assessed by EDS analysis performed using a combined scanning electron microscope/focused ion beam system LYRA I XMU (Tescan) equipped with EDS microanalyzer (Quantax, Bruker). The specific surface area of bare μSiO_2 and $\mu\text{SiO}_2@\text{Cr(VI)-IIL}$ particles was determined by N_2 adsorption–desorption isotherms at 77 K using a Quantachrome NOVA 1200 apparatus (Quantachrome UK Ltd. England). The carbon, hydrogen and nitrogen (wt. %) content in the synthesized samples was determined by elemental microanalysis technique using an automatic CHNS-O elemental analyzer EuroEA 3000 (EuroVector, Italy). Thermogravimetric analysis of bare μSiO_2 and $\mu\text{SiO}_2@\text{Cr(VI)-IIL}$ spheres was performed on apparatus type STA 781 DTA 675 Stanton Redcroft in air, at a heating rate of 10°C/min .

The concentrations of Cr were measured by Electrothermal AAS (ETAAS, Perkin Elmer Model AAnalyst 400 atomic absorption spectrometer equipped with an HGA 900). Pyrolytically coated graphite tubes were used as atomizers and sample solutions (10–20 μL) were introduced into the graphite furnace using the Perkin Elmer AS 800 autosampler. All measurements were carried out with at least three replicates and based on integrated absorbance. Pretreatment temperature of 1100°C and atomization temperature of 2500°C were used for ETAAS measurements of Cr in effluates and eluates solutions.

A microprocessor pH-meter (Hanna Instruments, Portugal) was used for all pH measurements. An EBA 20 centrifuge (DJB Labcare Ltd., UK) was used to separate

modified silica and extracted metal solution in batch experiments.

2.3 Synthesis procedure

Micron-sized silica spheres with low polydispersity were obtained from submicrospherical silica seeds by modified seeded growth technique originally developed by Bogush et al. [30]. Silica seeds were prepared using an optimized Stöber procedure [31] where solution of TEOS in absolute ethanol was rapidly mixed with ammonia in water-ethanol solution under stirring at constant temperature of $30 \pm 1^\circ\text{C}$ (as illustrated in Figure 1). The total volume of reaction mixture was 60 mL and the reactant concentrations were 0.25 mol/L TEOS, 1.00 mol/L NH_3 , and 5.00 mol/L H_2O . After 4 h the reaction was completed and further amounts of TEOS and H_2O were added stepwise (1 mL TEOS and 0.2 mL H_2O at each step) to an aliquot (20 mL) of the silica seed dispersion. The mixture was stirred for 12 h at each step. Fifteen seeded growth steps were conducted without any signs of secondary nucleation. Finally, the residual reagents were removed by centrifugation and enlarged micron-sized silica spheres were washed three times with absolute ethanol and three times with distilled water. The solid product, denoted as bare μSiO_2 , was dried at 50°C for 24 h. The surface chemical modification of bare μSiO_2 consists of three steps as presented in Figure 1 and followed already developed procedure [29]. The final composite material, denoted as $\mu\text{SiO}_2@\text{Cr(VI)-IL}$ (micrometer-sized SiO_2 coated with Cr(VI) imprinted ionic liquid layer), was dried under vacuum at room temperature for 8 h.

2.4 Studies on extraction efficiency and adsorption capacity

Experiments for optimization of extraction parameters of $\mu\text{SiO}_2@\text{Cr(VI)-IL}$ sorbent toward Cr(VI) were conducted according to the published procedures [29]. A portion of 50 mg $\mu\text{SiO}_2@\text{Cr(VI)-IL}$ was mixed with 10 mL aqueous solution containing 2 μg Cr(VI) or Cr(III), and adjusted to the pH value in the range 1–8 by adding HNO_3 or NH_4OH . The samples were shaken for 20 minutes and then centrifuged. Supernatant solution was removed and analyzed by ETAAS as an effluent in order to determine degree of analyte sorption. The sorbent was washed with deionized water and treated with 2 mL eluent solution. The degree of elution was assessed after centrifugation and analyte measurement in the supernatant by ETAAS.

Figure 1: Schematic representation of (a) procedure for synthesis of micrometer-sized silica particles, (b) synthesis of ionic liquid and its coordination with chromate anion and (c) grafting Cr(VI)-IL complex onto SiO_2 surface.

Kinetics of sorption for Cr(VI) was studied by batch procedure: the sorbent particles (50 mg) were placed in a plastic tube and total volume was brought to 10 mL by adding 0.001 mol/L nitric acid containing 3.846 $\mu\text{mol/L}$ Cr(VI). Then the sample was vigorously shaken for 60 minutes and 200 μL aliquots of supernatant solution were recurrently removed and Cr concentration was immediately measured by ETAAS. Kinetics of desorption was studied after loading of the $\mu\text{SiO}_2@\text{Cr(VI)-IL}$ particles (50 mg) with 10 μg Cr(VI) followed by treatment with 10 mL freshly prepared solution of ascorbic acid in 2 mol/L HNO_3 . Samples were shaken for 60 minutes while 200 μL aliquots from the eluate solution were recurrently removed and Cr concentration was immediately measured by ETAAS.

In order to determine adsorption capacity of $\mu\text{SiO}_2@\text{Cr(VI)-IL}$, 50 mg of adsorbent was mixed with 10 mL of Cr(VI) solution with increasing initial concentration (10–70 $\mu\text{mol/L}$) under optimum conditions (pH 3, 10 mL sample volume, 50 mg sorbent) at temperature 25°C . The equilibrium Cr(VI) concentration after adsorption

was measured by ETAAS. The linearized Langmuir and Freundlich equations were applied to the data to provide an insight into the mechanism of the adsorption [32].

2.5 Sample analysis

Textile samples were prepared according to the International Standard ISO 105-E04: a sample of each fabrics (1.0 g) was cut to 10mm×10mm pieces, placed in a plastic tube and soaked in 50.0 mL artificial sweat solution (0.5 g L-histidine, 5.0 g NaCl and 2.2 g $\text{NaH}_2\text{PO}_4 \cdot 2\text{H}_2\text{O}$ were dissolved in 1 L deionized water and pH was adjusted to 5.5 ± 0.2 or 8 ± 0.2 with 0.1 mol/L sodium hydroxide solution for acidic or alkaline artificial sweat, respectively [33]). The samples were shaken for 12 h at 37°C using a water bath. Finally, the textiles were removed, sample solutions were filtered and immediately acidified to pH 3 with 0.1 mol/L HNO_3 . Sorbent particles (50 mg) were added to aliquot sample of 10 mL and shaken for 10 min. After centrifugation supernatant was removed, sorbent washed with doubly distilled water, retained Cr(VI) eluted (for 10 min) with 2 mL 3 mmol/L ascorbic acid in 2 mol/L HNO_3 and quantified by ETAAS.

Ethical approval: The conducted research is not related to either human or animal use.

3 Results and discussion

3.1 Synthesis and characterization

Micron-sized monodisperse silica spheres (bare μSiO_2) with high solid mass fraction were obtained by a controlled multistage growth process of pre-synthesized monodisperse silica seeds. The initial average diameter of these seeds ($436 \text{ nm} \pm 21 \text{ nm}$) was obtained at molar ratio of the reagents $\text{TEOS} : \text{NH}_3 : \text{H}_2\text{O}$ equal to 0.25 : 1.0 : 5.0. In the growth process, the particles obtained at the previous stage play a role of ‘seeds’ for the next growth stage upon their surface chemical reaction with TEOS, added in the same reaction medium. The reaction conditions were adjusted in order to inhibit the formation of new silica seeds and thus to prepare monodisperse micrometer-sized silica particles.

The growth sequence of silica seeds is illustrated by the SEM micrographs shown in Figure 2. Perfect spherical morphology and smooth particle surface of both seeds and enlarged silica particles are obtained. A very good monodispersity of the silica spheres at each growth stage

was observed. The relative standard deviation of their diameters was in the range of 2–5% and average size of 1041 nm was achieved at the final fifteenth step. Moreover, the developed synthesis procedure demonstrates the applicability of Bogush equation [30] for accurate prediction of the enlarged particle size after each addition of TEOS (see Supplementary, P1, Figure S1).

The bare μSiO_2 particles were used as substrates to immobilize Cr(VI)-IL complex *via* covalent grafting through reaction of the methoxy groups with silanol groups on the SiO_2 surface (as illustrated in Figure 1). SEM micrographs and corresponding particle size distribution histograms for typical μSiO_2 samples before and after immobilization of Cr(VI)-imprinted ionic liquid layer are shown in Figure 3. It should be noted that after formation of Cr(VI)-imprinted ionic liquid layer onto the surface of μSiO_2 the resulting core-shell $\mu\text{SiO}_2@\text{Cr(VI)-IIL}$ particles still keep the morphological homogeneity of the bare μSiO_2 , i.e. they are still spherical, non-aggregated, and with a smooth surface. However, the SEM image in Fig 3c also reveals some particle coalescence through formation of interparticle necks that are possibly due to the presence of the Cr(VI)-imprinted ionic liquid layer covering the surface of silica particles [34]. The comparison of particle size distribution histograms (Figure 3) for bare μSiO_2 and $\mu\text{SiO}_2@\text{Cr(VI)-IIL}$ shows practically identical average sizes. This result was further confirmed by the measured specific surface area of $\mu\text{SiO}_2@\text{Cr(VI)-IIL}$ spheres ($3.1 \text{ m}^2/\text{g}$) which is nearly the same as the measured S_{BET} value of bare μSiO_2 particles ($2.9 \text{ m}^2/\text{g}$). Furthermore, the calculated value of geometrical surface area of $\mu\text{SiO}_2@\text{Cr(VI)-IIL}$ ($2.8 \text{ m}^2/\text{g}$) is on the same magnitude as the measured S_{BET} value suggesting virtually nonporous nature of the synthesized sorbent particles (see Supplementary, P2).

Additional evidences for the formation of Cr(VI)-imprinted ionic liquid layer on the bare μSiO_2 were obtained by EDS analysis, elemental microanalysis, and thermogravimetric measurements. EDS peak due to nitrogen has been detected on the surface of $\mu\text{SiO}_2@\text{Cr(VI)-IIL}$ sample (Figure 4). This result was further confirmed by elemental microanalysis performed on the same $\mu\text{SiO}_2@\text{Cr(VI)-IIL}$ sample (0.55 wt.% N). Ionic liquid loading of 1.6 wt.% calculated from the elemental microanalysis agrees well with the results of thermogravimetric measurements. The thermogravimetric curves of bare μSiO_2 and $\mu\text{SiO}_2@\text{Cr(VI)-IIL}$ particles are presented in Figure S2 (see Supplementary, P3). In the temperature range of 200–600°C, $\mu\text{SiO}_2@\text{Cr(VI)-IIL}$ particles exhibit a higher mass loss than bare μSiO_2 obviously due to the loss of organic moieties attached on the silica surface. Overall results obtained undoubtedly show that the immobilization of

Figure 2: SEM micrographs of silica particles grown from (a) seeds with average diameter of $436 \text{ nm} \pm 5.0\%$ to various particle sizes: (b) $638 \text{ nm} \pm 2.7\%$ (third step of multistage growth), (c) $882 \text{ nm} \pm 2.2\%$ (ninth step of multistage growth), and (d) $1041 \text{ nm} \pm 3.3\%$ (the last fifteenth step of multistage growth)

Figure 3: SEM micrographs and particle size distribution histograms of bare μSiO_2 ((a) and (b)) and $\mu\text{SiO}_2@\text{Cr(VI)-IIL}$ ((c) and (d)).

Figure 4: EDS spectrum of $\mu\text{SiO}_2\text{@Cr(VI)-IIL}$, shown in the inset with an EDS map.

Cr(VI)-imprinted ionic liquid layer on the surface of silica micron-sized spheres has been successful.

3.2 Extraction efficiency of $\mu\text{SiO}_2\text{@Cr(VI)-IIL}$

Experiments performed for the characterization of extraction efficiency of $\mu\text{SiO}_2\text{@Cr(VI)-IIL}$ toward Cr(III) and Cr(VI) followed routine procedures [29]. Briefly: results obtained for the influence of pH of sorption media (studied in the range 2–8) showed that Cr(VI) is quantitatively retained (above 97%) at pH 2 to 5 while the sorption of Cr(III) starts at pH 4 and reaches 50% at pH 7–8. The excellent separation of Cr species is achieved at pH 2–3 where the degree of sorption for Cr(VI) is $(98 \pm 3)\%$ while the degree of sorption for Cr(III) is less than 2%. The high selectivity toward Cr(VI) in presence of Cr(III) at this pH range could be attributed to the electrostatic attraction of HCrO_4^- and CrO_4^{2-} with the positively charged methylimidazolium fragments on the surface of $\mu\text{SiO}_2\text{@Cr(VI)-IIL}$ against the backdrop of negligible adsorption of positively charged Cr(III) species as already reported [22, 29].

3.3 Kinetics of sorption and modelling

Kinetics of the sorption process of Cr(VI) onto $\mu\text{SiO}_2\text{@Cr(VI)-IIL}$ particles, investigated in a batch mode, at pH 3, initial Cr(VI) concentration $3.846 \mu\text{mol/L}$ and 25°C , is shown in Figure 5.

Figure 5: Effect of contact time on Cr(VI) adsorption onto $\mu\text{SiO}_2\text{@Cr(VI)-IIL}$ at temperature 25°C (pH 3; sorbent dose = 5 g/L ; $c_0 = 3,846 \mu\text{mol/L}$).

The retention of Cr(VI) is relatively fast process and 10 minutes are completely enough to achieve equilibrium. As can be seen from Figure 5, more than 90% of the total sorption of Cr(VI) occurs within the first 5 min. This fast adsorption of Cr(VI) onto the surface of sorbent particles is mainly due to the micron-sized silica spheres, used as support material in this study. It might be assumed that the uniform spherical surface of micro-sized silica particles ensures coverage with monomolecular IL layer imprinted with Cr(VI), which is easier and faster accessible for the analyte species than the silica gel support used in our previous study [29]. Unlike the widely used silica gel, the

uniform spherical surface of micro-sized silica particles ensures coverage with monomolecular IL layer imprinted with Cr(VI), which is the main advantage of the developed sorbent. This suggestion was further confirmed by the kinetics data modelling. Three kinetic models (pseudo-first-order model, pseudo-second-order model and intra-particle diffusion models) have been used to fit with the experimental adsorption data. The linear forms of the equations for these models can be represented as [35]:

$$\text{pseudo-first-order model: } \ln(q_e - q_t) = \ln q_e - k_1 \times t$$

$$\text{pseudo-second-order model: } t/q_t = 1/(q_e^2 \times k_2) + t/q_e$$

$$\text{intra-particle diffusion model: } q_t = k_{\text{diff}} \times t^{1/2} + c$$

where: q_e , q_t - amounts of analyte retained per mass unit of $\mu\text{SiO}_2@\text{Cr(VI)}\text{-IIL}$ at equilibrium and at time t , ($\mu\text{mol/g}$), respectively; k_1 , k_2 - rate constants of pseudo-first kinetic model (1/min) and pseudo-second order kinetic model ($\text{g}/\mu\text{mol min}$), respectively; k_{diff} - intra-particle diffusion rate constant ($\mu\text{mol/g min}^{1/2}$); c - analyte concentration in aqueous solution at equilibrium ($\mu\text{mol/L}$).

The linear plots of pseudo-first-order and pseudo-second-order models are shown in Fig S3 and Fig S4. The corresponding kinetic parameters as well as correlation coefficients are depicted in Table 1.

The higher correlation coefficient achieved in the simulation of obtained experimental data by pseudo-second-order model shows that this kinetic model gives better fit than the pseudo-first-order model. In addition, the value of equilibrium sorption capacity calculated from the pseudo-second order equation agrees better with the corresponding experimental value. This means that the rate limiting step is the complexation between analyte ions and sorbent, thus confirming strong interactions of methylimidazolium fragments in $\mu\text{SiO}_2@\text{Cr(VI)}\text{-IIL}$ with template ions.

The intra-particle diffusion model, which takes into account the role of diffusion process, could not describe completely all kinetics data; however, two straight lines simulate very well experimental results (Figure S5). The values of kinetic parameters are presented in Table 2.

The slope of the line for the first region (responsible for the mass transfer effect in the boundary layer) is higher than the slope of the line for the second region (corresponding to intra-particle diffusion) which confirms that the active sorption sites on the sorbent surface are freely available for chromate ions from solution with insignificant penetration into the core material.

Table 1: Kinetic parameters for adsorption of Cr(VI) ions onto the $\mu\text{SiO}_2@\text{Cr(VI)}\text{-IIL}$ at temperature 25°C.

Kinetic parameter	Pseudo-first order	Pseudo-second order
R^2	0.9844	0.9982
k_1 (1/min)	0.4327	
k_2 ($\text{g}/\mu\text{mol min}$)		0.9732
$q_{e,\text{calc}}$ ($\mu\text{mol/g}$)	0.6688	0.8441

$$c_0 = 3.846 \mu\text{mol/L}; q_{e,\text{exp}} = 0.772 \mu\text{mol/g}$$

Table 2: Kinetic parameters of an intra-particle diffusion model for adsorption of Cr(VI) ions onto the $\mu\text{SiO}_2@\text{Cr(VI)}\text{-IIL}$ at temperature 25°C.

Kinetic parameter	Region 1	Region 2
R^2	0.9960	0.9782
k_{diff} ($\mu\text{mol/g min}^{1/2}$)	0.2297	0.0131
c ($\mu\text{mol/L}$)	0.1617	0.7197

$$c_0 = 3.846 \mu\text{mol/L}$$

3.4 Desorption studies

Various eluents have been studied for desorption of retained Cr(VI). Experiments performed undoubtedly showed that even 4 mol/L nitric acid could not efficiently elute the analyte, most probably because Cr(VI) ion associates formed on the sorbent surface are very stable. That is why reduction of Cr(VI) with ascorbic acid was examined as an appropriate way to destroy ion associates thus ensuring fast and quantitative elution of Cr(VI). The elution of Cr(VI) with this eluent (3 mmol/L ascorbic acid in 2 mol/L HNO_3 [29]) is also very fast process (10 min), which can be explained with the monomolecular IL layer on the spherical silica particles.

3.5 Sorbent capacity, matrix effects and reusability

3.5.1 Capacity and adsorption isotherms

The adsorption capacity is an important characteristic to evaluate sorbent binding properties and to determine the sorbent' amount required for quantitative extraction of the analyte. Adsorption isotherms constructed with the experimental data showed that the amount of adsorbed Cr(VI) per unit mass of the sorbent increased with the

Figure 6: Adsorption isotherm curve of $\mu\text{SiO}_2\text{@Cr(VI)-IIL}$ for Cr(VI) in aqueous solutions. Experimental conditions: 10 mL sample volume, 50 mg sorbent, pH 3, at temperature 25°C.

initial concentration of Cr(VI), and leveled off after 9.4 $\mu\text{mol/g}$ (Figure 6).

The experimentally achieved adsorption capacity of $\mu\text{SiO}_2\text{@Cr(VI)-IIL}$ is almost 50% higher than the capacity of sorbent supported on silica gel [29]. Subsequently, two isotherm models - Langmuir and Freundlich were used to analyze the equilibrium experimental data [32]. The obtained results are presented in Figure S6 and Figure S7. The isotherm parameters calculated from linear analysis are summarized in Table 3 and could be interpreted as follow: (i) Higher R^2 value (> 0.99) achieved by Langmuir equation for the adsorption of Cr(VI) shows that this adsorption model gives better fit than the Freundlich isotherm model. This might be accepted as a proof that sorption process occurs in a surface monolayer of homogeneous sites; (ii) The theoretical (monolayer) adsorption capacity 9.26 $\mu\text{mol/g}$ (calculated from the slope of the curve (Figure S7) agreed very well with experimentally obtained values 9.4 $\mu\text{mol/g}$, thus confirming the validity of assumptions for adsorption in monomolecular layer.

3.5.2 Matrix effects and reusability

Considering the composition of model solutions of artificial sweat (sodium chloride, sodium dihydrogen phosphate and L-histidine) the possible matrix interferences on the selectivity of separation of Cr(III) and Cr(VI) should be evaluated. Batch experiments were carried out with 5 parallel samples, containing different concentrations of Cr(III), chloride, phosphate and L-histidine ions as well as of 10 mL artificial acidic or alkaline sweat solution, spiked with Cr(III) and Cr(VI) and 50 mg $\mu\text{SiO}_2\text{@Cr(VI)-IIL}$. The solid phase extraction was performed under defined

Table 3: Adsorption parameters of the Langmuir and Freundlich isotherm models for adsorption of Cr(VI) ions onto the $\mu\text{SiO}_2\text{@Cr(VI)-IIL}$ at temperature 25°C.

Adsorption isotherm model*	Parameter	$\mu\text{SiO}_2\text{@Cr(VI)-IIL}$
Langmuir $C_e/Q_e = C_e/Q_{\max} + 1/(b \times Q_{\max})$	$Q_{\max}$, $\mu\text{mol/g}$	9.26
	b , $\text{L}/\mu\text{mol}$	0.54
	R^2	0.997
Freundlich $\ln Q_e = \ln k_f + n^{-1} \ln C_e$	k_f	15.56
	n	2.90
	R^2	0.966

*In the Langmuir and Freundlich equations:

C_e ($\mu\text{mol/L}$) is the equilibrium concentration of Cr(VI) in the solution, Q_e ($\mu\text{mol/g}$) is the adsorption capacity of the adsorbed chromate anions onto the sorbent at equilibrium,

$Q_{\max}$ ($\mu\text{mol/g}$) is the theoretical maximum adsorption capacity,

b ($\text{L}/\mu\text{mol}$) is the Langmuir constant that relates to the affinity of binding sites;

k_f and n are Freundlich constants incorporating all factors that affect the adsorption process such as capacity and intensity.

optimal conditions: pH 3, sorption time 10 min, elution time 10 min with 2 mL eluent solution. Concentrations of Cr, determined by ETAAS measurements, and the calculated degrees of sorption and elution undoubtedly showed very good separation of Cr species and absence of matrix suppression effects on the extraction efficiency for Cr(VI) (see Table 4).

Obviously, imprinting the target analyte during the synthesis as well as the high sorbent capacity due to the uniform spherical surface of submicronized silica are the main reasons for the lack of interferences from sorption of competitive ions, even smaller, e.g. chloride. Furthermore, it was experimentally verified that extraction efficiency and selectivity toward Cr(VI) is equal for the sorbents prepared by different synthesis batches. In addition, each sorbent can be used over 60 sorption/elution cycles without significant loss of activity which confirms its better mechanical stability and reusability (see Figure S8).

3.6 Analytical figures of merit and application

The analytical figures of merit of analytical procedure developed for Cr(VI) determination in artificial sweat according to ISO105-E04 (see paragraph 2.5) were obtained by parallel analysis of 5 different blank samples and 5 samples of acidic and alkaline extracts of artificial sweat (obtained from different types of textiles) spiked

Table 4: Recoveries for Cr(VI) in the presence of Cr(III) and competitive anions (components of artificial sweat).

Competitive ion	Concentration, mg/L	Recovery, %
Cr(III)	10	98±3
Cl ⁻	1000	97±3
	2500	95±3
	5000	96±3
H ₂ PO ₄ ⁻	500	97±3
	1000	95±4
	2500	94±4
L-histidine	250	96±3
	500	95±3
Acidic, artificial sweat*	10 mL	98±3
Alkaline, artificial sweat*	10 mL	97±3

* - prepared according to the published data

Table 5: Added/found method for Cr(VI) determination in textiles.

Sample	Added, µg/L	Found, µg/L	Recovery, %
Wool/polyester/ elastane	5.0	4.93 ± 0.03	99 ± 3
	2.0	1.92 ± 0.08	97 ± 5
Cotton (100%)	5.0	4.92 ± 0.04	98 ± 4
	2.0	1.95 ± 0.06	95 ± 5
Polyester	5.0	4.89 ± 0.04	96 ± 4
	2.0	1.95 ± 0.07	96 ± 3
Polyester/ polyamide/ elastane	5.0	4.95 ± 0.03	98 ± 4
	2.0	1.92 ± 0.06	96 ± 4
Polyamide	5.0	4.86 ± 0.04	98 ± 3
	2.0	1.96 ± 0.06	98 ± 5

at concentration levels of Cr(VI) ten times lower than the permissible limit (0.5 µg/g). The sensitivity of ETAAS measurement is enough high and the purpose of developed procedure is not to achieve a high concentration factor but to realize a rapid and selective separation of the chromium species thus ensuring the reliable determination of Cr(VI) in relatively complicated matrix of textile extracts in artificial sweat solutions. The calculated characteristics could be summarized as follow: application of added/found method shows very good accuracy of the developed analytical procedure (Table 5); detection limit (3σ, blank) is 0.005 µg/g; determination limit (10σ, blank) is 0.015

µg/g; relative standard deviations varied in the range 3-8% for the studied concentration levels. The linear range for ETAAS measurements is relatively short (0.015-0.5 µg/g) and in case of higher Cr(VI) concentration the volumes of sample and eluate solutions could be easily changed. The analytical method developed was applied to different textile materials presented as samples for Cr(VI) determination in accredited laboratory in Bulgaria. In all acidic and alkaline extracts obtained according to ISO105-E04 the content of Cr(VI) was far below the permissible limit. It is worth mention that the standard procedure based on selective spectrophotometric determination of Cr(VI) using 1,5-diphenylcarbazide could not be used for colored extracts from textile materials, which confirms the applicability of developed procedure for routine laboratory practice.

4 Conclusion

In the present work newly synthesized core-shell particles were used as an effective and selective sorbent for determination of leachable Cr(VI) in textile samples. The synthesis procedure includes seeded growth process to prepare micrometer-sized silica spheres followed by surface deposition of chromate-imprinted methylimidazolium ionic liquid layer. The experiments performed demonstrate a good repeatability of the synthesis procedure, a good reusability of the prepared sorbent and an applicability of the developed analytical procedure for routine quality control of textile materials.

Acknowledgement: This study was financially supported by Bulgarian National Scientific Foundation (Grant № DNTS India 01/3). Authors are grateful to Operational programme „Science and Education for Smart Growth“, project BG05M2OP001-2.009-0028.

Conflict of interest: Authors declare no conflict of interest.

References

- [1] Anderson R.A., Chromium as an essential nutrient for humans, Regul. Toxicol. Pharmacol., 1997, 26, 35–41.
- [2] Costa M., Klein C.B., Toxicity and carcinogenicity of chromium compounds in humans, Crit. Rev. Toxicol., 2006, 36, 155–163.
- [3] Lunk H.-J., Discovery, properties and applications of chromium and its compounds, ChemTexts, 2015, 1:6. DOI 10.1007/s40828-015-0007-z.

- [4] Beukes J.P., du Preez S.P., van Zyl P.G., Paktunc D., Fabritius T., Paatalo M., et al., Review of Cr(VI) environmental practices in the chromite mining and smelting industry - Relevance to development of the Ring of Fire, Canada, *J. Clean. Prod.*, 2017, 165, 874–889.
- [5] Kant R., Textile dyeing industry an environmental hazard, *Natural Science*, 2012, 4, 22–26.
- [6] Pouzar M., Prusová M., Prokopčáková P., Cernohorsky T., Wiener J., Krejkova A., LIBS analysis of chromium in samples of dyed wool fabric, *J. Anal. At. Spectrom.*, 2009, 24, 685–688.
- [7] Tonetti C., Innocenti R., Determination of heavy metals in textile materials by atomic absorption spectrometry: verification of the test method, *AUTEX Res. J.*, 2009, 9, 66–70.
- [8] Holme I., Recent developments in colorants for textile applications, *Surf. Coat. Int. B: Coat. Trans.*, 2002, 85, 243–264.
- [9] Nygren O., Wahlberg J.E., Speciation of chromium in tanned leather gloves and relapse of chromium allergy from tanned leather samples, *Analyst*, 1998, 123, 935–937.
- [10] Commission Decision of 5 June 2014 establishing the ecological criteria for the award of the EU Ecolabel for textile products (notified under document C(2014) 3677) (Text with EEA relevance) (2014/350/EU).
- [11] OekoTex standard 100, edition 02.2018. General and special conditions for the authorization to use the Oeko-Tex®Standard 100 mark.
- [12] Rezić I., Zeiner M., Determination of extractable chromium from leather, *Monatsh Chem.*, 2009, 140, 325–328.
- [13] Choe E.K., Kim Y.-Z., Cho Y.D., Son S.H., Study on analytical scheme for human ecological quality control of chromium-complex acid dyes, *Text. Res. J.*, 2016, 86, 1847–1858.
- [14] Pyrzynska K., Non-chromatographic speciation analysis of chromium in natural waters, *Int. J. Environ. Anal. Chem.*, 2011, 92, 1262–1275.
- [15] Karadjova I., Dakova I., Yordanova T., Vasileva P., Nanomaterials for elemental speciation, *J. Anal. At. Spectrom.*, 2016, 31, 1949–1973.
- [16] Tseng W.C., Hsu K. C., Shiea C.S., Huang Y.L., Recent trends in nanomaterial-based microanalytical systems for the speciation of trace elements: A critical review, *Anal. Chim. Acta*, 2015, 884, 1–18.
- [17] Tan Z.Q., Liu J.F., Pang L. Advances in analytical chemistry using the unique properties of ionic liquids. *TRAC-Trend. Anal. Chem.*, 2012, 39, 218–227.
- [18] Nawala J., Dawidziuk B., Dziedzic D., Gordon D., Popiel S., Applications of ionic liquids in analytical chemistry with a particular emphasis on their use in solid-phase microextraction, *TRAC-Trend. Anal. Chem.*, 2018, 105, 18–36.
- [19] Sadeghi S., Moghaddam A.Z., Preconcentration and speciation of trace amounts of chromium in saline samples using temperature-controlled microextraction based on ionic liquid as extraction solvent and determination by electrothermal atomic absorption spectrometry, *Talanta*, 2012, 99, 758–766.
- [20] Wen S., Wu J., Zhu X., Room temperature ionic liquid-based dispersive liquid–liquid microextraction combined with flame atomic absorption spectrometry for the speciation of chromium(III) and chromium(VI), *J. Mol. Liq.*, 2013, 180, 59–64.
- [21] Kumar A.S.K., Gupta T., Kakan S.S., Kalidhasan S., Manasi, Rajesh V., et al., Effective adsorption of hexavalent chromium through a three center (3c)co-operative interaction with an ionic liquid and biopolymer, *J. Hazard. Mater.*, 2012, 239–240, 213–224.
- [22] Gao B., Wang X., Zhang Y., Preparation of chromate anion surface-imprinted material IIP-PVI/SiO₂ based on polyvinylimidazole-grafted particles PVI/SiO₂ and its ionic recognition characteristic, *Mater. Chem. Phys.*, 2013, 140, 478–486.
- [23] Yamini Y., Seidib S., Latifeh F., Ionic liquid-modified silica-coated magnetic nanoparticles; promising anion-exchange sorbent for extraction of Cr(VI), *Int. J. Environ. Anal. Chem.*, 2017, 97, 1223–1236.
- [24] Dinker M.K., Kulkarni P.S., Recent advances in silica-based materials for the removal of hexavalent chromium: a review, *J. Chem. Eng. Data*, 2015, 60, 2521–2540.
- [25] Wang Z., Ye C., Wang X., Li J., Adsorption and desorption characteristics of imidazole-modified silica for chromium(VI), *Appl. Surf. Sci.*, 2013, 287, 232–241.
- [26] Chen M.-L., Zhao Y.-N., Zhang D.-W., Tian Y., Wang J.-H., The immobilization of hydrophilic ionic liquid for Cr(VI) retention and chromium speciation, *J. Anal. At. Spectrom.*, 2010, 25, 1688–1694.
- [27] Li Y., Gao B., Du R., Studies on preparation and recognition characteristic of surface-ion imprinting material IIP-PEI/SiO₂ of chromate anion, *Sep. Sci. Technol.*, 2011, 46, 1472–1481.
- [28] Sadeghi S., Moghaddam A.Z., A new method for separation and determination of Cr(III) and Cr(VI) in water samples by high-performance liquid chromatography based on anion exchange stationary phase of ionic liquid modified silica, *Environ. Monit. Assess.*, 2015, 187, 725–736.
- [29] Mitreva M., Dakova I., Yordanova T., Karadjova I., Chromate surface-imprinted silica gel sorbent for speciation of Cr in surface waters, *Turkish Journal of Chemistry*, 2016, 40, 921–932.
- [30] Bogush G.H., Tracy M.A., Zukoski IV C.F., Preparation of monodisperse silica particles: control of size and mass fraction, *J. Non-Cryst. Solids*, 1988, 104, 95–106.
- [31] Stöber W., Fink A., Bohn E., Controlled growth of monodisperse silica spheres in the micron size range, *J. Colloid Interf. Sci.*, 1968, 26, 62–69.
- [32] Alberti G., Amendola V., Pesavento M., Biesuz R., Beyond the synthesis of novel solid phases: review on modelling of sorption phenomena, *Coord. Chem. Rev.*, 2012, 256, 28–45.
- [33] ISO105-E04:2013. Textiles-tests for colour fastness-part E04: colour fastness to perspiration (sixth edition).
- [34] Sidhpuria K.B., Daniel-da-Silva A.L., Trindade T., Coutinho J. A., Supported ionic liquid silica nanoparticles (SILnPs) as an efficient and recyclable heterogeneous catalyst for the dehydration of fructose to 5-hydroxymethylfurfural, *Green Chem.*, 2011, 13, 340–349.
- [35] Nemeş L., Bulgariu L., Optimization of process parameters for heavy metals biosorption onto mustard waste biomass, *Open Chem.*, 2016, 14, 175–187.