

Speciation of Chromium in Water Samples by Solid-Phase Extraction on a New Synthesized Adsorbent

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Poly(1,3-thiazol-2-yl methacrylamide-co-4-vinyl pyridine-co-divinylbenzene) was prepared and used as a sorbent for the solid-phase extraction of Cr(VI) ions from aqueous solution. Two forms of chromium showed different exchange capacities at different pH values; Cr(VI) was selectively retained especially at pH 2. The total chromium was determined after the oxidization of Cr(III) to Cr(VI) by potassium permanganate as an oxidizing agent. Then, Cr(III) was calculated by subtracting the Cr(VI) concentration from the total chromium concentration. The optimum conditions were found for species of Cr(VI) (pH 2; eluent, 4 mol L⁻¹ NH₃; sample flow rates, 2 mL min⁻¹ and eluent flow rates, 1 mL min⁻¹ etc.). The adsorption capacity and binding equilibrium constant were calculated to be 80.0 mg g⁻¹ and 0.018 L mg⁻¹, respectively. A preconcentration factor of 30 and a three-sigma detection limit of 2.4 µg L⁻¹ (*n* = 20) were achieved for Cr(VI) ions. The developed method was applied to stream water and waste water samples. At the same time, the polymer was applied to a certified reference material (CRM) (TMDA-52.3) sample.

Keywords Chromium speciation, chelating resin, solid-phase extraction, flame atomic absorption spectrometry

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Introduction

Chromium is a relatively common element and occupies the 21st position on the index of elements occurring most commonly in the earth crust.¹ It can be also released to the environment from anthropogenic sources because it is widely used in manufacturing processes, such as tanning, steel works, plating, corrosion control, chromate and chrome pigment production.² Chromium occurs in the environment mainly in two oxidation states: Cr(III) and Cr(VI). Cr(III) is considered to be a non-labile, inert element in the environment and essential for mammals in trace amounts, whereas Cr(VI) is much more labile, toxic and carcinogenic for a variety of organisms.³

Usually, the speciation analysis of chromium is carried out by the separation and determination of Cr(VI), and then by the determination of total chromium. For the separation of Cr(VI) methods, such as coprecipitation,^{4,6} solvent extraction,^{7,8} ion exchange,^{9,10} HPLC separation technique^{11,12} and solid-phase extraction¹³⁻¹⁵ were used most frequently. In the present work a solid-phase extraction (SPE) method was developed. This type of extraction is often used for the preconcentration and speciation of heavy metals because of many advantages, such as simplicity, high enrichment factor, high recovery, rapid phase separation, low cost and ability for combinations with different detection techniques.^{16,17} Many instrumental techniques commonly used for the determination of chromium, such as graphite furnace and flame atomic adsorption spectrometry (GFAAS and FAAS),^{18,19} inductively coupled plasma atomic emission spectroscopy (ICP-AES)²⁰ and inductively coupled

plasma mass spectrometry (ICP-MS)²¹, can only yield the total amount of chromium.²

Chelating resins are superior in selectivity to solvent extraction and ion exchange due to their triple function of ion exchange, chelate formation and physical adsorption. Chelating and/or ion exchange-type sorbents used in speciation pretreatment have shown a preferential affinity for a single oxidation state of chromium. Thus, Cr(III) could be oxidized with a suitable oxidizing agent; this method would enable the determination of total Cr by the retention of the original and oxidized Cr(VI) species on the resin.²²⁻²⁵

In this study, a newly synthesized resin, poly(1,3-thiazol-2-yl-methacrylamide-co-4-vinyl pyridine-co-divinyl benzene), was used for the speciation of Cr(VI) and Cr(III). The Cr(VI) was separated from Cr(III) and preconcentrated by using a column packed with this resin. The total chromium was determined after oxidizing Cr(III) to Cr(VI). The Cr(III) concentration was estimated indirectly by subtracting the Cr(VI) concentration from the total Cr concentration. The effects of various analytical parameters on the recovery of the Cr(VI), such as the pH of the solution, concentration, type and volume of eluent, flow rate of the sample solution, sample volume and interfering ions, have been investigated. The adsorption capacity of the sorbent for Cr(VI) was also studied. The proposed method was applied in the determination and speciation of chromium in various water samples.

Experimental

Reagents and chemicals

All chemicals used were of analytical grade. Cr(III) and Cr(VI) stock solutions (1000 mg L⁻¹) were prepared from

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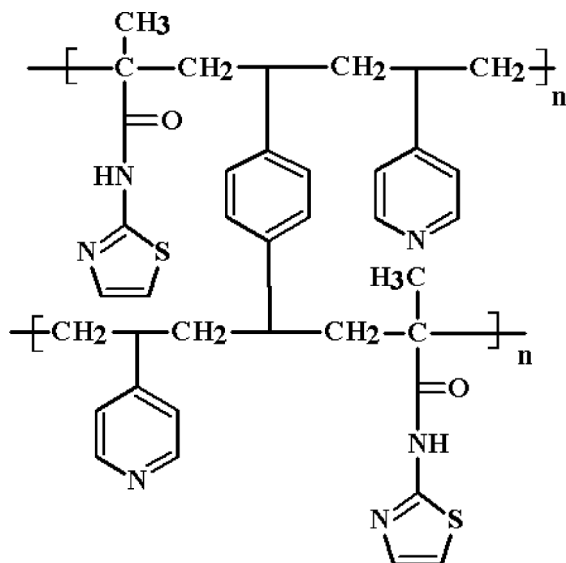


Fig. 1 Resin structure.

$\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ and $\text{K}_2\text{Cr}_2\text{O}_7$ (Merck, Darmstadt, Germany), respectively. Working solutions of the metals were obtained by appropriate dilution of the stock solutions. Stock solutions of interfering ions were prepared from their high-purity compounds (Merck). The required pH adjustments were made by the use of buffer solutions. For pH 2, KCl/HCl (Sigma-Aldrich, Steinheim, Germany) buffer was used. $\text{CH}_3\text{COOH}/\text{CH}_3\text{COONH}_4$ buffer was used to adjust the pH in the range of 4–6. The oxidation of $\text{Cr}(\text{III})$ to $\text{Cr}(\text{VI})$ was carried out using potassium permanganate (Merck) as the oxidizing agent.

2,2'-Azobisisobutyronitrile (AIBN) was recrystallized from chloroform-methanol. Divinylbenzene (DVB) and 4-vinyl pyridine (VP) (Merck) were commercial products of analytical grade, and used as received unless otherwise noted.

Apparatus

A Perkin Elmer Analyst 800 model flame atomic absorption spectrometer (FAAS, Waltham, MA) was used for the determination of $\text{Cr}(\text{III})$ and $\text{Cr}(\text{VI})$. The operating conditions were as follows: wavelength, 357.9 nm; lamp current, 25 mA; bandpass, 0.7 nm; and acetylene/air flow rates, 2.9/17 L min^{-1} . A Consort C931 model digital pH meter (Turnhout, Belgium) was used for all pH measurements. Infrared spectra were measured on a Perkin Elmer 400 FTIR spectrometer (Perkin Elmer, Inc., Shelton, CT). Elemental analyses were carried out using by a Leco CHNSO-932 auto microanalyser (St. Joseph, MI).

Synthesis of the chelating polymer

1,3-Thiazol-2-yl methacrylamide monomer was prepared as reported in the literature.²⁶ The synthesis of poly(1,3-thiazol-2-yl-methacrylamide-co-4-vinyl pyridine-co-divinyl benzene) (Fig. 1) resin was carried out with a radical initiator in a dimethylformamide solution. To a polymerization flask, two appropriate monomers 1,3-Thiazol-2-yl methacrylamide (1.34 g, 8.0 mmol) and 4-vinyl pyridine (0.84 g, 8.0 mmol), the crosslinking reagent DVB (0.52 g, 4.0 mmol), and the initiator AIBN (0.033 g, 0.2 mmol) were added. The system was kept under N_2 for 12 h at $70 \pm 0.1^\circ\text{C}$. Subsequently, the resin was filtered and washed with distilled water and dried under a vacuum at 50°C until a constant weight was obtained.

Preparation of the column

The synthesized resin (350 mg) was packed into a glass column (Vensil; size, 7 mm diameter; 12 cm length). Glass wool was placed at the top and bottom of the column for allowing the adsorbent to settle properly. The column was thoroughly washed with distilled water, and then preconditioned to the desired pH before passing chromium ions containing solutions.

General preconcentration procedure for $\text{Cr}(\text{VI})$

The pH of standard solutions of 50 mL including 0.6 mg L^{-1} of $\text{Cr}(\text{VI})$ was adjusted to pH 2 using a KCl/HCl buffer. The column was preconditioned by passing a buffer solution with pH 2 through the column, and then the standard solutions were passed through the column at a flow rate of 2 mL min^{-1} . The chromium ions retained on the resin were eluted with 20 mL of a 4 mol L^{-1} NH_3 solution. The eluate was evaporated to 0.5–1 mL on a hot plate. The residue was dissolved and diluted to 5 mL. The concentration of the chromium in the eluate was determined by FAAS.

Determination of total chromium

In order to determine the total chromium, standard solutions containing different amounts of $\text{Cr}(\text{VI})$ and $\text{Cr}(\text{III})$ were prepared. Then, oxidation of $\text{Cr}(\text{III})$ ions to $\text{Cr}(\text{VI})$ in the model solutions was performed by a procedure given in the literature.²⁷ The pH of the spiked sample solution was adjusted to 2–3 using a sulfuric acid solution. Then, three drops of a KMnO_4 solution and 1 mL of concentrated H_2SO_4 were added. The beaker was covered with a watch glass and heated until boiling for about 20 min to complete oxidation. After the oxidation of $\text{Cr}(\text{III})$ to $\text{Cr}(\text{VI})$, the pH was adjusted to 2, and the volume of the solution was made up to 50 mL with distilled water. The described preconcentration procedure was applied, and the total chromium was determined by FAAS. The concentration of $\text{Cr}(\text{III})$ was calculated by subtracting the concentration of $\text{Cr}(\text{VI})$ from the total chromium concentration.

Procedure for the analysis

Stream water and waste-water samples were collected from Yozgat stream and the water input and output of Yozgat Waste Water Treatment Institution. The polyethylene bottles were cleaned with a detergent, water, diluted nitric acid and water in sequence. The samples were immediately filtered through a cellulose filter membrane (pore size, $0.45 \mu\text{m}$), and then acidified to pH 2 for storage; 100 mL of water samples were taken into 250 mL of beakers ($n = 4$). Thirty milliliter; of the TMDA-52.3 standard reference material sample was taken into a 100-mL of beaker ($n = 4$). Sample solutions were adjusted to pH 2 using a KCl/HCl buffer. Analysis of chromium species in water samples were made as described above.

Results and Discussion

Characterization of the resins

The structure of the chelating resin and its FTIR spectrum are illustrated in Fig. 2. The FTIR spectrum of poly(1,3-thiazol-2-yl-methacrylamide-co-4-vinyl pyridine-co-divinyl benzene) resin shows a band at 3186 cm^{-1} , which is attributed to N-H. The peak at 3020 cm^{-1} corresponds to C-H stretching of the aromatic system. The absorption at 1673 cm^{-1} could be assigned to C=O band. The band at 1420 cm^{-1} could be C=N stretching vibration in the aromatic ring. A band at 1317 cm^{-1} is attributed to C-S (thiazole). The molar ratios of the resins, as calculated

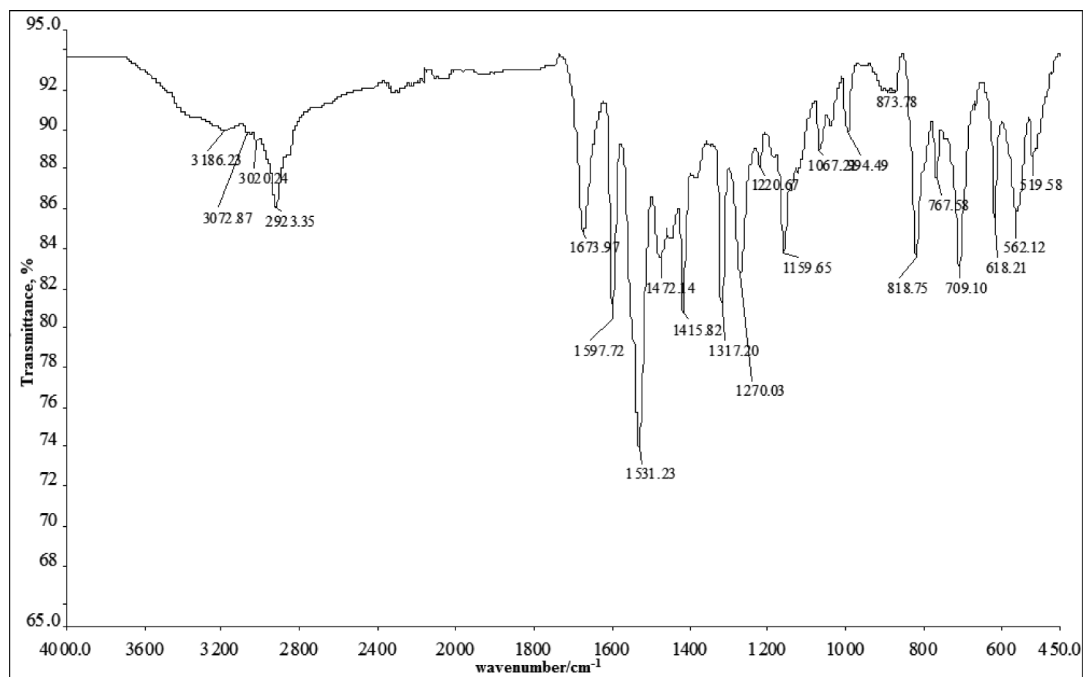


Fig. 2 FT-IR spectra of the resins.

Table 1 Result of elemental analyses and molar ratios of poly(1,3-thiazol-2-yl methacrylamide-co-4-vinyl pyridine-co-divinylbenzene)

Elemental analyses result, %				Molar ratio, %		
C	H	N	S	TMA ^a	4-VP ^b	DVB ^c
70.23	6.36	10.66	5.83	Feed ratio	40	20
				Composition of copolymer	23	27

a. TMA: 1,3-thiazol-2-yl methacrylamide; b. 4-VP: 4-vinyl pyridine; c. DVB: Divinyl benzene.

from C/H/N/S stoichiometry based on the elemental analysis data, are given in Table 1.

Effect of pH

The effect of the pH on the retention of Cr(III) and Cr(VI) on the column was studied by passing Cr solutions containing one of the species. The pH of the solution was adjusted over a range of 2 – 6 by using relevant buffer solutions. Retained ions were eluted by 20 mL of 4 mol L⁻¹ NH₃. Cr(III) and Cr(VI) in the eluate were determined by FAAS. Figure 3 shows the effect of the pH on the recoveries of both Cr(III) and Cr(VI) on the column. The quantitative recovery (≥95%) for Cr(VI) was found of pH 2, whereas the recovery for Cr(III) at this pH was rather low. For all subsequent experiments, pH 2 was selected as being optimal. This situation can be explain why pyridine is an anion exchange, and thiazole cannot be complex with Cr(III) at this pH. Cr(VI) is an anion that mainly exists as an oxy-anion in the aqueous phase in the form of CrO₄²⁻, HCrO₄⁻ or Cr₂O₇²⁻, dependent on the pH and the total concentration of the solution. Cr(VI) in an acidic solution demonstrates a very high positive redox potential, which denotes that it is strongly oxidizing and unstable in the presence of electron donors. Above pH 7, only

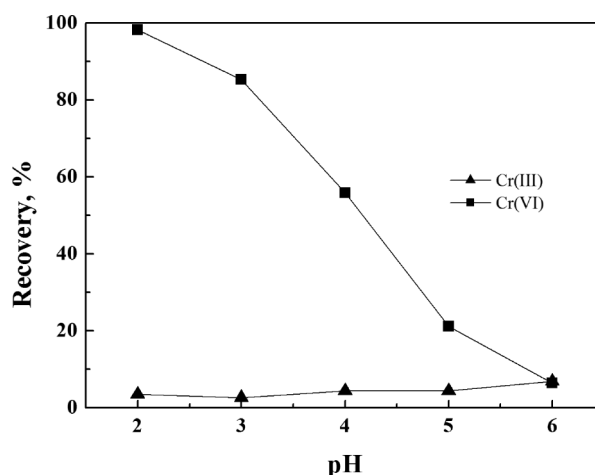


Fig. 3 Effect of the pH on the recovery of chromium.

CrO₄²⁻ ions exist in the solution throughout the concentration range; at pH 1 and 6, HCrO₄⁻ is predominant. Cr(VI) can be quantitatively adsorbed at this pH because our resin has anion exchange groups. The thiazole group has a nitrogen atom in the thiazole ring (-N=), like the pyridine nitrogen atom (-N=), so it can work like anion exchange with pyridine. The reaction mechanisms are shown in below:^{28,29}

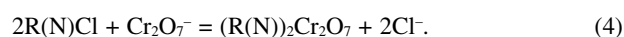
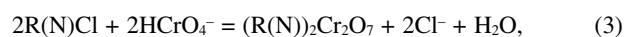


Table 2 Effect of the type, concentration and volume of the eluent

Concentration of eluent	Volume/mL	$R \pm s, \%$
1 mol L ⁻¹ NaOH	20	81 ± 5
2 mol L ⁻¹ NaOH	20	85 ± 3
2 mol L ⁻¹ NH ₃	20	87 ± 5
4 mol L ⁻¹ NH ₃	10	86 ± 4
	20	98 ± 1
	30	90 ± 4

Table 3 Effect of matrix ions on the recovery of Cr(VI)

Ion	Salt	Concentration/mg L ⁻¹	$R \pm s, \%$
Na ⁺	NaCl	5.000	97 ± 3
K ⁺	KCl	5.000	98 ± 3
Ca ²⁺	CaCl ₂	1.000	96 ± 1
Mg ²⁺	Mg(NO ₃) ₂ ·6H ₂ O	100	92 ± 3
SO ₄ ²⁻	Na ₂ SO ₄	500	97 ± 2
Al ³⁺	Al(NO ₃) ₃ ·9H ₂ O	50	93 ± 4
Mn ²⁺	Mn(NO ₃) ₂ ·4H ₂ O	50	98 ± 0
Cu ²⁺	CuCl ₂ ·2H ₂ O	50	95 ± 6
Fe ³⁺	Fe(NO ₃) ₃ ·4H ₂ O	50	93 ± 3
Zn ²⁺	Zn(NO ₃) ₂ ·6H ₂ O	50	98 ± 0
Ni ²⁺	NiCl ₂ ·6H ₂ O	50	95 ± 2
Cr ³⁺	Cr(NO ₃) ₃ ·9H ₂ O	500	99 ± 3

Effect of the type and concentration and volume of the eluent solution

Two different bases were investigated as an eluent for the recovery of Cr(VI) from the solid phase. Eluent studies were performed with 2 and 4 mol L⁻¹ ammoniac, 1 and 2 mol L⁻¹ sodium hydroxide solutions. The studied eluent volumes were between 10 and 30 mL. The results are given in Table 2. In all further studies, 20 mL of 4 mol L⁻¹ NH₃ was used.

Effect of the flow rate

The effect of the flow rate of the sample and the eluting solutions from the column on the retention and recovery of Cr(VI) ions was studied in the range of 0.5 – 5.0 mL min⁻¹ under the optimal condition. It was found that a quantitative retention of Cr(VI) occurred in the column for sample solution flow rates in the range of 1.0 – 2.0 mL min⁻¹. A quantitative desorption of Cr(VI) ion from the column was achieved in a flow rate range of 0.5 – 1.0 mL min⁻¹. Hence, all subsequent experiments were performed at a sample flow rate of 2.0 mL min⁻¹ and an eluent flow rate of 1 mL min⁻¹.

Effect of the sample volume

The effect of the sample volume on the Cr(VI) retention on chelating polymer was studied. For this purpose, 50 – 250 mL volumes of standard solutions containing 30 µg of Cr(VI) were passed through the column under the optimum conditions. The recovery of Cr(VI) was quantitative for 150 mL. In this work, the highest preconcentration factor (PF) was 30, because the elution volume was adjusted to be 5 mL.

Effect of a matrix

The effect of a matrix on the determination of Cr(VI) was studied. To a 50 mL of solution containing 0.6 mg L⁻¹ of Cr(VI) was added individually interfering ions having different concentrations, and the proposed method was applied. The

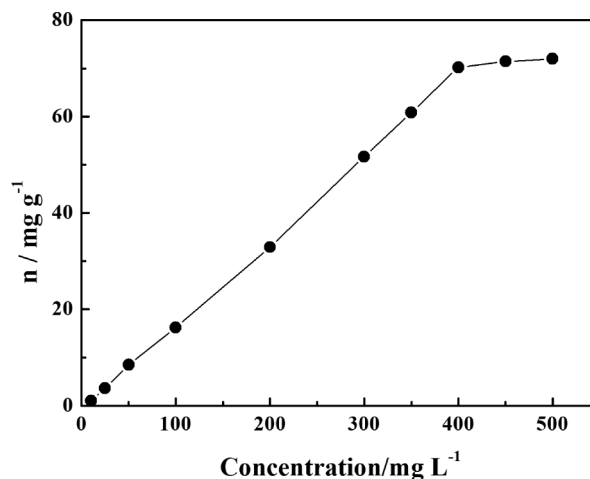


Fig. 4 Adsorption isotherm of the resin for Cr(VI).

recovery values obtained and the ratio of interfering ions to Cr(VI) are given in Table 3. As can be seen, the presence of large amounts of alkali, alkaline earth and transition metals had no significant effect on the recovery of Cr(VI). These results show that Cr(VI) can be determined quantitatively in stream water and waste-water samples.

Precision studies and limit of detection

In order to determine the detection limit (DL) of the proposed method, the pH of blank solutions of 150 mL ($n = 20$) was adjusted to pH 2 using KCl/HCl buffer and applying the preconcentration method. The DL, calculated as three-times the standard deviation of the blank solutions divided by the slope of the calibration curve was 2.4 µg L⁻¹ for Cr(VI). The precision of the method under the optimum conditions (0.6 mg L⁻¹ Cr(VI); pH 2; flow rate of sample, 2 mL min⁻¹) was determined by performing 7 successive retention and elution cycles, followed by FAAS. It was found that the recovery of Cr(VI) was 94.5 ± 3.2%.

Adsorption isotherm and adsorption capacity

The adsorption capacity of the resin was determined for Cr(VI) by using the column technique. Therefore, 50 mL portions of model solutions containing 10 – 500 mg L⁻¹ Cr(VI) at pH 2 were passed through a column filled with 350 mg of the resin at a flow rate of 2.0 mL min⁻¹. The retained Cr(VI) ions were eluted from the resin with 4 mol L⁻¹ NH₃. The concentrations of Cr(VI) in the eluate were determined by FAAS. The concentration of adsorbed metal ion (n) in mg/g was studied as a function of the metal-ion concentration (C /mg L⁻¹) in the initial solution. Figures 4 and 5 ($y = 0.693 + 0.0125x$, $R^2 = 0.9995$) show adsorption isotherms for Cr(VI) ions, which conform to the Langmuir equation.³⁰ The adsorption capacity (n_m) of the resin for chromium was calculated from the Langmuir equation. The equation is.

$$\frac{C}{n} = \frac{1}{n_m K} + \left(\frac{1}{n_m} \right) \times C. \quad (5)$$

The adsorption capacity (n_m) and the binding equilibrium constant (K) were calculated from the slope and the intercept of the regression plot obtained by the least-squares method, respectively. The adsorption capacity of the resin for Cr(VI) was found to be 80.0 mg g⁻¹ (1.54 mmol g⁻¹), and the binding

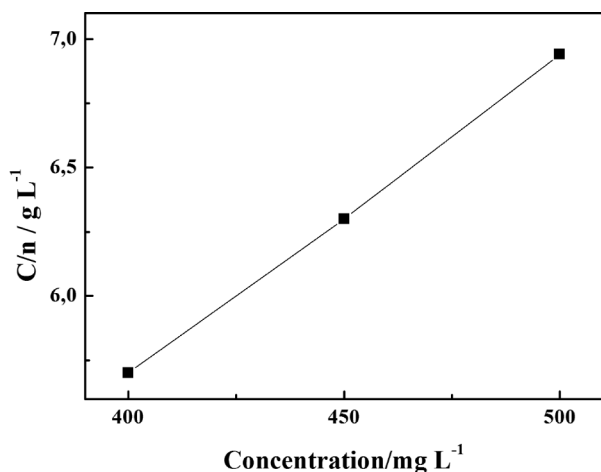


Fig. 5 Langmuir plot for the adsorption of Cr(VI) on the resin.

Table 4 Comparison of the adsorption capacity of SPE materials prepared by using various sorbents for Cr(VI)

SPE material	Adsorption capacity for Cr(VI)	
	mmol g ⁻¹	Ref.
Acetylacetone modified XAD-16	0.723	[13]
Polystyrene divinylbenzene copolymer with azophenolcarboxylate (ONO)	0.690	[31]
Ammonium pyrrolidine dithiocarbamate (APDC) chelate	0.183	[32]
Dowex M 4195 chelating resin	0.571	[33]
Poly(1,3-thiazole-2-ly-methacrylamide-co-4-vinylpyridine-co-divinylbenzene)	1.539	This work

equilibrium constant was found to be 0.018 L mg⁻¹. As can be seen in Table 4, the adsorption capacity of the resin for Cr(VI) ions is higher than that at chelate modified SPE procedures reported in the literature up to now. On the other hand, the resin could be successfully regenerated over 250 operating cycles by the column method without any loss in its sorption capacity.

Validation and application of the proposed method

The proposed method was applied to stream and waste-water samples. To validate the method, a certified reference material (TMDA 52.3; fortified lake water sample) was analysed. Recovery studies were performed in which an analyte was added to the water samples at known concentrations. The concentrations of Cr(VI) ion added to the water samples were 300 and 600 µg L⁻¹. The analysis results of the water samples are given in Table 5. A good agreement was obtained between the added and found analyte contents. While the recovery values for the chromium ion are 95 and 100%, the relative standard deviation values for the samples are 1.0 and 3.0%, respectively. The results obtained by analysing the CRM for the Cr(VI) ion are given in Table 6. The found and certified values are in good agreement for validation studies of the method.

Conclusions

In this paper, a new adsorbent was synthesized and characterized by FTIR and elemental analyses. Then, the SPE procedure was

Table 5 Results for tests of the addition/recovery for chromium determinations speciation in water samples ($n = 4$)

Sample		Added/µg L ⁻¹	Found/µg L ⁻¹	R ± s, %
Stream water	Cr(III)	0	BDL ^a	—
	Cr(VI)	0	BDL ^a	—
		300	292 ± 7	98 ± 2
		600	571 ± 7	95 ± 1
Yozgat Waste Water Treatment Instution (input)	Cr(III)	0	BDL ^a	—
	Cr(VI)	0	BDL ^a	—
		300	296 ± 7	99 ± 2
		600	604 ± 7	100 ± 3
Yozgat Waste Water Treatment Instution (output)	Cr(III)	0	BDL ^a	—
	Cr(VI)	0	BDL ^a	—
		300	299 ± 5	100 ± 2
		600	593 ± 9	99 ± 2

a. Below detection limit.

Table 6 Analysis of CRM (TMDA 52.3: Fortified lake water sample)

	Concentration/µg L ⁻¹		
	Certified value ^a	Our value ^a	Relative error, %
Cr(VI)	165 ± 12	162 ± 3	-1.8

a. At 95% confidence level, $\bar{x} \pm \frac{t \times s}{\sqrt{N}}$, $n = 4$.

developed by using this resin for the speciation of chromium in water samples. This SPE method has a good potential for the speciation of Cr(VI) from Cr(III) and the host of co-existing alkali and alkaline earth ions. The proposed method is simple and the sorption capacity of the resin is much higher than the other similar SPE materials given in Table 4. The resin has high mechanical and chemical strength, and the reusability was as high as 250 cycles without any loss in its sorption behavior. The applied method provided good precision with relative standard deviations lower than 3.0%, and high accuracy was obtained with a quantitative recovery of Cr(VI). Thus, the resin offers reliable analyse of Cr(VI) and Cr(III) in water samples.

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