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A MWCNTs@$CuAl_2O_4$@SiO_2 Nanocomposite for the Speciation of Cr(III), Cr(VI), and Total Chromium Prior to High-Resolution Continuum Source Flame Atomic Absorption Spectrometric Determination

Hassan Elzain Hassan Ahmed · Mustafa Soylak

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Abstract A solid-phase microextraction (SPME) method had been applied to speciate chromium in natural and wastewater samples. MWCNTs@$CuAl_2O_4$@SiO_2 nanocomposite was synthesized by sol–gel and calcination methods and then characterized using SEM, FTIR, and XRD techniques. MWCNTs@$CuAl_2O_4$@SiO_2 was used to extract Cr(VI) as pyrrolidine dithiocarbamate chelates. Some analytical parameters involving pH, ligand (APDC) and adsorbent amounts, sample initial and final volume, and the effects of matrices were tested and optimized. For the oxidation of Cr(III) to Cr(VI), potassium permanganate was used, and after that, the presented method was applied to determine the total chromium levels. The calculations were carried out to obtain Cr(III) concentration by finding differences between total chromium and Cr(VI) concentrations. The limit of detection (LOD) and limit of quantification (LOQ) were found to be 6.2 µg L^{-1} and 20.8 µg L^{-1}, respectively. The proposed method was successfully applied for chromium speciation in wastewater samples.

Keywords Speciation · Chromium · Solid-phase microextraction · MWCNTs@$CuAl_2O_4$@SiO_2 · Flame atomic absorption spectrometry

H. E. H. Ahmed · M. Soylak (✉)
Department of Chemistry, Faculty of Sciences, Erciyes University, 38039 Kayseri, Turkey
e-mail: soylak@erciyes.edu.tr

H. E. H. Ahmed · M. Soylak
Technology Research & Application Center (TAUM), Erciyes University, 38039 Kayseri, Turkey

H. E. H. Ahmed
Sudan Atomic Energy Commission (SAEC) – Chemistry and Nuclear Physics Institute, Khartoum, Sudan

H. E. H. Ahmed
Chemistry Section, Scientific Laboratories Department, College of Science, Sudan University of Science and Technology (SUST), Khartoum, Sudan

M. Soylak
Turkish Academy of Sciences (TUBA), Cankaya 06670, Ankara, Turkey

1 Introduction

Pollution by heavy metals is one of the most important environmental problems. Heavy metals have toxic impacts on humans and animals because they can accumulate in their bodies throughout the food chain (Akdogan et al., 2016; Demirel et al., 2008; Filik et al., 2004; Hu et al., 2009; Kowalski, 1994). Chromium is deemed a high-priority environmental pollutant. Chromium is found in nature as ores and in several other natural materials in its compound form. It can be found in electroplating, leather tanning, textile factories, metal finishing, wood preservation, some fertilizers, chromate preparation, etc. (Saracoglu et al., 2007; Shen et al., 2010). It can also enter aquatic systems through the discharge of concentrated industrial effluents. In general, there are two different

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oxidation states of chromium (Cr(III) and Cr(VI)) in nature (Cheng et al., 2022; Hu et al., 2009; Karatepe et al., 2010; Prabhakaran et al., 2009; Tuzen & Soylak, 2006). The toxicity of chromium depends on the existence of Cr oxidation states and the concentration of Cr species (Marques et al., 2000; Outridge & Scheuhammer, 1993). Cr(III) is a fundamental trace element that is necessary for the normal functioning of living organisms. It has a significant role in carbohydrates, proteins, and lipid metabolism, and its deficiency could cause an illness called chromium deficiency (Hu et al., 2009; Ozturk et al., 2021). The National Research Council recommendation for Cr(III) is 50–200 mg per day (Arain et al., 2018; Gjerde et al., 1993).

In contrast, Cr(VI) is toxic to the human biological system. It is water soluble, extremely irritating, and has high toxicity to humans due to its oxidation potential and permeability to biological membranes (Bağ et al., 2000; Krishna et al., 2004; Narin et al., 2008). Cr(VI) compounds are approximately 100 times more dangerous and 1000 times more mutagenic than Cr(III) salts. This is because its oxidation potential is high, and it readily permeates biological membranes (Narin et al., 2008; Rahman & Singh, 2019; Tripathi et al., 1998). In humans, Cr(VI) exposure may also easily inhibit DNA, RNA, and protein syntheses; increase the death rate; and increase the incidence of certain types of cancer, such as throat, lung, and bladder cancers, as well as other diseases like pneumonia, bronchitis, hypersensitivity, gastrointestinal hepatic, and renal impairments (Balali-Mood et al., 2021; Erarpat et al., 2022; Nriagu & Nieboer, 1988). The International Agency for Research on Cancer (IARC) has categorized Cr(VI) as a Class I carcinogen, while the US Environmental Protection Agency (EPA) has rated it as very hazardous (Islam et al., 2016; Mashhadizadeh & Amoli-Diva, 2013; Ouejhani et al., 2003). The maximum permitted content of Cr(VI) in drinking water, according to the World Health Organization (WHO), is 0.05 mg L^{-1} (Ozkantar et al., 2020; Saracoglu et al., 2012).

Depending on chromium oxidation states that may be essential or toxic, these oxidation forms must be determined individually by speciation analysis methods (Michalke & Caroli, 2013; Narin et al., 2008; Wang et al., 2020). The approach to estimating the total concentration of Cr by studying its physical and chemical forms is known as speciation. According to research on environmental contamination and public health, the need for chromium evaluation at trace amounts in environmental samples has risen. Inductively coupled plasma mass spectrometry (ICP-MS), inductively coupled plasma atomic emission spectrometry (ICP-AES), atomic absorption spectrometry (FAAS and ETAAS), energy-dispersive X-ray fluorescence (EDXRF), and UV–VIS spectrophotometry are commonly used techniques for total Cr determination. Ion exchange techniques have also been used to remove chromium from wastewater and determine it properly (Bulut et al., 2009; El-Feky et al., 2023; Kanberoglu et al., 2019; Musielak et al., 2024; Narin et al., 2002, 2008; Ozkantar et al., 2020; Yalçin et al., 2001).

FAAS is a trustworthy, cost-effective, and precise technique for determining metal ions at low levels. However, it has two limitations: lower amounts of analytes are below the detection limits, and matrix components of the tested samples influence the results (Guo et al., 2003; Shemirani et al., 2004; Tel et al., 2004; Dadfarnia and Shabani, 2010; Sarafraz-Yazdi & Amiri, 2010; Soylak et al., 2022). Atomic absorption spectroscopy cannot directly measure chromium species. Speciation of chromium species by preconcentration and separation procedures such as solid-phase extraction (SPE) (Fig. 1), liquid–liquid extraction (LEE), and others in conjunction with FAAS or ETAAS is frequently insensitive for chromium traces (Duran et al., 2007; Jagirani & Soylak, 2020; Khan et al., 2020). Most chromium speciation procedures involve the separation and enrichment of Cr(VI). Following the oxidation of Cr(III), the total chromium was determined in several published experiments (Marguí & Torrent, 2023).

In the presented work, MWCNTs@$CuAl_2O_4$@SiO_2 nanocomposite was synthesized by sol–gel methodology to be employed as an adsorbent in the speciation of chromium species. MWCNTs, $CuAl_2O_4$, and SiO_2 have demonstrated significant utility in preconcentration applications across diverse fields. Their unique properties, including high surface area, tunable surface chemistry, and mechanical stability, make them highly effective sorbents for adsorbing and preconcentrating target analytes from environmental samples (Alavi et al., 2022; Li et al., 2017; Soylak et al., 2024a, b). The MWCNTs@$CuAl_2O_4$@SiO_2 nanocomposite is a potential sorbent material for SPME applications because of its distinct

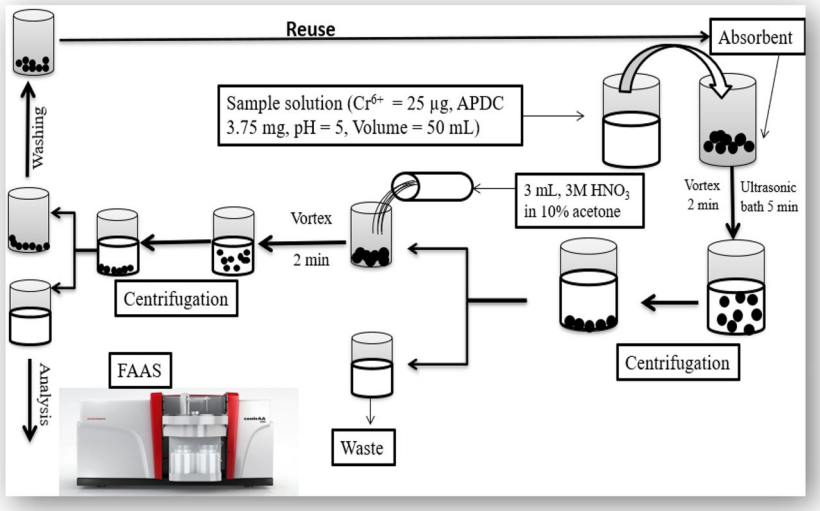


Fig. 1 Schematic presentation of the presented solid-phase microextraction method of Cr(VI)

combination of MWCNTs, copper–aluminum spinel, and SiO_2. This combination provides a large surface area and active sites for effective adsorption of target analytes, increasing extraction efficiency. The composition of the nanocomposite enables the selective extraction of analytes from complicated matrices thanks to the various interactions between the components. The nanocomposite's structural integrity promotes stability and durability during SPME processes, reducing loss and maintaining consistent results over numerous cycles. Its large surface area and porous structure allow quick mass transfer kinetics, resulting in reduced extraction times and greater adsorption. Its compatibility with analytical procedures makes it appropriate for various applications, including environmental, medicinal, and food analysis (Deak et al., 2007; Bouali et al., 2023; Soylak et al., 2024a, b) . Since ammonium pyrrolidine dithiocarbamate (APDC) is a highly selective chelating agent for Cr(VI), it is commonly used as a suitable ligand. Cr(VI) was assessed FAAS after being separated-preconcentrated as its APDC complex on MWCNTs@$CuAl_2O_4$@SiO_2. Total chromium was measured in a similar manner after oxidizing Cr(III) to Cr (VI). The difference between the total chromium and the Cr(VI) contents was used to calculate the Cr(III) content. The analytical conditions, including pH, amount of adsorbent, APDC quantity, and interferent impacts, were optimized.

2 Experimental

2.1 Instruments

A flame atomic absorption spectrophotometer (model contrAA 800) with a xenon arc lamp was utilized, and all measurements were performed in an air/acetylene flame in this work. The analysis parameters of the analyzed element were adjusted as recommended by the manufacturer. For shaking the model and real sample solutions, a Weightlab (Turkey) ultrasonic bath and a Fisons WhirliMixer Vortex Shaker Cyclone Mixer model 12,665 were used. The Nüve Nf 400 (16×15 ml at 4.100 rpm) model centrifuge was also used for the separation of solid-phase adsorbents from solutions.

2.2 Chemicals and Solutions

All chemical reagents used in this study are AR-grade and were used as-is without any purification. Deionized water (Milli-Q Millipore 18.2 MΩ cm^{-1} conductivity) was used for all work. Ammonium pyrrolidine dithiocarbamate (APDC) solution (0.5%, w/v) was freshly prepared in water with ethanol (3:1, v/v). Multiwalled carbon nanotubes (MWCNTs) were purchased from Aldrich, Milwaukee, WI, USA. Potassium permanganate (KMnO4) (Sigma-Aldrich) solution (0.02 M) was prepared for oxidation purposes.

Chromium standard solutions (Cr(III) and Cr(VI)), HNO_3, and H_2O_2 used in this work were prepared and diluted from stock solutions (1000 mg L^{-1}) that were purchased from Sigma-Aldrich. Other solutions for elements were obtained by preparing high-purity compounds. INCT-OBTL-5 Oriental Basma tobacco leaves CRM from INCT, Warsaw, Poland, and TMDA-64.3-fortified water CRM from NWRIC, Burlington, ON, Canada. Phosphate ($HPO_4^{2-}/H_2PO_4^-$, $H_2PO_4^-/H_3PO_4$), acetate, and ammonium buffer solutions were prepared as pH = 2, 3, 6, and 7; 4 and 5; and 9 and 10, respectively.

2.3 *Synthesis of MWCNTs@$CuAl_2O_4$@SiO_2*

A total of 20 mL of 10% (v/v) HCl was added to 1 g of MWCNTs and stirred for 2 h for their surface activation. The obtained MWCNTs were separated using filter paper and dried at 85 °C for 5 h. Then 0.75 g was taken and suspended in 60 mL of concentrated H_2SO_4 and concentrated HNO_3 mixture (3:1). The mixture solution was also stirred overnight at 80 °C. Then, it was washed with deionized water till its pH reached 7 then dried at 85 °C for 12 h.

Using the sol–gel method, 0.4 g of $Cu(NO_3)_2{\cdot}3H_2O$ and 0.6 g of $Al(NO_3)_3{\cdot}9H_2O$ were dissolved in deionized water. A total of 0.75 g of oxidized MWCNTs was added to the above mixture and stirred using a stirrer till a light blue-colored solution appeared. Then 0.9 g of citric acid was added to the above mixture and stirred for 30 min at 70 °C. The pH of the mixture was set to 2–3 using an ammonia solution until the solution color changed to a deep blue. The dark blue gel was formed after the solution temperature was adjusted to 70 °C. The gel was placed in an oven at 90 °C for 8 h until it became completely dry and turned into a porous gel. The dried porous gel was put in a furnace at 400 °C for 4 h (Kwak et al., 2012).

MWCNTs@$CuAl_2O_4$ nanoparticles obtained in the above step were coated on their surfaces by SiO_2 nanoparticles using the Stöber method (Habila et al., 2016). A total of 1 g of prepared MWCNTs@$CuAl_2O_4$ nanoparticles were used as cores and dispersed in 10 mL ethanol then added to a round-bottom flask containing 200 mL ethanol and 50 mL deionized water. The mixture was stirred for 20 min, and then 5 mL of ammonia solution (25%) was added drop by drop. The mixture was placed in the stirrer for 15 min, and 3 mL of TEOS was added drop by drop using a burette for 5 min. The round-bottom flask content was stirred for 8 h to carry out the silica coating. The prepared MWCNTs@$CuAl_2O_4$@SiO_2 nanoparticles were centrifuged to separate the solution phase, washed using deionized water and ethanol, and dried in an oven at 85 °C for 12 h (Saravanan & Dubey, 2020).

2.4 Test Procedure for Cr(VI)

A total of 2 mL of buffer solution (pH = 5) and 0.75 mL of APDC solution were added to 5 mL of solution in a centrifuge tube that contains 25 µg of Cr(VI). Deionized water was used to bring the final volume to 50 mL, and 20 mg of sorbent was added. The tube content was put in an ultrasonic bath for 5 min, shaken on a vortex for 2 min, and then centrifuged for 5 min. After decantation, 3 mL of HNO_3 (3 M) dissolved in 10% acetone was added to the remaining solid phase in the tube and shaken well using the vortex for 5 min and then put again in the centrifuge for 5 min. The eluent was separated into another tube for measurement of Cr(VI) concentrations via FAAS.

2.5 Oxidation of Cr(III) to Cr(VI) and Determination of Total Chromium

The oxidation step had been carried out using the procedures described in the previous studies (Ghosh et al., 2013; Tarigh et al., 2020). The Cr(III) quantity in the 10-ml model solution was 25 mg. Four to five drops of (0.02 M) $KMnO_4$ solution and 1 mL of 2 M H_2SO_4 were added to three separate beakers containing 50 mL. To finish the oxidation process, the beakers were covered with watch glasses and heated at 70–80 °C for 30 min. After cooling the solutions, sodium hydroxide solution (2.5% w/v) was added drop by drop to remove the excess $KMnO_4$. The pH of the solution was checked with a pH meter and set to 5. Each solution was quantitatively transferred to a 50-mL volumetric flask, completed with deionized water, and shaken well. Overall, 5 mL from each solution was taken to centrifuge tubes separately. Then 0.75 mL of 0.5% APDC solution and 2 mL of acetate buffer solution were added, and the final volume was completed with deionized water until 50 mL and mixed well. A total of 20 mg of sorbent was added, and the steps mentioned in Sect. 2.4 were applied. FAAS was applied to determine the total chromium in the model and real sample solutions. The level of Cr(III) is obtained from the difference between the concentrations of total chromium and Cr(VI).

2.6 Total Chromium Levels of Certified Reference Materials

A 100-mg amount of INCT-OBTL-5 Oriental Basma tobacco leaves CRMs sample was added to 10 mL of concentrated nitric acid, and the solution was heated and evaporated near dryness. The above process was done again with 10 mL of HNO_3:H_2O_2 (1:1). A total of 10 ml of distilled water was added to the beaker, and the suspension was centrifuged for 5 min. Then, 5 mL was taken from the upper layer, and the above enrichment method was applied. The same procedure was also performed on the blank solutions. Using FAAS, the concentration of total chromium was determined.

The presented extraction procedure was directly applied to determine the total chromium of the TMDA-64.3-fortified water CRM sample.

2.7 Applications to Real Samples

Water samples, including wastewater, Erciyes University tap water, and mineral water, were filtered through cellulose filter paper. The same method given above was applied, and Cr(VI) concentrations in the samples were measured by FAAS. After the oxidation process was applied to Cr(III), the total chromium levels in water samples were measured.

3 Results and Discussion

3.1 Characterization

To characterize the synthesized MWCNTs, MWCNTs@$CuAl_2O_4$, and MWCNTs@$CuAl_2O_4$@SiO_2 nanocomposite, FTIR analysis was carried out in the range of 4000–400 cm^{-1} (Fig. 2a, b, and c, respectively). In Fig. 2, bands at 3430 cm^{-1} belong to the OH stretching vibrations (Saravanan & Dubey, 2020). Spectrum bands at 2810 and 2790 cm^{-1} are the alkyl chains cleaved from the nanotube surface (Jalbani & Soylak, 2015). Furthermore, bands at 1270 and 1190 cm^{-1} could be attributed to CH-CH3 and C-O peaks (Soylak et al., 1993). Moreover, the bands from 1090 to 850 cm^{-1} can belong to C–C and C=O groups. The broad band at 550 cm^{-1} is attributed to metal–oxygen stretching frequencies associated with the symmetric and asymmetric Si–O–Si stretching and vibration

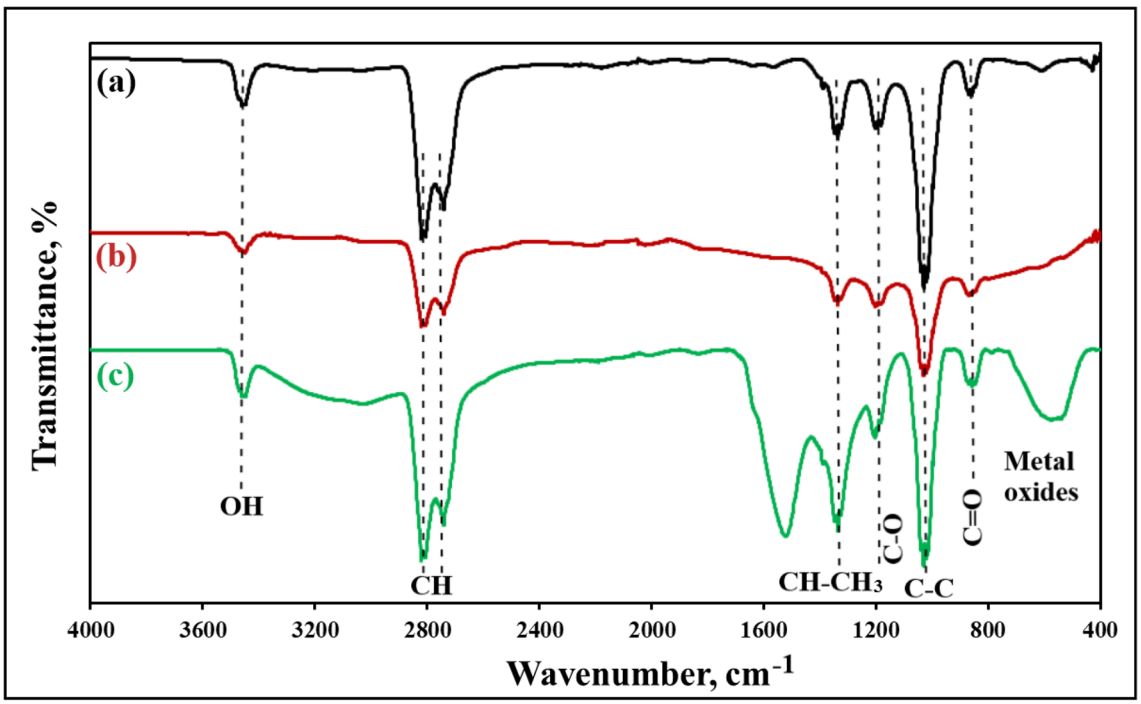


Fig. 2 IR spectra of (**a**) MWCNTs, (**b**) MWCNTs@$CuAl_2O_4$, and (**c**) MWCNTs@$CuAl_2O_4$@SiO_2

bonds and Cu–O, Al–O, and Cu–O–Al vibration bonds (Gholami & Maddahfar, 2016; Jalbani & Soylak, 2015; Saravanan & Dubey, 2020; Soylak et al., 1993).

The typical XRD profiles of oxidized MWCNTs, MWCNTs@$CuAl_2O_4$, and MWCNTs@$CuAl_2O_4$@SiO_2 are given in Fig. 3. In (a), according to Miller indices, typical (002) and (110) peaks of oxidized MWCNTs were gotten and observed at diffraction angles (2θ) of 26°, 43.8°, and 45°, respectively, which are acceptable and related to the literature values (Gholami & Maddahfar, 2016). The XRD pattern of MWCNTs@$CuAl_2O_4$@SiO_2 nanocomposite, as given in (b), collects reflection peaks of (220), (311), (400), (422), (511), (440), (420), and (533) for $CuAl_2O_4$ and (002) diffraction lines for MWCNTs with a space group of *Fd3m* (JCPDS card no. 44–0160) (Lee et al., 2005). MWCNTs@$CuAl_2O_4$@SiO_2 diffraction peaks show a clear difference from the MWCNTs@$CuAl_2O_4$ peaks (c) (Khomenkova et al., 2011).

Figure 4A, B, and C shows the SEM images of magnetic MWCNTs, MWCNTs@$CuAl_2O_4$, and MWCNTs@$CuAl_2O_4$@SiO_2 nanocomposites, respectively. These characterizations show that all nanocomposites have a different morphology from each other. Homogenous formation of $CuAl_2O_4$ nanoparticles on the MWCNTs and homogenous formation of SiO_2 on the MWCNTs@$CuAl_2O_4$ nanocomposite surface were obtained (Saleh, 2016).

3.2 Optimization of the Developed SPME Procedure

3.2.1 Effects of pH

The speciation mechanism by which Cr(III) and Cr(VI) interact with APDC is generally dependent on pH-dependent interactions and complexation reactions. In complexation reactions, APDC forms stable complexes with metal ions, including Cr(III) and Cr(VI), by reacting as a chelating agent. When APDC is present, Cr(III) coordinates with the APDC ligand to form a complex as Cr(III)-APDC at pH ranging from 4 to 8. Cr(VI) reacts with APDC at pH 2.0–6.0 to produce Cr(VI)-APDC complexes. MWCNTs@$CuAl_2O_4$@SiO_2 nanocomposite adsorbs Cr(VI)-APDC on its surface. The nanocomposite possesses a high surface area and a variety of functional groups, such as hydroxyl (−OH) and carboxyl (−COOH) groups, which can adsorb Cr(VI)-APDC chelates through electrostatic attraction, ion exchange, and surface complexation. Adsorption of Cr(VI)-APDC chelates onto the nanocomposite surface is typically favored under acidic conditions (pH < 7) (Salihu & Bakar, 2018; Yan et al., 2023). The impacts of pH (Fig. 5) on both Cr(III) and Cr(VI) recovery values were tested in the range of 2–10 pH. Related to the results presented in Fig. 5, Cr(III) recovery values were below 10% in all pH ranges from 2 to 6, so this work was done in the same

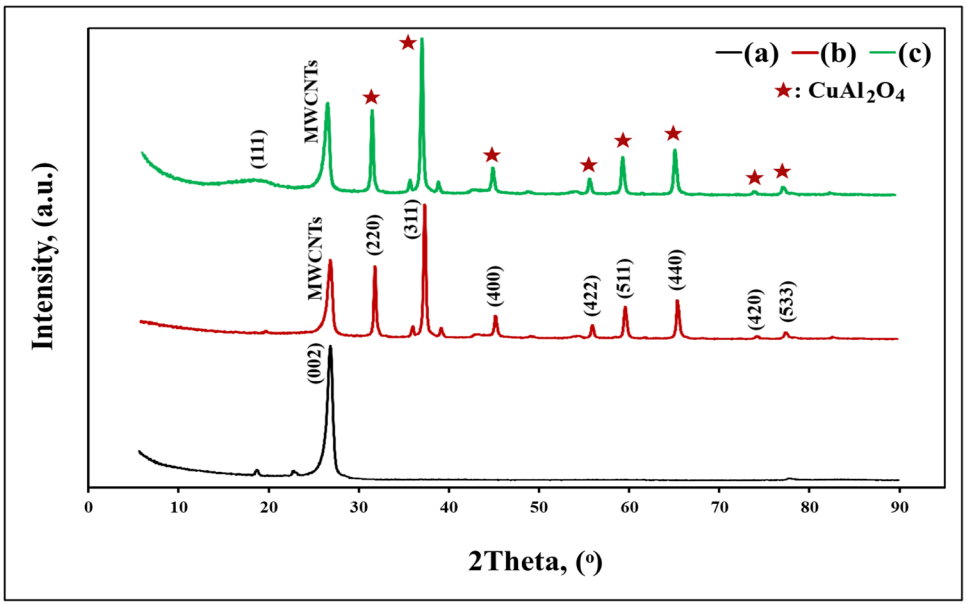


Fig. 3 XRD patterns of MWCNTs (**a**), MWCNTs@$CuAl_2O_4$ (**b**), and MWCNTs@$CuAl_2O_4$@SiO_2 (**c**)

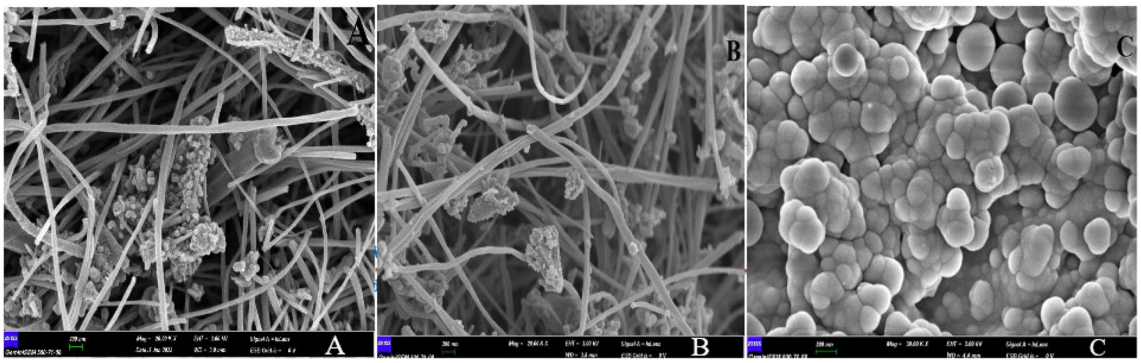


Fig. 4 SEM images of MWCNTs (A), MWCNTs@$CuAl_2O_4$ (**B**), and MWCNTs@$CuAl_2O_4$@SiO_2 (**C**)

range. In contrast, Cr(VI) was quantitatively recovered in the range of 4.5–5.5 of pH as Cr(VI) chelates. The given results prove that the Cr(III) and Cr(VI) speciation is possible at a pH range of 4.5–5.5, and all remaining works were continued at pH 5.0 for chromium speciation.

3.2.2 *Effects of APDC Amount*

APDC is a reagent that can react with about 30 mineral ions, including Cr (VI), to form stable complexes (Bahadir et al., 2016; Saber Tehrani et al., 2004). APDC is commonly used in preconcentration-separation works and is preferred by researchers because of its properties. The influence of APDC on the recovery values of Cr(VI) on the adsorbent was also studied, and the results are given in Fig. 6. The recovery of Cr(VI) was not quantitative at 0 mg APDC, then started increasing with the quantity of APDC. The values of recovery became quantitative after using 3.75 mg of APDC, and the remaining work was carried out using this amount of the chelating agent.

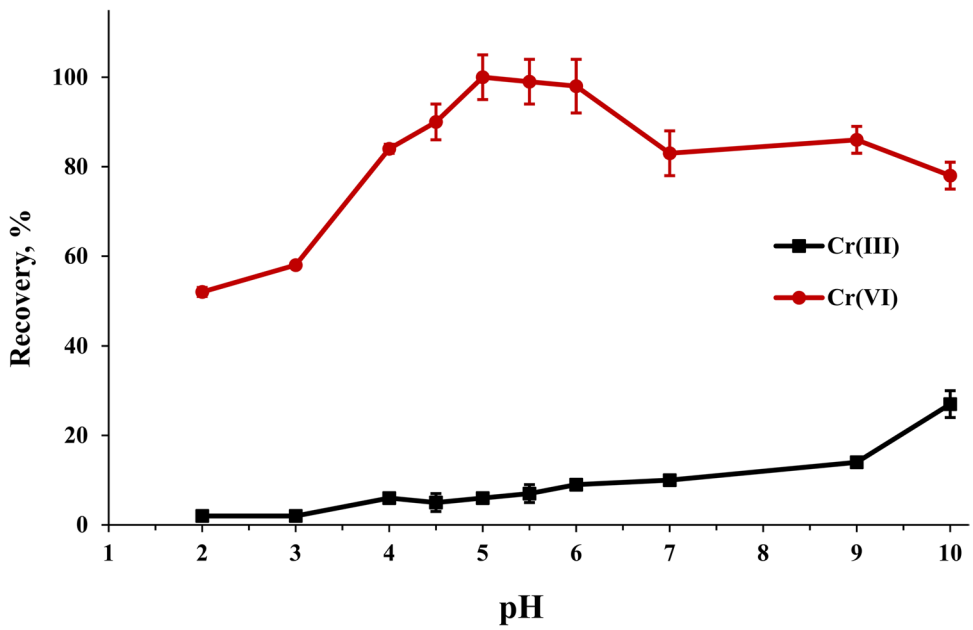


Fig. 5 Effects of pH on the recoveries of Cr(III) and Cr(VI), ($N = 3$)

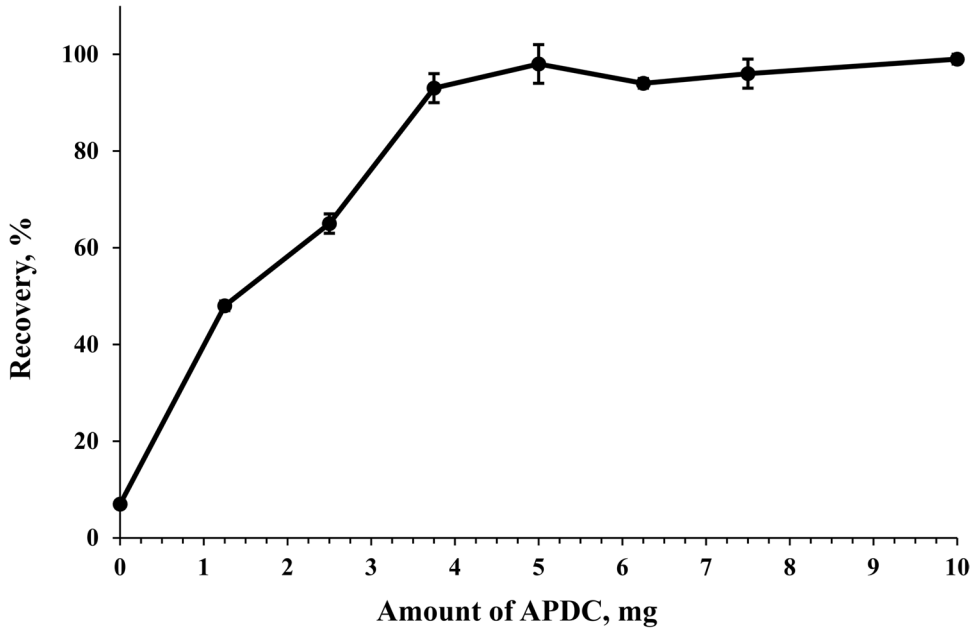


Fig. 6 Effect of chelating agent amount on the recoveries of Cr(III) and Cr(VI), ($N = 3$)

3.2.3 Effects of Adsorbent Quantity

In this step, different amounts of modified adsorbent were studied. The range of 5–40 mg of adsorbent was tested, and the results are given in Fig. 7. Related to the obtained results, all used amounts have given quantitative recoveries of Cr(VI) except 5 mg. Further work was done using 20 mg of adsorbent.

3.2.4 Effect of Eluent Type

The type and volume of eluent are also significant factors that affect the recovery values. The elution condition optimizations were carried out to get the best recovery values with a minimal volume of the eluent. In this work, different eluents (5 mL) were tested, and the results are given in Table 1. As can be seen, the Cr(VI) ions were quantitatively eluted from the solid phase with 3 M HNO_3 in 10% acetone, and this eluent was used in all subsequent studies.

3.2.5 Effect of Sample Volume

The sample volume effect on the recovery values of Cr(VI) was tested using different sample volumes of 10–50 mL. This indicates that Cr(VI) recoveries are quantitative in this range (Fig. 8). The lowest eluent volume was 3 mL (Fig. 9). So the preconcentration factor was calculated as 17.

3.2.6 Effect of Matrix Components

Different metal cations and anions were added individually to the model solutions to test the presented method mentioned in Sect. 2. Sequences shown in Table 2 indicate that most of these matrices remained in the adsorption liquid phase. Some heavy metal ions were used in this work, and their levels were low and suitable for the Cr(VI) separation–enrichment in the real samples tested.

3.3 Figure of Merits

After the preconcentration-separation method was applied to the blank solutions, the limit of detection (LOD) and the limit of quantification (LOQ) were obtained under optimum experimental conditions. LOD and LOQ of Cr(VI) and R^2 were 6.2 µg L^{-1} and 20.8 µg L^{-1} and 0.997, respectively. The precision of Cr(VI) determination for this procedure was evaluated, as mentioned above. The presented method was repeated 10 times for Cr(VI).

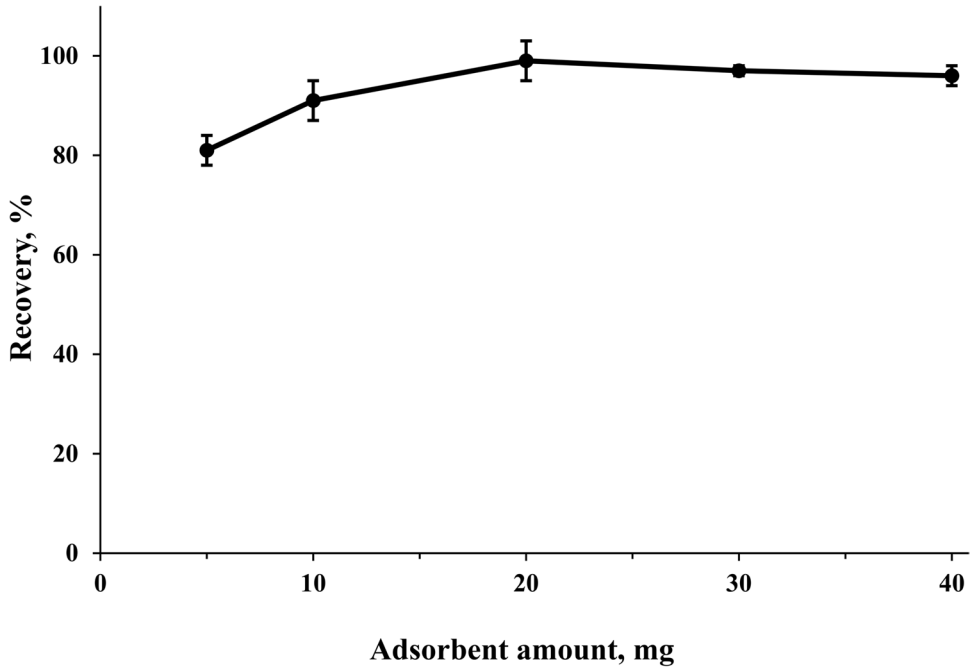


Fig. 7 Effect of adsorbent quantity on the recoveries of Cr(III) and Cr(VI), ($N=3$)

Table 1 Effect of the eluent type on the recoveries of chromium (VI), ($N=3$)

Eluent type (5 mL)	Recovery (%)[a]
3 M HCl	53 ± 2
3 M HNO_3	63 ± 3
3 M HCl in 5 v% acetone	78 ± 3
3 M HNO_3 in 5% acetone	70 ± 2
3 M HCl in 10% acetone	89 ± 3
3 M HNO_3 in 10% acetone	97 ± 4

[a]Mean ± standard deviation

At a 95% confidence level, the recovery of Cr(VI) was 98 ± 5%.

3.4 Determination of Total Chromium

Model solutions and natural water samples that contain different quantities of Cr(VI) and Cr(III) were prepared to determine total chromium. 0.5 mL of H_2SO_4, and drops of $KMnO_4$ were added to these sample solutions to oxidize Cr(III) ions to Cr(VI) (Lopez-Garcia et al., 2012; Sereshti et al., 2011). The mixture was heated at 70–80 °C for 30 min to achieve the oxidation process. To obtain quantitative recovery values for Cr(VI), the pH of the solution was adjusted to pH = 5 using sodium hydroxide, followed by adding 2 mL of acetate buffer solution at pH = 5. The method given in Sect. 2 was applied to these solutions, and the results are presented in Table 3. Total chromium recovery in distilled water varied from 89 to 99% for various spiked concentrations, suggesting high recovery rates. With comparatively small standard deviations and observed values that were within an acceptable range, the measurement was precise. This implies that the technique works well for speciating chromium in samples of distilled water. Similarly, total chromium recovery varied from 96 to 107% in Erciyes University tap water and from 94 to 97% in mineral water samples. These results show how dependable and resilient the approach is in a variety of water matrices. The method's accuracy in quantifying chromium species in complicated water samples is shown by the constant recovery rates seen across all tested concentrations. The results indicate that the present SPE procedure can be suitable for total chromium determination in aqueous solutions.

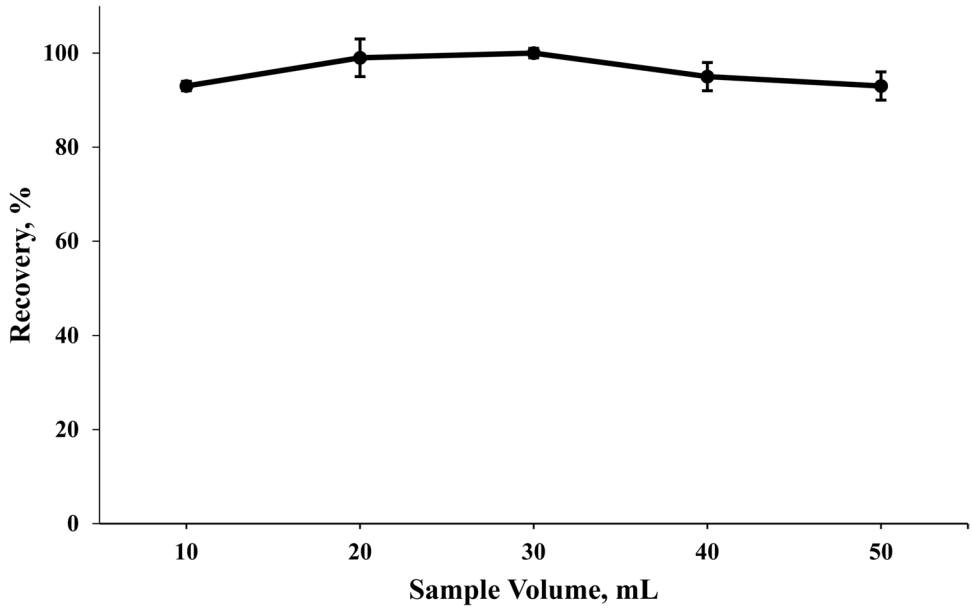


Fig. 8 Effects of sample volume on the recoveries of Cr(III) and Cr(VI), ($N=3$)

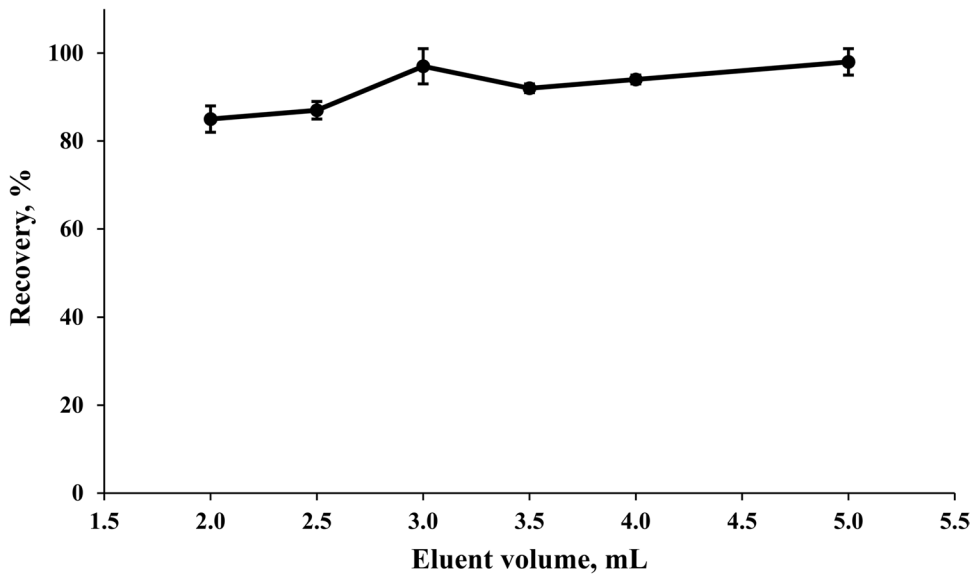


Fig. 9 Effects of eluent volume on the recoveries of Cr(III) and Cr(VI), ($N=3$)

The presented procedure was also applied to TMDA-64.3-fortified water and INCT-OBTL-5 Oriental Basma tobacco leaves CRMs for chromium separation and preconcentration. The results in Table 4 were obtained in three replicates and correspond well with the certified chromium values. The analysis of TMDA-64.3-fortified water and INCT-OBTL-5 Oriental Basma tobacco leaves has shown recovery rates of $96 \pm 5\%$ and $94 \pm 4\%$, respectively. These recovery rates indicate the method's effectiveness in accurately quantifying total chromium in different sample matrices. The close agreement between the certified and

Table 2 Effect of some foreign ions on the recoveries of chromium (VI), ($N=3$)

Ions	Salt	Concentration (ppm)	Recovery (%)[a]
K^+	KCl	5000	94 ± 3
Na^+	NaF	5000	98 ± 3
Mg^{2+}	$MgCl_2$	1000	94 ± 3
Ca^{2+}	$CaCl_2$	1000	108 ± 6
Co^{2+}	$CoCl_2$	5	97 ± 3
Mn^{2+}	$Mn(NO_3)_2$	5	76 ± 3
Zn^{2+}	$ZnCl_2$	5	95 ± 2
Fe^{3+}	$Fe(NO_3)_3$	5	94 ± 1
CO_3^{2-}	Na_2CO_3	1000	96 ± 4
SO_4^{2-}	Na_2SO_4	2000	70 ± 3
Cl^-	$CaCl_2$	1750	96 ± 2
NO_{3-}	$NaNO_3$	2000	95 ± 2
F−	NaF	4000	98 ± 3

[a]Mean ± standard deviation

found concentrations demonstrates the reliability and accuracy of the presented method. The relative standard deviation (RSD%) range of CRMs was 4–5%.

3.5 Applications to Wastewater Samples

Using the standard addition method, the presented speciation procedure was applied to three different samples of wastewater collected from Kayseri Industrial Region in Kayseri City. The reliability of the new method was confirmed by spiking experiments. The results are shown in Table 5. The findings presented in Table 5 indicate that the chromium concentrations of the examined samples varied considerably, with Water C containing the maximum quantities of both Cr(III) and Cr(VI). The significance of speciation analysis in clarifying the source and possible toxicity of chromium contamination in wastewater is underscored by these results. The concentrations that have been observed emphasize the critical need for efficient monitoring and management approaches to reduce chromium pollution and the hazards it poses to the environment and human health. The efficacy of the method described in this study in precisely quantifying chromium species within intricate matrices such as effluent reaffirms its practicality in the realms of environmental monitoring and regulatory compliance.

Table 3 Speciation chromium in spiked test solutions, (volume, 50 mL; $N=3$)

Sample	Added (µg)			Found (µg)[a]	
	Cr(VI)	Cr(III)	Total chromium	Total chromium	Recovery (%)
Distilled water	0	25	25	22.3 ± 2.0	89 ± 6
	15	10	25	24.8 ± 1.0	99 ± 5
	20	5	25	24.5 ± 0.6	98 ± 2
	25	0	25	24.5 ± 0.6	98 ± 2
Tap water from Erciyes University	0	25	25	25.5 ± 0.8	102 ± 3
	15	10	25	25.3 ± 0.8	101 ± 3
	25	0	25	26.7 ± 0.6	107 ± 2
Mineral water	0	25	25	24.0 ± 0.3	96 ± 1
	15	10	25	24.3 ± 0.6	97 ± 2
	25	0	25	23.5 ± 0.6	94 ± 2

[a]Mean ± standard deviation

Table 4 The level of total chromium in the standard reference materials after application of the presented method, ($N=3$)

CRMs	Total chromium		Recovery (%)
	Certified	Found	
TMDA-64.3-fortified water	0.283 (µg/mL)	0.271 (µg/mL)	96 ± 5[a]
INCT-OBTL-5 Oriental Basma tobacco leaves	6.30 (µg/g)	5.940 (µg/g)	94 ± 4

[a]Mean ± standard deviation

Table 5 Chromium speciation in wastewater samples, (volume, 50 mL; $N = 3$)

Wastewater sample	Cr(III) (μg/L)[a]	Cr(VI) (μg/L)	Total Cr (μg/L)
Water A	483 ± 15	106 ± 0	589 ± 18
Water B	625 ± 36	336 ± 14	988 ± 57
Water C	1741 ± 35	520 ± 17	2261 ± 45

[a]Mean ± standard deviation

4 Conclusions

Chromium in wastewater samples was speciated using a novel, rapid, reliable, and simple procedure. The procedure was effectively carried out to measure chromium species in different wastewater samples. In this method, a new nanocomposite was synthesized as multi-walled carbon nanotubes and copper (II) aluminate nanoparticles coated by silicon dioxide nanoparticles (MWCNTs@$CuAl_2O_4$@SiO_2). High recovery rates over a variety of spiking concentrations were shown by the total chromium recovery in distilled water, which varied from 89 to 99%. The tap water and mineral water samples from Erciyes University showed varying recovery rates, ranging from 96 to 107% and 94 to 97%, respectively. These steady recovery rates show how the technique is resilient and dependable in a variety of water matrices. TMDA-64.3-enriched water and INCT-OBTL-5 Oriental Basma tobacco leaves

Table 6 Comparative data from some recent studies on Cr(III) and Cr(VI) speciation

Technique	System	Media	Detection system	PF	DL (μg/L)	RSD (%)	Ref
SPE	Sorption of Cr(III) and reduction of Cr(VI)	*Saccharomyces cerevisiae* immobilized on sepiolite	FAAS	75	94	< 5	Bağ et al. (2000)
SPE	Cr(VI)-DPC[b] and oxidation of Cr(III)	*Funaria hygrometrica* immobilized in a polysilicate matrix	ICP-MS and FAAS	20	0.15 and 145	< 10	Krishna et al. (2004)
SPE	Cr(VI)-acetyltrimethyl ammonium bromide and oxidation of Cr(III)	C-18 bonded-phase silica SPE disks	FAAS	45	15–20	< 5	Saber Tehrani et al. (2004)
SPE	Cr(III)-dithizone and reduction of Cr(VI)	Chromosorb 108	FAAS	71	0.75	< 9	Tuzen and Soylak (2006)
DLLME[c]	Cr(VI)-DPC and oxidation of Cr(III)	Methanol and CCl_4[d]	TXRF[e]	200	0.8	< 12	Bahadir et al. (2016)
LLE[f]	Cr(VI)-DPC and oxidation of Cr(III)	*n*-pentanol	Spectrophotometry		7.5	5	Chen et al. (2005)
UA-DLLME[g]	Cr(VI)-TBP[h] and oxidation of Cr(III)	TBP, HCl, and NaCl	ETAAS	240	0.002	5.2–8.6	Dokpikul et al. (2018)
DLLME	Cr(VI)-Na-DDTC[i]	CCl_4	ICP-OES	8	0.27	6.2–9	Sereshti et al. (2011)
IL-DLLME[j]	Cr(VI)-APDC and oxidation of Cr(III)	($[C_8MIm][NTf_2]$)[h]	ETAAS	300	0.002	8	López-García et al. (2013)
SPE	Cr(VI)-APDC and oxidation of Cr(III)	Magnetic MWCNTs/$CuAl_2O_4$/SiO_2	FAAS	17	6.2	5	This work

DPC[b] diphenylcarbazide, *DLLME*[c] dispersive liquid–liquid microextraction, CCl_4[d] carbon tetrachloride, *TXRF*[e] reflection x-ray fluorescence, *LLE*[f] liquid–liquid extraction, *UA-DLLME*[g] ultrasound-assisted dispersive liquid–liquid microextraction, *TBP*[h] Octakis (*p*-tert-butylphenyl), *DDTC*[i] diethyldithiocarbamate, *IL-DLLME*[j] ionic liquid-dispersive liquid–liquid microextraction

[h]($[C_8MIm][NTf_2]$) 1-methyl-3-octylimidazolium bis[trifluoromethylsulfonyl]imide

showed recovery rates of 96 ± 5% and 94 ± 4%, respectively, suggesting that the approach is a good fit for precisely measuring total chromium in various sample matrices. The considerable differences in chromium concentrations found in wastewater samples under examination, especially in Water C, highlight the significance of speciation analysis in determining the level of chromium pollution in wastewater. These findings highlight the urgent need for effective management and monitoring strategies to lower chromium pollution levels and the risks they pose. Chromium speciation data from some late studies and this work were compared and given in Table 6. The optimal conditions of the presented method and the chromium speciation detection limit were studied. The new synthesized nanocomposite speciation method is superior to some of the reported methods in terms of detection and quantification limits, selectivity, simplicity, amount of adsorbent, and used solvents.

Author Contribution Hassan Elzain Hassan Ahmed: methodology, visualization, and writing—review and editing. Mustafa SOYLAK: methodology, visualization, supervision, and writing—review and editing.

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Data Availability Datasets of selected element concentrations were added as supplementary information.

Declarations

Ethical Approval The work on this manuscript met all ethical standards required for research publication. No experiments with animals were performed.

Consent to Participate Human beings were not studied in this work.

Consent for Publication All authors willfully took part in this study, contributed to its content, and were informed on the progress of manuscript preparation.

Competing Interests The authors declare no competing interests.

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