Synthesis and Characterization of GO/MOF-199/MoSe2 for use as a Solid Phase Extractant for Flame AAS Determination of the Speciation of Cr in Natural and Wastewater Samples

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ABSTRACT: This study investigates a new approach to synthesizing molybdenum diselenide nanoflowers doped on metal-organic frameworks-graphene oxide (GO/MOF-199/MoSe2) nanocomposite. The nanocomposite has been used for chromium speciation analysis. Various analytical methods, such as Fourier transform infrared (FT-IR), X-ray diffraction (XRD), and field-emission scanning electron microscopy (FE-SEM), validated the proper preparation and unique structural properties of the nanocomposite. Optimizations were conducted on several analytical parameters, including pH (9.0), ligand (1-(2-pyridylazo)-2-naphthol (PAN)), adsorbent amount (15 mg), sample and eluent volumes (30 and 2 mL), and the interference effects. The method shows outstanding sensitivity, accuracy, and efficiency, as shown by low detection and quantification limits of Cr(III) (0.11 and 0.39 µg L⁻¹) and a relatively low RSD (6.5%). The proposed method was applied to natural water, wastewater samples, and certified reference materials (CRMs) to demonstrate its adaptability and usefulness in various environmental samples.

INTRODUCTION

Heavy metals are one of the most significant contaminants in the environment. Excessive levels of heavy metals are toxic and may result in health problems for humans. Chromium is one of the major heavy metal contaminants that pollutes the environment.¹,² Because of the importance of chromium species to human health, analyzing chromium contamination is an essential aspect of analytical chemistry. Chromium and its compounds are extensively employed in electroplating, leather tanning, wood preservation, dyeing, photography, and textile sectors, making chromium species easily discharged into water bodies. Trivalent chromium (Cr (III)) and hexavalent chromium (Cr (VI)) are the most common and stable forms of the element.³⁴ These species vary in their characteristics. Cr (VI) holds carcinogenic properties and potentially contributes to the development of certain illnesses, including gastrointestinal, kidney, liver, and lung cancers. The US Environmental Protection Agency (USEPA) and the International Agency for Research on Cancer (IARC) have classified Cr(VI) as carcinogenic. The USEPA and World Health Organization set limit concentrations of 100 and 50 µg L⁻¹, respectively, for total chromium and Cr(VI) in drinking water.⁵ Chromium (III) is the most common chemical type of present in foods and is required for several enzyme systems and appropriate glucose metabolism.⁶⁻¹⁰ Therefore, it is essential to separate these two species from...
environmental samples and estimate their corresponding abundances. There is a growing need to determine the concentrations of chromium species rather than only the total chromium.\textsuperscript{10}

Trace or ultra-trace chromium frequently be determined directly because of the low amounts involved, which often fall below the detection limits of traditional analytical techniques. Furthermore, the inclusion of complex matrices complicates the analysis since it may interfere with the detection technique. Sample preparation methods, like matrix elimination strategies and preconcentration techniques, are used to keep chromium levels within the detection limits of analytical instruments and reduce interference from matrix components, which makes it easier to measure chromium levels accurately.\textsuperscript{11–13} Liquid-liquid extraction (LLE), solid phase extraction (SPE), ion exchange, electroanalytical techniques, membrane filtration, cloud point extraction (CPE), coprecipitation, and solid phase micro-extraction (SPME) are the common sample preparation techniques.\textsuperscript{11,14,15} High-performance liquid chromatography (HPLC) with sensitive detectors, inductively coupled plasma-mass spectrometry (ICP-MS), inductively coupled plasma-optical emission spectroscopy (ICP-OES), X-ray fluorescence spectroscopy (XRF), and atomic absorption spectroscopy (AAS) are some of the most common analytical techniques to measure chromium concentrations in different samples.\textsuperscript{12,16–19}

Each type of sample preparation method and analytical technique possesses its own set of advantages and limitations. Considerations including the concentration range of chromium, the complexity of the sample matrix, the required detection limits, and the instrumentation and expertise at hand all influence the selection of the most appropriate method. When complementary sample preparation methods and analytical techniques are combined, the overall performance and dependability of chromium analysis on a variety of sample types can frequently be improved. Dispersive micro-solid phase extraction (D-μSPE) is a simple and adaptable method for analyzing chromium that requires limited sample preparation and provides good sensitivity and selectivity.\textsuperscript{15,17,19} D-μSPE simplifies the process by immediately extracting analytes onto an adsorbent, reducing solvent use, which promotes eco-friendly practices. This approach’s flexibility enables the examination of multiple sample matrices, allowing for the sampling of many sample types without requiring extensive method development. On the other hand, flame atomic absorption spectrometry (FAAS) provides good chromium determination selectivity and sensitivity. FAAS technique is widely accessible and reasonably priced, making it appropriate for regular analysis in labs with limited resources.\textsuperscript{11,20,21} An efficient method for chromium analysis in a variety of sample matrices is offered by the combination of FAAS for precise quantification and D-μSPE for effective sample preparation. This approach offers dependable outcomes for industrial analysis, environmental monitoring, and other applications.\textsuperscript{15}

Metal-organic frameworks, or MOFs, are crystalline materials with various structures and properties that make them valuable in gas storage, catalysis, analytical chemistry, and environmental remediation. Metal ions, or clusters, coordinate with organic ligands to form MOFs.\textsuperscript{21} Graphene oxide (GO) is a carbon-based substance that is generated from graphene. It has excellent mechanical qualities, a large surface area, and chemical reactivity due to its oxygen-containing functional groups.\textsuperscript{19,22} Molybdenum diselenide nanoflowers (MoSe\textsubscript{2} NFs) have emerged as attractive choices for solid-phase extraction (SPE) thanks to their flower-like structure, large surface area, and unique electrical and optical characteristics. The unique properties of MoSe\textsubscript{2} NFs allow them to be used as selective adsorbents in SPE applications.\textsuperscript{23} This makes it easier to adsorb analytes from complex environments. A combination of these three nanomaterials (Gio, MOFs, and MoSe\textsubscript{2} NFs) offers a wide range of advantages for selective adsorption. In optimal conditions, the GO/MOF-199/MoSe\textsubscript{2} nanocomposite is very good for extracting chromium species from water. This is due to its large surface area, functional groups, and porous structure. The GO/MOF-199/MoSe\textsubscript{2}: NFs exhibit a distinctive octahedral pyramidal and flower-like shape that makes this material an essential tool in the extraction and separation of chromium. This nano-sorbent boasts a notable capacity for chromium adsorption, exhibits selectivity, and demonstrates reusability. Such characteristics render them an attractive option for environmental remediation and chromium-related analytical applications.\textsuperscript{19,21,24,25} The GO/MOF-199/MoSe\textsubscript{2} NFs exhibit a distinctive octahedral pyramidal and flower-like shape that makes this material an essential tool in the extraction and separation of chromium. This nano-sorbent boasts a notable capacity for chromium adsorption, exhibits selectivity, and demonstrates reusability. Such characteristics render them an attractive option for environmental remediation and chromium-related analytical applications.\textsuperscript{3,4,26,27}

This study aims to provide a reliable and strong approach by using a novel nanomaterial (GO/MOF-199/MoSe\textsubscript{2} NFs) for chromium speciation in samples of environmental water. More precisely, the goals are to improve the analytical technique’s sensitivity and selectivity, eliminate interference from other species in complicated sample matrices, and validate the method’s performance through experimental testing. Through the achievement of these goals, the work will be able to close the gaps in the existing chromium speciation techniques and further analytical chemistry in environmental monitoring.

**EXPERIMENTAL**

**Instruments and chemicals.** Total chromium measurements
were performed using an Analytik Jena AG contraAA 800 atomic absorption spectrometer equipped with a xenon arc lamp and air-acetylene flame. The instrument operational parameters followed the manufacturer’s guidelines. Centrifugation of both model and real sample solutions was carried out using a Nuve NF400 centrifuge (4 × 50 mL/4100 rpm). Solution agitation during adsorption and desorption steps was achieved using a Fisons WhirliTm™ Vortex Shaker Cyclone mixer model 12665. pH values were adjusted using a WTW 3110 pH meter with a glass electrode. For characterization purposes, a Thermo Nicolet 5700 Fourier Transform Infrared (FTIR) spectrophotometer, BRUKER AXS D8 ADVANC X-ray diffraction (XRD) instrument, ZEISS Gemini 550 field-emission scanning electron microscope (FE-SEM), FE-SEM-EDX for energy dispersive X-ray spectroscopy, and Micromeritics Gemini VII analyzer for BET-N2 surface analysis were employed.

All chemicals were analytical reagent (AR) grade from Sigma-Aldrich and Merck Company (Darmstadt, Germany). Double distilled deionized water (18.2 MΩ cm, Millipore). Stock solution of Cr(VI) SRM solution (1000 mg L⁻¹) was obtained from LabSert, Chemical Reference Standard, Mersin, Turkey. 0.1% w/v 1-(2-pyridylazo)-2-naphthol (PAN) was prepared in methanol. Graphite, sodium nitrate, sulfuric acid (98%), potassium permanganate, hydrogen peroxide (30%), benzen-1,3,5-tricarboxylic acid (BTC), copper (II) nitrate hemi-penta-hydrate, ethanol, sodium molybdate dihydrate, selenium powder, hydrazine hydrate, chromium (III) nitrate nonahydrate, nitric acid (65%), and hydrochloric acid (35%) were obtained from Sigma-Aldrich and Merck Company (Darmstadt, Germany). Cr(III) stock solution (1000 mg L⁻¹) was prepared from chromium (III) nitrate nonahydrate salt, and the diluted standard solutions were prepared from stock solution. TMDA-64.3 fortified water CRM was obtained from LabStandards, Budapest, Hungary. SPS-WW2 waste water CRM was sourced from Spectrapure Standards AS, Oslo, Norway. Matrix ion solutions were prepared in different concentrations.

**Synthesis of GO/MOF-199/MoSe2 NFs.** As shown in Fig. 1A, in a round-bottom flask, 3 g of graphite powder and 1.5 g of sodium nitrate were mixed with 50 mL of concentrated sulfuric acid (98%). The entire process took place in an ice bath with continuous stirring. Subsequently, 6 g of potassium permanganate was slowly added to the above mixture as the oxidizing agent at a temperature below 20 °C, ensuring thorough mixing. The resulting mixture was stirred at room temperature for 2 h. To this mixture, 100 mL of DI water was added slowly in an ultrasonic bath for an hour. Following this, the reaction mixture was diluted with 300 mL of DI water. To remove the excess potassium permanganate, 30% H₂O₂ was added. The resulting solid GO was washed with DI water several times with repeated centrifugation. The GO was collected and subsequently dried in an oven at 80 °C for 24 h.

Separately, 0.805 g of BTC and 1.6 g of copper (II) nitrate hemi-penta-hydrate were dissolved in 10 mL of ethanol and 10 mL of DI water, respectively. The two solutions were combined and stirred using a magnetic stirrer for 20 min. Subsequently, 1.0 g of GO was added to the mixture and stirred for an additional 30 minutes. The resulting mixture was transferred to a Teflon reactor, then placed inside an autoclave and subjected to an oven

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Fig. 1 Schematic presentation of the adsorbent’s synthesis method (A) and presented D-µSPE general procedure (B).
temperature of 120 °C for a duration of 24 h. The newly obtained GO/MOF-199 composite was thoroughly washed using deionized water and ethanol, followed by drying at 80 °C for 12 h.21

To synthesize GO/MOF-199/MoSe2 NFs, 1.0 g of sodium molybdate dihydrate and 1.0 g of GO/MOF-199 were added to a mixture of deionized (DI) water and ethanol (20:30 mL), resulting in solution A. Similarly, 0.632 g of selenium powder was dissolved in 15 mL of hydrazine hydrate. The color of the solution instantly changed from colorless to dark red and remained stable for 24 h under room temperature, forming solution B. Subsequently, solutions A and B were thoroughly mixed with continuous stirring and transferred into a Teflon-lined stainless-steel autoclave. The reaction mixture was then aged at 200 °C for 24 h and allowed to cool to room temperature. The resulting black precipitate was collected through centrifugation and subjected to multiple washes using DI water (three times) and ethanol (one time). The obtained GO/MOF-199/MoSe2 was dried at 80 °C for 12 h, yielding the final product of GO/MOF-199/MoSe2 NFs.28

Extraction procedure. As shown in Fig. 1B, 2 mL of ammonium buffer solution with a pH of 9 and 0.1 mL of PAN solution (0.1 % w/v) were added to a centrifuge tube. A 0.5 mL of Cr(III) solution (10 mg L⁻¹) was added to the mixture. The final volume was adjusted to 20 mL using DI water, and then 15 mg of the GO/MOF-199/MoSe2 NFs adsorbent was added to the mixture. The contents of the tube were subjected to vortex shaking for 30 s, followed by centrifugation for 2 min. After decantation, 2 mL of 3M HNO₃ was added to the remaining solid phase in the tube. The mixture was vigorously shaken for 1 min using a vortex and then centrifuged for 3 min. Cr(III) was measured using FAAS. Cr(VI) is determined as the difference between total chromium and Cr(III) concentrations.

Applying the present method to tap water and wastewater samples. We collected all tap water samples from various locations in Kayseri, Turkey. We put the tap water samples in 1 L polyethylene bottles. We washed these bottles with detergent, deionized distilled water, diluted HNO₃ (1%), and deionized water before using them. Tap water samples were filtered through a Millipore cellulose membrane with 0.45 μm pores. After filtering, we transferred the samples to 1 L polyethylene bottles, acidified them with 1% nitric acid, and refrigerated them at 4 °C. Two different metal treatment factories in Kayseri, Turkey, provided the wastewater samples. We also applied the above-mentioned preservation method to these two samples.

For tap water samples, 15 mL was added to every tube. Different amounts of Cr(III) and Cr(VI) were placed into different tubes. We divided the tubes into two groups, each containing an equal number of tubes. We used the first group to determine total chromium, performing three replications per spiked concentration. We used the second group to determine Cr(III) (without reduction) using three replications per spiked concentration. For total chromium, 2 mL of ethanol and 0.5 mL of concentrated H₂SO₄ were added to some tubes. After the reduction, the pH of the solutions was set using sodium hydroxide solution (5 mol L⁻¹) near 9. 2 mL of ammonium buffer solution with a pH of 9 and 0.1 mL of PAN solution (0.1 % w/v) were added. After adjusting the final volume to 20 mL using DI water, 15 mg of the GO/MOF-199/MoSe2 NFs adsorbent was added to the tubes. The contents of the tube were subjected to vortex shaking for 30 s, followed by centrifugation for 2 min. After decantation, 2 mL of 3M HNO₃ was added to the remaining solid phase in the tube. The mixture was vigorously shaken for 1 minute using a vortex and then centrifuged for 3 min. Total chromium was measured using FAAS.

For Cr(III) speciation, the pH of the solutions was set using sodium hydroxide solution (5 mol L⁻¹) near 9. 2 mL of ammonium buffer solution with a pH of 9 and 0.1 mL of PAN solution (0.1 % w/v) were added. After adjusting the final volume to 20 mL using DI water, 15 mg of the GO/MOF-199/MoSe2 NFs adsorbent was
added to the tubes. The contents of the tube were subjected to vortex shaking for 30 s, followed by centrifugation for 2 min. After decantation, 2 mL of 3M HNO₃ was added to the remaining solid phase in the tube. The mixture was vigorously shaken for 1 minute using a vortex and then centrifuged for 3 min. After the elution step, Cr(III) was determined using FAAS. Cr(VI) is determined as using a vortex for 1 min, followed by centrifugation for three minutes. Total chromium was measured using FAAS.

For wastewater samples, 15 mL were taken to two groups of centrifuge tubes. Their pH was set using sodium hydroxide solution (5 mol L⁻¹) near 9. The first group was used for total chromium, and the second one for Cr(III). Total chromium was measured after performing the reduction method. Cr(III) was determined using the method without reduction.

The validation of method using CRMs. 10 mL of TMDA-64.3 fortified water and 10 mL of SPS-WW2 wastewater were added to separated centrifuge tubes. Subsequently, 0.1 mL of a 0.1% w/v PAN solution and 2 mL of pH 9 (ammonium buffer solution) were added to the mixture. 15 mg of the GO/MOF-199/MoSe₂ NFs adsorbent was added, and the final volume was adjusted to 20 mL using DI water. After centrifuging the tube contents for 2 min, they were vortexed for 30 s. The residual solid phase in the tube was eluted with 2 mL of 3M HNO₃. The eluate was vigorously agitated using a vortex for 1 min, followed by centrifugation for three minutes. Total chromium was measured using FAAS.

**RESULTS AND DISCUSSION**

Characterization of GO/MOF-199/MoSe₂ NFs. Figure 2A shows the FT-IR spectra for three compounds: GO (i), GO/MOF-199 (ii), and GO/MOF-199/MoSe₂ NFs (iii). The bands in Fig. 2A show typical peaks for the presence of O-H stretching bands (3500–3600 cm⁻¹, OH groups) in all materials (i, ii, and iii). The peaks associated with C=O and C–O bonds at 1620 cm⁻¹ and 1060 cm⁻¹, respectively, indicate the presence of carbonyl and ether functional groups in all materials (i, ii, and iii). The integration of metal oxide species, as indicated by metal oxide (C–M) peaks, such as Mn–O (from KMnO₄ in the synthesis of GO), Cu–O–C (from MOF-199), and Mo–O–C and Se–O–C (from MoSe₂), improves the structural composition of GO/MOF-199 and GO/MOF-199/MoSe₂.

If we compare the spectra of GO, GO/MOF-199, and GO/MOF-199/MoSe₂ NFs side by side, any changes or shifts in the locations of the peaks could indicate that the chemical environment or the interactions between the parts have changed. Adding MoSe₂ NFs to the GO/MOF-199 mix might change the FT-IR peaks that were seen, which could mean that the structure of MoSe₂ is changing or that it is interacting with the other parts.

XRD was performed to determine the structure of the nanocomposite that was synthesized. This analysis served to confirm the successful synthesis of the nanocomposite. The XRD analysis was conducted using a Bruker D8 ADVANCE diffractometer, which utilized Cu Kα radiation with a wavelength of 1.54060 Å. The XRD patterns of graphene oxide (GO) are depicted in Fig. 2B (i). The XRD pattern of the graphene oxide exhibited peaks at 2θ = 11.2° and 28.0° corresponding to the (001) and (100) crystallographic planes, respectively. These peaks provide evidence supporting the successful synthesis of GO.

Fig. 2 (A): IR spectra of (i) GO, (ii) GO/MOF-199, and (iii) GO/MOF-199/MoSe₂ NFs; (B): XRD patterns of (i) GO, (ii) GO/MOF-199, and (iii) GO/MOF-199/MoSe₂ NFs; (C): FE-SEM images of (a) GO, (b) GO/MOF-199, and (c, d, e, and f) GO/MOF-199/MoSe₂ NFs; (D): SEM-EDX analysis of GO/MOF-199/MoSe₂ NFs (i) and elemental composition of GO/MOF-199/MoSe₂ NFs (ii).
The remaining diffraction peaks exhibited a strong agreement with the known XRD patterns of MOF-199 reported in the literature\textsuperscript{21, 34}. Notably, the diffraction peaks are marked with (♦) symbol that corresponds to graphene oxide (GO). FE-SEM images (Fig. 2B (iii)) illustrate the patterns of GO/MOF-199/MoSe\textsubscript{2} NFs. The XRD spectrum of MoSe\textsubscript{2} NFs exhibited notable diffraction peaks at 12.44°, 29.01°, 38.34°, and 55.94°, represented by the (♦) symbol. These XRD results confirmed the successful formation of the flower-like 2D-MoSe\textsubscript{2} phase on the hexagonal surface of MOF-199, as evidenced by its agreement with the JCPDS No. 29-0914 reference.\textsuperscript{35} However, the XRD spectra of MoSe\textsubscript{2} did not exhibit highly sharp peaks, suggesting the presence of semi-crystalline MoSe\textsubscript{2} NFs within the nanocomposite. Furthermore, the XRD analysis indicated the successful synthesis of the GO/MOF-199/MoSe\textsubscript{2} NFs through the hydrothermal method.\textsuperscript{36, 37}

Figure 2C in the present study displays the FE-SEM images of the synthesized GO (a), GO functionalized with M-1 (b), and GO/MOF-199/MoSe\textsubscript{2} NFs (c). The Image in Fig. 2C(a), reveal a distinctive two-dimensional structure characterized by a layered and wrinkled sheet-like morphology of GO. The oxidized graphene sheets exhibit relatively large dimensions and resemble thin sheets. The surface of the functionalized GO exhibits a comparatively higher level of roughness. The significant thickness of GO nanosheets can be attributed to the presence of oxygen-containing functional groups on both sides.\textsuperscript{24} The presence of covalently bonded oxygen and the slight displacement of sp\textsuperscript{2}-hybridized carbon atoms above and below the original graphene plane\textsuperscript{38} are expected to contribute to the increased thickness of the GO sheets. The FE-SEM images in Fig. 2C(b) demonstrated that the surface of GO/MOF-199 exhibited a slight increase in roughness, accompanied by the presence of small sheets on the MOF-199 surface. This modified structure resulted in a larger surface area, facilitating improved loading of the new nanoparticles (MoSe\textsubscript{2} NFs) onto the surface. Additionally, the FE-SEM images of MOF-199 revealed a distinct octahedral shape with well-defined edges and smooth surfaces, as evident in the images.\textsuperscript{21} The morphologies and microstructures of GO/MOF-199/MoSe\textsubscript{2} NFs were also investigated using FE-SEM. The typical FE-SEM micrographs, depicted in Fig. 2C (c, d, e, and f), reveal the presence of nanoflowers on the surface of GO/MOF-199 with small shallow channels. These nanoflowers consist of several nanosheets with a thickness of approximately 50 nm. The observations suggest that the MoSe\textsubscript{2} NFs exhibit a solid interior and possess a core-corona architecture.\textsuperscript{28}

FE-SEM-EDX analysis was conducted to investigate the surface elemental compositions of the newly synthesized nanoflower composite (Fig. 2D). The FE-SEM image (Fig. 2D (ii)) clearly shows the presence of octahedral shapes. The elemental composition results are presented in Fig. 2D (ii), and are consistent with the literature findings.\textsuperscript{21}

Figure 2(E) displays a SEM-Mapping image of GO/MOF-199/MoSe\textsubscript{2} nanoflowers, which provides evidence of the effective synthesis of the adsorbent. The elements exhibit uniform distribution, with weight percentages of 29%, 39%, 17%, 8%, and 6% for C, O, Mo, Cu, and Se, respectively. Mo and Se are concentrated on the surface of MOF-199, while Cu is concentrated in the center of MOF-199. As seen in FE-SEM images (Fig. 2C(i)), this shows that the GO/MOF-199/MoSe\textsubscript{2} core-shell nanocomposite is octahedral. Cu is the metal in the middle, and the other GO and MoSe\textsubscript{2} are spread out on the octahedral surface.

Optimization of parameters for Cr speciation analysis

Effect of pH. pH optimization plays a crucial role in chromium speciation analysis. Because chemical reactions happen at different pH levels, the pH level has a big effect on the formation, hydrophobicity, and stability of the complex. In acidic conditions, the nitrogen atom of the pyridine group in the PAN structure undergoes reactions and becomes positively charged, while in basic environments, hydrogen from the hydroxyl group is ionized. These pH-dependent reactions determine the complex’s behavior and properties.\textsuperscript{39} In the determination of aquo species of Cr(III) and Cr(VI), pH optimization is necessary to achieve the desired separation. Aquo species of Cr(III) are more stable and less soluble at higher pH values, typically around pH 6–9. In contrast, aquo species of Cr(VI) are more stable and soluble under acidic conditions, typically at lower pH values.\textsuperscript{40, 41} A pH investigation was conducted on both Cr(III) and Cr(VI) in their PAN-chelates forms at pH values ranging from 1 to 10. Based on the results depicted in Fig. 3(i), when pH increases, Cr(III)-PAN’s extraction efficiency increases. At pH 6, the recovery rate is 94%. Beyond this range, the recovery values became fixed, with a little decrease at pH 10. In contrast, Cr(VI)-PAN has the best extraction efficiency at lower pH values, beginning with 97% at pH 1 and gradually decreasing as pH levels rise. Interestingly, at pH 6, the recovery of Cr(VI)-PAN extraction drops significantly to 21%, then to as low as 5% at pH 10. The optimal pH was selected as 9, since it results in a quantitative recovery for Cr(III)-PAN while simultaneously having the lowest recovery value for Cr(VI)-PAN.

Amount of ligand (PAN). PAN was chosen as a chelating agent in this study because of its tendency to form stable complexes with transition metals such as chromium. PAN’s distinctive properties, such as metal-binding capability and hydrophobic nature, make it easier to form a complex with Cr(III) and separate from the matrix. Compared to other chelating compounds, such as diphenylcarbazone, PAN may provide advantages such as better stability constants, improved selectivity, or increased extraction efficiency. PAN forms coordination bonds with its functional groups (hydroxyl or nitrogen) to preferentially bind metal ions such as Cr(III). This action serves as a chelating agent during the adsorption process. However, its solubility limitations, especially in water, may limit the quantity that may be added during the
Fig. 3 (i): Effects of pH on the recoveries of Cr(III) (5 µg) and Cr(VI) (5 µg); (ii): Effect of ligand amount on the recovery of Cr(III) (5 µg); (iii): Effect of adsorbent amount on the recovery of Cr(III) (5 µg); (iv): Effect of adsorption and desorption times on the recovery of Cr(III) (5 µg); (v): Effect of centrifugation time on the recovery of Cr(III) (5 µg); (vi): Effect of eluent type and concentration on the recovery of Cr(III) (5 µg); (vii): Effect of sample volume on the recovery of Cr(III) (5 µg); (viii): Effect of eluent volume on the recovery of Cr(III) (5 µg), (N = 3).

Chelating process. Exceeding PAN’s maximum solubility in a solvent may result in the formation of precipitates or gels, which can impede the adsorption process and make processing difficult.\textsuperscript{39,42,43} When using D-µSPE to study chromium speciation, optimizing the ligand is a key step to make sure that the right chromium species are separated and extracted quantitatively. Choosing a suitable ligand that can strongly bind to chromium is very important for accurately and quickly finding different forms of chromium in complex samples. This ligand optimization process is crucial for achieving reliable results in chromium speciation analysis using D-µSPE.\textsuperscript{18,44} Many researchers use PAN extensively in preconcentration-separation studies because of its distinct characteristics. This study looked at how PAN affected the recovery of Cr(III), and the results are shown in Fig. 3(ii). At 25–
around 1 to 3 min. A similar occurrence of extended desorption vortex time 0.5 minute. Afterwards, the recovery stabilized at recovery rate improved from 84% at vortex time 0 to 103% at exhibit variations in accordance with the vortex time. The demonstrates that the adsorption and desorption efficiencies was conducted within a time frame of 0 to 3 min.

It is important to balance amongst these parameters increase the number of interactions, but they temporal progression of these processes. Longer adsorption times may allow Cr(III) PAN chelates to bind efficiently with GO/MOF-199/MoSe₂ nanoflowers. Van der Waals forces, or electrostatic interactions with metal ions or organic molecules. The hydrogen atom of one molecule (like PAN) can form hydrogen bonds with an electronegative atom in the adsorbent. These bonds could aid in attracting the Cr(III)-PAN chelates to the GO/MOF-199/MoSe₂ nanoflowers. Van der Waals forces, which are temporary dipoles caused by changes in electron distribution, might help the adsorption process even more by making it easier for the adsorbent and Cr(III)-PAN chelates to stick together. Moreover, electrostatic interactions caused by the attraction of charged species increase the adsorbent's adsorption capacity. These intermolecular forces may allow Cr(III)-PAN chelates to GO/MOF-199/MoSe₂ nanoflowers.

In this experimental stage, various quantities of GO/MOF-199/MoSe₂ adsorbent were investigated. The range of adsorbent amounts tested ranged from 2.5 to 20 mg, and the corresponding results are presented in Fig. 3(iii). Based on the obtained results, complete recoveries of Cr(III) were achieved only at 15 and 20 mg of adsorbent. Therefore, subsequent experiments and analyses were conducted using 15 mg of adsorbent, as it demonstrated satisfactory quantitative recovery of Cr(III).

**Effect of adsorbent amount.** The quantity of adsorbent used in D-µSPE is crucial for efficient extraction. It should be optimized to ensure maximum extraction efficiency without using excessive amounts that can lead to problems like saturation of the adsorbent surface sites. The ideal quantity depends on factors such as the analyte, adsorbent properties, and sample matrix. It is possible for the GO/MOF-199/MoSe₂ nanocomposite to form hydrogen bonds, van der Waals forces, or electrostatic interactions with metal ions or organic molecules. The hydrogen atom of one molecule (like PAN) can form hydrogen bonds with an electronegative atom in the adsorbent. These bonds could aid in attracting the Cr(III)-PAN chelates to the GO/MOF-199/MoSe₂ nanoflowers. Van der Waals forces, which are temporary dipoles caused by changes in electron distribution, might help the adsorption process even more by making it easier for the adsorbent and Cr(III)-PAN chelates to stick together. Moreover, electrostatic interactions caused by the attraction of charged species increase the adsorbent's adsorption capacity. These intermolecular forces may allow Cr(III)-PAN chelates to bind efficiently with GO/MOF-199/MoSe₂ nanoflowers.

In this experimental stage, various quantities of GO/MOF-199/MoSe₂ adsorbent were investigated. The range of adsorbent amounts tested ranged from 2.5 to 20 mg, and the corresponding results are presented in Fig. 3(iii). Based on the obtained results, complete recoveries of Cr(III) were achieved only at 15 and 20 mg of adsorbent. Therefore, subsequent experiments and analyses were conducted using 15 mg of adsorbent, as it demonstrated satisfactory quantitative recovery of Cr(III).

**Study of adsorption and desorption times.** Optimization of adsorption and desorption periods is essential for effective extraction. Sorbent properties and analyte concentration dictate the temporal progression of these processes. Longer adsorption times increase the number of interactions, but they are time-consuming. Shorter desorption times allow for faster elution, but the analytes may only be partially recovered. So, the optimal durations are important to balance amongst these parameters. The investigation was conducted within a time frame of 0 to 3 min. Fig. 3(iv) demonstrates that the adsorption and desorption efficiencies exhibit variations in accordance with the vortex time. The Cr(III) recovery rate improved from 84% at vortex time 0 to 103% at vortex time 0.5 minute. Afterwards, the recovery stabilized at around 1 to 3 min. A similar occurrence of extended desorption time occurred. With an increase in the desorption vortex duration from 0 to 1 minute, there is a significant increase in the recovery percentage, which rises from 58% to 101%. These results show that a longer time does not make it easier, but rather simply provides sufficient time to allow the desorption of Cr(III) ions from GO/MOF-199/MoSe₂ surface to become more quantitative. After 1 min of vortex, the recovery percentage stays consistently steady, with little fluctuations ranging from 90% to 92%. This suggests that extending the duration of desorption may not substantially enhance the effectiveness of recovering beyond a certain limit.

**Study of centrifugation intervals.** To achieve an effective separation with low analyte loss, the centrifugation time in D-µSPE must be tuned. The sorbent material's density and particle size, the sample volume, and the centrifugation speed all affect the length of the centrifugation process. Finding the perfect timing entails conducting experiments to develop and refine the technique. Centrifugation durations often range from a few minutes to several tens of minutes, forming a balance between achieving complete separation while maintaining overall extraction efficiency and speed. Durations ranging from 1–5 min was examined in this stage, as shown in Fig. 3(v). During the process of adsorption centrifugation, the recovery increased from 70% to 98% at 1 and 2 minutes, respectively. Quantitative recoveries were evident in all remaining periods within the range of 3-5 min. The desorption centrifugation process was performed for 3 min to ensure there were no tiny parts of the adsorbent suspended in the separated eluent.

**Study of elution process.** The eluent is an important component of SPME, assisting in the elution of the analyte from the adsorbent. It needs to be compatible with both the adsorbate and the adsorbent to break the bonds between the two and free the analytes. The pH of the eluent solution affects the charge and speciation of analytes and adsorbents, which affects the desorption kinetics. The eluent's complexing capacity is critical for complex sample matrices or analytes. This stage included testing two different acids (HNO₃ and HCl) at various concentrations (1, 2, and 3 mol L⁻¹). In general, HNO₃ produced better recovery values than HCl. Increasing the concentrations of eluent results in higher recovery values (see Fig. 3(vi)). The highest recovery was obtained using the highest concentrations of each eluent. 3 mol L⁻¹ HNO₃ and 3 mol L⁻¹ HCl had the greatest recoveries (101% and 103%, respectively). The best eluent was selected as 3 mol L⁻¹ HNO₃.

**Effect of sample and eluent volumes.** Optimizing sample volume in D-µSPE is critical for reliable analysis findings. Enrichment factors rise as sample volumes increase and eluent volumes decrease. The sample volume was studied in the range of 10–50 mL. 15 mg of adsorbent, 100 µg of PAN, and 0.5 mL of Cr(III) solution (10 mg L⁻¹) were used in this step. Fig. 3(vii) indicates a clear inverse relationship between sample volume and the recovery.
of Cr(III) ions. As the sample volume increases, the efficiency of the recovery process gradually decreases, with lower recovery percentages observed at larger sample volumes. The reason for this decrease in recovery efficiency is the dilution effect. Higher sample volumes result in a more diluted Cr(III) solution, which makes it difficult for the Cr(III) ions to be adsorbed on the nanocomposite surface. At sample volumes of 10 and 20 mL, the recovery values were 100% and 94%, respectively, indicating quantitative recoveries of Cr(III) ions. For eluent volume optimization, volumes ranging from 1–5 mL of 3 mol L\(^{-1}\) of HNO\(_3\) (see Fig. 3(viii)). Except for 1 mL, other volumes showed quantitative recovery values (94–102%) of Cr (VI) (Fig. 3(viii)). The optimal sample and eluent volumes were chosen as 20 and 2 mL, respectively.

**Interferences.** Since the presence of foreign ions may have a significant influence on the accuracy and reliability of the recovery process, matrix effects must be taken into account when speciating Cr(III) in real samples. To keep these effects to a minimum and get accurate results of Cr(III) levels in complex sample matrices, the technique may need to be optimized, and the recovery strategy must be carefully chosen. Na\(^+\), K\(^+\), Ca\(^{2+}\), Mg\(^{2+}\), Cr\(^{3+}\), Cu\(^{2+}\), Ni\(^{2+}\), Zn\(^{2+}\), Fe\(^{3+}\), Cl\(^-\), NO\(_3^-\), CO\(_3^{2-}\), SO\(_4^{2-}\) were examined. Table 1 demonstrates that various ions in the matrix affect the Cr recovery percentages. The recovery percentages range from 91% to 101%. From these results, it can be concluded that there is no significant effect from foreign ions on the recovery efficient of Cr(III).

**Performance of the method.** A certain formula was used to find the limit of detection (LOD) and the limit of quantification (LOQ) of Cr(III) are defined as follows: LOD = 3 \(\times\) the standard deviation (\(\sigma\)) of the mean concentration determined in 10 blank samples following the outlined procedure the LOD = 3.33 times the LOD. The LOD was 0.11 \(\mu\)g L\(^{-1}\), whereas the limit of quantification (LOQ) was 0.39 \(\mu\)g L\(^{-1}\). The correlation of determination (\(R^2\)) of Cr(III) was 0.9979, showing a significant connection between absorbance and concentration. The linear equation derived from the calibration curve of Cr(III) was \(y = 0.0289x + 0.0004\). Additionally, the relative standard deviation (RSD%) of Cr(III) at concentration of 2.5 \(\mu\)g L\(^{-1}\) was found to be 6.5%, indicating high measurement accuracy. The preconcentration factor (PF) was calculated by dividing the initial volume (\(V_{\text{initial}}\)) of the sample by the final volume (\(V_{\text{final}}\)) of the eluent after preconcentration, whereas the enhancement factor (EF) was estimated by comparing the slopes of the calibration curves with and without preconcentration. PF of Cr(III) was found to be 20, which shows the level of concentration reached in the preconcentration phase. EF of Cr(III) was found to be 20.6, which shows the level of signal enhancement achieved during the analytical process. These metrics together give information on the sensitivity, and efficacy of the analytical approach used in this research.

![Table 1. Interference effect on the recovery of Cr(III)](image)

<table>
<thead>
<tr>
<th>Ions / Added as</th>
<th>Added Concentration, mg L(^{-1})</th>
<th>Recovery, %*</th>
<th>RSD</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na(^+) / NaNO(_3^-)</td>
<td>2000</td>
<td>97 ± 3</td>
<td>3.1</td>
</tr>
<tr>
<td>K(^+) / KCl</td>
<td>2000</td>
<td>94 ± 2</td>
<td>2.1</td>
</tr>
<tr>
<td>Ca(^{2+}) / Ca(NO(_3^-))</td>
<td>200</td>
<td>100 ± 2</td>
<td>2.0</td>
</tr>
<tr>
<td>Mg(^{2+}) / Mg(NO(_3^-))(_2)H(_2)O</td>
<td>200</td>
<td>100 ± 5</td>
<td>4.8</td>
</tr>
<tr>
<td>Co(^{3+}) / Co(NO(_3^-))(_2)H(_2)O</td>
<td>2.5</td>
<td>94 ± 4</td>
<td>4.3</td>
</tr>
<tr>
<td>Cu(^{2+}) / Cu(NO(_3^-))(_3)H(_2)O</td>
<td>2.5</td>
<td>92 ± 1</td>
<td>1.4</td>
</tr>
<tr>
<td>Ni(^{2+}) / Ni(NO(_3^-))(_2)H(_2)O</td>
<td>5</td>
<td>95 ± 4</td>
<td>4.1</td>
</tr>
<tr>
<td>Zn(^{2+}) / Zn(NO(_3^-))(_2)H(_2)O</td>
<td>5</td>
<td>101 ± 3</td>
<td>3.0</td>
</tr>
<tr>
<td>Fe(^{3+}) / Fe(NO(_3^-))(_3)H(_2)O</td>
<td>2</td>
<td>96 ± 5</td>
<td>5.2</td>
</tr>
<tr>
<td>Cl(^-) / KCl</td>
<td>1800</td>
<td>94 ± 2</td>
<td>2.2</td>
</tr>
<tr>
<td>NO(_3^-) / NaNO(_3^-)</td>
<td>5300</td>
<td>97 ± 3</td>
<td>3.5</td>
</tr>
<tr>
<td>CO(_3^{2-}) / Na(_2)CO(_3)</td>
<td>100</td>
<td>91 ± 1</td>
<td>4.4</td>
</tr>
<tr>
<td>SO(_4^{2-}) / Na(_2)SO(_4)</td>
<td>100</td>
<td>93 ± 4</td>
<td>4.4</td>
</tr>
</tbody>
</table>

*a Mean ± Standard deviation, (N=3).

The findings of the total chromium analysis in CRMs using the proposed method are shown in Table S1. The results show that the total chromium concentration was determined with a high degree of accuracy and precision. Over 94% of the chromium that was in the SPS-WW2 wastewater (Spectrapure Standards AS, Oslo, Norway) was recovered, and over 95% of the chromium that was in the TMDA-64.3-fortified water (LabStandards, Budapest, Hungary) was recovered as well. These findings show how well the suggested method works for precisely determining the total chromium content of CRMs. Both CRMs’ comparatively low relative standard deviations (RSDs), which range from 3.2% to 4.1%, show that the procedure is accurate and repeatable. By using a significance level of 0.05 and a confidence level of 95%, the t-test statistical analysis was performed on the measured levels of CRMs. The p-value was calculated as 0.34, which indicates that there is no significant difference between the certified and found total chromium concentrations.

**Applications.** The proposed method was applied to natural water and wastewater samples. The chromium speciation in spiking test solutions (prepared in deionized water) and the associated recovery percentages are shown in Table S2. The total chromium detected in the test solutions remained constant across all chromium concentrations spiked (Cr(III) and Cr(VI)) with slight differences. This demonstrates the analytical method’s effectiveness in precisely detecting both chromium species. The recovery percentages for both Cr(III) and Cr(VI) were in the range of (91–99%), indicating good recovery and technique accuracy even at low levels. The variations in the recovery values stay within a reasonable range, demonstrating the analytical procedure’s durability and dependability in all spiked concentrations.

The recovery values of Cr(III), Cr(VI), and total chromium from tap water samples using the suggested D-\(\mu\)SPE approach are shown in Table S3. The findings emphasize several important findings.

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[www.at-spectrosc.com/as/article/pdf/2024052](www.at-spectrosc.com/as/article/pdf/2024052)
findings. The Incesu Tap Water sample contained 0.11 µg of Cr(III) at a concentration of 7.3 µg L⁻¹, while the Talas Tap Water sample contained 0.3 µg of Cr(VI) at a concentration of 20 µg L⁻¹. The effectiveness of the approach in extracting and speciating chromium species in tap water is shown by the recovery values for both Cr(III) and total chromium, which are consistently above 90% across all samples and spiked levels. Most of the values are between 90 and 98%, which suggests that there is a slight negative bias for Cr(III) recovery. This could mean that the concentration of Cr(III) is lower than it really is, possibly because of too few extraction or analysis losses. On the other hand, total chromium recoveries for this species are consistently within the range of 91–98%, suggesting little bias and excellent precision.

In addition, the very constant recovery percentages found for various tap water sources imply that matrix variations in the analyzed samples have little effect on the proposed D-µSPE approach. Relative standard deviations (RSDs) within the acceptable range, often less than 10%, indicate an acceptable level of procedure repeatability. Finally, the observation of Cr(VI) traces in the Talas tap water sample indicates the need for additional research to determine the source and possible health effects of chromium (VI) pollution in this area. The difference between total chromium and Cr(III) levels was used for calculating Cr(VI) values.

The results given in Table 2 illustrate the D-µSPE method’s effectiveness in detecting chromium species (Cr(III), Cr(VI), and total chromium) in wastewater samples collected from the Kayseri Industrial Region, Türkiye. Wastewater-1 and Wastewater-2 had Cr(VI) concentrations of 10.15 and 97.7 µg L⁻¹, respectively. The total chromium level in these wastewater samples exceeded the limit of detection (LOD) at 115.2 and 10.15 µg L⁻¹, respectively, with no Cr(III) in Wastewater-1. This data offers an expanded view of the chromium concentrations in the wastewater samples. The wastewater samples collected from the outflow of metal treatment factories (Kayseri, Turkey) represent a significant source of chromium and Cr(III) levels was used for calculating Cr(VI) values.

<table>
<thead>
<tr>
<th>Wastewater sample</th>
<th>Concentration found, µg L⁻¹</th>
<th>Cr(III)</th>
<th>Cr(VI)</th>
<th>Total chromium</th>
<th>Cr(III) RSD%</th>
<th>Cr(VI) RSD%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wastewater-1</td>
<td>&lt;LOD</td>
<td>10.15 ± 0.74</td>
<td>10.15 ± 0.74</td>
<td>&lt;LOD</td>
<td>7.3</td>
<td>7.3</td>
</tr>
<tr>
<td>Wastewater-2</td>
<td>17.4 ± 1.2</td>
<td>97.7 ± 8.1</td>
<td>115.2 ± 7.6</td>
<td>6.9</td>
<td>6.5</td>
<td>6.6</td>
</tr>
</tbody>
</table>

* Mean ± standard deviation, N=3

**Table 5. Application of the proposed method to wastewater samples (volume: 30 mL)**

### CONCLUSION

The successful synthesis of GO/MOF-199/MoSe₂ NFs offer a workable way to separate chromium species in complex environmental matrices. The study not only confirmed that the nanocomposite material could be prepared well, but it also shed light on some of its unique structural features, such as the addition of MoSe₂ nanoflowers to the GO/MOF-199 nanocomposite’s surface. The structural properties of the SPE material used in this study are much better after MoSe₂ nanoflowers are added to the GO/MOF-199 nanocomposite. The addition of MoSe₂ nanoflowers imparts different properties that have the potential to improve the adsorbent’s effectiveness. Optimizing the pH and selecting the suitable chelating agent (PAN) were important steps in making sure that the chromium speciation was accurate and reliable. Managing pH is an important part of selectively extracting and measuring chromium species. The process of optimizing pH shows how complicated the relationship is between the pH of the solution and the chemical speciation of Cr(III) and Cr(VI). Using PAN as the chelating agent showed that it could make stable complexes with chromium (III) ions. Due to its low LOD and LOQ, high correlation coefficient (R²), and relatively small RSD%, the technique is very sensitive, precise, and effective in this investigation. Together, these tests show that the suggested method is stable and reliable, making it a useful tool for studying chromium speciation in a variety of environmental applications. The high recovery rates and negligible matrix effects found in this study demonstrated the method’s effectiveness in precisely determining and speciating chromium species.

In this study, the authors have added a different approach for chromium speciation from water and wastewater samples. According to earlier research on chromium speciation, Tuzen et al. (2007) focused on the quantitative biosorption of Cr(III) using *Bacillus Sphaericus*-loaded Diaion SP-850. They then reduced Cr(VI) and calculated Cr(VI) as the difference between the total chromium content and Cr(III) content. This method shows a limit of detection of 0.50 µg L⁻¹ for Cr(III).³⁹ Researchers Hassan and Soyglak did a study in 2024 that used a MWCNTs@CuAl₂O₄@SiO₂ nanocomposite to speciate Cr(VI) as pyrrolidine dithiocarbamate chelates from natural water and wastewater.³⁸ In this work, Cr(III) was oxidized to Cr(VI) using KMnO₄. The method indicates a limit detection of 6.2 µg L⁻¹. Lastly, Erbas et al. (2024) used magnetic solid-phase extraction
This work improves our knowledge of chromium speciation fundamentally and provides useful information for the development of modern analytical methods for pollution management and environmental monitoring.

ASSOCIATED CONTENT

The supporting information (Tables S1–S4) is available at www.at-spectrosc.com/as/home

AUTHOR INFORMATION

Prof. Mustafa Soylak is working on Environmental Analytical Chemistry, Nanotechnology, Nanomaterials, Nanocomposites, Separation/Preconcentration Techniques including Solid Phase Extraction, Coprecipitation, Cloud point extraction, membrane filtration, speciation and microextraction of trace organic and inorganic species. Dr. Soylak has an h-index of 111 (Web of Science). He has over 725 papers in Web of Science, 8 book chapters and reviews, two textbooks (in Turkish), one textbook on microextraction techniques (Elsevier, 2020). He is Editor-in-Chief of Comprehensive Sampling and Sample Preparation (Elsevier, 2022). He was visiting professor at King Saud University-Saudi Arabia on 2010-2016 and at Near East University-Cyprus on 2018-2019. He is now Professor at Erciyes University, Department of Chemistry, Kayseri-Turkey. He is the editorial board member of Atomic Spectroscopy, Journal of Hazardous Materials, International Journal of Environmental Analytical Chemistry, Arabian Journal of Chemistry, Turkish Journal of Chemistry, and Journal of Nanostructure in Chemistry. He has TUBITAK (Turkish Scientific and Technological Research Council) Encouragement Award in 2001. He is the recipient of the highest prestigious science award in Turkey, TUBITAK Science Award in 2020. He has also IIIM Yama Award from IIIM Yama Foundation in 2021. He has been a principal member of the Turkish Academy of Sciences (TUBA) since 2020. He has obtained a TÜBİTAK 2247-A National Fellowship for Outstanding Researchers (2021).

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Notes

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