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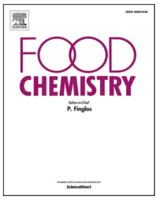

Determination of chromium in foodstuffs by using novel adsorbent in vortex assisted-dispersive solid phase micro-extraction method: An application of multivariate techniques

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ABSTRACT

A new graft copolymer composed of polystyrene and polylinoleic acid (PLinas) with the sodium salt of iminodiacetate (Ida) was synthesized and used as an adsorbent. The vortex-assisted dispersive solid-phase micro-extraction (VA-dSPμE) method was used for the extraction and pre-concentration of chromium. Multivariate methodologies, such as factorial design and 3D surface plots, were applied for screening and optimizing effective extraction parameters. The influence of diverse analytical parameters, such as pH, sample volume, and interfering ions, on the extraction of chromium was studied. The calibration standard curve exhibited a linear range from 0.01 to 0.50 μg L^{-1}. The relative standard deviation and limit of detection were found to be 1.65 % and 0.003 μg L^{-1}, respectively. Extraction recoveries were found in the range of 96 to 99 % by using certified reference materials (CRMs). The adsorbent capacity of PLinas-Ida was found to be 112 mg g^{-1}. The VA-dSPμE method demonstrated its effectiveness in the pre-concentration and determination of chromium within samples of foodstuffs by graphite furnace-atomic absorption spectrometry (GF-AAS).

1. Introduction

Chromium (Cr) is found naturally in the earth's crust, usually in the form of chromite ore from which it is extracted (Ahmed et al., 2022). Cr has several important uses and applications; one of the most well-known uses is in the production of stainless steel, where it is added in varying amounts to impart corrosion resistance, hardness, and a shiny appearance to the steel. Cr plating provides a protective and decorative coating on various surfaces, including automobiles, household fixtures, and appliances (Pedeferri, 2018). A thin layer of Cr on surfaces improves corrosion and wear resistance. Cr compounds find applications in industrial processes and products, such as potassium dichromate in pigment production for paints, dyes, and inks. Despite Cr being an essential trace element for human health in small amounts, precautionary safety measures are necessary when handling it and its compounds (Prasad et al., 2021). Cr is a naturally occurring trace element found in various food sources, though the concentrations may vary based on the specific type of food (Shaheen et al., 2016). The Cr plays a vital role in diverse human metabolic processes. In food, there are two primary forms: trivalent Cr, which is biologically active and deemed safe in appropriate quantities; and hexavalent Cr, which is more toxic and commonly encountered in industrial settings rather than in food (Seby and Vacchina, 2018). Certain foodstuffs naturally contain Cr. Whole wheat, oats, barley, and other whole grain products are rich sources of Cr. Additionally, broccoli, green beans, potatoes, lettuce, and various vegetables contain varying amounts of Cr (Mulyaningsih et al., 2021). Apples, bananas, oranges, and grapes are examples of fruits that provide some Cr. Beef, poultry, fish, and seafood can contain small amounts of Cr. Almonds, Brazil nuts, flaxseeds, and sunflower seeds are among the nuts and seeds that contain Cr (Amer et al., 2019; Bae et al., 2022). Essential in small amounts for proper metabolic function, Cr toxicity depends on its chemical form and dosage (Bhalakiya et al., 2019).

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Hexavalent Cr is a known carcinogen linked to lung cancer in animals. Studies reveal that it can cause DNA damage, respiratory distress, and gastrointestinal problems, as well as damage to the liver, kidneys, and reproductive system (Balali-Mood et al., 2021; Hossini et al., 2022). The Cr content in food varies based on factors like soil composition, agricultural practices, and processing methods. The bioavailability of Cr from food is still under study, with individual differences in absorption and metabolism influencing its utilization. The recommended dietary intake for Cr varies by age, sex, and life stage. While there's no established recommended dietary allowance for Cr, an adequate intake (AI) has been set (Farag et al., 2023). The AI for Cr in adults is 25–35 μg per day. A healthcare professional recommends obtaining essential nutrients, including calcium, from a varied and balanced diet rather than relying on supplements, unless specifically advised otherwise.

Sample preparation for Cr analysis involves steps to separate different forms for accurate measurement. Common acid digestion methods include heating the sample with strong acids like nitric and hydrochloric acid to break down the matrix and release Cr. This technique is widely used for solid samples such as food, soil, sediments, and biological tissues before further analysis (Ali et al., 2021; Ali et al., 2019b). Solid phase extraction (SPE) selectively extracts from a sample matrix using solid sorbents with an affinity for Cr metal. The sample passes through the SPE column, where different species are selectively retained and removing unwanted interference. We use different materials, like resins or agents depending on what kind of chromium test we're doing (Herrero-Latorre et al., 2018). Liquid-Liquid Extraction (LLE) concentrates and separates Cr in a liquid sample through partitioning between two immiscible liquid phases. Usually, an organic solvent such as methyl isobutyl ketone or ethyl acetate is used to remove chromium from the water phase (Beni et al., 2019; Noah et al., 2018). To analyze chromium in solid materials, we use methods like X-ray fluorescence, X-ray diffraction, GF-AAS, inductively coupled plasma atomic emission spectrometry, and inductively coupled plasma mass spectrometry (Halko et al., 2022; Marguí et al., 2022). We've developed a budget-friendly adsorbent for pre-concentration of Cr, utilizing cost-effective GF-AAS instead of pricier instruments. Block and graft copolymers combine properties from their constituent polymer blocks, creating versatile and innovative materials (Hazer, 1996; Yıldız, Hazer, 1998). Atmospheric oxygen interacts with unsaturated plant oils or fatty acids, forming macroperoxide plant oil initiators capable of triggering free radical polymerization of vinyl monomers (Erdem et al., 2022; Hazer, 2023) in a process known as autoxidation. Unreacted carboxylic acid terminals in fatty acid-vinyl polymers can undergo condensation reactions with amine-terminated oligomers like amine-terminated polydimethyl siloxane and polyethylene glycol. This study utilized an autoxidized polylinoleic acid macroperoxide initiator to catalyze free radical polymerization of styrene, aiming to synthesize a graft copolymer (PLinas) of polystyrene and polylinoleic acid. The process extended to merge terminal carboxylic acid groups in PLinas with secondary amine functional groups in sodium iminodiacetate (Ida) salt, resulting in the novel adsorbent PLinas-Ida.

The main goal is to create a fast and accurate VA-dSPμE method for extracting and concentrating Cr in digested food. This method utilizes a unique adsorbent PLinas-Ida graft copolymer and incorporates microwave-assisted digestion. Researchers applied multivariate techniques to investigate how the adsorbent and extraction parameters affect chromium determination in the VA-dSPμE process. The developed method's analytical performance and its application to various foodstuffs, such as fruits, vegetables, natural products, and meat samples, were thoroughly examined.

2. Materials and methods

2.1. Chemicals and materials

The experimental setup involved the utilization of high-quality reagents and standards. Double-distilled water employed for experimental purposes was sourced from the Milli-Q® water system in Bucks, UK. An analytical-grade chemical such as hydrochloric acid (37 % purity) and nitric acid (65 % purity) was procured from Merck in Darmstadt, Germany. A stock standard solution of Cr with a concentration of 1000 mg/L was acquired from Sigma-Aldrich, USA. To prepare working standard solutions for Cr analysis, the stock solution underwent a precise dilution step using nitric acid. To maintain the desired pH levels, a stock buffer solution was formulated using the sodium salt of acetic acid. Various food items, including fruits, vegetables, natural products, and meats, were systematically collected from local markets. The accuracy and reliability of the method were rigorously validated using apple leaves (SRM-1515) and tea leaves (INCTTL-1) obtained from the National Institute of Standards and Technology (NIST) in the United States Department of Commerce.

2.2. Instrumentations

The determination of Cr content in the digested food samples was conducted using a Perkin Elmer GF-AAS model AAS-700, Norwalk, CT, USA. This spectrometer was equipped with a D_2 background corrector to enhance accuracy. The recommended manufacturer used operating parameters for chromium analysis via GF-AAS. For the characterization of the PLians-Ida graft copolymer, several instrumental techniques were employed. These included a Perkin-Elmer FT-IR spectrum 400, Waltham, MA, USA. Furthermore, scanning electron microscopy (SEM) was carried out using a Gemini SEM 500-71 instrument. To facilitate the dispersion of metal particles in solution, an ultrasonic water bath from Norwalk, CT, USA, was employed. In the various stages of sample preparation, adsorption, and desorption, several devices were used, including a vortex from Ika Werke in Staufen, Germany. A universal centrifuge from Hettich in London, England; a digital pH meter from JP Selecta in Barcelona, Spain; and a Milestone Ethos microwave digestion system from Italy.

2.3. Sample collection and preprocessing

In this study, a random selection process was employed to choose fifteen (15) local markets within Tokat city as the sources for obtaining samples of 12 distinct fruits, namely (apple, apricot, banana, grape, hazelnut, walnut, tomato, plum, mulberry, pear, fig, and rosehip), 7 different vegetables, including broccoli, garlic, mushroom, onion, potato, spinach, and tea, as well as 6 diverse natural and meat products (egg, fish, honey, meat, salami, and sausage). A comprehensive collection of 125 samples was systematically gathered for analysis, comprising 5 samples from each fruit category and totaling 60 fruit samples. Each type of vegetable contributed five samples, totaling 35 vegetable samples, while each variety of natural and meat products provided five samples each, resulting in a total of 30 meat samples. The majority of these samples were sourced from prominent food establishments situated within the Tokat city markets. In an effort to maintain the integrity of the samples and minimize the potential loss of Cr concentration, which is vital for subsequent analysis, all food samples intended for human consumption were aseptically gathered and securely stored in polyethylene plastic bags. Following that, the samples were swiftly transported to the laboratory and kept in dry conditions to minimize the risk of contamination. This meticulous storage procedure was imperative, particularly in preparation for the subsequent microwave-assisted acid digestion process, which is a critical step in the digestion of the food samples for further analysis.

2.4. Microwave-assisted digestion

All harvested food items, including fruits, vegetables, natural products, and meat, were thoroughly washed with double-distilled water prior to microwave-assisted digestion (Ali et al., 2017b). Subsequently, the edible portions were carefully cut using a knife. Weighed exactly 1.0 g of each food sample and transferred it into Teflon tubes, then added 6 mL of nitric acid solution (65 %) and 2.0 mL of hydrogen peroxide (30 %). After securely closing the Teflon tube caps, the tubes were placed into the microwave-assisted digestion system. The same program and procedures were applied to all samples and certified reference materials (CRMs) with minor adjustments, involving four steps: Step 1 (2 min at 80 °C, 250 W), Step 2 (5 min at 130 °C, 1000 W), Step 3 (3 min at 180 °C, 500 W), and Step 4 (5 min at 200 °C, 600 W) (Ali et al., 2015; Ali et al., 2017c). Following this, the residues from the digestion process were dissolved in water and diluted to a final volume of 10 mL to enable the application of the microwave-assisted digestion procedure. Additionally, a blank sample was prepared similarly to evaluate potential analytical contamination in the reagents. An important benefit of employing microwave-assisted digestion is its capacity to accelerate the digestion process while avoiding the oxidation of metal ions. As a result, the necessary chemical conditions for the oxidation of chromium species are not reached during the microwave-assisted digestion step (Ali et al., 2019a; Ali et al., 2019b).

2.5. Synthesis of the novel adsorbent PLinas-Ida graft copolymer

2.5.1. Synthesis of PLinas

The PLinas was synthesized using the modified procedure we reported (Ance et al. 2016). Shortly, PLina-OX macroperoxide was prepared after 32 days of autoxidation of 5.0 g of linoleic acid at room temperature under air oxygen in a Petri dish (Φ = 7 cm). A mixture of 6.50 g PLINA-OX and 13.5 g styrene was polymerized at 90 °C for 270 min under argon. The yield of the obtained PLinas was 11.0 g. We carried out the condensation of 1.89 g PLinas with an aqueous iminodiacetate (Ida) solution (0.5 g Ida/3.0 g H2O) via film curing at 110 °C for 2.0 h following a procedure similar to that reported by Ullah et al. (2023). Finally, the yield of PLinas-Ida was 1.66 g with an 8 % water uptake.

2.5.2. Preparation and of PLinas-Ida graft copolymer

Begin the free radical polymerization of styrene using the autoxidized polylinoleic acid macroperoxide initiator. This results in the formation of the polystyrene-polylinoleic acid (PLinas) graft copolymer. Mix the free carboxylic acid ends of the PLinas graft copolymer with the sodium salt of iminodiacetate (Ida). The reaction involves the coupling of the secondary amine groups of Ida with the carboxylic acid groups of PLinas. This reaction forms iminodiacetate-functionalized PLinas, where Ida units are linked to the polymer chains as depicted in Fig. 1a.

2.5.3. Purification and characterization of the PLinas-Ida graft copolymer

Clean the synthesized iminodiacetate-functionalized PLinas graft copolymer (PLina-Ida) to get rid of any leftover reagents or byproducts. The PLinas-Ida graft copolymer was characterized using various techniques such as Fourier-transform infrared spectroscopy (FTIR), nuclear magnetic resonance (NMR), and differential scanning calorimetry (DSC) to confirm its structure and properties.

2.5.4. Application of PLinas-Ida as adsorbent

Use the newly synthesized iminodiacetate-functionalized PLinas graft copolymer as a fresh adsorbent for detecting chromium in food. Its unique properties resulting from the grafting of Ida moieties onto the polymer chains can make it effective for various adsorption applications, such as removing specific ions or molecules from solutions. It is noteworthy that the particular reaction conditions, reagents, and procedures may vary depending on the details of the experiment. Careful optimization of the reaction parameters is essential to achieving the desired grafting efficiency and product quality.

2.6. Procedure of the VA-dSPμE method

The development of the VA-dSPμE method involved several key steps and considerations. The first step was the choice of an appropriate adsorbent material. In this case, a graft copolymeric material called PLinas-Ida was synthesized and selected for its ability to efficiently extract chromium. To begin the procedure, a sample solution containing Cr standard at a concentration of 0.50 μg/L was prepared. This solution served as the test matrix for evaluating the effectiveness of the VA-dSPμE method. 40 mg of the PLinas-Ida adsorbent was added to the sample solution. The adsorbent's role is to selectively capture the Cr species in the digested foodstuffs. The pH of the digested food sample solution was adjusted to a specific level of pH 6.5 using an acetate buffer solution. Controlling pH is essential for optimizing the adsorption process. After pH adjustment, the volume of the digested solution was adjusted to 10 mL. To boost chromium adsorption onto the PLinas-Ida adsorbent material, we mixed the mixture vigorously at room temperature. This step helps ensure that the adsorption is complete. After mixing, the tubes containing the mixture were centrifuged at 3000 rpm for 3 min. Centrifugation separates the PLinas-Ida material, now loaded with adsorbed Cr, from the rest of the solution. The supernatant solution was carefully decanted, leaving the PLinas-Ida material at the bottom of the tube. The adsorbed Cr metal was then eluted from the PLinas-Ida using 1.5 mL of HCl. This step effectively desorbs the Cr ions from the adsorbent for subsequent analysis. Finally, the concentration of Cr in the eluted sample was determined using GF-AAS.

2.7. Multivariate technique for optimization of the extraction variables

Optimization variables are essential for attaining maximum Cr recovery through the VA-dSPμE method. These variables, including eluent volume and adsorbent (PLinas-Ida) dosage, adsorption time, pH, sample volume, and desorption time, underwent comprehensive examination to assess their influence. Using multivariate techniques can greatly help us understand how separation and extraction methods work together, especially when it comes to optimizing variables for extraction. Factorial design is commonly used in the initial screening to identify significant factors, whereas center composite design is employed for optimizing effective extraction parameters.

3. Results and discussion

3.1. Structure of the PLinas-Ida graft copolmer

Iminodiacetate-functionalized polystyrene-polylinoleic acid (PLinas-Ida) graft copolymers are complex macromolecules that combine two distinct polymer chains through a grafting process. The structure of such a copolymer can be described as follows: The backbone of the copolymer consists of a polystyrene chain. This backbone provides mechanical stability and hydrophobic properties for the copolymer. Polylinoleic acid, a natural fatty acid, is grafted onto the polystyrene backbone. Polylinoleic acid is rich in double bonds and has hydrophobic properties (Ali et al., 2019b; Hazer, 2023). The polylinoleic acid chains have carboxylic acid groups that allow them to interact with other molecules and be further modified. Iminodiacetate functional groups are attached to the polystyrene backbone or the polylinoleic acid chains. These groups contain two carboxylic acid groups and a nitrogen atom, providing coordination sites for metal ions. This functionalization enables the copolymer to complex with metal ions and can be used for various applications, such as metal ion removal from solutions (Ali et al., 2019b; Ali et al., 2016). The structure of the synthesized PLinas-Ida graft copolymer is represented in Fig. 1a. Please note that the specific arrangement and distribution of the grafted polylinoleic acid chains and iminodiacetate functional groups can vary based on the synthetic methods used, copolymerization conditions, and other factors. The structure described above is a simplified representation of the

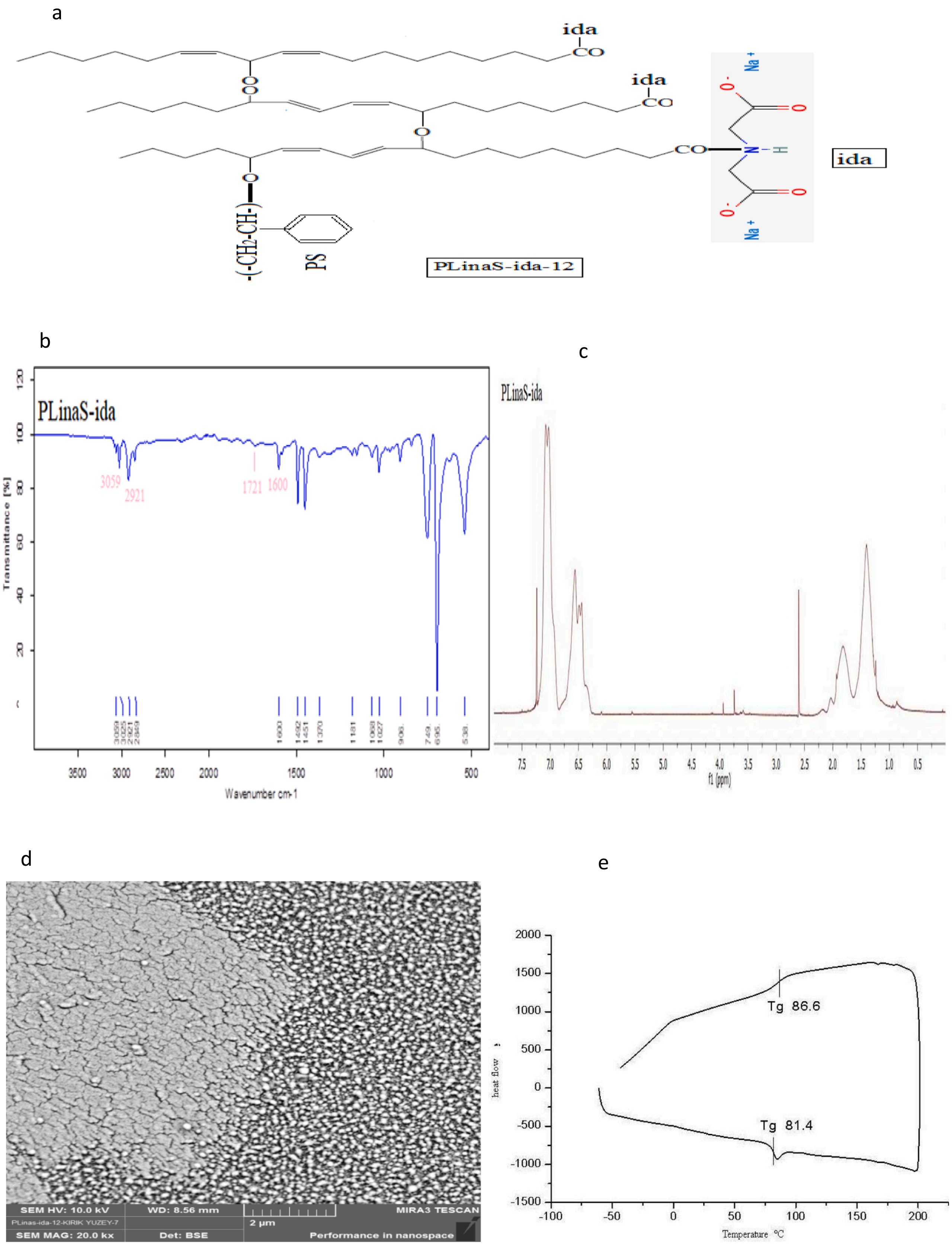

Fig. 1. (a) The chemical structure of the PlinaS-ida graft copolymer; (b) FTIR spectrum; (c) 1H NMR spectrum; (d) SEM micrograph; (e) DSC curve.

copolymer's main components. The actual structure might have more complexity and variations, depending on the synthesis and processing conditions.

3.2. Characterization of the PLinas-Ida graft copolymer

3.2.1. Characterization by FT-IR technique

We analyzed the new adsorbent PLinas-Ida graft copolymer and identified peaks in the FT-IR spectrum, as shown in Fig. 1b. A broad peak around 1700–1725 cm^{-1} is indicative of the carboxylic acid groups present in both the polylinoleic acid and the iminodiacetate functional groups. It may exhibit peaks around 1600 cm^{-1} corresponding to the C═C stretching vibration in the polylinoleic acid chains (Ali et al., 2019b). The carbonyl groups in the iminodiacetate functional groups could result in a peak around 1721 cm^{-1}. Peaks in the range of 1492 cm^{-1} could indicate the presence of aromatic rings in the polystyrene backbone. Peaks around 2921 cm^{-1} would correspond to the aliphatic carbon-hydrogen bonds present in the polylinoleic acid chains. The nitrogen–hydrogen stretching vibration in the iminodiacetate functional groups might be observable around 3059 cm^{-1}. Additionally, it might also observe peaks related to other functional interactions that could be present in the copolymer. The relative intensities, positions, and shapes of these peaks can provide information about the chemical composition and structure of the graft copolymer. It's important to compare the observed spectrum with the reference spectra of the individual components (polystyrene, polylinoleic acid, and iminodiacetate) to aid in the interpretation. The actual spectrum could vary based on factors such as the degree of functionalization, copolymerization conditions, and measurement techniques.

3.2.2. Characterization by 1H NMR technique

The characterization of a new adsorbent PLinas-Ida graft copolymer in chloroform by 1H NMR spectrum was observed with peaks at 6.25–7.25 ppm (Fig. 1c). These peaks correspond to the protons on the aromatic rings of the polystyrene backbone (Ali et al., 2016). The multiplicity of these peaks could be complex due to coupling interactions between the aromatic protons. Aliphatic proton signals from the polylinoleic acid chains might appear in the range of 1.25–2.0 ppm. This region could display multiple peaks due to the presence of various types of aliphatic protons in the polylinoleic acid chains. Protons from the methylene groups in the polylinoleic acid chains could resonate around 2.65 ppm. The multiplicity of these peaks might vary based on neighboring protons and the degree of saturation in the fatty acid chains. Solvent peaks also observe residual solvent peaks around 7.25 ppm due to chloroform itself. It's important to note that NMR spectra can be quite complex, and the above description provides the exact positions, shapes, and relative intensities of the peaks of the PLinas-Ida copolymer structure and experimental conditions.

3.3. Morphology and thermal properties of the PLinas-Ida graft copolymer

3.3.1. Surface topography by SEM technique

The SEM image of the broken surface of the PLinas-Ida graft copolymer shows a varied and intricate structure (Fig. 1d). The fracture surface exhibits a mixture of different features, indicative of the underlying polymer structure and the interplay of its components (Ali et al., 2017a). The fracture surface appears rough and irregular, suggesting a lack of long-range order. Large-scale voids, cracks, and irregularities are distributed across the surface, highlighting the presence of phase separation within the graft copolymer. The surface displays regions of contrast with varying shades and textures. This suggests phase separation between the polystyrene backbone and the polylinoleic acid grafts. Domains of differing sizes are observed, ranging from micrometer to sub-micrometer scales. These domains likely arise from the immiscibility of the hydrophobic polystyrene and the polylinoleic acid chains. Along the fracture surface, irregular protrusions and variations in height are evident. These may correspond to points of grafting, where polylinoleic acid chains are covalently bonded to the polystyrene backbone. The polylinoleic acid chains appear to extend from the polystyrene backbone like branches, forming a complex network of intertwined structures (Gurel et al., 2023). Within the domains, a granular structure can be discerned. This suggests the presence of small clusters of polymer chains, potentially due to the self-assembly of the agglomeration of functional groups. The fracture surface exhibits micro-scale roughness, resulting from the different hardness and flexibility of the components in the graft copolymer. The rugged surface is consistent with the irregular distribution of polylinoleic acid grafts. Within certain areas, elevated concentrations of functional groups may give rise to distinct features in the micrograph. This can indicate regions rich in carboxylic acid or iminodiacetate groups. The SEM micrograph of the fracture surface provides insight into the complex morphology of the PLinas-Ida graft copolymer. The presence of phase separation, grafting points, microstructural heterogeneity, and the distribution of functional groups all contribute to the intricate pattern observed on the surface (Fig. 1d). The fracture surface reflects the interplay between the various components, providing valuable information about the copolymer's structure and properties (Ali et al., 2016).

3.3.2. Thermal stability by DSC technique

The PLinas-Ida graft copolymer exhibits distinct surface topography and thermal properties (Chrzanowska and Derylo-Marczewska, 2019). It shows characteristic transitions such as the glass transition of PLinas and the potential melting/crystallization of Ida chains. Differential scanning calorimetry (DSC) curves can provide insights into these properties. The DSC is a technique used to study the thermal properties of materials by measuring the heat flow (enthalpy changes) associated with physical and chemical changes as a function of temperature. A DSC curve typically shows heat flow on the y-axis and temperature on the x-axis. In PLinas-Ida graft copolymers, polystyrene is a common thermoplastic polymer with a high glass transition temperature (Tg) (Ali et al., 2020). The DSC curve of the PLinas-Ida sample can be seen in Fig. 1e. The plasticized effect of linoleic acid content lowered the glass transition temperature from 100 °C to 81 °C. It's widely used in various applications due to its favorable mechanical properties. Polylinoleic acid could be a polymer or a polymer derivative based on linoleic acid, which is a polyunsaturated fatty acid. The specific properties and behavior of polylinoleic acid depend on the polymerization and functionalization processes. Graft copolymer is a polymer that contains two or more different polymer chains covalently bonded together. In this case, have polystyrene as the main polymer backbone and polylinoleic acid as the grafted side chains. The DSC curve of PLinas-Ida graft copolymers displays thermal changes related to the components and structural shifts within the copolymer. The curve might exhibit a step-like change in heat flow corresponding to the glass transition of the polystyrene backbone. This temperature represents the point at which the polymer transitions from a rigid, glassy state to a more flexible, rubbery state (Ishaq and Giustozzi, 2023). If the polylinoleic acid chains in the graft copolymer have a crystalline nature, observe endothermic (heat-absorbing) peaks corresponding to melting or exothermic (heat-releasing) peaks corresponding to crystallization. The DSC curve might reveal any phase transitions between the polystyrene backbone and the polylinoleic acid side chains. These could manifest as changes in the observed thermal transitions. Depending on the specific copolymerization processes involved, you might observe other transitions related to the iminodiacetate groups present in the copolymer. Remember, the interpretation of the DSC curve is highly dependent on the specific properties and characteristics of the materials involved. The position, shape, and intensity of the peaks can provide valuable insights into the copolymer's structure, composition, and behavior during heating or cooling processes.

3.4. Optimization of extraction parameters using multivariate techniques

Multivariate techniques encompass a suite of statistical tests used for the simultaneous interpretation of data resulting from various extraction parameters. These techniques take into consideration the interrelationships between extraction parameters to provide a comprehensive understanding of the resulting dataset. For optimization of the VA-dSPμE method, we specifically employed multivariate techniques, including factorial design and central composite design (CCD). The construction of a Pareto chart to screen effective extraction variables was facilitated using Minitab-16 statistical software. During this process, the impacts standardized on the percentage recovery were visualized at an alpha value of 0.05. The screening test using the Pareto chart produced results with a critical value of 2.57, as illustrated in Fig. 2a. Extraction parameters were considered to have substantial effects when their experimental values surpassed this critical threshold. Various extraction parameters, including eluent volume, adsorbent PLinas-Ida dosage, adsorption time, pH, sample volume, and desorption time, were examined. The Pareto chart was instrumental in quantifying the estimated effects of these extraction parameters and their efficiency on the process.

3.4.1. Variable screening via factorial design

The factorial design method is widely employed for efficiently identifying the most influential extraction parameters in the proposed pre-concentration technique. In a factorial design, various factors are systematically adjusted at different levels, and the resulting response variable is measured for each unique combination of factor settings. We used a factorial design method at a 95 % confidence level to thoroughly study essential extraction factors, such as eluent volume, PLinas-Ida amount, adsorption time, pH, sample volume, and desorption time. This meticulous examination aimed to assess the impact of these extraction parameters on the process. Fig. 2a illustrates that the most significant extraction parameters are eluent volume, adsorbent PLinas-Ida dosage, and adsorption time. In contrast, pH, sample volume, and desorption time exhibit a comparatively weaker influence on the recovery of Cr from digested food samples. The findings indicate that eluent volume, PLinas-Ida dosage, and adsorption time are significant extraction factors because they surpass the critical alpha value of 2.571,

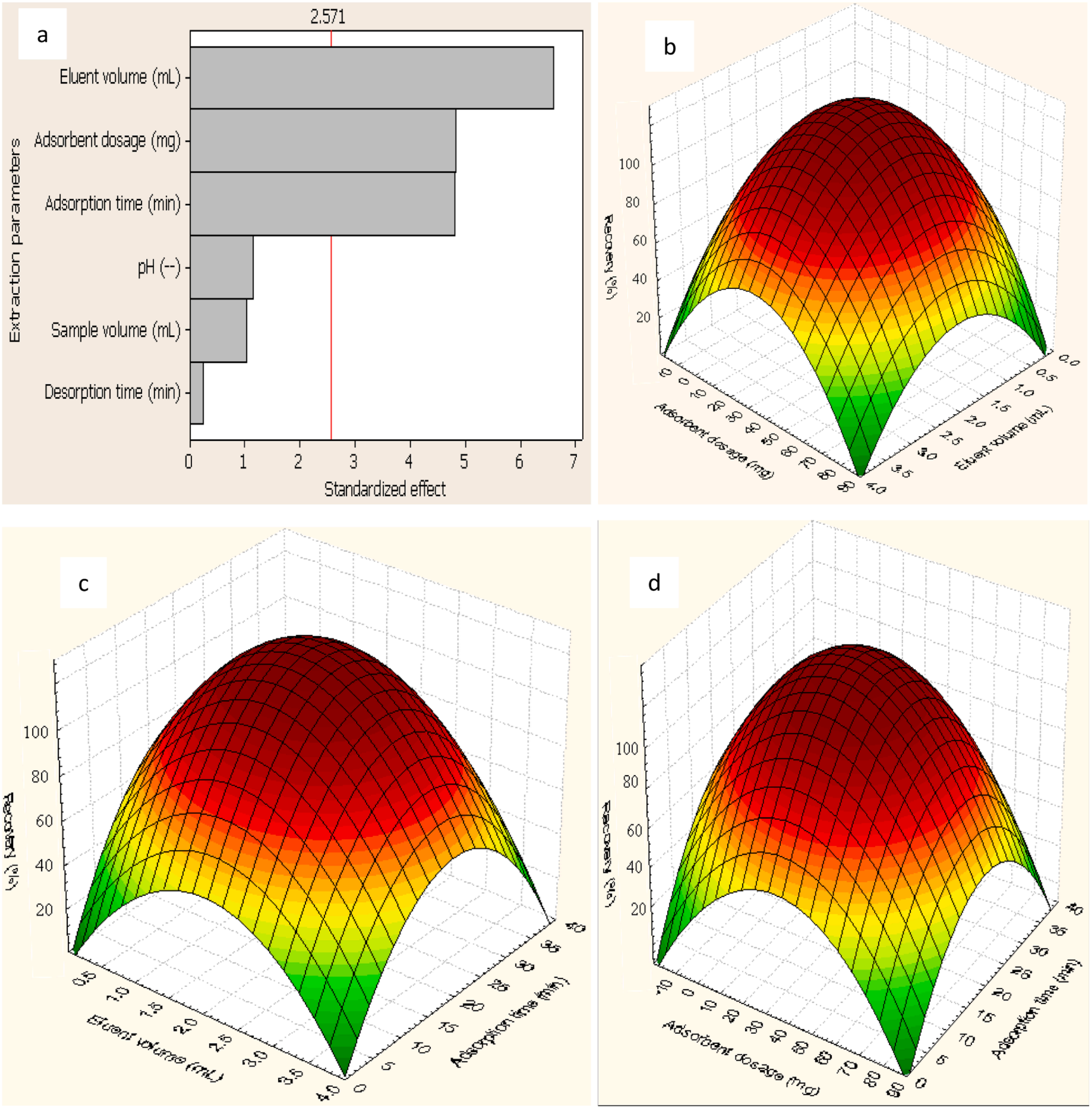

Fig. 2. (a) Pareto chart of standardized effect in factorial design for screening out the efficient effective extraction parameters; (b) 3D surface plot of adsorbent dosage Vs eluent volume; (c) 3D surface plot of eluent volume Vs adsorption time; (d) 3D surface plot of adsorbent dosage Vs adsorption time.

as shown in Fig. 2a. These parameters significantly affect the recovery of Cr in food samples that underwent microwave-assisted acid digestion. Conversely, factors such as pH, sample volume, and the volume of HCl used for desorption exerted a lesser impact. In conclusion, our findings show that eluent volume, PLinas-Ida dosage, and adsorption time are crucial factors in chromium extraction using the developed VA-dSPμE method. Factorial designs involve systematically varying multiple factors, and observing their effects on the response variable, providing valuable insights into the relationships between these factors, and the desired outcome. They are particularly useful for efficiently screening numerous parameters, and identifying those deserving further investigation.

3.4.2. *Multivariate optimization of key extraction parameters*

This method integrates factorial, and response surface designs to systematically explore the response variable space, and determine optimal settings for significant parameters. After constructing the response surface model, optimization techniques are applied to identify critical parameters that maximize or minimize response variables. In this study, CCD was employed for optimizing significant variables, primarily through second-order response surface modeling. To improve the VA-dSPμE method, we used a central 23 + star orthogonal composite design, testing six extraction parameters across twenty experimental runs. We found that eluent volume, PLinas-Ida dosage, and adsorption time are crucial for achieving the best results in the VA-dSPμE method. Less significant extraction parameters, such as pH, sample volume, and desorption time, were set at predetermined suitable values (6.50, 100 mL, and 1.50 min) for subsequent experiments. We carefully observed how important extraction factors like eluent volume, PLinas-Ida dosage, and adsorption time affect chromium recoveries. The optimized values for these three parameters were determined as follows: eluent volume at 1.50 mL, adsorbent PLinas-Ida dosage at 40 mg, and adsorption time at 20 min. remarkably, these optimal values were found to align closely with those obtained through CCD, affirming their reliability in maximizing Cr recovery.

After identifying these crucial extraction variables using factorial design, CCD was utilized to refine them, and attain the maximum Cr recovery. This statistical approach looked at how adsorbent PLinas-Ida dosage interacts with eluent volume, eluent volume interacts with adsorption time, and adsorbent PLinas-Ida dosage interacts with adsorption time. These interactions were visualized through three-dimensional response surface graphs (Fig. 2b) aiding in identifying conditions. We used a quadratic equation to predict how the response surface data would look, helping us find the best values for the key extraction parameters that give maximum recovery. These theoretical values, including eluent volume (1.50 mL), adsorbent PLinas-Ida dosage (40 mg), and adsorption time (20 min), closely resembling those obtained through CCD in the developed VA-dSPμE method, lead to subsequent experiments being carried out using these optimized values to validate their effectiveness in maximizing Cr recovery. This comprehensive approach combines factorial design with response surface modeling, and CCD, providing valuable insights into the relationships between parameters and the response variable. It enables efficient exploration of parameter space, and the identification of optimal settings for significant parameters, ultimately leading to improved process performance.

3.5. *Reusability and adsorption capacity of the novel adsorbent*

The economic benchmark for the VA-dSPμE procedure hinges on how frequently PLinas-Ida can be utilized for Cr extraction. In this scenario, the important thing is that PLinas-Ida can be used again in adsorption–desorption experiments without losing much of its adsorption ability. We tested the reusability of 40 mg of PLinas-Ida in adsorption–desorption experiments over 15 cycles under the best conditions we found. During the initial 10 cycles, there was no notable decrease in the adsorption capacity, and we achieved full recovery for Cr ions. However, after the tenth utilization, as the adsorption capacity of PLinas-Ida decreased, the recovery rate for Cr ions dropped from 90 % to 45 %.

To assess the adsorption capabilities of the newly developed adsorbent, 40 mg of PLinas-Ida was added to a 100 mL sample solution containing Cr ions. The mixture underwent 30 min of vigorous vortex mixing to promote adsorption. Following this, the resulting solution was filtered into a separate tube, and the targeted ions were quantified using GF-AAS. After these procedures, the adsorption capacity was determined using the provided formula.

$$Adsorptioncapacity = \left\{ V\left(C_i - C_f\right) \right\} / W$$

In this context, the variables are defined as follows: V represents the volume of the standard Cr solution; Ci and Cf denote the initial, and final concentration values of Cr, respectively, after ten cycles of VA-dSPμE. W represents the quantity of the newly introduced copolymer used as the adsorbent. It's worth mentioning that the adsorption capacity for the new graft copolymer, PLinas-Ida, was measured at 112 mg g^{-1}. It's worth highlighting that our adsorptive polymeric materials exhibit a notably high adsorption capacity when compared to other reported adsorbents found in the literature.

3.6. *Analytical performance of the developed method*

Utilizing the proposed VA-dSPμE method, successful separation and pre-concentration of Cr from digested food samples were achieved, followed by a comprehensive investigation of its analytical performance. All optimization parameters for the present VA-dSPμE technique are detailed in Table 1a. The range of linearity for the suggested VA-dSPμE method applied to Cr spanned from 0.01 to 0.50 μg/L while maintaining a pH of 6.5. For the determination of both the limit of detection (LOD) and the limit of quantification (LOQ), specific formulas were applied: LOD = 3SD/m, and LOQ = 10SD/m. Here, SD corresponds to the standard deviation derived from the analysis of 10 blank samples, and m represents the slope of the linear graph originating from the analysis of these blank samples. The resultant LOD, and LOQ values for our innovative VA-dSPμE technique are notably minimal, measuring at 0.003 μg/L, and 0.01 μgL^{-1}, respectively. In contrast to other micro-extraction methods using different adsorbents for detecting chromium in fruits, vegetables, natural samples, and meat, which reported higher values, our suggested VA-dSPμE method shows a much higher enrichment factor (EF) of about 72.8 compared to previous studies on chromium analysis. This EF value is computed by establishing the ratio between slopes extracted from linear calibration graphs with and without the pre-concentration step, facilitated by the newly developed micro-extraction approach. Regarding precision, the percentage relative standard deviation (RSD) was computed at 1.65 % under conditions of n = 10, and a concentration of 0.65 μgL^{-1}, utilizing the recommended method for Cr determination.

Table 1a
Analytical figure of merits of the developed method for chromium.

Analytical performance parameters	Values
Regression equation	A = 0.33Cr + 0.02
Correlation coefficient (r^2)	0.999
Working standards calibration (μg L^{-1})	0.01–0.50
Limit of detection (μg L^{-1})	0.003
Limit of quantification (μg L^{-1})	0.01
Percentage relative standard deviation (n = 10, 0.65 μg/L)	1.65
Enrichment factor	72.8
Pre-concentration factor	66.7
pH	6.5
Adsorption volume (mL)	100
Desorption volume (mL)	1.50

3.7. Interference ions assessment

It's crucial to study how selective the new adsorbent PLinas-Ida is for chromium determination, especially since we're using model solutions to optimize VA-dSPμE steps. This prompted a thorough evaluation of PLinas-Ida's selectivity towards Cr within the context of coexisting foreign ions. To accomplish this, various conceivable foreign ions were introduced into model solutions containing 0.50 μg/L Cr, followed by the execution of the VA-dSPμE procedure. Subsequent to each foreign ion introduction, computations were performed to determine the tolerance concentration, and recovery values. Tolerance concentration, in this context, signifies the concentration level at which relative errors exceeding or falling below 5 % emerge concerning the determination of Cr. The outcomes of this comprehensive investigation are succinctly presented in Table 1b. The results clearly show that the adsorbent PLinas-Ida has excellent selectivity for chromium, as it can tolerate high concentrations and achieve full recoveries. Furthermore, the results distinctly indicate the absence of significant matrix effects.

3.8. Implementation of the developed method

The efficacy of the VA-dSPμE method was established through the evaluation of a variety of CRMs originating from apple leaves (NIST-SRM-1515), and tea leaves (INCTTL-1) for Cr determination. The ascertained concentrations of total Cr within these CRMs demonstrated remarkable concordance with reported values, resulting in a calculated recovery rate of 96.7 % for apple leaves, and 98.4 % for tea leaves (Table 2a). This underscores the exceptional selectivity, and sensitivity of the VA-dSPμE method in gauging trace level Cr content across a diverse range of food items obtained from varied markets within Tokat city, Turkiye. To validate, and ensure the robustness of the developed VA-dSPμE approach, CRMs derived from apple, and tea leaves were employed. The innovative VA-dSPμE technique, utilizing the novel adsorbent PLinas-Ida was proficiently applied for assessing trace concentrations of total Cr across an extensive array of foodstuffs. Various foodstuffs like fruits (apple, apricot, banana, grape, hazelnut, walnut, tomato, plum, mulberry, pear, fig, and rosehip), vegetables (broccoli, garlic, mushroom, onion, potato, spinach, and tea), natural, and meat products (egg, fish, honey, meat, salami, and sausage) are presented in (Table 2b). The findings concerning Cr concentrations in diverse foodstuffs (fruits, vegetables, natural products, and meat) consistently adhered to the recommended values established by WHO, and USEPA, except for apricot, plum, and mushroom samples. While conducting Cr assessments, a significant observation emerged regarding the predominance of Cr in comparison to other trace elements within the examined human food items, aligning with existing literature. Notably, the levels of Cr estimated through the VA-dSPμE method surpassed those reported in the literature. This divergence could potentially be attributed to geographical variations.

Table 1b

Tolerance limits of interfering ions for chromium by developed method (n = 3).

Foreign Ions	Added as	Tolerance limits (mg L^{-1})	Recovery (%)
Na^+	NaCl	5000	98 ± 2.7
K^+	KCl	3000	97 ± 3.2
Ca^{2+}	$CaCl_2$	1500	99 ± 2.9
HCO_3^-	$NaHCO_3$	1500	96 ± 2.8
Mg^{2+}, Mn^{2+}, Co^{2+}, Sn^{2+}	Respective salts	300	95 ± 3.4
As^{3+} Al^{3+}, Fe^{3+}		250	96 ± 2.8
Zn^{2+}, Cu^{2+}, Cd^{2+}, Ni^{2+}, Sr^{2+}		100	94 ± 3.4
F^-	NaF	3000	96 ± 2.8
Cl^-	NH_4Cl	7000	97 ± 3.1
NO_3^-	$NaNO_3$	2000	99 ± 2.5
PO_4^{3-}	K_3PO_4	1000	96 ± 3.2
SO_4^{2-}	K_2SO_4	1000	98 ± 2.9

Table 2a

Results of chromium concentration in CRMs (n = 3).

Certified Reference Materials	Certified values (mg kg^{-1})	Measured values (mg kg^{-1})	Recovery (%)
Apple leaves (NIST-SRM-1515)	0.30 ± 0.02[a]	0.29 ± 0.02	96.7 ± 3.1
Tea leaves (INCTTL-1)	1.91 ± 0.22	1.88 ± 0.09	98.4 ± 2.6

Key: [a] Mean ± standard deviation

3.9. The developed method compared to other existing techniques

We measured the concentration of chromium using GF-AAS with the VA-dSPμE method and found higher levels than those reported in existing literature. This discrepancy could potentially be attributed to variations in geographical locations (Pytlakowska et al., 2016). Surprisingly, the Cr concentrations in food products collected from different markets in Tokat Turkiye, were found to exceed the recommended levels. Furthermore, we compared the novel adsorbent in the VA-dSPμE method with methods documented in the literature, as outlined in Table 3. The VA-dSPμE method exhibited exceptional selectivity, and sensitivity in determining Cr concentrations in a wide range of food items, including fruits, vegetables, natural products, and meat products. The LOD and RSD for the VA-dSPμE method were determined to be 0.003 μg/L and 1.65 % respectively, which are lower than those reported in existing literature for Cr determination (Ali et al., 2019a). Furthermore, we determined the enhancement factor (EF) by comparing the slopes of calibration curves obtained with and without preconcentration using the VA-dSPμE method. This method demonstrated an impressive adsorption capacity of 112 mg/g, surpassing previously reported values for Cr in the literature, except as reported in (Jia et al., 2016; Ulusoy et al., 2022). Table 3 shows a detailed assessment of the analytical performance of the VA-dSPμE method for detecting chromium in food using the new PLinas-Ida adsorbent. All key parameters, like sample analysis, adsorption capacity, pH, LOD, PF/EF, RSD, adsorption time, and recovery, were found to be as good as or better than values reported in the literature using different adsorbents (Ali et al., 2019b; Assi et al., 2019; Bahadir et al., 2016; Chanthasakda et al., 2016; Pang et al., 2021; Zeng et al., 2012). Hence, the current VA-dSPμE method provides a convenient and accurate approach for quantifying chromium levels in food products.

4. Conclusions

The synthesized PLinas-Ida graft copolymer served as the pivotal adsorbent material for selective extraction and sensitive Cr detection within digested food samples. This was accomplished utilizing a microwave-assisted digestion process followed by GF-AAS examination. Our PLinas-Ida graft copolymer showed excellent adsorption abilities without affecting its natural hydrophobic properties. We effectively achieved chromium ion adsorption onto the solid phase using a vortex-assisted mixing technique. The standout features of our methodology are the pioneering utilization of PLinas-Ida for the purpose of Cr ion preconcentration. Our approach treads lightly on chemical usage, aligning seamlessly with the principles of green chemistry. The PLinas-Ida graft copolymer showcased impressive chemical stability and could be employed multiple times. Our methodology, by virtue of omitting a heating step, boasts a considerably shorter extraction time in comparison to traditional LLE techniques. The VA-dSPμE method, based on the deployment of the PLinas-Ida graft copolymer, emerged as a highly effective means for Cr determination within a diverse array of foodstuffs. The method demonstrated commendable accuracy, and precision, with CRM recovery rates of 97 %, and 99 %. Furthermore, the iminodiacetate-functionalized PLinas graft copolymer, employed as an adsorbent for Cr ions exhibited a markedly superior adsorption capacity

Table 2b
Concentration of chromium in foodstuffs by developed method.

(b) Human foodstuffs (Fruits)					
Sr.No	Fruit name	Concentration (μg g^{-1})	Sr.No	Fruit name	Concentration (μg g^{-1})
01	Apple	0.78 ± 0.01	07	Tomato	0.03 ± 0.01
02	Apricot	2.38 ± 0.22	08	Plum	2.25 ± 0.22
03	Banana	0.05 ± 0.01	09	Mulberry	1.05 ± 0.06
04	Grape	1.85 ± 0.21	10	Pear	1.93 ± 0.09
05	Hazelnut	0.06 ± 0.01	11	Fig	1.97 ± 0.11
06	Walnut	0.04 ± 0.01	12	Rosehip	0.93 ± 0.05
(c) Human foodstuffs (Vegetables)					
Sr.No	Vegetable name	Concentration (μg g^{-1})	Sr.No	Vegetable name	Concentration (μg g^{-1})
01	Broccoli	0.07 ± 0.01	05	Potato	0.07 ± 0.01
02	Garlic	0.11 ± 0.02	06	Spinach	0.14 ± 0.03
03	Mushroom	2.53 ± 0.13	07	Black tea	5.33 ± 0.27
04	Onion	0.08 ± 0.01	08	Green tea	4.58 ± 0.23
(d) Natural and meat products					
Sr.No	Product name	Concentration (μg g^{-1})	Sr.No	Product name	Concentration (μg g^{-1})
01	Egg	0.08 ± 0.02	04	Meat	0.11 ± 0.01
02	Fish	1.66 ± 0.08	05	Salami	0.77 ± 0.03
03	Honey	0.02 ± 0.01	06	Sausage	0.21 ± 0.02

Table 3
Comparison of the developed method with literature reported methods for chromium in foodstuffs.

Techniques	Methods	Adsorbents	Sample mL	AC[a] (mg g^{-1})	pH –	LOD[b] (μg L$^{-1)}$	PF/ EF[c]	RSD[d] (%)	Time (min)	Recovery (%)	References
EDXRF[e]	MSPE[f]	GO-Gly[g]	50	250	6.0	0.15	55.0	2.30	10	97–99	Pytlakowska et al. (2016)
UV–Vis[h]	HF-LPME[i]	SLM[j]	28	–[k]		3.5	200	9.00	5.0	96–101	Chanthasakda et al. (2016)
TXRF[l]	DLLME[m]	APDC[n]	50	–	6.0	0.80	200	12.0	30	92–106	Bahadir et al. (2016)
HPLC/DAD[o]	MB-ME/IT-SPME[p]	MBCC[q]	5.0	40.0	5.5	0.50	57.0	4.20	5.0	84–115	Pang et al. (2021)
ETAAS[r]	MSPE[s]	MGO-NCP[t]	100	250	2.2	1.00	182	8.50	90	85–99	Jia et al. (2016)
	SPμEM[u]	PH-DTT-MPT[v]	50.0	42.4	7.0	0.006	90.0	1.17	2.0	88–102	Ali et al. (2019b)
	UA-DES-ME[w]	Calmagite	25.0	–	9.0	0.006	85.0	4.93	5.0	95–101	Ali et al. (2019a)
FAAS[x]	MSPE[y]	DPC-MNPs[z]	50	3.50	8.5	–	–	–	60	92–98	Assi et al. (2019)
	HF-LPME[x1]	RTILS[x2]	100	–	4.5	0.70	175	4.90	15	91–105	Zeng et al. (2012)
	SPE[x3]	PAM-CR[x4]	120	118	5.0	0.35	97.0	2.30	18	96–97	Ulusoy et al. (2022)
	GFAAS, VA-dSPμE[x5]	PLinaS-ida[x6]	100	112	6.5	0.003	72.8	1.65	20	96–99	This study

Key: [a] Adsorption capacity [b] Limit of detection, [c] Pre-concentration factor/Enrichment factor, [d] Related standard deviation, [e] Energy dispersive X-ray fluorescence spectrometry, [f] Dispersive micro solid-phase extraction, [g] Graphene oxide with glycine, [h] Ultraviolet–visible spectrometer, [i] Hollow fiber membrane liquid phase micro-extraction, [j] Supported liquid membrane, [k] Not reported, [l] Total-reflection X-ray fluorescence spectrometry, [m] Dispersive liquid–liquid micro-extraction, [n] Ammonium pyrrolidinedithiocarbamate [o] High-performance liquid chromatography-diode array detector, [p] Magnetism-assisted in-tube solid phase micro-extraction, [q] Monolith-based capillary column. [r] Electrothermal Atomic Absorption Spectrometry, [s]Magnetic solid-phase extraction, [t]Magnetic graphene oxide coated with poly (2-amino-thiazole) nanocomposite, [u] Solid phase micro-extraction method, [v] PH-DTT-MPT (poly-3-hydroxybutyrate-2-(dodecylthiocarbonothioylthio)-2-methylpropionat triester), [w] Ultrasonic assisted deep eutectic solvent micro-extraction, [x] Flame Atomic Absorption Spectrometry, [y] Magnetic solid-phase extraction, [z] 1,5-diphenylcarbazide modified magnetic nanoparticles, [x1] Hollow fiber liquid phase micro-extraction, [x2] Room temperature ionic liquids, [x3] Solid phase extraction and [x4] Polyacrylamide and carmine, [x5] Vortex Assisted-solid phase micro-extraction and [x6] Polystyrene and polylinoleic acid functionalized iminodiacetate graft copolymer.

when juxtaposed with previously reported materials employed in Cr determination. We employed multivariate techniques to identify the most efficient and effective parameters. Utilizing Pareto charts and CCD enabled us to screen, and optimize the most influential extraction parameters, resulting in a significant enhancement in Cr extraction efficiency from digested fruits, vegetables, natural products, and meat products. The VA-dSPμE methodology proved to be a resounding success in both the determination, and pre-concentration of Cr across a broad spectrum of food products.

CRediT authorship contribution statement

Jamshed Ali: Writing – original draft, Validation, Software, Methodology, Formal analysis, Data curation, Conceptualization. **Mustafa Tuzen:** Writing – review & editing, Writing – original draft, Validation, Supervision, Formal analysis. **Wahid Bux Jatoi:** Writing – review & editing, Writing – original draft, Methodology, Investigation, Formal analysis, Data curation, Conceptualization. **Mushtaque Ahmed Jakhrani:** Writing – review & editing, Writing – original draft, Software. **Baki Hazer:** Writing – review & editing, Writing – original draft, Validation, Software, Methodology, Investigation, Formal analysis, Data curation, Conceptualization.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

The data that has been used is confidential.

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