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ORIGINAL PAPER

Synthesis, characterization, and application of polyacrylamide/carmine polymer nanomaterial as an effective solid-phase material for ultrasonic-assisted solid-phase microextraction of aluminum and chromium in vegetable samples

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Abstract

Here, a new and inexpensive polymer nanomaterial consisting of polyacrylamide and carmine (PAM-CR) was synthesized to provide selective extraction of aluminum and chromium from vegetable samples prior to their determination by flame atomic absorption spectrometry. Various characterized techniques including scanning electron microscopy, Fourier transform infrared spectroscopy and X-ray powder diffraction were applied to investigate the structure and morphology of the PAM-CR. Important factors were investigated and optimized to improve the effectiveness of the adsorbent. Under optimized conditions, calibration graphs for Al(III) and Cr(III) were linear in the range from 0.2 to 400.0 μg L^{-1} and 1.0 to 500.0 μg L^{-1}, respectively. Satisfied recoveries between 93.1% and 102.7% were obtained with detection limits of 0.06 μg L^{-1} and 0.35 μg L^{-1} for Al(III) and Cr(III), respectively. The relative standard deviation was in range of 2.0–2.3%. The PAM-CR can be reused 8 times without significant loss in the recovery. After validation study with certified reference material, the proposed method was successfully applied to the pre-concentration and determination of Al(III) and Cr(III) in vegetable samples.

Keywords Al(III) · Cr(III) · Polymeric nanomaterial · Solid-phase extraction · Vegetables

Introduction

Aluminum (Al) is one of the most common elements found in the earth's crust and therefore can be found at relatively high levels in nature, air, water, plants, and consequently in all the food chain (López et al. 2000). Recent studies have shown that acid rain decreases the pH in the soil, so that the dissolved Al passes into the soil through the ground water (Bojórquez-Quintal et al. 2017). The Al has no important function in the human metabolism. It is thought that the presence of trace levels (above 5.0 μg L^{-1}) may cause some health problems such as renal failure, encephalopathy, microcytic anemia and sleep disorders (Almeida Pereira et al. 2004). Chromium (Cr) has an important function in carbohydrate, lipid, protein, mineral, and other metabolisms (Mateos et al. 2003). The Cr(III) is considered an essential nutrient in humans, although the Cr(VI) is toxic. It has been reported that the Cr(VI) which has toxic effect may play a role in the pathogenesis of some diseases such as lung and gastrointestinal cancer (Tripath et al. 2018). Because of these properties, the development of new analytical methods for the determination of trace amounts of Al and Cr in vegetable samples remains popular.

Sample preparation is a very important step in most analytical approaches. Depending on the extraction procedure, sample preparation strategies are categorized into solid-phase extraction (SPE) and liquid-phase extraction. Analytical laboratories use SPE to concentrate, purification samples for analysis, and preconcentration of various types of analytes (Płotka-Wasylka et al. 2015; Öner et al. 2021). The SPE procedure is widely used in extraction studies due to its cheapness, simple operation, high extraction efficiency and rapid phase separation. Up to now, various configurations

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of SPE such as ultrasonic-assisted SPE (Jalilia et al. 2020), dispersive-SPE (Chisvert et al. 2019), magnetic-SPE (Vasconcelos and Fernandes, 2017), molecularly imprinted-SPE (Sarafraz-Yazdi and Razavi, 2015; Abdollahi et al., 2020), vortex-assisted SPE (Bagheri et al. 2016), matrix solid-phase dispersion-SPE (Arabi et al. 2016), and multiwalled carbon nanotube-SPE (Krawczyk and Jeszka-Skowron 2016) have been developed to increase the efficiency of the analytical methods. SPE-based methods are generally applied by two ways: Column and batch approaches. Because column methods require a special equipment for filtration and more time for this process, batch type solid-phase extraction methods are preferable for most analysist. Succession of this process is generally based on feasibility (durability, selectivity, reusability, etc.) of adsorbent material. So, it is a challenge to obtain new material in order to use in SPE-based methods. As a useful polymer, polyacrylamide (PAM) is a kind of hydrogel and can be used as potential carrier for new adsorbents. PAM is known an inert material for most of metal ions in adsorption studies. But, its adsorptive properties can be improved by grafting organic ligands with active functional groups. These type molecules increase surface properties of adsorbent and provide selectivity for target ions. So, SPE-based methods may be more sensitive and selective. The SPE methods were combined with many determination techniques such as high performance liquid chromatography-ultra violet (Bagheri et al. 2016), high-resolution mass spectrometry (Stravs et al. 2016) inductively coupled plasma mass spectrometry (Manousi et al. 2020), flame atomic absorption spectrometry (FAAS) (Altunay et al. 2018), graphite furnace atomic absorption spectrometry (López-García et al. 2020) and inductively coupled plasma-optical emission spectroscopy (Nyaba and Nomngongo, 2020). Compared to other techniques the FAAS offers cheapness, easy operation and short analysis time (Altunay et al. 2019). But its sensitivity is less than other methods. To overcome this, a suitable SPE procedures may be employed prior to determination step. Sonication has proven to be a very useful tool in intensifying the mass transfer process and breaking the affinity between sorbet and analyte (Hamdaoui and Naffrechoux, 2009). As a result of sonication, cavitation occurs in the aqueous solution. In this way, the interaction of the analyte ions with the sorbent increases. This indirectly leads to an increase in adsorption (Breitbach et al. 2003).

In the current study, a new inexpensive polymer nanomaterial consisting of polyacrylamide and carmine (PAM-CR) was synthesized to provide selective extraction of Al(III) and Cr(III) from various vegetable samples prior to their determination by FAAS. The PAM-CR nanomaterial was characterized in detail. Under optimized conditions, the good compatibility of the analytical data obtained in the analysis of the reference material with the certified values shows that the proposed method is practically applicable to vegetable samples. After application, quantitative recoveries and low relative standard deviations were obtained. As far as we know, this nanomaterial synthesized is the first application for the simultaneous extraction and determination of Al(III) and Cr(III) ions.

Experimental

Apparatus

Determinations of Al(III) and Cr(III) in the final phase were carried out with a flame atomic absorption spectrometer (FAAS, Shimadzu AAS-6300 model, Kyoto, Japan), equipped with a D_2 background corrector. Operating parameters of the FAAS for aluminum and chromium were set up as follows: lamp current, 10 mA and 4.0 mA; wavelength, 309.3 nm and 357.9 nm; slit width, 0.2 nm and 0.4 nm, and burner height, 11 mm and 7.0 mm, respectively. For characterization of the PAM-CR nanomaterial, Perkin-Elmer Spectrum 400 Fourier transform infrared spectrophotometer (FT-IR, Waltham, MA, USA), Raman spectrometer (WITec alpha 300 M + micro-Raman system with 532 nm laser source), advanced XRD diffractometer (Bruker AXS D8) instruments were used. FE-SEM was performed on a Gemini SEM 500–71-08. An ultrasonic water bath (Norwalk, CT, USA) was used to dispersion of the nanoparticles in solution phase. Devices including vortex (Ika-Werke Staufen, Germany), ultrasonic bath (SK5210LHC Kudos, Shanghai, China), centrifuge (Universal Hettich, London, England), digital pH meter (JP Selecta, Barcelona, Spain) and microwave digestion system (Milestone Ethos, Italy) were used in the sample preparation, adsorption and desorption steps. Ultra-pure water used throughout the current experiment was prepared by Milli-Q water purification system (Bedford, USA).

Reagents

Stock solutions (1000 mg L^{-1}) of Al(III) and Cr(III) ions were prepared by dissolving appropriate amount of their nitrate salts in water (Carlo Erba, Milan, Italy) and were stored at 4 °C. The required working solutions (in range of 0.1–1000 µg L^{-1}) were daily prepared in the same vessel by mixing the appropriate amounts of the stock solutions. N,N′-methylenebisacrylamide (≥ 99.0%, Bis–AA) was purchased from Merck (Darmstadt, Germany). Ammonium persulfate $(NH_4)_2S_2O_8$) was purchased from Sigma (St Louis, MO, USA). Methanol (Sigma), ethanol (Merck), tetrahydrofuran (Sigma), carmine (Sigma), acetonitrile (Merck), 1-octanol (Carlo Erba) and acetone (Merck) were used for desorption of the analytes from the solid adsorbent. Acetate buffer solution (0.1 M, pH 5.0) was prepared by dissolving of sodium acetate and acetic acid in the water.

Synthesis study

A new polymer nanomaterial as adsorbent was synthetized and characterized for SPE experiments by using a simple procedure as explained in our previous studies (Köseoğlu et al. 2020; Şimşek and Ulusoy, 2018). According to this approach, 2.0 g of acrylamide monomer was weighed carefully and dissolved in 10 mL ultrapure water. This solution moved on a magnetic stirrer and mixed 100 rpm. Then, 0.2 g of N,N′-methylenebisacrylamide (Bis–AA) as cross-linker was transferred to solution slowly on magnetic stirrer. After a clear solution was obtained, 0.2 g of carmine (CR) molecules was added to mixture while it was being stirred on constant rate. Polymerization reaction was started by adding 100 mg of $(NH_4)_2S_2O_8$ while stirring rate was increasing to 200 rpm. Finally, 100 µL of N,N,N',N'-Tetramethyl-ethylenediamine was added to solution drop by drop to stabilize the polymers. The reaction chamber was cooled in an ice bath because it is an exothermic reaction. The obtained polymeric material was washed with ultrapure water for 5 times and ethanol for 2 times. Then the solid material was dried in a vacuum oven at 50 °C for 48 h. The grain size of the solid material was reduced by grinding in a mortar. Finally, the material was sieved by using a sieve (18 Mesh) in order to use same size particles in experiments.

Microwave-assisted digestion

Vegetable samples analyzed (broccoli, mushrooms, spinach, eggplant, paprika, cabbage, carrot, leek, zucchini) in the study were purchased from local greengrocer in Sivas, Turkey. Certified reference material (CRM, Tea Leaves INCT-TL-1) was purchased from Institute of Nuclear Chemistry and Technology (Warsaw, Poland). All vegetable samples were washed with the water before microwave-assisted digestion, followed by cutting the edible parts with a knife. 1.0 g of vegetable samples were weighed on an analytical balance and transferred to Teflon tubes. Then, 15 mL of 5 mol L^{-1} of HNO_3 and 1 mL of H_2O_2 were added and the caps of Teflon tubes were closed and placed in the microwave digestion system. Same program was then applied to all samples (Bakkali et al. 2009) with a few modifications. The used program has 4 steps including the step-1 (2 min, 80 °C, 250 W), step-2 (5 min, 130 °C, 00 W), step-3 (3 min at 180 °C, 500 W) and step-4 (5 min at 200 °C, 600 W). Then, the obtained residues were dissolved in water and diluted to 5 mL for the application of the SPE procedure. Moreover, a blank sample was carried out in the same way to test the possible analytic contaminations in the reagents used. One of the main advantages of use of microwave digestion is fast digestion process by avoiding oxidation of metal ions. Therefore, the necessary chemical environment for the oxidation of chromium species is not obtained in the microwave digestion step (Van Niekerk et al., 2007; Lin 2002).

Optimized procedure

The SPE procedure based on synthesized polymeric nanomaterial (PAM-CR) was performed as follows. First, 5.0 mL of the sample solution containing Al(III) (10 µg L^{-1}) and Cr(III) (30 µg L^{-1}) was added to 50-mL conical centrifuge tubes. 30 mg of the PAM-CR was added to the sample solution and then the pH of the sample solution was adjusted to pH 5.0 using 2.5 mL of the acetate buffer solution. After, the final volume of the tubes was completed to 50 mL, the obtained mixture was sonicated at room temperature in an ultrasonic bath to accelerate the adsorption of the Al(III) and Cr(III) ions to the PAM-CR. After sonication, the tubes were centrifuged at 4000 rpm for 3 min. This step allowed that the PAM-CR to be collected at the bottom of the tube. After decantation of the aqueous portion, the adsorbed metal ions on the PAM-CR were eluted with 2 mL of methanol using vortex (1 min). Finally, the amounts of analytes in the elute were determined by FAAS.

Results and discussion

Characterization studies

In the analyzed PAM-CR formulation, polyacrylamide was treated with a crosslinker and the product after reaction was treated with the final product carmine dye. Considering the FT-IR spectrum (see Fig. 1a) taken for Carmine, the asymmetric stresses of N–H bonds in secondary amines give a characteristic peak at 3398 cm^{-1}. The peak seen at 1617 cm^{-1} appears as vibration bands supporting each other of C=O bonds combined with C=C stress. Also, the C–N bonds of the amine group in the range of 1350–1000 cm^{-1}. The weak asymmetric trend appears in the literature as vibration peaks. The peak in the range of 735–770 cm^{-1} is also attributed to C–H bonds, apart from plane bends in the aromatic group. When these observed bands are compared with the literature, it confirms that Carmine dye has characteristic peaks. In the FT-IR spectrum of the PAM component, it is characterized by the characteristic dominant OH^- peak at 3571 cm^{-1} and asymmetric trend bands at 1066 cm^{-1}. The vibration bands at 1651 and 1591 cm^{-1} are due to the C=O and C=C bands in the PAM structure, and these peaks are also confirmed in the literature. It appears to include bands with frequencies of 1443, 1441, 1310 and 1108 cm^{-1}. The frequencies between 1650–1510 cm^{-1} correspond to

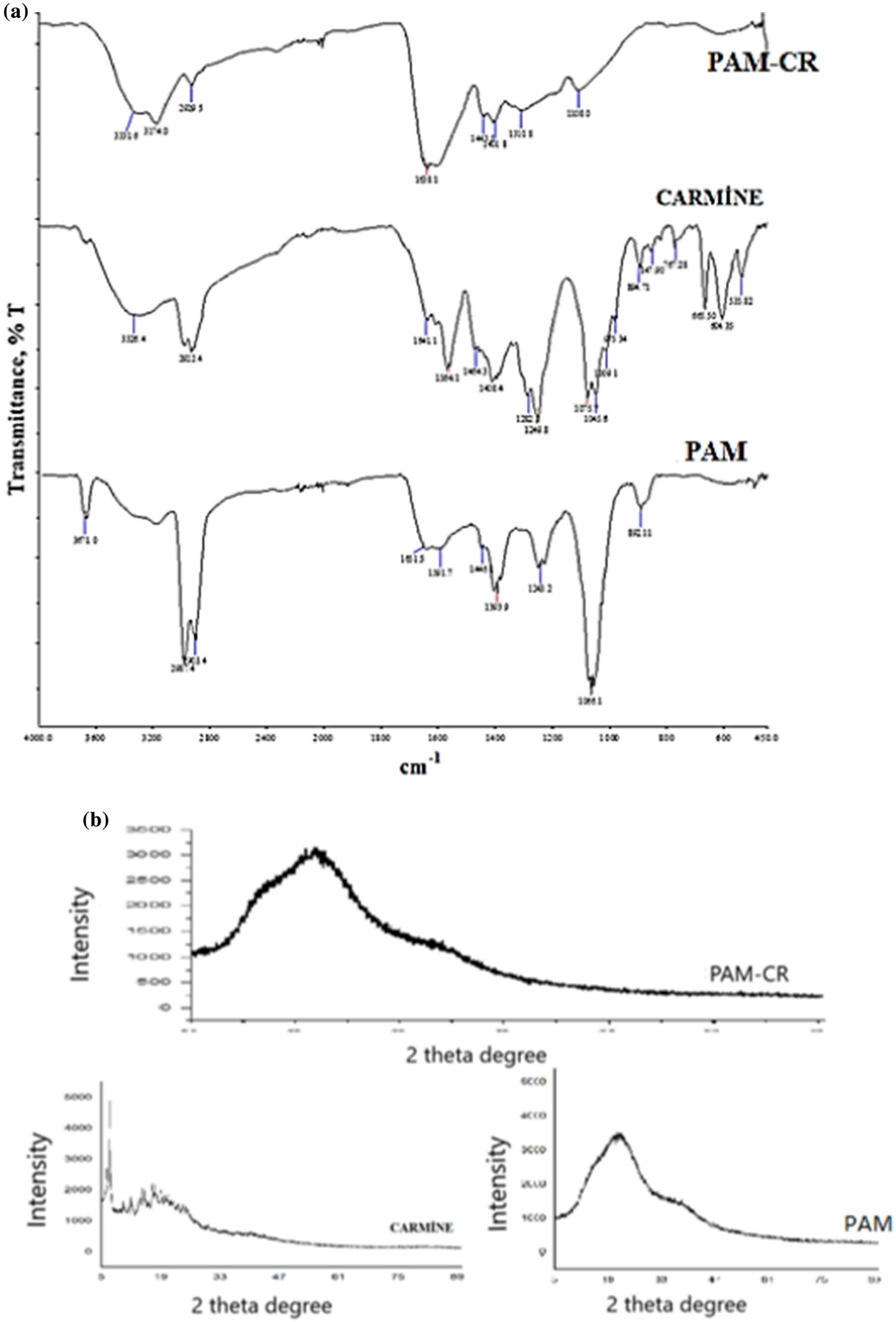

Fig. 1 **a** FT-IR spectrum of PAM, Carmine, PAM-CR. **b** XRD spectrum of new polymeric nanomaterials

the stretching and bending vibrations of the (C=C) group. The spectrum seen at 3174 cm^{-1} wavelengths is due to C-H asymmetric stresses. The spectrum at 2922.4 cm^{-1} is due to the OH^{-}, which is also seen in some organic structures, and the peak with a frequency of 3331 cm^{-1} originates from the asymmetric symmetric N–H bands.

In the analysis of the PAM-CR component performed by X-ray diffraction method, characteristic peaks of the Carmine dye material at 7, 10, 12, 14, 15, 17 and 19 2θ (theta) degrees are observed. Since the PAM component formed as a result of the treatment of acryl amide with a cross binder is polymeric and has an amorphous structure, it is seen Fig. 1b that significant peaks cannot be seen in XRD analysis and that the characteristic peaks of carmine dye have been damped.

In the images taken by scanning electron microscopy, specific cubic views of carmine substance are clearly displayed in Fig. 2. When looking at the images b, and c, it was seen that the initial cubic structures disappeared and a more general structure appeared after the distribution of the synthesis product and the carmine dye in the images of the final synthesis product PAM-CR components.

Optimization studies

Our main aim is to investigate the feasibility of the synthesized solid material for the adsorption of AI(III) and Cr(III) ions. To achieve this, important variables (pH, adsorption time, amount of polymer nanomaterial, type and volume of eluent, desorption time, sample volume) affecting the SPE procedure should be investigated and optimized. In all optimization studies, the amounts of analytes were taken as 75 µg L^{-1} and performed in triplicate. The optimization studies were carried out by with a one-at-a-time strategy. Percent recovery (R%) was used as a reference in optimization studies. Calculations related to the R% were made according to the following formula.

$$\mathrm{R}\ \% = \frac{C_{\mathrm{init}\,.}V_{\mathrm{init}} - C_{\mathrm{final}}.V_{\mathrm{final}}}{C_{\mathrm{init}}.V_{\mathrm{init}}} \times 100$$

where C_{init} amount of analyte in the initial sample volume V_{init}, and C_{final} amount of analyte in the phase of volume V_{final}.

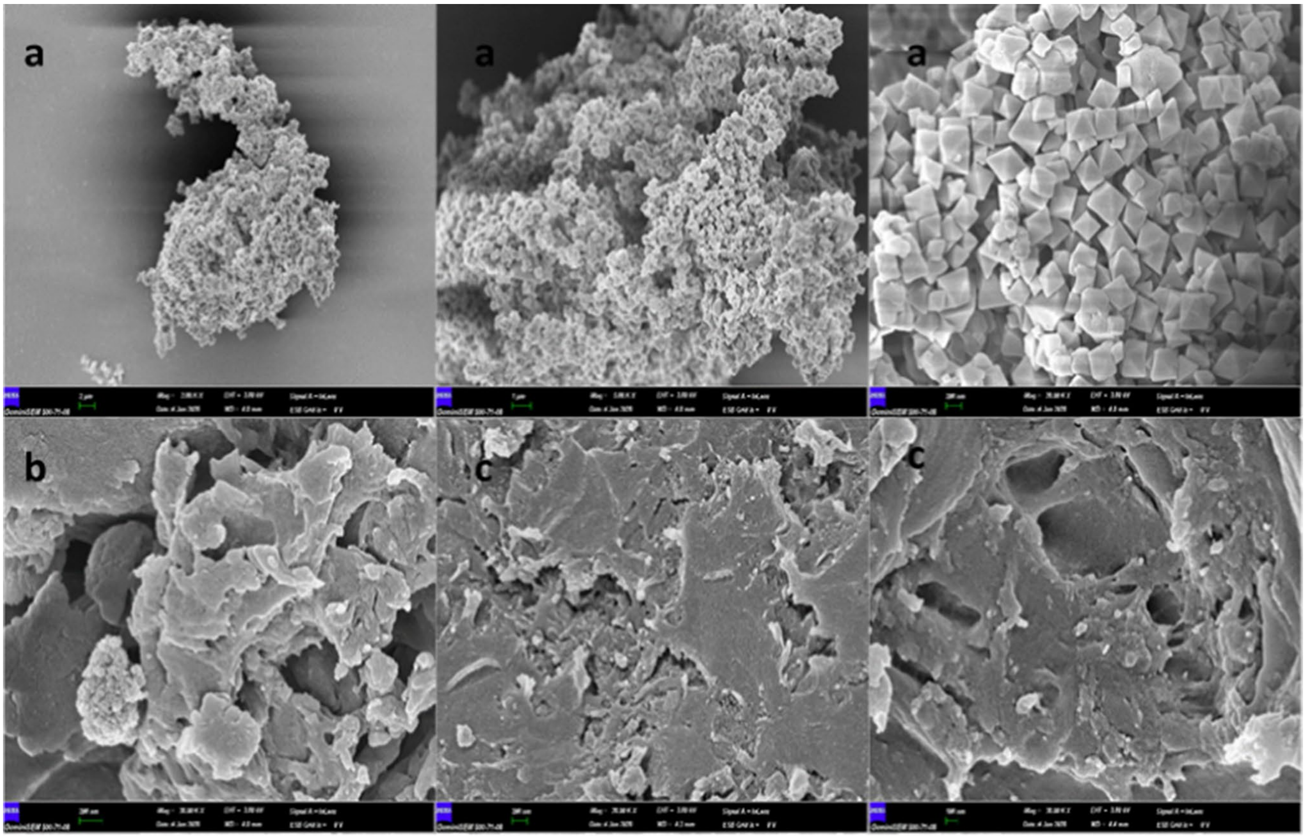

Fig. 2 SEM images of **a** Carmine (×2.0), (×5.0), (×10.0) **b** PAM (×20.0) **c** PAM-CR (×20.0), (×30.0)

Effect of pH

In the SPE procedure, the adsorption of Al(III) and Cr(III) ions to the polymer nanomaterial surface may also vary according to pH of sample solution since it is a chemical interaction. For this purpose, the effect of pH of sample solvent on the adsorption and recovery of Al(III) and Cr(III) ions was investigated in the range of pH 3.0–10.0 using different buffer solutions. As shown in Fig. 3a, the R% values of Al(III) and Cr(III) ions were sharply depends on the pH of the sample solution, so that quantitative recovery and adsorption of Al(III) and Cr(III) were provided pH in the range of 5.0–6.5. So, pH 5.0 of acetate buffer solution was chosen as the optimum pH for subsequent studies.

Effect of adsorbent amount

The second important factor to be optimized in this method is the adsorbent amount. If the adsorbent amount is insufficient, quantitative extraction of the target analytes cannot be done efficiently. Accordingly, unreliable results are obtained in analytical data such as recovery and relative standard deviation. The appropriate amount of adsorbent must be determined in order to obtain both cost and quantitative analytical data. The amount of PAM-CR in the model solution should be sufficient to allow the adsorption of Al(III) and Cr(III) ions onto the polymer nanomaterial. Furthermore, the adsorption effectiveness of the polymer nanomaterial is directly related to its amount. Therefore, to monitor the effect of the amount of the PAM-CR on the recovery of Al(III) and Cr(III), the PAM-CR in the range of 5–50 mg were added to the sample solution. The recovery % for both analytes was increased with increasing amount of the adsorbent in range of 5–50 mg and then remained constant at higher amounts. Figure 3b shows these analytical results. So, 30 mg was chosen as the PAM-CR amount for subsequent studies.

Effect of adsorption time

After adding the newly synthesized polymer nanomaterial to the model solution, the time required for the adsorption of the Al(III) and Cr(III) ions in the sample to PAM-CR should be optimized. If sufficient time is not determined, the Al(III) and Cr(III) ions cannot be adsorbed onto the PAM-CR and therefore no quantitative recovery can be achieved. In addition, an extraction procedure should be as fast and practical as possible. Ultrasound, shaking and vortexing were generally performed to ensure effective and short-term adsorption (Ulusoy et al. 2019; Yilmaz et al. 2015). In this context, the effect of adsorption time on the recovery of the Al(III) and Cr(III) ions was tested in the range of 5–60 min using ultrasonic bath. Results are shown in Fig. 3c. It had been found that adsorption time of 15 min was enough to establish the Al(III) and Cr(III) ions partition equilibrium between the sample solution and solid phases, and that after this time the recovery values of the Al(III) and Cr(III) ions were almost the same. So, 15 min of ultrasonic time was chosen as the adsorption time for subsequent studies.

Effect of eluent type and its volume

The solvent must be strong enough to could desorb all of the adsorbed analyte from the newly synthesized polymeric nanomaterial. In order to achieve optimum desorption conditions, different elution solutions were investigated and the highest recovery was obtained for the Al(III) and Cr(III) ions. In this context, 250 µL of the of different eluents solvents such as water, ethanol, methanol, pH 5 buffer solution, acetone, acetonitrile and 1 M HNO_3 was studied for desorption analytes from the PAM-CR. As shown in Fig. 3d, the highest recovery for both analytes was obtained in presence of methanol. So, methanol was chosen as the eluent solvent for subsequent studies. Optimization of the desorption solvent volume is a critical variable both for separating the Al(III) and Cr(III) ions from the PAM-CR and for achieving high sensitivity. The effect of methanol volume on desorption performance was investigated in range of 0.5–4.0 mL. The results (Fig. 3e) shown that the optimal desorption volume for both analytes was 2.0 mL. The recovery was decreased for both analytes in volumes greater than 2.0 mL. The main reason for this is the decrease in analyte concentration in the final volume due to the increasing eluent volume. So, 2.0 mL of methanol was chosen as the eluent volume for subsequent studies.

Effect of desorption time

In order to achieve quantitative recoveries and reproducible results, the Al(III) and Cr(III) ions adsorbed onto the PAM-CR should be completely passed to the aqueous phase prior to the FAAS determination. In this context, to determine the optimal desorption time for the analytes, vortex was applied in range of 10–180 s after addition of eluent solvent. As a result of experimental studies, quantitative recoveries for both analytes were obtained using vortexing 1 min. So, 1 min vortexing was chosen as the desorption time for subsequent studies.

Effect of sample volume

In order to obtain high preconcentration factor (PF) in microextraction studies, sample volume should be optimized. The PF is defined as the ratio of sample volume to final volume. The optimization of the sample volume was performed as follows. The vegetable samples prepared as described in the

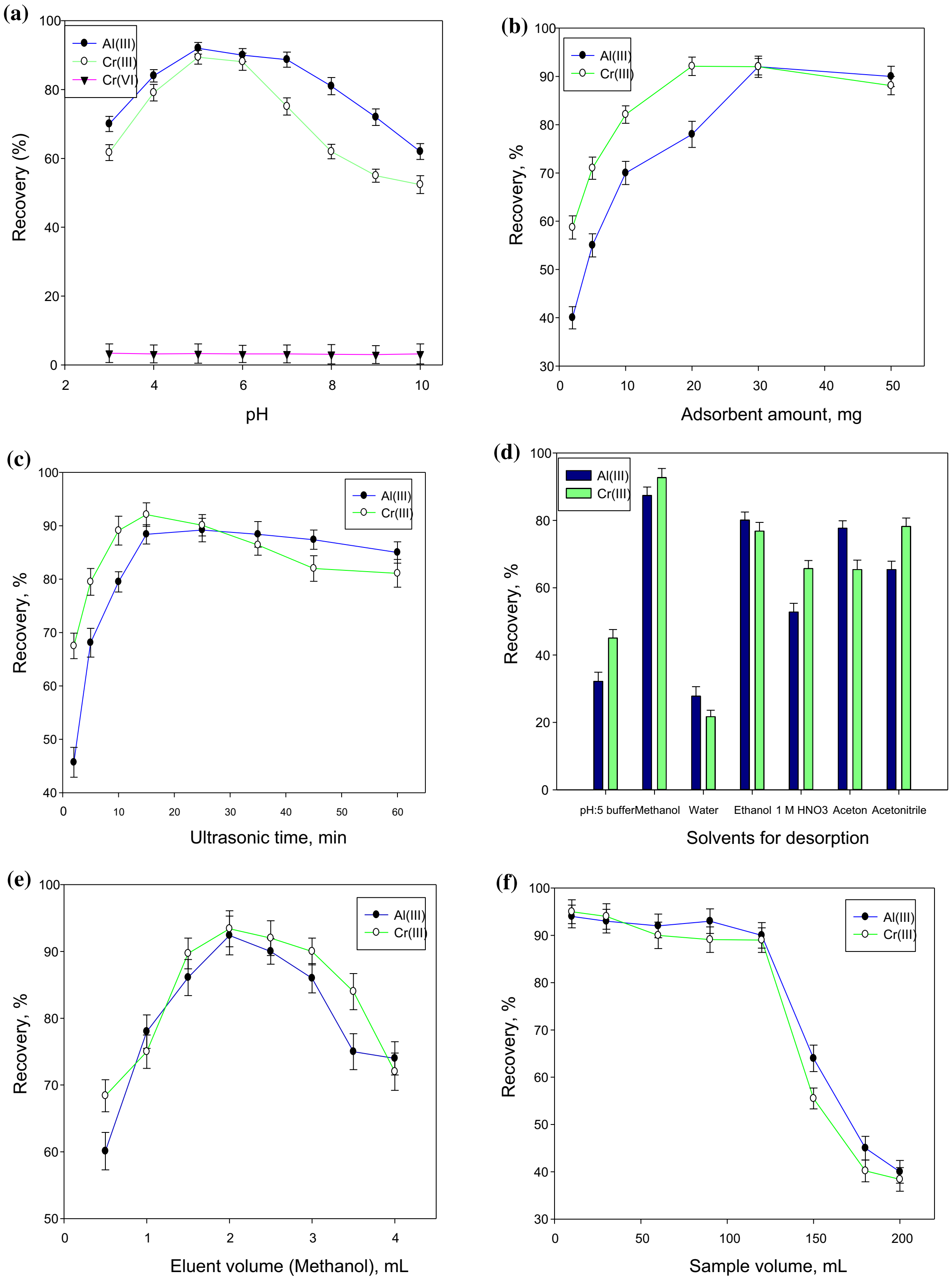

Fig. 3 **a-f** Results of the continued optimization studies for SPE procedure. Optimum conditions: pH 5.0; adsorbent amount, 30 mg: adsorption time, 15 min; desorption solvent type and volume, methnaol and 2.0 mL; sample volume; 120 mL, centrifuge rate and time; 4000 rpm and 3 min

microwave-assisted digestion are diluted with water to different volumes (20, 40, 60, 90, 120, 150 180 and 200 mL). Subsequently, the SPE procedure was applied to each sample diluted to different volumes. The results of the study are given in Fig. 3f. Quantitative recovery for both analytes was obtained in the sample volume range of 20–120 mL. However, at volumes higher than 120 mL, recoveries values were decreased from 95 to 35%. In view of the results obtained, the sample volume was taken as 120 mL to obtain high the PF. Based on the above definition, the PF was calculated as 60.

Regeneration and reusability

The economic indicator of the SPE procedure is how many times the PAM-CR can be used for the extraction of Al(III) and Cr(III) ions. In this regard, the reusability of the PAM-CR in adsorption–desorption experiments without significant change in adsorption capacity is an important feature. Under the optimum conditions obtained, the re-usability of 30 mg of the PAM-CR was tested in the adsorption–desorption experiments for 15 times. No significant change in the adsorption capacity was observed in the re-use of the synthesized PAM-CR 8 times for both analytes. Also quantitative recoveries were obtained for Al(III) and Cr(III) ions in these uses. However, after 8 times using, because the adsorption capacity of the PAM-CR was reduced, the recovery of the Al(III) and Cr(III) ions was decreased from 95 to 30%.

Matrix effect

The selectivity of the PAM-CR for the Al(III) and Cr(III) ions is another important variable that needs to be investigated, because model solutions were used for optimization of SPE steps. Therefore, the selectivity of the PAM-CR for Al(III) and Cr(III) ions was investigated in the presence of foreign ions. In this context, the possible foreign ions were added to the model solutions containing 50 µg L^{-1} Al(III) and Cr(III) ions and then the SPE procedure were applied. Tolerance concentration and recovery values were then calculated for each foreign ion. The tolerance concentration of foreign ions is defined as the ions concentration that causes relative error lower or greater than 5% with respect to the determination of Al(III) and Cr(III) ions. The results are summarized in Table 1. The high tolerance concentration and quantitative recoveries obtained from these studies indicate that the PAM-CR has high selectivity for Al(III) and Cr(III) ions. It is also clear from the results that there is no significant matrix effect.

Adsorption capacity

To investigate the adsorbent capacity, 30 mg of the PAM-CR was added to 120 mL of the sample solution containing the target ions. The obtained solution was vortexed for 30 min to ensure adsorption. The aqueous solution was filtered into another tube and the target ions were determined via FAAS.

Table 1 Results of selectivity study for 50 µg L^{-1} of Al(III) and Cr(III) ions of PAM-CR in the presence of foreign ions (N = 3)

Foreign ions	Added as	Al(III)		Cr(III)	
		*Tolerance concentration	Recovery (%)	*Tolerance concentration	Recovery (%)
K^+	KCl	2000	98 ± 2	2000	99 ± 3
Na^+	NaCI	2000	97 ± 3	2000	97 ± 2
F^-	NaF	2000	97 ± 3	2000	98 ± 2
NO_3^-	$NaNO_3$	2000	99 ± 2	1500	97 ± 3
Cl^-	NH_4Cl	1500	98 ± 3	1500	99 ± 3
Ca^{2+}	$CaCl_2$	1500	97 ± 3	1000	98 ± 2
HCO_3^-	$NaHCO_3$	1000	97 ± 3	1000	96 ± 2
PO_4^{3-}	Na_3PO_4	1000	96 ± 2	500	96 ± 3
Sr^{2+}	$Sr(NO_3)_2$	500	98 ± 3	100	96 ± 2
Ni^{2+}	$Ni(NO_3)_2$	500	98 ± 1	100	96 ± 1
Co^{2+}	$Co(NO_3)_2$	200	97 ± 1	200	98 ± 1
Sn^{2+}	$SnCI_2$	200	96 ± 3	200	97 ± 2
Zn^{2+}	$Zn(NO_3)_2$	200	97 ± 2	50	95 ± 2
Cu^{2+}	$Cu(NO_3)_2$	100	95 ± 2	50	95 ± 1
Cd^{2+}	$Cd(NO_3)_2$	100	96 ± 3	100	97 ± 3
Fe^{3+}	$Fe(NO_3)_3$	100	94 ± 2	250	98 ± 3
All ions above are mixed at equal concentrations		50	94 ± 1	100	96 ± 2

* mg L^{-1}

Next, the adsorption capacity was calculated using the formula below.

$$Qe = (Ci - Ce)\ V\ W^{-1} \tag{1}$$

where Qe (mg g^{-1}), V (mL), W (g), Ci (mg L^{-1}), and Ce (mg L^{-1}) were adsorbent capacity, sample volume, amount of the PAM-CR, the spiked target ions amount, and determined analytes amounts, respectively. Finally, the adsorbent capacity for Al(III) and Cr(III) was found as 91.5 mg g^{-1} and 118.6 mg g^{-1}, respectively.

Analytical performance

Analytical performance of the SPE procedure was determined following the optimum condition (pH 5.0, elution solvent, methanol; the PAM-CR amount, 30 mg; adsorption time, 15 min, desorption time, 1.0 min; stirring rate, 200 rpm, and elution solvent volume; 2.0 mL). The matrix matched solutions were utilized to determine the calibration curve and figures of merit of the SPE procedure. The matrix matched solutions were prepared by adding standard Al(III) and Cr(III) solutions at different concentrations to the prepared vegetable samples. The working ranges for Al(III) and Cr(III) were in the range of 0.2–400.0 µg L^{-1} and 1.0–500.0 µg L^{-1}, respectively. Detection (LOD) and quantification (LOQ) limits were calculated according to the formula the LOD = $3S_{blank}$/m and the LOQ = $10S_{blank}$/m, where s is the standard deviation of the blank solution and m is the slope of the calibration curve. The LOD and LOQ for Al(III) were 0.06 µg L^{-1} and 0.2 µg L^{-1}, respectively, while the same parameters for Cr(III) were 0.35 µg L^{-1} and 1.0 µg L^{-1}, respectively. Enrichment factor (EF), defined as the ratio of the slopes of the calibration curves obtained before and after the SPE, was 115 and 97 for Al(III) and Cr(III), respectively. In addition, the main quality parameters of the SPE procedure were described in Table 2.

The validation study is essential for the reliability of analytical results. In this context, validation of the SPE procedure was evaluated with certified reference material (CRM, Tea Leaves INCT-TL-1) containing analytes. The CRM was diluted before analysis to bring the analyte quantities to the detection limits of the proposed method. The result obtained for Al(III) and Cr(III) was good agreement compared to the certified value using a t-test at 95% confidence limits. There was a quantitative agreement between the standard addition amount and the measured analyte quantities. The recovery for Al(III) and Cr(III) was found to be in the range of 98.4–99% and 99.1–99.5%, respectively. These recovery values confirm that the SPE procedure is independent of the matrix effect. The comprehensive results of the validity study of the proposed method are given in Table 3.

The repeatability and reproducibility of the SPE procedure were evaluated by studies carried out for three different

Table 2 Analytical parameters for matrix-matched calibration solutions using the SPE procedure

Parameters	Al	Cr
Regression equation	$Abs = 0.0054C_{Al(III)} + 0.003$	$Abs = 0.0083C_{Cr(III)} + 0.007$
r^2	0.9973	0.9981
Working range, µg L^{-1}	0.2–400	1–500
LOD, µg L^{-1}	0.06	0.35
LOQ, µg L^{-1}	0.2	1.0
RSD (%) (N:10, 30 µg L^{-1})	2.0	2.3
Average recovery (%)	96.4	97.3
[a]PF	60	60
[b]EF	115	97

[a] PF were calculated as V_{sample} volume (120 mL) /V_{final} volume (2 mL)

[b] EF was calculated by using the ratio of calibration slopes before and after SPE

Table 3 Results for certified reference material (CRM, Tea Leaves INCT-TL-1) (N = 5)

CRM	Al (mg.kg^{-1})				Cr (mg.kg^{-1})			
	Added	Obtained value	Recovery (%)	* t_{exp}	Added	Obtained value	Recovery (%)	* t_{exp}
[a]Tea Leaves INCTTL-1	–	2240 ± 115	97.8	0.97	–	1.89 ± 0.8	98.9	0.56
	100	2338 ± 100	98.0	–	100	100.99 ± 3.7	99.1	–
	200	2438 ± 110	99.0	–	200	200.70 ± 5.8	99.4	–

[a]Certified value were 2290 ± 280 mg kg^{-1} for Al and 1.91 ± 0.22 mg kg^{-1} for Cr

*The t_{exp} was calculated by using $\mu = x_{average} \pm \frac{t.s}{\sqrt{N}}$ for five replicate measurements at a confidence interval of 95% (critical t-value is 2.31) concentrations of Al(III) and Cr(III) ions. This study was conducted for 5 µg L^{-1} (low), 100 µg L^{-1} (middle) and 300 µg L^{-1} (high) of Al(III) and Cr(III) ions. In the repeatability study, the selected concentrations were analyzed in triplicate in one day, while in the reproducibility study, the same concentrations were evaluated in triplicate analyzes on three consecutive days. In the repeatability study, the RSD value for Al(III) varied from 1.4% to 2.7%, while the RSD value for Cr(III) ranged from 1.3% to 2.9%. In addition, in the reproducibility study, the RSD value for Al(III) varied from 1.9% to 3.3%, while the RSD value for Cr(III) ranged from 1.7% to 3.8%.

Applications

Following the validation study, the applicability of the SPE procedure to vegetable samples was tested by standard addition. From the recovery results obtained in the range of 92.7–103.5% for analytes, it can be seen that the SPE procedure is applicable for the determinations and extractions of Al(III) and Cr(III) ions in the vegetable samples without a significant matrix effect. In addition to these results, obtaining low the RSD% values for Al(III) and Cr(III) ions emphasizes the effectiveness of the SPE procedure in applying to the vegetable samples. The analytical results are detailed in Table 4.

A method comparison should be made to more easily explain the analytical effectiveness of the SPE procedure. Therefore, the comparison of the SPE procedure to the other preconcentration procedure and detection techniques in the literature is given extensively in Table 5. As shown in Table 5, the SPE procedure was evaluated with other methods in terms of different analytical features such as working range, LOD, RSD (%), extraction time, recovery (%) and EF/PF. As it is understood from the results, the proposed method for both analytes had wide working range and quantitative recoveries comparable to expensive and expert user-requiring techniques. The LODs in the proposed procedure were generally lower than the other methods. Further, RSDs% were low, and EFs were relatively high. The most

Table 4 The amounts of analytes in vegetable samples after applying the SPE procedure (N = 5)

Samples	Added Al(III)/Cr(III) (µg L^{-1})	Al (Mean value ± standard deviation)			Cr (Mean value ± standard deviation)		
		Found (µg L^{-1})	RSD (%)	Recovery (%)	Found (µg L^{-1})	RSD (%)	Recovery (%)
Mushrooms	–	15.4 ± 0.4	2.6	–	57.9 ± 1.9	3.3	–
	50	63.2 ± 1.4	2.2	95.5	109.0 ± 2.8	2.6	102.2
	100	112.6 ± 2.3	2.0	97.2	159.4 ± 4.0	2.5	101.5
Spinach	–	88.2 ± 2.1	2.4	–	156.3 ± 3.7	2.4	–
	50	136.4 ± 3.2	2.3	96.3	204.0 ± 4.0	2.0	95.4
	100	186.8 ± 4.1	2.2	98.6	253.6 ± 4.6	1.8	97.3
Eggplant	–	102.6 ± 2.9	2.9	–	198.5 ± 7.7	3.9	–
	50	151.4 ± 4.0	2.7	97.5	246.0 ± 8.1	3.3	94.9
	100	201.0 ± 4.6	2.3	98.4	296.1 ± 8.9	3.0	97.6
Paprika	–	3.8 ± 0.8	2.1	–	76.3 ± 2.0	2.6	–
	50	50.4 ± 1.0	2.0	93.1	124.5 ± 2.8	2.2	96.3
	100	99.1 ± 1.7	1.7	95.3	174.8 ± 3.7	2.1	98.5
Cabbage	–	52.9 ± 1.4	2.6	–	152.3 ± 2.6	1.7	–
	50	101.1 ± 2.5	2.5	96.3	203.5 ± 3.1	1.5	102.4
	100	150.9 ± 3.0	2.0	98.0	253.2 ± 4.0	1.6	100.9
Broccoli	–	144.8 ± 5.4	3.7	–	66.4 ± 1.7	2.6	–
	50	196.2 ± 6.8	3.5	102.7	113.1 ± 2.6	2.3	93.3
	100	246.0 ± 7.6	3.1	101.2	162.9 ± 3.3	2.0	96.5
Zucchini	–	27.4 ± 0.5	1.8	–	10.5 ± 0.3	2.9	–
	50	76.2 ± 1.1	1.4	97.5	59.4 ± 1.5	2.5	97.7
	100	125.7 ± 2.6	2.0	98.3	108.8 ± 2.6	2.4	98.3
Leek	–	85.2 ± 3.3	3.9	–	144.8 ± 5.7	3.9	–
	50	136.4 ± 5.3	3.7	102.3	192.8 ± 6.2	3.2	95.9
	100	186.7 ± 6.5	3.5	101.5	242.2 ± 7.5	3.1	97.4
Carrot	–	91.5 ± 2.4	2.6	–	153.5 ± 4.0	2.6	–
	50	139.8 ± 3.5	2.5	96.6	202.3 ± 4.8	2.4	97.5
	100	188.9 ± 4.3	2.3	97.4	252.3 ± 5.7	2.3	98.8

Table 5 Comparison of the proposed method with literature values for the preconcentration and determination of Al and Cr

Sample type and analyte	Adsorbent	Preconcentration procedure	Detection system	Working range (µg L^{-1})	LODs (µg L^{-1})	EF/PF	RSD (%)	Recovery (%)	Time (min)	Refs
Al, hair samples		SM-SB-LLME	UV–VIS	2.5–150	0.47	30	0.3	94–101	20	(Khan and Soylak, 2015)
Cr, waters	ZnAl-ASP-LDH	DSPE	FAAS	10–700	3.13	–	2.95	–	16	(Leite et al. 2020)
Cr, blood samples		CP-DILLME	ET-AAS	0.02–1.7	0.0054	25.2	3.8	95–102	6	(Shirkhanloo et al. 2016)
Cr, Foods	*Bacillus altitudinis* immobilized nanodiamond	SPE	ICP-OES	0.25–12.5	0.023	80	4.4	95–97	–	(Özdemir et al., 2017)
Al, scalp hair		TIL-DLLME	FAAS	50–200	0.56	85	4.74	96.8–99.0	20	(Arain et al. 2015)
Al, water		CPE	FAAS	5–800	1.43	50	2.7	98.4–99.8	15	(Ulusoy et al. 2011)
Cr, Foods		M-IL-CIA-DLLME	FAAS	2–50	0.7	60	2.7	92–102	6	(Zeeb et al. 2013)
Al, Cr, Vegetables		VA-IL-DLLME	FAAS	0.1–100, 0.2–80	0.02, 0.05	95, 135	1.7, 1.9	96.7,103.2	7	(Altunay et al. 2018)
Cr, Natural water	Al_2O_3/nano-G	DSPE	EDXRF	2–50	0.04	–	3.5	92.2–96.5	12	(Baranik et al. 2018)
Cr, Waters and foods	Carbon-coated Fe_3O_4	MSPE	ICP-MS	–	0.002	37.5	9.4	87–106	8	(Habila et al. 2017)
Cr, Waters and foods	mGO/SiO_2@coPPy-Th	SPE	FAAS	1.0–50	0.36	36	6.3	92–102	20	(Molaei et al. 2017)
Al, Cr, vegetables	PAM-CR	SPE	FAAS	0.2–400, 1–500	0.06, 0.35	115, 97	2.0, 2.3	96.4, 97.3	18	Current study

VA-IL-DLLME: vortex-assisted ionic liquid-based dispersive liquid–liquid microextraction, M-IL-CIA-DLLME: modified ionic liquid cold-induced aggregation dispersive liquid–liquid microextraction, CPE: cloud point extraction, TIL-DLLME: temperature controlled dispersive liquid–liquid microextraction, SPE: solid-phase extraction, ICP-OES: inductively coupled plasma—optical emission spectrometry, ET-AAS: electro-thermal atomic absorption spectrometry, CP-DILLME: cloud point assisted dispersive ionic liquid–liquid microextraction, SDME: single drop microextraction, DRS-FTIR: diffuse reflectance Fourier transform infrared spectroscopic. SM-SB-LLME: supramolecular solvent-based liquid–liquid microextraction, UV–VIS: UV-Spectrophotometry; ZnAl-ASP-LDH: A zinc–aluminum layered double hydroxide intercalated with the amino acid L-aspartic acid, DSPE: dispersive solid-phase extraction, Al_2O_3/nano-G: Aluminum oxide-coated nano-graphite, EDXRF: Energy-dispersive X-ray fluorescence spectrometry, MSPE: Magnetic solid-phase extraction, ICP-MS: inductively coupled plasma mass spectrometry: mGO/SiO_2@coPPy-Th: SiO_2-coated magnetic graphene oxide modified with a pyrrole-thiophene important reason of high PF/EF is to use special ligands in the polymer nanomaterial synthesis process.

Conclusions

In this study, the newly polymeric nanomaterial as a potential solid-phase material was synthesized, characterized and used as useful solid phase for simultaneous pre-concentration and separation of Al(III) and Cr(III) ions from vegetable samples before their determination by flame-AAS. The ultrasonic effect was utilized for the adsorption of analyte ions to the solid phase. The innovations of our method can be listed as follows. (I) This is the first application of the PAM-CR for simultaneous preconcentration of Al(III) and Cr(III) ions. (II) The consumption of chemicals is quite low, which makes green chemistry properties more prominent. (III) The PAM-CR exhibits good chemical stability and reusability. (IV) Since there is no heating step, the extraction time of this study is shorter than liquid–liquid extraction methods. It has been shown that the new solid material formed by immobilizing an inert polymer, PAA hydrogel, can be used in enrichment studies of Al(III) and Cr(III) ions. Considering the structure of the carmine dye, the presence of electronegative regions formed by the large number of oxygen atoms it carries indicates that it has an interaction potential with cations. It is thought that the carmine dye, which is taken into the matrix of Al(III) and Cr(III) ions, binds through these electronegative atoms that have not interacted with the polymer (Dapson 2007). Finally, it can be said that the SPE procedure could be successfully applied to the determination and pre-concentration of Al(III) and Cr(III) ions in vegetables (mushrooms, spinach, eggplant, paprika, cabbage, broccoli, zucchini, leek, and carrot) with acceptable accuracy and high precision. The results from real samples suggested that the SPE-FAAS method could be used as a simple and effective method for simultaneous preconcentration and determination of Al(III) and Cr(III) in complex matrices. As far as we know, this nanomaterial synthesized is the first application for the simultaneous extraction and determination of Al(III) and Cr(III).

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Declarations

Conflict of interest The authors have declared that there is no conflict of interest.

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