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# Solid-phase extraction for simultaneous separation and preconcentration of Fe (III) and Zn(II) traces using three chelatants and Ramelak bark-derived activated carbon as a new bio-sorbent

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## ABSTRACT

This article introduces a comparative study for the simultaneous separation and preconcentration of Fe (III) and Zn(II) traces in various water samples using three well-known ligands as chelating agents and activated carbon (AC) derived from Ramelak bark as a new bio-sorbent prior to the determination by flame atomic absorption spectrometry. The chelating agents were 4,4'-[(4-Cyano-phenyl)methylene]bis (3-methyl-1-phenyl-1H-pyrazol-5-ol) (CMBM), diethyldithiocarbamate (DDTC) and ammonium pyrrolidine dithiocarbamate (APDC). CMBM was synthesized by a procedure reported in the literature. The newly prepared AC was characterized by Scanning Electron Microscopy (SEM) and Fourier-Transform Infrared (FTIR) Spectrometry. The analytical parameters affecting the separation efficiency of the analytes including pH, shaking time, chelating agent volume (concentration), sorbent mass, sample flow rate and elution conditions were investigated and discussed. Common coexisting ions did not seriously interfere with the separation, showing the good selectivity of the proposed method. The calibration graph was linear in the range of 0.35–70, 0.50–80, 0.9–100, 0.55–75, 0.75–90 and 1.0–120 ng mL<sup>-1</sup> for Fe-CMBM, Fe-DDTC, Fe-APDC, Zn-CMBM, Zn-DDTC and Zn-APDC, respectively. Under optimized conditions, the limits of detection were 0.11, 0.13, 0.27, 0.16, 0.22 and 0.30 ng mL<sup>-1</sup> for Fe-CMBM, Fe-DDTC, Fe-APDC, Zn-CMBM, Zn-DDTC and Zn-APDC, respectively. The proposed method has been applied to the determination of Fe(III) and Zn(II) in different water samples with satisfactory recovery percentages. The developed method, validated with standard reference materials, was used successfully in determining the concentrations of metal ions in water samples.

## KEYWORDS

Activated carbon; biosorbent; flame atomic absorption spectrometry; iron(III); solid-phase extraction; zinc(II)

## Introduction

In recent years, the release of various harmful heavy metal ions into the environment has attracted great attention worldwide because of their toxicity and widespread use. Trace metals play an important role in human metabolism and either excess or deficiency of them in the living organism can lead to biological disorder.<sup>[1]</sup> Iron is vital for almost all living organisms due to the fact that it occurs in a wide variety of metabolic processes, including oxygen transport, DNA synthesis and electron transport. However, iron concentrations in body tissue must be carefully regulated, because excessive iron leads to tissue damage as a result of the formation of free radicals.<sup>[2]</sup> Zinc is an essential element in the nutrition of animals and humans. It works with the enzymes that make genetic material, manufacture heme, digest food, metabolize carbohydrate, protein and fat, liberate vitamin A from storage in the liver and dispose of damaging free radicals.

Zinc is a relatively nontoxic element; however, it can be toxic if consumed in large quantities. A high zinc intake is known to produce copper-deficiency anemia by inducing the intestinal cells to synthesize large amounts of a protein that captures copper in a nonabsorbable form.<sup>[3]</sup>

The interest in the determination of trace heavy metal ions, such as iron and zinc, in environmental waters has increased immensely during the last few decades because of environmental problems and public health studies. Therefore, the monitoring of environmental pollutants, such as iron and zinc, at trace or ultra-trace levels in different environment matrices directly related to human health has a high importance. It thus needs the effective preconcentration and selective separation of trace Fe(III) and Zn(II) from natural waters.

Solid-phase extraction (SPE) is one of the most employed preconcentration methods that can be applied

in offline or online systems, with the advantage of possible automatization. SPE consists of the retention of metal species (or their derivatives) on an appropriate solid sorbent packed in a column or microcolumn and its later desorption with the adequate solvent. Thus, the concentration and separation of the analyte from the rest of the sample matrix are achieved.<sup>[4]</sup> Owing to its flexibility, absence of emulsion, simplicity, sampling in the field, safety and ease of automation, SPE is a preferred method for the separation and enrichment of the target. SPE requires that the adsorbent possess a strong, selective adsorption ability.<sup>[5]</sup>

Activated carbon (AC) is one of the most frequently used adsorbents for the removal of metal ions from aqueous solution due to its large surface area, high adsorption capacity, porous structure, selective adsorption and high purity standards. However, without any surface treatment, AC presents an insufficient adsorption capacity for metal ions,<sup>[6]</sup> because metal species exist in solution either as simple ions or as hydrous ionic complexes. For this reason, modification and impregnation techniques have long been used to increase surface adsorption and to add removal capacity and selectivity to AC. Thus, several recent reports concern the modification techniques of AC with chelating collectors for metal ions, namely Cu(II), Co(II), Cd(II), Mn(II), Ni(II), Fe(III), Zn(II) and Pb(II), used to increase the adsorption capacity, metal enrichment and selectivity.<sup>[7–21]</sup>

This work presents the preparation of a new kind of AC from Ramelak tree bark as a new bio-sorbent for the adsorption of Fe(III) and Zn(II) from aqueous solutions. In fact, various, abundant biological materials can be used to remove, at very low cost, even small amounts of toxic heavy metals from effluents. The newly prepared AC was characterized by Scanning Electron Microscopy (SEM) and Fourier-Transform Infrared (FTIR) Spectrometry. A comparative study for the simultaneous separation and preconcentration of Fe(III) and Zn(II) traces using three chelating agents, namely 4,4'-[(4-Cyano-phenyl)methylene]bis(3-methyl-1-phenyl-1H-pyrazol-5-ol) (CMBM), diethyl-dithiocarbamate (DDTC) and ammonium pyrrolidine dithiocarbamate (APDC) using the SPE procedure, was performed. CMBM was synthesized according to a procedure reported in the literature<sup>[22]</sup> with a slightly different catalyst. Finally, after retaining metal ions onto the sorbent and desorption by a suitable eluent, the eluent was analyzed for the determination of metals by Flame Atomic Absorption Spectrometry (FAAS). Parameters that can affect the adsorption and elution efficiency of the metal ions were studied. Furthermore, the method was applied to different water samples and validated with certified reference materials.

## Materials and methods

### Instrumentation

A Metrohm pH-meter with a combined glass-calomel electrode (model 691, Switzerland) was used in order to adjust the pH at desirable values. A Chemtech Analytical Instrument model CTA-3000 atomic absorption spectrometer (Bedford, England) equipped with a flame burner was used for the analysis of the metals; the lamp current (5 mA) and wavelengths (248.3 nm for Fe and 213.9 for Zn) were those recommended by the manufacturer. All metals were determined under optimized operating conditions by FAAS with an air-acetylene flame. The FTIR spectra (KBr) were recorded on an FT-IR JASCO 460 Plus spectrometer. <sup>1</sup>H and <sup>13</sup>C NMR spectra were obtained using a Bruker AVANCE-DRX-400 instrument at 400 MHz and 100 MHz, respectively (in DMSO-d<sub>6</sub>,  $\delta$  in ppm and J in Hz). Elemental analyses (C, H and N) were performed with a Heraeus CHN-O-Rapid analyzer.

The shape and surface morphology of the AC were investigated with a field emission scanning electron microscope (FE-SEM, Hitachi S4160) under an acceleration voltage of 15 kV.

### Synthesis and characterization of 4,4'-[(4-Cyano-phenyl)methylene]bis(3-methyl-1-phenyl-1H-pyrazol-5-ol)

Here, we introduce an efficient method for the synthesis of CMBM, using readily available starting materials, catalyzed by the supported ionic liquid, [(EtO)<sub>3</sub>Sipmim] HSO<sub>4</sub> SiO<sub>2</sub> [silica supported 1-methyl-3-(triethoxysilylpropyl)imidazolium hydrogen sulfate]. This well-known ionic liquid acts as a 'green catalyst' and can be recycled. Briefly, 2.0 mmol of 5-methyl-2-phenyl-2,4-dihydro-3H-pyrazol-3-one, 1.0 mmol of aromatic aldehyde in the presence of 0.15 g of [(EtO)<sub>3</sub>Sipmim] HSO<sub>4</sub> SiO<sub>2</sub> was completely dissolved in 12 mL of ethanol. Afterward, the solution was heated up to 80 °C and stirred thoroughly under reflux. Following the end of the reaction, verified by thin layer chromatography (TLC), the compound was filtered. Solidification was accelerated by cooling. The product was rinsed and recrystallized from ethanol. The yield was 91% and the melting point was 205–208°C.<sup>[22]</sup>

The characterization of CMBM gave the following information:

IR: 3481 (OH), 3055 (CH arom), 2900 (CH aliph), 2205 (CN), 1607 (C=C), 1498 (C=C), 1410, 1290 (C=N), 2100 (CN), 1018, 830, 790, 745, 670 cm<sup>-1</sup> (Fig. S1)

<sup>1</sup>H NMR:  $\delta$  (ppm, from TMS) = 2.31 (6H, s, 2 CH<sub>3</sub>), 4.96 (1H, s, CH), 7.23 (2H, t, J = 8.5 Hz, 2 CH), 7.43–7.46

(6H, m, 6 CH), 7.71–7.73 (6H, m, 6 CH), 13.96 (1H, br.s, OH) (Fig. S2).

$^{13}\text{C}$  NMR:  $\delta$  (ppm, from TMS) = 12.01 ( $\text{CH}_3$ ), 33.27 (CH), 104.48 (C), 121.17 (C), 121.70 (C), 122.22 (CH), 126.31 (CH), 129.44 (CH), 130.17 (C), 134.82 (CH), 137.49 (CH), 145.01 (C), 146.78 (C), 148.24 (C) (Fig. S3).

The IR,  $^1\text{H}$ -NMR and  $^{13}\text{C}$ -NMR spectra are shown in Figs. S1, S2 and S3, respectively, in the Supporting Information.

### Standard solutions and reagents

Reagents of analytical and spectral purity were used for all experiments and doubly distilled water was used throughout. Standard labware and glassware were repeatedly cleaned with  $\text{HNO}_3$  and rinsed with double-distilled water, according to a reported procedure.<sup>[7]</sup>

Acids and bases of the highest purity (99%, from Merck, Darmstadt, Germany) were used as received. Stock solutions ( $1000 \text{ mg L}^{-1}$ ) of Fe(III) and Zn(II) were prepared by dissolving appropriate amounts of  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$  (Merck, 99.0%) and  $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  (Merck, 98.5%) in doubly distilled water, respectively. The stock solutions were diluted with doubly distilled water. Nitrate salts of lead, cadmium, mercury, cobalt, nickel, copper, zinc, magnesium, calcium, barium, silver, sodium and potassium (all from Merck, 99%) were of the highest purity available and used without any further purification. DDTc and APDC were purchased from Sigma-Aldrich.

### Preparation of AC

Ramelak barks collected from Yasouj City environment were washed with tap water, dried and ground in a laboratory mill, and then dried again. The dried precursors were soaked in 45 wt.%  $\text{H}_3\text{PO}_4$  (as a chemical activating agent) overnight at a ratio of 2.3:1 ( $\text{H}_3\text{PO}_4$ : Ramelak, wt./wt.), carbonized and activated in a muffle furnace at  $450^\circ\text{C}$  for 60 min, then allowed to cool naturally to room temperature. The produced material was washed with distilled water until a constant near-neutral pH was observed, and then dried at  $105^\circ\text{C}$  for 8.0 h and allowed to cool to room temperature.<sup>[23]</sup>

### Preparation of the column

Prepared AC was loaded into a  $10 \text{ mm} \times 150 \text{ mm}$  glass column blocked by glass frit resin supports at both ends. Before each use,  $2.0 \text{ mol L}^{-1}$   $\text{HNO}_3$  solution and water were passed through the column in order to clean it. Then, the column was conditioned to the desired pH values with buffer solutions. The column was conditioned

with distilled water during the passing time for the next experiment.

### Preconcentration procedure

After the loading of a desired mass of sorbent into the column and preconditioning with a buffer solution, a series of standard or sample solutions containing Fe (III) and Zn(II) were transferred into a 25 mL beaker. The chelating agents were then added to form the metal–ligand complexes. After that, the solutions were adjusted to the desired pH values and passed through the column gravitationally. Afterwards, the metal–ligand complexes retained on AC were eluted with  $2.0 \text{ mol L}^{-1}$   $\text{HNO}_3$  solution and the analytes were determined by FAAS.

### Sample preparation

The water samples including well water, spring water and tap water were collected from Yasouj, Iran. Before the analysis, the samples were filtered through PTFE Millipore filter of pore size  $0.45 \mu\text{m}$ . The organic content of the water samples was oxidized in the presence of 1.0%  $\text{H}_2\text{O}_2$  and concentrated nitric acid. After acidification to 1.0 % with concentrated nitric acid, they were stored in polyethylene bottles. After adjusting to the desired pH values, the solutions were passed through the column gravitationally. Subsequently, the procedure in the above section was applied.

## Results and discussion

### AC characterization

The SEM images of the AC surface depict the porous and rough surface of the AC, which is suitable for adsorption (Fig. 1). The FTIR spectrum in the  $4000\text{--}400 \text{ cm}^{-1}$  wave number range (Fig. 2) shows the functional groups and surface properties of the adsorbent. The peak obtained at  $3459.5 \text{ cm}^{-1}$  corresponds to the free and intermolecular bonded hydroxyl groups. Peaks around  $1608 \text{ cm}^{-1}$  are assigned to C=O stretching. The peaks at  $1450.7 \text{ cm}^{-1}$  indicate the C=C groups present in AC. The peak around  $877 \text{ cm}^{-1}$  (C-H bending) shows the presence of benzenoid rings on the surface of AC.

### Effect of pH on sorption

The pH value plays an important role with respect to the adsorption of different ions on the oxide surfaces. Solution acidity affects metal ion adsorption: in acid medium, the binding sites of the chelating agents are



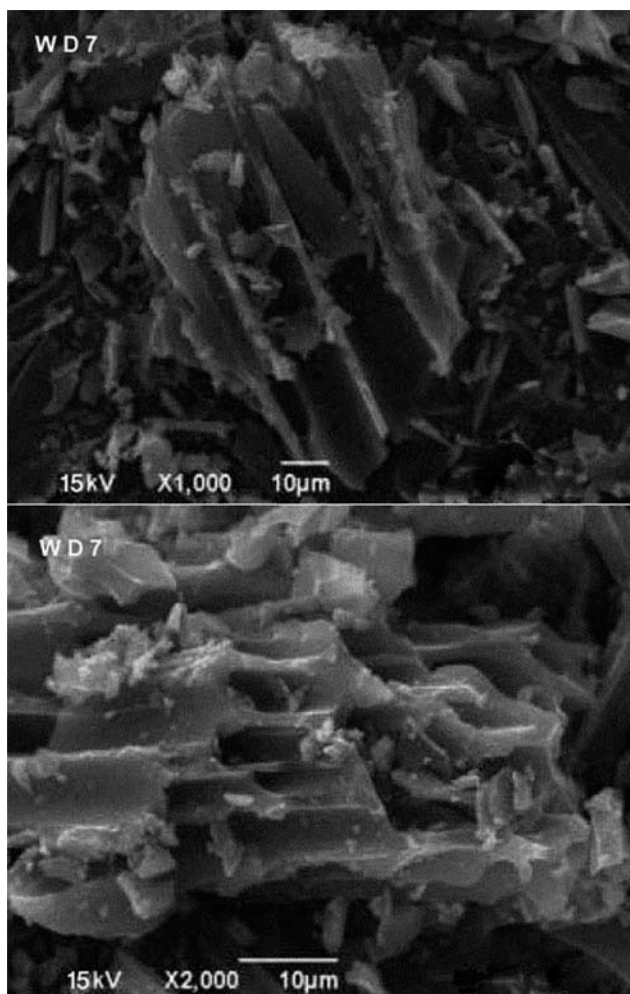


Figure 1. SEM images of activated carbon.

protonated, and, in alkaline medium, hydroxide may complex and precipitate many metals.<sup>[6]</sup> Therefore, pH is the first parameter to be optimized. To evaluate the effect of pH, two metal ions, *viz.* Fe(III) and Zn(II),

were tested and determined at different pH values in the range of 1–8 with the three chelating agents. The results are shown in Fig. 3.

Several trends are notable. The metal capacity value strongly depends on pH and first increases with pH. At lower pH values, the complexation is incomplete, probably because of the competition between metal and hydrogen ions for ligand binding. Then, the metal recovery values (>95%) of Fe(III) and Zn(II) are at maximum in the pH range 3.0–5.0. Hydrolysis rate of metal ions increases with pH and metal ion concentration. That is why a fixed pH value cannot be stated for the starting of aqua Zn(II) and Fe(III) hydrolysis. To avoid hydrolysis at higher pH and determine these elements simultaneously, pH 4.0 was chosen for further studies.

#### Effect of the amount of chelating agent

To determine the amounts of ligand required for quantitative recoveries of Fe(III) and Zn(II) ions, the effect of various quantities of chelating agents (CMBM, DDTC and APDC) on the retention of metal ions was examined.

As presented in Fig. 4, the recoveries of analytes increase with increasing amounts of ligand added and reach quantitative values (over 95%) with at least 4.0 mL, 3.0 mL and 2.0 mL of CMBM (reported here as PMBP), DDTC and APDC, respectively. Therefore, these values were recommended as optimum ligand values for quantitative recoveries. At lower concentrations, the amount of ligands is insufficient to extract all the analytes from the solution. On the other hand, further addition of ligand shows no significant change on metal recovery. The fact that different minimum amounts of ligand are needed to achieve the maximum

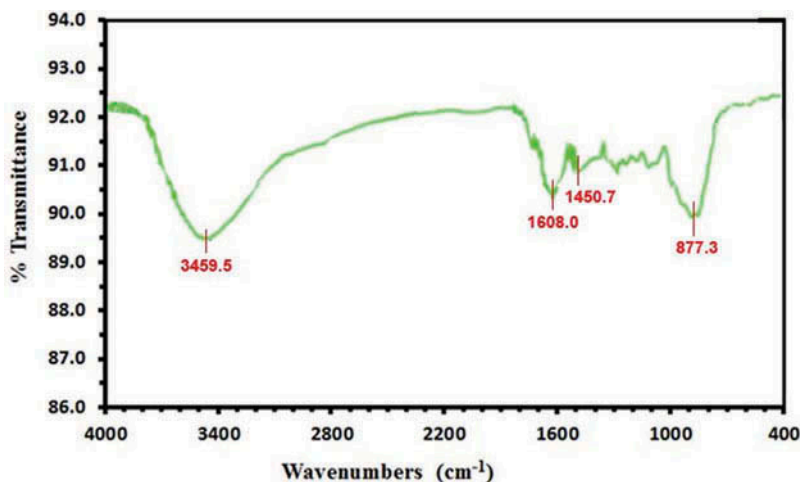


Figure 2. IR characterization of activated carbon.

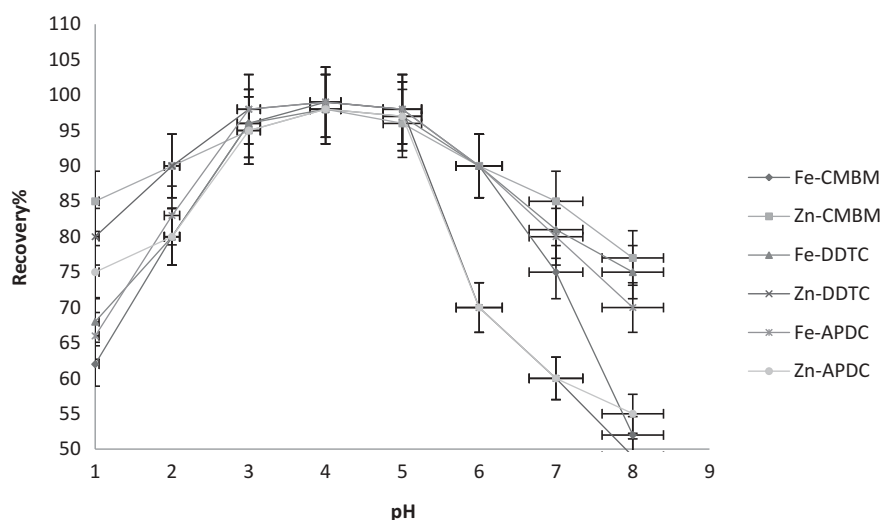


Figure 3. Effect of pH on the recoveries of the metal ions (N = 3.0).

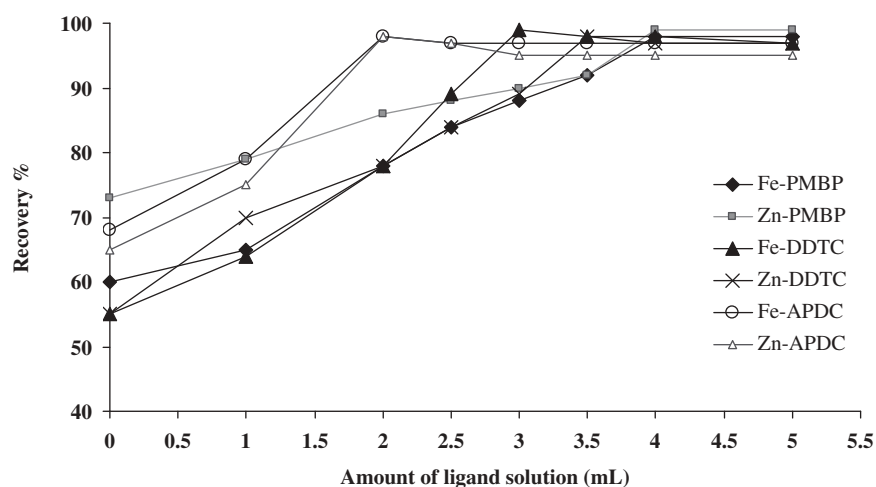


Figure 4. Effect of amount of ligand solution on the recoveries of analytes (N = 3.0).

extraction rate of a given metal ion is due to the conditions of electron transfer between the metal ion and the ligand (nature and number of electron donors in the ligand).

#### Effect of eluent type and volume

A suitable eluent should effectively elute the analytes from the column with small volume. Various eluting solutions, such as HCl, HNO<sub>3</sub> and H<sub>3</sub>PO<sub>4</sub> at various concentrations, were examined to identify the best eluent for the adsorbed metal complex-activated carbon (ML-AC). The results are summarized in Table 1. The results indicate that a concentration of 2.0 mol L<sup>-1</sup> HNO<sub>3</sub> is sufficient for quantitative elution (>95%). Subsequently, the influence of eluent volume (1.0–8.0 mL) on the recoveries was studied by using 2.0 mol L<sup>-1</sup>

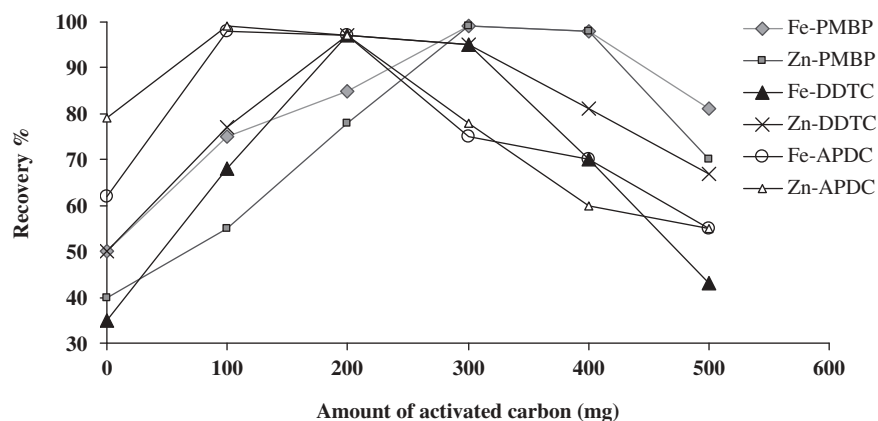
HNO<sub>3</sub>. It is obvious that 5.0 mL of 2.0 mol L<sup>-1</sup> HNO<sub>3</sub> in acetone is sufficient for the quantitative recovery of adsorbed analytes from AC.

#### Effect of the amount of AC

In the adsorption step, an appropriate amount of solid phase filled to column should be used to obtain quantitative retention of metal. This amount is thus a main parameter for the quantitative recoveries of analytes. However, it is also notable that the adsorbent mass has a significant effect on removal efficiency. In fact, an excess amount of adsorbent can prevent the quantitative elution of the retained metals by a small volume of eluent.<sup>[24]</sup> As can be seen in Fig. 5, the retention of the metal ions increases on increasing the adsorbent mass, and then decreases above an optimum value. In

**Table 1.** Effect of various eluents on analyte ion recoveries. (Optimum conditions: pH: 4.0; Eluent: 5.0 mL; Sample volume: 500 mL; Sample and eluent flow rates: 3.0 mL min<sup>-1</sup>, N = 3.0).

Eluent	Recovery (%)					
	CMBM		DDTC		APDC	
	Fe(III)	Zn(II)	Fe(III)	Zn(II)	Fe(III)	Zn(II)
1.0 mol L <sup>-1</sup> HNO <sub>3</sub> in acetone	92.1 ± 0.6	90.9 ± 1.0	96.7 ± 0.8	91.4 ± 0.7	94.6 ± 0.9	92.1 ± 1.2
1.5 mol L <sup>-1</sup> HNO <sub>3</sub> in acetone	95.4 ± 0.9	94.5 ± 0.8	97.1 ± 0.6	95.1 ± 0.6	93.1 ± 0.5	91.1 ± 0.8
2.0 mol L <sup>-1</sup> HNO <sub>3</sub> in acetone	99.4 ± 2.3	98.3 ± 3.1	99.4 ± 0.8	98.5 ± 1.3	97.9 ± 0.9	99.5 ± 0.7
1.0 mol L <sup>-1</sup> HCl	81.1 ± 0.7	86.2 ± 1.8	90.8 ± 0.9	88.4 ± 0.8	89.2 ± 1.0	89.2 ± 0.7
1.5 mol L <sup>-1</sup> HCl	85.4 ± 0.6	89 ± 0.8	90.8 ± 0.9	88.1 ± 0.8	92.4 ± 1.1	95.1 ± 0.8
2.0 mol L <sup>-1</sup> HCl	90.4 ± 1.0	91.4 ± 1.1	90.8 ± 1.1	91.4 ± 0.7	93.2 ± 1.0	96.1 ± 1.0
2.0 mol L <sup>-1</sup> HCl in acetone	94 ± 0.6	96.3 ± 0.9	93.5 ± 1.2	94.4 ± 0.6	93.5 ± 0.9	96.8 ± 1.1
1.0 mol L <sup>-1</sup> H <sub>3</sub> PO <sub>4</sub>	65 ± 1.0	75 ± 1.3	63.8 ± 0.9	64.3 ± 0.8	72.2 ± 1.1	76.6 ± 1.0
1.5 mol L <sup>-1</sup> H <sub>3</sub> PO <sub>4</sub>	75.5 ± 0.9	74.6 ± 0.9	70.3 ± 1.1	71.4 ± 0.7	69.2 ± 1.0	75.1 ± 1.0
2.0 mol L <sup>-1</sup> H <sub>3</sub> PO <sub>4</sub>	79 ± 1.1	77 ± 1.0	81.4 ± 1.0	83.4 ± 0.8	83.5 ± 1.0	86.7 ± 1.1



**Figure 5.** Effect of amount of activated carbon on the recoveries of analytes (N = 3.0).

fact, it makes sense that a sufficient amount of adsorbent should be used to ensure quantitative retention of the metal ion, but also that an excess of sorbent prevents the quantitative elution of the retained metal. Quantitative recovery values for the examined analytes were obtained in the ranges of 300–400 mg for CMBM, 200–300 mg for DDTC and 100–200 mg for APDC. Therefore, in further experiments, the column was filled with 300, 200 and 100 mg for CMBM, DDTC and APDC, respectively.

### Effect of sample volume

To explore the possibility of adsorbing low concentrations of analytes from large volumes of solution, the effect of sample volume on the retention of metal ions was also investigated. To study the preconcentration factor, various volumes of sample solutions (50, 100, 200, 300, 400 and 500 mL) containing each Fe(III) and Zn(II) complexes with chelating agents were passed through the column with the optimum flow rate. Quantitative recovery (>95%) was obtained for the sample volume of 500 mL for Fe(III) and Zn(II) and, for larger volumes, the recovery percentages decreased.

The decreased recovery with increasing sample volume may be due to the low concentration of metal ions in the solution.<sup>[25]</sup> Therefore, a volume of 500 mL of sample solution was adopted for the preconcentration of analytes. The adsorbed metal ions could be eluted with 5.0 mL of 2.0 mol L<sup>-1</sup> HNO<sub>3</sub> in acetone, so the preconcentration factor achieved by this method was calculated as 100.

### Flow rates of sample and eluent solutions

The flow rate of the sample solution affects the retention of cations on the adsorbent and the duration of complete analysis. Therefore, the effect of the flow rate of sample solution on the recoveries of metal complexes on AC was examined in the range of 1.0–5.0 mL min<sup>-1</sup>. It was found that, under the optimum conditions (pH, eluent, etc.), when the flow rates of the sample and eluent solutions were in the range of 1.0–3.0 and 1.0–4.0 mL min<sup>-1</sup> the recoveries of the analytes were quantitative. At higher flow rates, there was a decrease in the recovery because of a too short contact time between the AC and the sample solution.<sup>[26]</sup> Thus, a flow rate of 3.0 mL min<sup>-1</sup> was employed in this work.



## Adsorption capacity

The adsorption capacity is an important factor in that it determines how much adsorbent is required to quantitatively remove a specific amount of metal ions from the solutions. The capacity of AC for the adsorption of Fe(III) and Zn(II) ions was studied by passing 500 mL portions of aqueous solutions containing 100 mg of Fe-CMBM-AC, Fe-DDTC-AC, Fe-APDC-AC, Zn-CMBM-AC, Zn-DDTC-AC and Zn-APDC-AC at optimal pH through the column. The results show that the adsorption capacity of various metal ions probably differ due to their size, degree of hydration and value of their binding constant with the adsorbent. The maximum adsorption capacities have been found to be 65.8, 56.1, 43.7, 65.8, 56.1 and 43.7 mg g<sup>-1</sup> for Fe-CMBM-AC, Fe-DDTC-AC, Fe-APDC-AC, Zn-CMBM-AC, Zn-DDTC-AC and Zn-APDC-AC, respectively, as shown in Table 2.

## Effect of foreign ions

In order to assess the possible analytical applications of the recommended preconcentration procedure, the effect of some foreign ions on the adsorption of Fe(III) and Zn(II), which could interfere with their determination, was investigated. A tolerable limit was defined as the highest amount of foreign ions that produced recovery error not exceeding 5.0% by the combination of SPE and atomic absorption spectrometric determination. The results are presented in Table 3 and prove that the ions, up to a 1800-fold concentration in the most favorable cases, do not have any meaningful interference: this high selectivity enables accurate and precise determination of Fe(III) and Zn(II) ions in water samples.

**Table 2.** Effect of the interference of some ions (N = 3.0).

Ions	Tolerance limit (ion)/(Fe(III) or Zn(II))		
	CMBM	DDTC	APDC
Li <sup>+</sup> , Na <sup>+</sup> , K <sup>+</sup> , Ag <sup>+</sup> , F <sup>-</sup> , Cl <sup>-</sup> , I <sup>-</sup>	1200	1300	1800
Mg <sup>2+</sup> , Br <sup>-</sup> , SO <sub>4</sub> <sup>2-</sup>	1000	1100	1500
Ni <sup>2+</sup> , CO <sub>3</sub> <sup>2-</sup> , C <sub>2</sub> O <sub>4</sub> <sup>2-</sup>	800	900	1200
NO <sub>3</sub> <sup>-</sup> , HCO <sub>3</sub> <sup>2-</sup> , PO <sub>4</sub> <sup>3-</sup>	700	800	1000
Al <sup>3+</sup> , CH <sub>3</sub> COO <sup>-</sup>	500	600	800
Ca <sup>2+</sup> , Mn <sup>2+</sup> , Mo(V)	400	300	700
Cr <sup>3+</sup> , Sn <sup>4+</sup>	250	250	450
Cd <sup>2+</sup> , Pd <sup>2+</sup>	100	150	300

**Table 3.** Specifications for each element and ligand.

Parameters	Fe(III)			Zn(II)		
	CMBM	DDTC	APDC	CMBM	DDTC	APDC
Linear range (µg L <sup>-1</sup> )	0.35–70	0.50–80	0.9–100	0.55–75	0.75–90	1.0–120
Detection limit (µg L <sup>-1</sup> )	0.11	0.13	0.27	0.16	0.22	0.30
Correlation coefficient	0.9998	0.9987	0.9987	0.9998	0.9987	0.9886
R.S.D (%)	1.1	1.8	1.9	0.7	0.9	1.2
Adsorption capacity (mg g <sup>-1</sup> )	65.8	56.1	43.73	65.8	56.1	43.73

## Analytical performances

The analytical features of the presented methods, such as linear ranges of the calibration curves, limits of detection, correlation coefficients and relative standard deviations (RSDs) are shown in Table 3, which indicate a wide linear range and applicability of the method for trace metal enrichment.

According to the definition of the International Union of Pure and Applied Chemistry, the detection limit of the method was calculated based on three times the standard deviation of 11 runs of the blank solution. The detection limits of this method for Fe(III) and Zn(II) are in the range 0.11–0.30 µg L<sup>-1</sup>, respectively. Under the selected conditions, nine samples of 1.0 µg L<sup>-1</sup> standard solutions were enriched and analyzed simultaneously following the column procedure. The RSDs were found to be lower than 3.0%, which indicates that the method has good precision for the analysis of trace Fe(III) and Zn(II) in solution samples.

## Analytical applications and comparison with other methods

To ascertain the accuracy of the proposed procedure, the method has been applied to the determination of trace iron and zinc in different water samples. The accuracy of the method was verified by the analysis of samples spiked with known amounts of the analytes and certified reference materials. The results are presented in Table 4. The recovery of the spiked samples is satisfactorily reasonable and was confirmed using the standard addition method, which indicates the suitability of the prepared AC for selective SPE and determination of analytes in water samples. Comparative information from some studies on the preconcentration of Fe(III) and Zn(II) ions by various methods for the figure of merits is given in Table 5. As seen from the data, the proposed method developed using CMBM, DDTC, APDC and AC has a relatively high capacity compared with the other methods reported.<sup>[7–16,19]</sup>

**Table 4.** Analytical results for the determination of trace iron and zinc ions in various water samples.

Modified solid phase For water samples	Ion	Added ( $\mu\text{g L}^{-1}$ )	Found <sup>a</sup> ( $\mu\text{g L}^{-1}$ )	Recovery (%)	RSD(%)
AC -CMBM <sup>b</sup>	Fe	-	10.18 $\pm$ 0.08	-	1.6
		10	20.94 $\pm$ 0.05	103.77	2.2
		20	30.1 $\pm$ 0.03	99.73	1.9
	Zn	-	17.78 $\pm$ 0.07	-	1.2
		10	28.20 $\pm$ 0.09	101.51	2.1
		20	37.55 $\pm$ 0.09	99.39	2.3
AC-DDTC <sup>c</sup>	Fe	-	5.55 $\pm$ 0.07	-	1.2
		5.0	10.91 $\pm$ 0.09	103.41	2.8
		10	15.89 $\pm$ 0.04	102.19	1.5
	Zn	-	11.84 $\pm$ 0.08	-	2.2
		5.0	16.56 $\pm$ 0.02	98.34	3.1
		10	20.99 $\pm$ 0.05	96.11	3.0
AC- APDC <sup>d</sup>	Fe	-	2.54 $\pm$ 0.08	-	1.4
		5.0	7.51 $\pm$ 0.05	99.60	2.2
		10	12.38 $\pm$ 0.09	98.74	1.5
	Zn	-	6.91 $\pm$ 0.07	-	2.1
		5.0	12.07 $\pm$ 0.09	101.34	1.3
		10	16.87 $\pm$ 0.08	99.74	1.5
Modified solid phase For CRM samples					
AC -CMBM <sup>e</sup>	Fe	29.5	28.4	96.27	1.9
	Zn	41.9	43.1	102.86	2.4
AC-DDTC <sup>f</sup>	Fe	21	20.4	97.14	.9
	Zn	39	40.5	103.85	1.0
AC- APDC <sup>g</sup>	Fe	16.5	16.4	99.39	3.1
	Zn	27.5	26.5	96.36	1.5

<sup>a</sup>  $\bar{x} \pm ts\sqrt{n}$  at 95% confidence (N = 5.0).  $\bar{x}$ , value for five determinations, s, standard deviation.

<sup>b</sup> Spring water; <sup>c</sup> Well water; <sup>d</sup> Tap water; <sup>e</sup> TM-25.3; <sup>f</sup> TM-26.3; <sup>g</sup> TM-28.3.

**Table 5.** Comparison of the proposed method with recent studies reported in the literature using modified activated carbon as adsorbent for the preconcentration of iron and zinc.

Analytes	Ligand <sup>a</sup>	pH	Eluent ( $\text{mol L}^{-1}$ )	Adsorption capacity ( $\text{mg g}^{-1}$ )	PF <sup>b</sup>	LOD <sup>c</sup>	References
Cr <sup>3+</sup> , Fe <sup>3+</sup> , Hg <sup>2+</sup> , Pb <sup>2+</sup>	EDA	4.0	2.0%(wt./v) thiourea in HCl (0.5)	28.9	133.3	0.22	[7]
Cr <sup>3+</sup> , Cu <sup>2+</sup> , Fe <sup>3+</sup> , Pb <sup>2+</sup>	1-(2-formamidoethyl)-3-phenylurea	4.0	HCl (2.0)	77.8	100	0.27	[8]
Cr <sup>3+</sup> , Fe <sup>3+</sup> , Pb <sup>2+</sup>	AMP	4.0	HNO <sub>3</sub> (1.0)	67.1	50	0.41	[9]
Fe <sup>3+</sup> , Cu <sup>2+</sup> , Zn <sup>2+</sup>	<i>p</i> -dimethylaminobenzyl 3, 3- dimethylbenzidene	5.0	10% HCl	NR <sup>d</sup>	20	0.9–1.8	[10]
Pb <sup>2+</sup> , Fe <sup>3+</sup>	Mono- <i>o</i> -Anisic acid, Bis- <i>o</i> -Anisic acid	3.0	HCl (0.1–0.5)	39.5–85.7	100	0.09–0.23	[11]
Cu <sup>2+</sup> , Zn <sup>2+</sup> , Pb <sup>2+</sup>	2[2-hydroxybenzylideneamino] 2- hydroxybenzimidazole	4.0	HNO <sub>3</sub> (3.0)	NR <sup>d</sup>	NR	0.65–1.9	[12]
Cr <sup>3+</sup> , Fe <sup>3+</sup>	Ethylenediamine	8.0	HNO <sub>3</sub> (3.0)	NR <sup>d</sup>	50	1.5–2.7	[13]
Zn <sup>2+</sup> , Cu <sup>2+</sup>	2-4-MBAT,	7.0	HNO <sub>3</sub> (4.0)	NR <sup>d</sup>	93.7–	1.62–2.34	[14]
	2-4-CBAPT				112.5		
Cr <sup>3+</sup> , Fe <sup>3+</sup> , Pb <sup>2+</sup>	Triethylenetetramine	4	HCl (0.5)	34.6–51.9	NR	0.35–0.71	[15]
Cr <sup>3+</sup> , Fe <sup>3+</sup> , Cu <sup>2+</sup> , Ni <sup>2+</sup> , Co <sup>2+</sup> , Zn <sup>2+</sup>	1,3- propan diimine (BSPDI)	9.0	HNO <sub>3</sub> (2.0) in acetone	2.1	175	0.27–0.33	[16]
Fe <sup>3+</sup> , Cr <sup>3+</sup> , Ni <sup>2+</sup>	<i>N,N'</i> -ethylene bis(ethanesulfonamide)	6.0-6.5	HCl (0.5)	NR <sup>d</sup>	10	0.06–0.38	[19]
Fe <sup>3+</sup> , Zn <sup>2+</sup>	CMBM, DDTC, APDC	4.0	HNO <sub>3</sub> (2.0) in acetone	43.73–65.8	100	0.11–0.30	This work

<sup>a</sup> EDA: ethylenediamine; AMP: 2-((2-aminoethylamino)methyl)phenol; 2-4-MBAT: 2-(4-methoxybenzylideneamino)thiophenol; 2-4-CBAPT: 2-(4-chlorobenzylideneamino) benzenethiol; <sup>b</sup> PF: Preconcentration factor; <sup>c</sup> LOD: Limit of detection; <sup>d</sup> NR: not reported.

## Conclusions

The present study introduces a simple SPE method for the preconcentration and determination of Fe(III) and Zn(II) ions based on adsorption of these ions as their different complexes onto newly prepared bio-sorbent (AC) prior to their atomic absorption spectrometric determination. The most important characteristics of the new sorbent are its environmental benignity, faster adsorption and desorption capacities and simplicity for the ions studied. Satisfactory sensitivity and selectivity, good detection limits and high

preconcentration factor (PF=100) are the other advantages of the proposed work. The high accuracy of the proposed method was confirmed by recovery tests with a standard addition method. The possible interference of some important ions was investigated and no important interference was encountered. In summary, the newly prepared AC has great potential for the preconcentration and separation of Fe(III) and Zn(II) species and can be applied easily and effectively to the routine analysis of those heavy metals in water samples.

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