Effect of oxidation of activated carbon on its enrichment efficiency of metal ions: Comparison with oxidized and non-oxidized multi-walled carbon nanotubes

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Abstract

The effect of oxidation of activated carbon (AC) with various oxidizing agents (nitric acid, hydrogen peroxide, ammonium persulfate) on preconcentration of metal ions (Cr³⁺, Mn²⁺, Pb²⁺, Cu²⁺, Cd²⁺ and Zn²⁺) from environmental waters prior to their flame atomic absorption spectroscopic analysis was investigated. The highest recoveries and adsorption capacities towards metal ions were achieved when using nitric acid-oxidized AC (sorbent AC-NA) as preconcentrating sorbent at pH 9. A preconcentration procedure was optimized using AC-NA as sorbent, which was then compared with non-oxidized AC in terms of analytical performance of the preconcentration method. Higher sensitivity, lower detection limits and wider linear ranges were achieved when AC-NA was used. The analytical performance of the method using AC-NA as preconcentrating sorbent was also compared with nitric acid-oxidized multi-walled carbon nanotubes (sorbent MWCNT-NA) and non-oxidized multi-walled carbon nanotubes (sorbent MWCNT). The analytical performance of the preconcentration method using AC-NA was close to MWCNT-NA, but AC-NA was better than non-oxidized MWCNT. Application of the optimized preconcentration method (using AC-NA sorbent) to environmental waters (tap water, reservoir water, stream water) gave spike recoveries of the metals in the range 63–104%.

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1. Introduction

Monitoring environmental pollutants at ultra-trace level needs an effective sample preconcentration step. Solid phase extraction (SPE) is the most common technique used for preconcentration of analytes in environmental waters. In SPE procedure, the choice of appropriate adsorbent is a critical factor to obtain full recovery and high enrichment factor. Many sorbents have been used for preconcentration of pollutants, such as activated carbon (AC), multi-walled carbon nanotubes (MWCNT), etc. Sometimes it is useful to consider the cost of sorbent, in addition to its analytical performance. AC is a relatively cheap sorbent, while MWCNT is a relatively expensive one.

AC is an excellent-common sorbent consisting of graphite sheets randomly substituted with hetero-atoms (mainly oxygen) [1]. The surface properties of AC may improve or hinder its ability to adsorb certain species. Reports have explored the role of surface chemistry, oxygen content and textural properties of ACs on its adsorption properties [2–6]. Characteristics of AC depend on the precursor and the activation technique employed in the manufacturing process of AC [6]. These characteristics may be altered by treatment of AC with certain oxidizing agents, such as nitric acid, ammonium persulfate, hydrogen peroxide, etc. By this treatment, it is possible to alter the textural properties of the AC and to generate acidic oxides (carboxylic, phenolic, lactonic) and/or basic groups (pyrone-like groups) on the surface of AC.

Authors have previously used AC for enrichment of metals from environmental samples prior to their analysis. Jankowski et al. [7] reported the preconcentration of cadmium, copper, chromium, iron, manganese, lead and zinc ions from water samples by adsorption on AC at pH 8–8.5 coupled with continuous powder introduction microwave induced plasma atomic emission spectroscopic analysis. Yusof et al. [8,9] reported the determination of some toxic metals from water samples after
preconcentration on modified AC (Zr/AC) and non-modified AC coupled with neutron activation analysis. They found that Zr/AC was capable of adsorbing As$^{5+}$, Se$^{6+}$, Cr$^{6+}$ and Hg$^{2+}$ ions at any pH, while AC was capable of adsorbing As$^{3+}$, Se$^{4+}$, Cr$^{3+}$ and Hg$^{+}$ ions at high pH values. Yaman et al. [10–12] reported the use of AC for speciation of copper, nickel and lead from soil samples. Yaman and Avcı [13] reported the determination of beryllium in solid samples after preconcentration on AC at various pH values. Beinrohr et al. [14] reported on-line preconcentration of Cr$^{3+}$ on AC from water samples at pH 7, while total chromium was determined after reduction of chromate into Cr$^{3+}$. Gil et al. [15,16] reported on-line preconcentration and speciation of Cr$^{6+}$ and Cr$^{3+}$ from water samples by sorption on conical mini-column packed with AC at pH 5. Sommer et al. [17] reported speciation of mercury by trapping on AC surface then desorption followed by gas chromatographic analysis. Granados et al. [18] reported preconcentration of radioactive Co$^{60}$ on AC. Adsorption of cadmium on AC was also reported by LeyvaRamos et al. [19], in which maximum adsorption occurred at pH 8. Preconcentration of Se$^{4+}$ from agricultural and natural water samples by precipitation on AC surface was reported by Berotino et al. [20], van der Hock et al. [21] and Castilla et al. [22]. Babel and Kurniawan [23] reported the use of AC modified with oxidizing agents (HNO$_3$ and H$_2$SO$_4$) for removal of Cr$^{6+}$ from synthetic wastewater. It was evident that nitric acid treated-AC showed better Cr$^{6+}$ removal than as-received AC in terms of adsorption rate and adsorption capacity. Zhang et al. [24] studied the role of physical and chemical properties of AC on lead speciation.

Multi-walled carbon nanotubes (MWCNT), which is an expensive sorbent, were previously used for preconcentration of metal ions, such as rare earth elements [25], copper [26,27], silver [28] and cadmium [27,29]. Munoz et al. [30] reported the speciation of organo-metallic compounds of lead, mercury and tin in environmental samples using MWCNT. Some researchers have tried to improve the properties of the MWCNT via oxidation with nitric acid. For example, Zhang et al. [31] reported that diameter of the single-walled carbon nanotubes may be enlarged by nitric acid treatment. Liang et al. [32] applied nitric acid-oxidized MWCNT to concentrate cadmium, manganese and nickel ions. Henrich et al. [33] reported the modification of adsorption properties of single-walled carbon nanotubes via nitric acid exposure. Chakraborty et al. [34] found that treatment of the carbon nanotubes with nitric acid/sulfuric acid mixture then baking at 1000 °C increased its surface area.

Although some works (such as those of Babel and Kurniawan [23] and Zhang et al. [24]) have reported the use of oxidized AC for adsorption (removal) of heavy metals from aqueous medium, however, to the best of our knowledge, it seems that nobody has studied the effect of oxidation of AC on its preconcentration performance towards metal ions from water samples. Additionally none of the researchers who conducted research on preconcentration of metal ions have compared the enrichment efficiency of oxidized AC with that of MWCNT.

In this work, the effect of oxidation of AC with various oxidizing agents (nitric acid, hydrogen peroxide, ammonium persulfate) on preconcentration of metals from environmental waters was reported. Metal ions selected were Cr$^{3+}$, Mn$^{2+}$, Pb$^{2+}$, Cu$^{2+}$, Cd$^{2+}$ and Zn$^{2+}$. Comparison between the analytical performance achieved by using oxidized AC and non-oxidized AC as preconcentrating sorbents for metal ions from water was reported for the first time in this work. Additionally the analytical performance of the oxidized AC was also compared with non-oxidized and nitric acid-oxidized MWCNT as preconcentrating sorbents for metal ions.

### 2. Experimental

#### 2.1. Standard solutions and reagents

Standard stock solutions (1000 μg mL$^{-1}$), of individual metals, were purchased from the following suppliers: Cd$^{2+}$ and Cr$^{3+}$ standard solutions from Aldrich; Pb$^{2+}$ standard solution from BDH; Cu$^{2+}$ standard solutions from Scharlau, Zn$^{2+}$ and Mn$^{2+}$ standard solutions from Panreac. Working standard solutions were prepared by appropriate dilution of the stock standard solutions. All the reagents used were of analytical grade or better. Doubly distilled water was used throughout the work. The following buffers were used to control the pH of water samples: hydrochloric acid–glycine (pH 1–3), sodium acetate–acetic acid (pH 3–6), disodium hydrogen phosphate–sodium dihydrogen phosphate (pH 6–8), and ammonium chloride–ammonia (pH 8–10).

Activated carbon (AC) was purchased from Sigma (untreated granular activated charcoal, 20–60 mesh, product number C3014). Multi-walled carbon nanotube (MWCNT) was purchased from Shenzhen Nanotechport Co. Ltd., Shenzhen, China. MWCNT was of 5–15 μm length and 10–30 nm external diameter. Before use, MWCNT was dried at 80°C for 2 h.

#### 2.2. Oxidation of sorbents

AC was oxidized with various reagents to study the effect of oxidation of AC on its on enrichment efficiency towards the targeted metal ions. Details of oxidation conditions are shown in Table 1. Oxidized sorbents were thoroughly washed with doubly distilled water and then dried. The produced sorbents were labelled AC-NA, AC-HP and AC-APS, which refers to AC sorbents oxidized with nitric acid, hydrogen peroxide and ammonium persulfate, respectively. AC refers to non-oxidized AC.

MWCNT was oxidized with nitric acid in a procedure similar to that of AC-NA, which is shown in Table 1. The produced sorbent was labeled MWCNT-NA. Sorbent MWCNT refers to non-oxidized MWCNT.

#### 2.3. Characterization of ACs

Characterization of the oxidized ACs and the non-oxidized AC involved determination of methylene blue relative surface area; determination of iodine numbers; and determination of surface oxides by Boehm titrations. Methylene blue (MB)-relative surface area [35,36] was estimated by introducing 25 mL of aqueous solutions of 10, 20, 30, 40, 50, 60, 70, 90, 110 mg L$^{-1}$ methylene blue separately into 50 mL conical flasks each con-
Table 1
Preparation conditions and characteristics of the oxidized ACs and non-oxidized AC with appropriate labelling of the sorbents

<table>
<thead>
<tr>
<th>Adsorbent abbreviation</th>
<th>Oxidation conditions</th>
<th>MB relative surface area (m² g⁻¹)</th>
<th>Iodine number (mg g⁻¹)</th>
<th>Boehm titrations</th>
</tr>
</thead>
<tbody>
<tr>
<td>AC – 303</td>
<td>200 mL of conc. HNO₃, 25 °C, 24 h</td>
<td>303</td>
<td>200</td>
<td>1.46</td>
</tr>
<tr>
<td>AC-NA</td>
<td>100 mL of conc. HNO₃, 25 °C, 24 h</td>
<td>240</td>
<td>140</td>
<td>0.121</td>
</tr>
<tr>
<td>AC-APS</td>
<td>100 mL of a saturated solution of (NH₄)S₂O₈ in 1 M H₂SO₄, 25 °C, 18 h</td>
<td>205</td>
<td>120</td>
<td>0.135</td>
</tr>
<tr>
<td>AC-HP</td>
<td>Mixture of 50 mL H₂O₂ and 50 mL 1 M H₂SO₄, 50 °C, 1 h</td>
<td>265</td>
<td>170</td>
<td>0</td>
</tr>
</tbody>
</table>

Note—(a) total basic group (mmol g⁻¹), (b) total acidic group (mmol g⁻¹), (c) phenolic groups (mmol g⁻¹), (d) lactonic groups (mmol g⁻¹), (e) carboxylic groups (mmol g⁻¹).

2.4. Apparatus

An Analyst 300 Perkin-Elmer atomic absorption spectrometer was used for the quantitative determination of all metals under the following conditions: optical path was 10 mm; slit width was 0.7 nm for all metals except for Mn it was 0.2 nm; wavelength was 279.5 nm for Mn, 357.9 nm for Cr, 217.0 nm for Pb, 228.8 nm for Cd, 324.8 nm for Cu, 213.9 nm for Zn; lamp current was 30 mA for Mn lamp, 25 mA for Cr lamp, 10 mA for Pb lamp, 4 mA for Cd lamp, 15 mA for Cu lamp, 15 mA for Zn lamp. Instrumental conditions for electro-thermal atomic absorption spectrometric (ET AAS) method were similar to those described by Sweileh [39].

A Cary 100 Bio UV–vis spectrophotometer was used for determination of the remaining concentrations of methylene blue. A visiprep-12-port vacuum manifold (from Supelco) connected to a vacuum pump (KNF NEUBERGER D-7800, Germany) was used to control the flow rate in the preconcentration procedure of metals.

2.5. Cartridge preparation

Cartridge was prepared by placing a specific mass of the sorbent in an empty 6 mL polypropylene SPE-tube “filtration tube” (from Supelco). Polyethylene frits “from Supelco” were used to hold the adsorbent packing in the cartridge. Cartridge was preconditioned by washing with 6 mL of 1.0 M HNO₃, then with 12 mL of doubly distilled water, then with 12 mL of the desired buffer solution, ahead of the preconcentration procedure.

2.6. General preconcentration procedure

The desired mass of the sorbent was packed into the SPE-cartridge and preconditioned as described in Section 2.5. Water sample (spiked with the desired concentration of metal ions and adjusted to the desired pH value) was then passed through the cartridge. The flow rate was maintained at 6 mL min⁻¹. Subsequently, metals retained on the cartridge were eluted with the desired volume and concentration of nitric acid solution.

2.7. Determination of adsorption capacity of the sorbents

Adsorption capacity of the sorbents was estimated in separate experiments at optimum pH by passing 50 mL of 10 µg mL⁻¹ of each metal ion solution (separately) into a 0.200 g of the sorbent packed in the cartridge and preconditioned as described above. The adsorbed metal was eluted with 10 mL of 1.0 M HNO₃ to ensure full elution.

2.8. Environmental water samples

Three types of environmental waters were used for evaluation of the proposed SPE method; tap water, reservoir water and stream water. Tap water samples were collected after flowing for 10 min from various water taps in our school at various days, and then pooled and used to generate a composite tap water sample. Reservoir water composite sample was generated by collecting various samples from local household reservoirs, which are known to store water for several weeks. Stream water composite sample was generated by collecting various samples from Al-Zarqa stream from various positions at various days. Before use, all the environmental water samples were filtered through 0.45 µm micropore membranes and stored in polyethylene bottles at 4 °C.

2.9. Application of the proposed method on real water samples

The optimum SPE procedure was applied first on un-spiked real water samples and then on real water samples spiked with the target metal ions. To ensure reproducibility of the results, SPE procedures were applied in five replicates (n = 5), after which each extract was analyzed for metal ions as separate sample.
3. Results and discussion

3.1. Characterization of the oxidized and non-oxidized ACs

The oxidized and non-oxidized ACs were characterized in our laboratory by relative surface area estimation by Methylene blue adsorption method, iodine number and Boehm titrations. The results are shown in Table 1. From Boehm titrations, it is noted that nitric acid oxidation produced maximum number of oxygen-containing groups in each category as classified by Boehm [37]. Hydrogen peroxide treatment significantly reduced the number of basic groups but enhanced number of acidic surface oxides. Ammonium persulfate treatment resulted in the generation of the greatest number of strongly acidic carboxylic groups.

From Table 1, it is noted that Methylene blue (MB) adsorption is less favored on oxidized activated carbon sorbents relative to non-oxidized activated carbon. It was reported by Krupa and Canon [40] that MB adsorption occurs mainly within large micropores and mesopores. The decrease in MB relative surface area is probably due to more carboxyl groups on the surface and thus forming water clusters, which blocks micropore openings [4] and hinders the passage of MB molecules inside micropores. Additionally El-Sheikh et al. [41] reported that nitric acid treatment decreases the surface area and pore volume of the AC. A similar trend was also observed in the results of iodine number (Table 1).

3.2. Adsorption capacity of the oxidized and non-oxidized ACs

Adsorption capacity of the oxidized and non-oxidized ACs towards metal ions was estimated as described in Section 2.7. The results are presented in Table 2. It is noted that the lowest adsorption capacity of AC was found towards Mn$^{2+}$ and Zn$^{2+}$. Oxidation of AC with various oxidizing agents generally increased the adsorption capacity towards all metal ions, but the highest increase was observed with AC-NA. This explains the highest recoveries achieved in the preconcentration process using AC-NA as the preconcentrating sorbent (see later Section 3.3.2).

3.3. Optimization of the preconcentration procedure using AC as sorbent

Optimization of preconcentration procedure is an important process to get appropriate enrichment efficiency and full recovery. The effect of oxidation of AC with various oxidizing agents was the main factor investigated in this work. Other variables that were investigated included: pH of water sample, concentration and volume of eluting solvent, mass of adsorbent and breakthrough volume.

3.3.1. Effect of pH of water sample

It is believed that pH of the solution affects the structure of adsorbent surface and the structure of adsorbate present in the aqueous solution. For example, at basic pH medium, metals are precipitated as their hydroxides while functional groups on adsorbent surface (carboxyl, phenolic, lactonic) exist in the deprotonated form. On the other hand, at acidic pH medium, free metal ions exist in solution while surface functional groups present in the protonated form. Thus the mechanism of metal uptake may vary at various pH values.

A series of experiments was performed to investigate the influence of sample pH over the range from pH 1 to 10. The three oxidized sorbents (AC-NA, AC-HP, AC-APS) and the non-oxidized AC were tested for preconcentration of the metal ions in aqueous solutions at various pH values. Variations of the percentage recovery of metal ions with changing the pH of water sample using various sorbents are shown in Figs. 1–4. It is generally noted that the highest recoveries were achieved at pH 9 for almost all metal ions with all the oxidized and the non-oxidized AC sorbents. Moderate recovery was sometimes achieved at pH 5 for some metals, such as for Pb$^{2+}$ using AC-APS sorbent (Fig. 3). The high recovery achieved for metal ions at pH 9 is probably due to precipitation of their hydroxides at this pH value, and thus metal hydroxides are captured inside the micropores of AC or stick to the surface of AC. On the other hand, at pH 5 metal ions uptake is probably due to direct binding of the metal ions with the acidic surface groups that are present on the activated carbon surface. However, recoveries achieved at pH 5 were not satisfactory and thus pH 9 was selected as the optimum pH of aqueous solution in the preconcentration process.

Table 2

<table>
<thead>
<tr>
<th></th>
<th>Mn$^{2+}$</th>
<th>Cr$^{3+}$</th>
<th>Pb$^{2+}$</th>
<th>Cd$^{2+}$</th>
<th>Cu$^{2+}$</th>
<th>Zn$^{2+}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>AC</td>
<td>0.095</td>
<td>0.117</td>
<td>0.336</td>
<td>0.280</td>
<td>0.225</td>
<td>0.076</td>
</tr>
<tr>
<td>AC-NA</td>
<td>0.248</td>
<td>0.178</td>
<td>0.555</td>
<td>0.392</td>
<td>0.366</td>
<td>0.270</td>
</tr>
<tr>
<td>AC-APS</td>
<td>0.221</td>
<td>0.102</td>
<td>0.186</td>
<td>0.121</td>
<td>0.107</td>
<td>0.255</td>
</tr>
<tr>
<td>AC-HP</td>
<td>0.228</td>
<td>0.195</td>
<td>0.505</td>
<td>0.352</td>
<td>0.304</td>
<td>0.262</td>
</tr>
</tbody>
</table>

Fig. 1. Effect of pH of the water sample on % recovery of the metal ions using non-oxidized AC sorbent: 25 mL water sample spiked with 0.30 μg mL$^{-1}$ metal (each), 0.200 g sorbent, elution with 10 mL of 0.50 M HNO$_3$. 
3.3.2. Effect of adsorbent oxidation

The preconcentration efficiency of the oxidized AC was compared with the non-oxidized AC sorbent at pH 9. The non-oxidized AC sorbent (Fig. 1) did not give satisfactory percentage recovery for all metal ions at pH 9, i.e. percentage recoveries are 80% for Pb$^{2+}$, 22% for Zn$^{2+}$, 58% for Cu$^{2+}$, 30% for Cr$^{3+}$, 68% for Cd$^{2+}$ and 28% for Mn$^{2+}$.

It is noted that using AC-NA sorbent has generally improved the recovery at pH 9 for all metal ions relative to the non-oxidized AC (Fig. 2). Thus at pH 9, the recovery increased for Mn$^{2+}$ from 28% to 85%; for Cd$^{2+}$ the recovery increased from 68% to 100%; for Cr$^{3+}$ the recovery increased from 30% to 60%; for Cu$^{2+}$ the recovery increased from 58% to 102%; for Zn$^{2+}$ the recovery increased from 22% to 85%; while the recovery of Pb$^{2+}$ was almost unchanged.

Treatment of AC with ammonium persulfate gave unexpected results (Fig. 3). It is noted that recoveries of Zn$^{2+}$ and Mn$^{2+}$ increased four times (Fig. 3) relative to the non-oxidized AC (Fig. 1); but unfortunately recoveries of Pb$^{2+}$, Cd$^{2+}$, Cu$^{2+}$ and Cr$^{3+}$ significantly decreased relative to the non-oxidized AC sorbent.

Treatment of AC with hydrogen peroxide gave recovery range 65–85% for metal ions at pH 9 (Fig. 4). These recoveries (Fig. 4) are generally higher than recoveries obtained with non-oxidized AC (Fig. 1), but they are generally lower than those obtained with AC-NA sorbent (except for Cr$^{3+}$) (Fig. 2).

Two postulates may be proposed to explain the highest recoveries achieved with AC-NA. The first postulate is that oxidation increases the oxygen content and thus increases the hydrophilicity of the surface (see Section 3.1 above), which in turn promotes the formation of water clusters on the activated carbon surface. This may facilitate the uptake process of metal hydroxides at pH 9, in which metal uptake is probably due to H-bonding of the metal hydroxides to the hydrophilic surface of AC. The second postulate is that nitric acid treatment may alter the porosity of the surface in a manner that makes it more capable of capturing precipitated metal hydroxides. El-Sheikh et al. [41] reported that nitric acid treatment decreases the surface area and pore volume of the AC. Thus a decrease in the diameter of the pore openings occurred. This may support the retaining process of the precipitated metal hydroxides inside the pores of AC.

Due to the highest recoveries achieved with AC-NA sorbent at pH 9, this sorbent was selected for subsequent optimization of the preconcentration SPE procedure of metal ions at pH 9.

3.3.3. Optimization of other parameters

Nitric acid was used as the eluting solvent in this work. The optimum concentration of nitric acid is 1.0 M HNO$_3$, while 10 mL of this eluting solvent is the optimum volume to elute maximum amount of the adsorbed metal ions. The optimum mass of AC-NA is 0.400 g, while the breakthrough volume is 400 mL.
3.3.4. The optimum preconcentration method

Based on the above discussion, the following optimized method is proposed for preconcentration of the metal ions using AC-NA as sorbent:

400 mL aqueous solution (containing the metal ions simultaneously) at pH 9 is passed through a 0.400 g of AC-NA packed inside the cartridge and preconditioned as described in Section 2.5. The retained metals are eluted with 10 mL of 1.0 M HNO₃ solution and then directly analyzed by the flame atomic absorption spectroscopy (FAAS) under the conditions stated in Section 2.4.

3.3.5. Effect of coexisting ions

The effect of coexisting ions on preconcentration of metal ions using AC-NA as sorbent at pH9 was investigated by adding the following amounts of interfering ions (separately) to water samples containing 0.30 µg mL⁻¹ of each metal ion: 1000 µg mL⁻¹ Na⁺, 1000 µg mL⁻¹ K⁺, 500 µg mL⁻¹ Al³⁺, 500 µg mL⁻¹ SO₄²⁻, 500 µg mL⁻¹ Ca²⁺, 500 µg mL⁻¹ Mg²⁺, 200 µg mL⁻¹ HCO₃⁻, 10 µg mL⁻¹ Fe³⁺. Water samples were then treated according to the optimum SPE procedure (see Section 3.3.4). Results are not given, but they indicated that the % recovery of all metals remained above 90%, even in the presence of the assigned concentrations of coexisting ions.

3.4. Comparing the enrichment efficiency of AC–NA with non-oxidized AC

For the purpose of comparing the enrichment efficiency of sorbent AC-NA with that of non-oxidized AC, the optimum preconcentration method (described in Section 3.3.4) was applied by using either AC-NA or the non-oxidized AC. The two sorbents will be compared in terms of linear range, detection limit and sensitivity of the preconcentration methods. For that purpose, 400 mL of doubly distilled water samples were spiked with various concentrations of the metal ions: 20, 50, 100, 150, 200, 250 and 300 ng mL⁻¹ and then enriched (using either AC-NA or non-oxidized AC) according to the optimized preconcentration method. Preconcentration experiments were performed in five replicates (n = 5) and the five extracts were analyzed as separate samples.

Precision was estimated as percent relative standard deviations (%RSD, n = 5). Linear ranges for the metal ions were estimated based on the value of the R-squared for the calibration curve. Sensitivity of the method (m) for each metal ion was estimated as the slope of the calibration curve. The detection limit for each metal ion was estimated as three times the standard deviation of the blank signal. The analytical parameters of the method using both sorbents (AC-NA and AC) are presented in Table 3.

Table 3
Analytical performance of the proposed SPE method using AC-NA, AC, MWCNT-NA and MWCNT towards the targeted metal ions

<table>
<thead>
<tr>
<th>Sorbent: AC-NA</th>
<th>Linear range (ng mL⁻¹)</th>
<th>R²</th>
<th>Detection limit (ng L⁻¹)</th>
<th>%RSD range (n = 5)</th>
<th>Slope</th>
<th>Intercept</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mn²⁺</td>
<td>20–300</td>
<td>0.9997</td>
<td>54</td>
<td>1.1–2.9</td>
<td>0.980</td>
<td>0.930</td>
</tr>
<tr>
<td>Cr³⁺</td>
<td>20–300</td>
<td>0.9939</td>
<td>88</td>
<td>1.1–3.5</td>
<td>0.845</td>
<td>0.793</td>
</tr>
<tr>
<td>Pb²⁺</td>
<td>20–300</td>
<td>0.9990</td>
<td>193</td>
<td>1.5–3.8</td>
<td>0.185</td>
<td>0.753</td>
</tr>
<tr>
<td>Cd²⁺</td>
<td>20–300</td>
<td>0.9998</td>
<td>42</td>
<td>1.5–3.9</td>
<td>1.720</td>
<td>0.680</td>
</tr>
<tr>
<td>Cu²⁺</td>
<td>20–300</td>
<td>0.9977</td>
<td>84</td>
<td>1.7–4.5</td>
<td>0.680</td>
<td>0.450</td>
</tr>
<tr>
<td>Zn²⁺</td>
<td>20–300</td>
<td>0.9832</td>
<td>33</td>
<td>1.1–3.1</td>
<td>4.189</td>
<td>0.516</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Sorbent: AC</th>
<th>Linear range (ng mL⁻¹)</th>
<th>R²</th>
<th>Detection limit (ng L⁻¹)</th>
<th>%RSD range (n = 5)</th>
<th>Slope</th>
<th>Intercept</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mn²⁺</td>
<td>20–100</td>
<td>0.9999</td>
<td>113</td>
<td>0.8–3.6</td>
<td>0.325</td>
<td>1.612</td>
</tr>
<tr>
<td>Cr³⁺</td>
<td>–</td>
<td>–</td>
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<td>–</td>
<td>–</td>
</tr>
<tr>
<td>Pb²⁺</td>
<td>20–100</td>
<td>0.9999</td>
<td>187</td>
<td>1.1–4.2</td>
<td>0.195</td>
<td>0.022</td>
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<tr>
<td>Cd²⁺</td>
<td>20–100</td>
<td>0.9911</td>
<td>465</td>
<td>0.9–3.3</td>
<td>0.450</td>
<td>5.628</td>
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<tr>
<td>Cu²⁺</td>
<td>20–100</td>
<td>0.9414</td>
<td>226</td>
<td>1.3–4.2</td>
<td>0.419</td>
<td>8.242</td>
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<tr>
<td>Zn²⁺</td>
<td>20–100</td>
<td>0.9345</td>
<td>302</td>
<td>1.6–3.6</td>
<td>2.923</td>
<td>61.08</td>
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</table>

<table>
<thead>
<tr>
<th>Sorbent: MWCNT-NA</th>
<th>Linear range (ng mL⁻¹)</th>
<th>R²</th>
<th>Detection limit (ng L⁻¹)</th>
<th>%RSD range (n = 5)</th>
<th>Slope</th>
<th>Intercept</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mn²⁺</td>
<td>20–150</td>
<td>0.9978</td>
<td>38</td>
<td>0.9–3.4</td>
<td>0.865</td>
<td>0.425</td>
</tr>
<tr>
<td>Cr³⁺</td>
<td>20–300</td>
<td>0.9990</td>
<td>37</td>
<td>1.1–3.9</td>
<td>0.901</td>
<td>0.339</td>
</tr>
<tr>
<td>Pb²⁺</td>
<td>20–300</td>
<td>0.9999</td>
<td>214</td>
<td>1.2–4.0</td>
<td>0.181</td>
<td>0.683</td>
</tr>
<tr>
<td>Cd²⁺</td>
<td>20–150</td>
<td>0.9973</td>
<td>24</td>
<td>1.3–3.1</td>
<td>1.402</td>
<td>0.161</td>
</tr>
<tr>
<td>Cu²⁺</td>
<td>20–300</td>
<td>0.9980</td>
<td>46</td>
<td>1.5–4.0</td>
<td>0.722</td>
<td>0.321</td>
</tr>
<tr>
<td>Zn²⁺</td>
<td>20–200</td>
<td>0.9936</td>
<td>9</td>
<td>1.3–3.5</td>
<td>4.179</td>
<td>0.365</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Sorbent: MWCNT</th>
<th>Linear range (ng mL⁻¹)</th>
<th>R²</th>
<th>Detection limit (ng L⁻¹)</th>
<th>%RSD range (n = 5)</th>
<th>Slope</th>
<th>Intercept</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mn²⁺</td>
<td>20–100</td>
<td>0.9324</td>
<td>310</td>
<td>1.3–3.6</td>
<td>0.116</td>
<td>0.339</td>
</tr>
<tr>
<td>Cr³⁺</td>
<td>20–100</td>
<td>0.985</td>
<td>378</td>
<td>1.5–4.1</td>
<td>0.170</td>
<td>0.683</td>
</tr>
<tr>
<td>Pb²⁺</td>
<td>20–100</td>
<td>0.9977</td>
<td>116</td>
<td>0.9–3.4</td>
<td>0.258</td>
<td>0.060</td>
</tr>
<tr>
<td>Cd²⁺</td>
<td>20–100</td>
<td>0.9780</td>
<td>47</td>
<td>1.1–3.8</td>
<td>0.557</td>
<td>0.323</td>
</tr>
<tr>
<td>Zn²⁺</td>
<td>20–150</td>
<td>0.9925</td>
<td>9</td>
<td>1.0–3.9</td>
<td>3.895</td>
<td>0.367</td>
</tr>
</tbody>
</table>
Table 4
Concentration of metal ions (µg L⁻¹ ± σ, n = 5) in the unspiked environmental waters and their spike recoveries (n = 5) using AC-NA according to the optimized SPE procedure

<table>
<thead>
<tr>
<th>Element</th>
<th>Tap water</th>
<th>Reservoir water</th>
<th>Stream water</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mn²⁺</td>
<td>ND⁴</td>
<td>ND⁴</td>
<td>77.2 ± 3.1b</td>
</tr>
<tr>
<td></td>
<td>85–95</td>
<td>97–100</td>
<td>85–100</td>
</tr>
<tr>
<td>Cr³⁺</td>
<td>ND⁴</td>
<td>ND⁴</td>
<td>20.1 ± 1.6b</td>
</tr>
<tr>
<td></td>
<td>90–100</td>
<td>88–100</td>
<td>98–102</td>
</tr>
<tr>
<td>Pb²⁺</td>
<td>ND⁴</td>
<td>ND⁴</td>
<td>22.7 ± 2.6b</td>
</tr>
<tr>
<td></td>
<td>63–100</td>
<td>77–100</td>
<td>95–100</td>
</tr>
<tr>
<td>Cd²⁺</td>
<td>ND⁴</td>
<td>ND⁴</td>
<td>26.3 ± 2.4b</td>
</tr>
<tr>
<td></td>
<td>98–104</td>
<td>97–103</td>
<td>97–101</td>
</tr>
<tr>
<td>Cu²⁺</td>
<td>ND⁴</td>
<td>ND⁴</td>
<td>52.6 ± 3.2b</td>
</tr>
<tr>
<td></td>
<td>63–100</td>
<td>98–102</td>
<td>97–102</td>
</tr>
<tr>
<td>Zn²⁺</td>
<td>ND⁴</td>
<td>ND⁴</td>
<td>63.7 ± 2.9b</td>
</tr>
<tr>
<td></td>
<td>79–101</td>
<td>85–99</td>
<td>73–100</td>
</tr>
</tbody>
</table>

a ND: not detected.
b Uncertainty is the standard deviation for five replicate runs.
c Added concentrations: 20, 50, 100, 150, 200, 250 and 300 ng mL⁻¹.

From Table 3, it was clear that the main difference between the two sorbents was in the linear range, in which AC-NA sorbent had wider linear range of the method for all the metal ions. This is probably due to higher adsorption capacity of AC-NA (see Table 2). It was also noted that sensitivity of the method was higher when AC-NA was used and thus lower detection limits were achieved with AC-NA (Table 3). The relative standard deviations %RSD, (n = 5) was always less than 4.5%.

3.5. Comparing the enrichment efficiency of AC–NA with MWCNT

For the purpose of comparison, MWCNT-NA and non-oxidized MWCNT were used separately for preconcentration of metal ions. Optimization of the preconcentration parameters gave similar procedure to that described in Section 3.3.4, except that 0.200 g of MWCNT-NA or MWCNT was optimum instead of 0.400 g. 400 mL of doubly distilled water samples were spiked with various concentrations of the metal ions: 20, 50, 100, 150, 200, 250 and 300 ng mL⁻¹ and then enriched (using either MWCNT-NA or non-oxidized MWCNT) according to the optimized preconcentration method described above in this section. Preconcentration experiments were performed in five replicates (n = 5) and the five extracts were analyzed as separate samples. The analytical parameters of the method using MWCNT-NA and non-oxidized MWCNT are presented in Table 3. These were compared with the analytical performance achieved with AC-NA.

It was noted that the sensitivities towards metal ions achieved with AC-NA and MWCNT-NA were close to each other, while the linear ranges were generally wider when AC-NA was used.

When non-oxidized MWCNT was used for preconcentration of metal ions, it was noted that the sensitivities towards metal ions achieved were noticeably smaller than those achieved with AC-NA. Additionally the linear ranges with non-oxidized MWCNT sorbent were noticeably narrower than AC-NA sorbent.

3.6. Analytical application

Environmental water samples (tap water, reservoir water and stream water) were used to validate the proposed preconcentration method of metal ions using AC-NA as sorbent (see Section 3.5). The concentrations of metals were determined using the optimum preconcentration method (using AC-NA as sorbent) and independent method (ET AAS) in Table 5.

Table 5
Concentrations of metals (µg L⁻¹ ± σ, n = 5) in un-spiked and spiked tap waters using the optimum preconcentration method (using AC-NA as sorbent) and independent method (ET AAS)

<table>
<thead>
<tr>
<th>Element</th>
<th>Added</th>
<th>Found</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Optimum SPE method (using AC-NA)</td>
</tr>
<tr>
<td>Mn²⁺</td>
<td>0</td>
<td>ND⁴</td>
</tr>
<tr>
<td></td>
<td>20</td>
<td>19.0 ± 1.3</td>
</tr>
<tr>
<td></td>
<td>50</td>
<td>46.5 ± 1.9</td>
</tr>
<tr>
<td>Cr³⁺</td>
<td>0</td>
<td>ND⁴</td>
</tr>
<tr>
<td></td>
<td>20</td>
<td>20.0 ± 1.1</td>
</tr>
<tr>
<td></td>
<td>50</td>
<td>49.0 ± 1.9</td>
</tr>
<tr>
<td>Pb²⁺</td>
<td>0</td>
<td>ND⁴</td>
</tr>
<tr>
<td></td>
<td>20</td>
<td>20.0 ± 1.1</td>
</tr>
<tr>
<td></td>
<td>50</td>
<td>45.5 ± 2.2</td>
</tr>
<tr>
<td>Cd²⁺</td>
<td>0</td>
<td>ND⁴</td>
</tr>
<tr>
<td></td>
<td>20</td>
<td>20.5 ± 1.3</td>
</tr>
<tr>
<td></td>
<td>50</td>
<td>49.0 ± 1.8</td>
</tr>
<tr>
<td>Cu²⁺</td>
<td>0</td>
<td>ND⁴</td>
</tr>
<tr>
<td></td>
<td>20</td>
<td>20.0 ± 0.9</td>
</tr>
<tr>
<td></td>
<td>50</td>
<td>45.5 ± 2.1</td>
</tr>
<tr>
<td>Zn²⁺</td>
<td>0</td>
<td>ND⁴</td>
</tr>
<tr>
<td></td>
<td>20</td>
<td>20.2 ± 1.3</td>
</tr>
<tr>
<td></td>
<td>50</td>
<td>48.5 ± 2.3</td>
</tr>
</tbody>
</table>

a ND: not detected.
Some metal ions were found in the unspiked real waters according to the proposed procedure, as shown in Table 4. Environmental waters were then spiked with the metal ions at various concentrations according to the linear ranges shown in Table 3. Spike recoveries of the target metal ions in real water samples are shown in Table 4. The spike recovery range of all metal ions was 63–104%. The results indicate that the proposed method is satisfactory and can be used for the analysis of the targeted metals.

In order to establish the validity of the proposed method, un-spiked and spiked tap water samples were analyzed twice, first by the optimum preconcentration method (using AC-NA as preconcentrating sorbent), second, by electro-thermal atomic absorption spectroscopy (ET AAS). The results are given in Table 5, from which it is clear that the results of the two methods are comparable to each other.

4. Conclusion

Oxidation of AC with various oxidizing agents produces sorbents of different enrichment efficiencies, although significant amount of acidic oxides is generated by the three oxidation schemes. Nitric acid treatment of activated carbon increases the enrichment efficiency of metal ions relative to the non-oxidized AC, AC-HP and AC-APS sorbents. This may be attributed to the fact that nitric acid treatment increases the hydrophilicity of the AC surface. Thus the precipitated metal hydroxides at pH 9 stick to AC-NA surface probably by hydrogen bonding between metal hydroxides and the acidic oxides on the surface. Treatment of AC with hydrogen peroxide increases the enrichment efficiency relative to non-oxidized AC, but it is lower than that achieved with AC-NA sorbent. On the other hand, ammonium persulfate treatment of AC do not improve the recovery of metal ions at pH 9.

Comparing the enrichment efficiency of AC with AC-NA reveals that the main difference between the two sorbents was in the limit of linearity, in which AC-NA gives wider linear ranges due to higher adsorption capacity of AC-NA towards all metal ions. AC-NA also gives higher method sensitivity and thus lower detection limits than non-oxidized AC.

Comparing the enrichment efficiency of AC-NA with non-oxidized MWCNT and MWCNT-NA indicates that the analytical performance of AC-NA is close to MWCNT-NA, but the analytical performance of AC-NA is much better than non-oxidized MWCNT.

Application of the optimum (proposed) method using AC-NA as preconcentrating sorbent on real environmental waters and comparison with independent method indicates that the proposed method can be recommended for preconcentration of metal ions from aqueous medium.

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References