Effect of Chemical Treatment of Multi-Walled Carbon Nanotubes with Various Oxidizing Agents on its Preconcentration Performance of Some Metals

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Abstract

Multi-walled carbon nanotube was oxidized with various oxidizing agents (nitric acid, hydrogen peroxide and ammonium persulphate) to produce multi-walled carbon nanotubes of various surface properties. The oxidized sorbents were used for the preconcentration of some metals (Mn²⁺, Pb²⁺, Cu²⁺, Cd²⁺, Zn²⁺) from environmental waters prior to their determination by flame atomic absorption spectroscopy. The best preconcentration performance was achieved with nitric acid-oxidized carbon nanotubes (sorbent CNT-NA) at pH 9. The effect of hydrogen peroxide treatment of carbon nanotubes was similar to nitric acid treatment in terms of increasing recovery at pH 9 and at pH5. A preconcentration method was optimized using CNT-NA. Comparing the analytical performance of CNT-NA with non-oxidized carbon nanotubes (sorbent CNT-NO) indicated that CNT-NA gave wider limit of linearity, higher sensitivity and lower limits of quantification. Applying the optimized method on environmental waters (tap water, reservoir water and stream water) gave spike recovery in the range 81-106 %.

Keywords: Multi-walled carbon nanotubes; Solid phase extraction; Preconcentration; Water samples; Atomic absorption spectrometry.

Introduction

The choice of appropriate sorbent is a critical factor in the preconcentration of pollutants in order to reach full recovery and high adsorption capacity [1]. Since carbon nanotubes were first prepared [2], they found many applications in analytical sciences [3, 4]. Due to their unique tubular structure [2], they were used as sorbents in preconcentration processes [5]. For example, multi-walled carbon nanotubes have been widely used for preconcentration of organic pollutants [6-22]. They were also used for the preconcentration of metal ions, such as those of rare earth elements [23], copper [24], cadmium [25], and silver [26]. Tarley et al. [27] reported the use of a simple flow injection mini-column preconcentration system with multi-walled carbon nanotubes for the determination of cadmium. Munoz et al. [28] reported the speciation of organo-metallic compounds of lead, mercury and tin in environmental samples using multi-walled carbon nanotubes and found them superior to graphitized carbon black and RP-C18.

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Other analytical applications of multi-walled carbon nanotubes for metal analysis were also reported [29-31].

Multi-walled carbon nanotubes is a carbon-based material, which can be visualized as graphite sheets [32] rolled up into a cylinder. As any carbon-based material, there is a possibility of altering the surface properties of the carbon nanotubes, e.g. by generating acidic oxides (carboxylic, lactonic, phenolic) or basic oxides (pyrone-like groups) on the graphite sheets, or even altering the surface area and porosity. Many authors have tried to improve the properties of carbon nanotubes via oxidation. For example, Zhang et al. [33] reported that the diameter of carbon nanotubes may be enlarged by nitric acid treatment. Hennrich et al. [34] reported the modification of the adsorption properties of carbon nanotubes applied for water treatment purposes via nitric acid exposure. Chakraborty et al. [35] found that treatment of carbon nanotubes with nitric acid/sulfuric acid mixture, then baking at 1000°C increased the surface area. Li et al. [36, 37] reported the adsorption of lead and cadmium on oxidized multi-walled carbon nanotubes. Liang et al. [38] reported the use of nitric acid-oxidized carbon nanotubes to concentrate cadmium, manganese and nickel ions. However they did not compare the preconcentration performance of the oxidized and non-oxidized carbon nanotubes.

Although the tubular structure gives multi-walled carbon nanotubes its unique structure and promising characteristics, its surface chemistry may also play a major role in the uptake of pollutants from aqueous medium. Unfortunately researchers who used multi-walled carbon nanotubes for the preconcentration of pollutants did not study the effect of oxidation of multi-walled carbon nanotubes on its preconcentration performance.

In this work, we report the effect of oxidation of multi-walled carbon nanotubes with various oxidizing agents (nitric acid, hydrogen peroxide, ammonium persulphate) on the preconcentration of some metal ions from environmental waters. We also report the first comparison between the enrichment efficiency of the oxidized and non-oxidized multi-walled carbon nanotubes towards some metals from environmental waters.

**Experimental**

*Standard solutions and reagents*

Standard stock solutions (1000 µg ml⁻¹) of individual metals were purchased from the following suppliers: Cd²⁺ standard solutions from Aldrich; Pb²⁺ standard solution from BDH; Cu²⁺ standard solutions from Scharlau, Zn²⁺ and Mn²⁺ standard solutions from Panreac. Working standard solutions were prepared by appropriate dilution of the standard stock 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). Multi-walled carbon nanotube was purchased from Shenzhen Nanotechport Co. Ltd., Shenzhen, China. Other characteristics of the carbon nanotubes provided by the manufacturer are as follows: length 1-5 µm, external diameter 10-30 nm, purity >95 v%; ash ≤0.2 wt%; amorphous carbon 2 %; specific surface area 40-300 m²/g. This sorbent was labeled as CNT-NO, which refers to the non-oxidized multi-walled carbon nanotubes.

**Oxidation of carbon nanotubes**

In order to study the effect of oxidation of CNT-NO with various oxidizing agents on enrichment efficiency of metal ions, carbon nanotubes were used to prepare three oxidized carbon nanotubes sorbents. Oxidation conditions are shown in Table 1. Sorbents were then washed with water to remove excess oxidizing agent and other water soluble species. The produced sorbents were labelled CNT-NA, CNT-HP and CNT-APS, which refers to multi-walled carbon nanotubes oxidized with nitric acid, hydrogen peroxide and ammonium persulphate, respectively (see Table 1). CNT-NO refers to the non-oxidized multi-walled carbon nanotubes.

**Table 1. Oxidation conditions and characteristics of the multi-walled carbon nanotube sorbents 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>CNT-NO</td>
<td>Non oxidized.</td>
<td>28</td>
<td>25</td>
<td>12</td>
</tr>
<tr>
<td>CNT-NA</td>
<td>100 ml of conc. HNO₃, 25°C, 24 hrs.</td>
<td>42</td>
<td>8</td>
<td>5</td>
</tr>
<tr>
<td>CNT-APS</td>
<td>100 ml of a saturated solution of (NH₄)S₂O₈ in 1 M H₂SO₄, 25°C, 18 hrs.</td>
<td>22</td>
<td>8</td>
<td>0</td>
</tr>
<tr>
<td>CNT-HP</td>
<td>Mixture of 50 ml H₂O₂ and 50 ml 1 M H₂SO₄, 50°C, 1 hr.</td>
<td>20</td>
<td>22</td>
<td>13</td>
</tr>
</tbody>
</table>

**TBG:** total basic group (µmol g⁻¹), **TAG:** total acidic group (µmol g⁻¹), **Phen:** phenolic groups (µmol g⁻¹), **Lact:** lactonic groups (µmol g⁻¹), **Carb:** carboxylic groups (µmol g⁻¹).

**Characterization of the sorbents**

Characterization of the oxidized and non-oxidized carbon nanotubes involved the determination of methylene blue relative surface area, the determination of iodine number and the determination of surface oxides by Boehm titrations. Methylene blue (MB)-relative surface area [39, 40] 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 containing 25 mg of the sorbent. The tubes were tightly stoppered and left for one week in the dark, with shaking from time to time. The
remaining concentrations were analyzed spectrometrically at 614 nm. Langmuir adsorption isotherms were plotted to find the monolayer capacity through which MB-relative surface areas were estimated \cite{39, 40}. The quantitative determination of surface oxides was performed as described by Boehm \cite{41}. Iodine numbers were estimated according to procedure described by ASTM \cite{42} (ASTM method D 4607–94).

**Apparatus**

An Analyst 300 Perkin Elmer flame atomic absorption spectrometer (FAAS) was used for the quantitative determination of all metals under study. Operational conditions of FAAS were similar to those described by Sweileh \cite{43}. A Cary 100Bio UV–VIS spectrophotometer was used for determination of the 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 of water sample.

**Cartridge preparation**

Carbon nanotubes cartridge was prepared by placing 0.200 g 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.

**General preconcentration procedure**

0.200 g of the oxidized or non-oxidized multi-walled carbon nanotubes sorbent was packed into the SPE-cartridge and pre-conditioned as described above. Water sample (spiked with the desired concentration of metal ions and adjusted to the desired pH value) was then passed through the cartridge. Subsequently, metal ions retained on the cartridge were eluted with the desired volume and concentration of nitric acid solution. In optimization of the preconcentration procedure, doubly distilled water was used.

**Environmental water samples**

Three types of environmental waters were used for the evaluation of the proposed SPE method: tap water, reservoir water and stream water. Tap water samples were taken after flowing for 10 min from various water taps in our school in different 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.

The optimum preconcentration 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, the preconcentration procedure was applied in three replicates (n=3), after which each extract was analyzed for metal ions as separate sample.

Results and Discussion

Metal contamination of the sorbents

Blank experiment was conducted by passing 10 ml of 1.0 M HNO₃ through 0.200 g of the oxidized and non-oxidized sorbents. Analysis of the eluates by FAAS showed that none of the targeted metals was detected.

Characterization of the non-oxidized and oxidized carbon nanotubes

To investigate the effect of oxidati on of carbon nanotubes on its surface properties, the oxidized and non-oxidized sorbents were characterized in our laboratory by relative surface area estimation by methylene blue (MB) adsorption method, iodine number and Boehm titrations. All of these characterization parameters were performed in aqueous medium, which is closer to reality and to the medium of our study (aqueous medium). The results are shown in Table 1.

It is generally noted that pre-treatment of the carbon nanotubes with ammonium persulphate and hydrogen peroxide reduced the MB relative surface area, which may be due to the formation of acidic groups and thus water clusters may be formed in the caps opening and thus blocked the cap openings. Nitric acid pre-treatment of the carbon nanotubes enhanced the MB relative surface area by 50 %. This may be due to opening the caps of the carbon nanotubes by nitric acid treatment and thus became more suitable to capture MB molecules. Iodine number decreased after oxidation with all oxidizing agents. As expected, a noticeable increase of the carboxyl group was observed for all the oxidized sorbents. This was in the order CNT-APS > CNT-NA > CNT-HP.

Effect of pH on the preconcentration process

Enrichment efficiency of metal ions is generally dependent on pH of water sample. This is because pH of solution affects the structure of adsorbent surface and the predominant structure of metal ions in the aqueous solution. For example, in basic solutions, metals are precipitated as their hydroxides, while surface groups (carboxyl, phenolic, lactonic) are present in the deprotonated form. On the other hand, in acidic solution, free metal ions exist while surface groups are present in the protonated form. Thus, the mechanism of metal uptake can be different at various pH values.
A series of experiments were performed to investigate the influence of sample pH over the range of pH 3–10. The three oxidized sorbents (CNT-NA, CNT-HP, CNT-APS) and the non-oxidized carbon nanotubes (CNT-NO) were tested for the preconcentration of the metals in aqueous solutions of various pH values. Results and details of the experimental conditions are shown in Fig. 1.
Figure 1. Effect of pH of aqueous sample solution on the recovery of metal ions using various sorbents. Sample volume: 25 ml, 300 µg l⁻¹ metal (each), 0.200 g sorbent, eluent: 10 ml of 0.50 M HNO₃. a: CNT-NO, b: CNT-NA, c: CNT-APS, d: CNT-HP.

It is generally noted that the highest recoveries occurred at pH 9 for almost all metal ions with all the oxidized and the non-oxidized carbon nanotubes sorbents investigated in this study. Other pH values gave lower recoveries. However, Cu²⁺ and Pb²⁺ exhibited two exceptional cases, where high recoveries were also obtained at pH 5. For Cu and Zn, the high recovery obtained at pH 9 is probably due to precipitation of metal hydroxides (very low solubility in aqueous medium) and thus metal hydroxides are captured inside the cylindrical carbon nanotubes.

Effect of sorbent oxidation on the preconcentration process

The preconcentration performance of the oxidized carbon nanotube sorbents was compared with the non-oxidized (CNT-NO) sorbent at pH 9 (see figure 1).

Non-oxidized sorbent CNT-NO

The non-oxidized sorbent (CNT-NO) did not give satisfactory % recovery for all metal ions at pH 9 (figure 1a), i.e. it gave 90 % for Pb²⁺, 95 % for Zn²⁺, 80 % for Cu²⁺, 55 % for Cd²⁺ and 17 % for Mn²⁺.

Sorbent CNT-NA

It is noted that nitric acid-oxidation of carbon nanotubes (sorbnet CNT-NA) has generally improved the recovery at pH 9 for all metal ions (see figure 1b) relative to CNT-NO (see figure 1a). At pH 9, the recovery increased for Mn²⁺ from 17 % to 80 %; for Cd²⁺ the recovery increased from 55 % to 90 %; while the recovery of other metals has slightly increased by the use of CNT-NA sorbent. At pH 5, it is noted that the recovery of Pb²⁺ and Cu²⁺ was 78 %.
**Sorbent CNT-APS**

Treatment of carbon nanotubes with ammonium persulphate did not give satisfactory recoveries for some metal ions at pH 9, where recoveries ranged between 30-85% (see figure 1c). It is noted that the recovery of Mn$^{2+}$ almost doubled at pH9 relative to the non-oxidized sorbent (CNT-NO); while the recovery of Pb$^{2+}$ decreased to 55%. At pH 5, the recovery of Cu$^{2+}$ was 85%; while the recovery of both Pb$^{2+}$ and Cd$^{2+}$ was 65%.

**Sorbent CNT-HP**

Treatment of carbon nanotubes with hydrogen peroxide gave recovery range of 75-80% for all metal ions at pH 9 (see figure 1d); except for Mn$^{2+}$ the recovery was 25%. At pH 5, 75% recovery was achieved for Cu$^{2+}$ and Pb$^{2+}$, which is similar to that at pH 9.

**Comparing various sorbents**

It seems that nitric acid treatment has two effects on the carbon nanotubes. First it generated new acidic groups on the surface of carbon nanotubes and thus may be used for capturing metal ions at pH5. Second it opened the caps of the carbon nanotubes and thus may facilitate the capturing process of the precipitated metal hydroxides at pH 9. On the other hand, treatment with ammonium persulphate has probably only one effect on carbon nanotubes, which was the generation of acidic surface groups (carboxyl groups) on the surface of carbon nanotubes, thus the recovery was improved for some metals at pH5 due to higher amount of acidic groups present, while the recovery was not improved at pH 9 relative to the non-oxidized CNT-NO sorbent.

Due to the highest recovery obtained with CNT-NA sorbent at pH 9, this sorbent was selected for subsequent optimization of the preconcentration procedure of metals at pH 9.

**Optimization of other preconcentration parameters using CNT-NA as sorbent**

A preconcentration procedure using CNT-NA as sorbent was optimized by studying various parameters (eluent concentration and volume; flow rate of water sample; volume of water sample).

**Effect of eluent volume and concentration**

Nitric acid was used as the eluent in this work. The effect of concentration and volume of nitric acid on the preconcentration process was investigated by passing 25 ml of water sample containing 300 µg l$^{-1}$ metal (each) at pH 9 through 0.200 g CNT-NA sorbent. Various concentrations (0.1, 0.5, 1.0, 1.5 and 2.0 M) and volumes (5, 10, 15, 20 ml) of nitric acid solutions were used. The optimum concentration of nitric acid was found to be 1.0 M HNO$_3$, while 10 ml of 1.0 M HNO$_3$ was optimum to elute maximum amount of the adsorbed metal ions and gave the highest recovery (>97%), above
which the recovery was almost constant. So that 10 ml and 1.0 M HNO₃ were selected as the optimum volume and concentration of eluent, respectively.

Effect of flow rate of aqueous sample solution

The effect of flow rate of aqueous sample solution was studied under the optimum conditions (25 ml water sample, 300 µg l⁻¹ metal (each), pH9, 0.200 g CNT-NA sorbent, 10 ml of 1.0 M HNO₃ as eluent). Several flow rates were investigated. It was found that the flow rate below 6 ml min⁻¹ had no significant effect on the recovery of the metals. Thus all subsequent experiments were performed at a flow rate of 6.0 ml min⁻¹.

Effect of aqueous sample volume

It is necessary to enrich small concentrations from large volumes. So that, 25, 50, 100, 200, 400, 800 and 1000 ml of water sample solutions containing 300 µg l⁻¹ metal (each) at pH 9 were passed through 0.200 g CNT-NA. It was found that quantitative recovery (>95%) of all metals was obtained for the samples volume up to 200 ml. Above 200 ml the recovery for metal ions decreased slightly. So that 200 ml was selected as the optimum aqueous sample volume in this work.

Comparing the analytical performance of CNT-NO and CNT-NA

Analytical performance of the optimized method was investigated in terms of limit of linearity of the calibration curve, limit of quantification and sensitivity. For that purpose, 200 ml of doubly distilled water samples were spiked with various concentrations of the metal ions (simultaneously): 20, 50, 100, 150, 200, 250 and 300 µg l⁻¹ and then enriched using the optimized preconcentration method using either CNT-NA or CNT-NO sorbents. Preconcentration experiments were performed in three replicates (n=3) and the three extracts were analyzed as separate samples. The analytical parameters of the method using sorbent CNT-NO and CNT-NA are shown in Table 2.

Limit of linearity for each metal ion was estimated based on the value of the R-squared for the calibration curve. The limits of quantification of the metal ions were estimated as ten times the standard deviation of the blank signal. Sensitivity of the method towards each metal ion was estimated based on the slope of the calibration curve.

From Table 2, it is clear that the main difference between the two sorbents is in the limit of linearity, in which CNT-NA gave higher limit of linearity of the method for all the metal ions. It is also noted that sensitivity of the method was higher when CNT-NA was used and lower limits of quantification were achieved with CNT-NA. So that CNT-NA was selected for application of the method on real water samples.
**Table 2.** Analytical performance of the optimum method using CNT-NO and CNT-NA as preconcentrating sorbent for metal ions

<table>
<thead>
<tr>
<th>Element</th>
<th>Limit of quantification*, µg l⁻¹</th>
<th>Sensitivity, AU µg⁻¹ l</th>
<th>Limit of linearity, µg l⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>CNT-NO</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cd²⁺</td>
<td>0.464</td>
<td>0.26</td>
<td>100</td>
</tr>
<tr>
<td>Pb²⁺</td>
<td>1.512</td>
<td>0.17</td>
<td>100</td>
</tr>
<tr>
<td>Cu²⁺</td>
<td>0.188</td>
<td>0.56</td>
<td>100</td>
</tr>
<tr>
<td>Zn²⁺</td>
<td>0.042</td>
<td>3.90</td>
<td>150</td>
</tr>
<tr>
<td>Mn²⁺</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td><strong>CNT-NA</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cd²⁺</td>
<td>0.106</td>
<td>1.40</td>
<td>150</td>
</tr>
<tr>
<td>Pb²⁺</td>
<td>0.856</td>
<td>0.18</td>
<td>300</td>
</tr>
<tr>
<td>Cu²⁺</td>
<td>0.184</td>
<td>0.72</td>
<td>300</td>
</tr>
<tr>
<td>Zn²⁺</td>
<td>0.040</td>
<td>4.18</td>
<td>200</td>
</tr>
<tr>
<td>Mn²⁺</td>
<td>0.152</td>
<td>0.87</td>
<td>150</td>
</tr>
<tr>
<td>Cd²⁺</td>
<td>0.106</td>
<td>1.40</td>
<td>150</td>
</tr>
</tbody>
</table>

* Limit of quantification is ten time the standard deviation of the blank.

**Analytical application of the method using CNT-NA sorbent**

The analytical application of the optimum method (using CNT-NA) was validated by applying the optimum preconcentration method (using CNT-NA) on environmental water samples followed by FAAS determination of the targeted metals.

The metal ions were found in the unspiked real water samples as shown in Table 3. Environmental waters were then spiked with the metal ions (simultaneously) at various concentrations (spiking ranges are shown in Table 3), then preconcentrated according to the optimum procedure (using CNT-NA) at pH 9. Spike recoveries of the metals are shown in Table 3. The spike recovery range of all metal ions is 81-106 %.

The results reveals that the optimum method gave satisfactory results and could be used for the analysis of Mn²⁺, Pb²⁺, Cd²⁺, Cu²⁺ and Zn²⁺ in real environmental waters.

**Table 3.** Concentration of metals (µg l⁻¹±σ, n=3) in environmental water samples and their spike recoveries according to the optimum method (using CNT-NA sorbent)

<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>Unspiked.</td>
<td>ND a</td>
<td>ND a</td>
</tr>
<tr>
<td>Spike recovery range, % (Spiking range: 20-150 µg l⁻¹).</td>
<td>87-100</td>
<td>89-106</td>
<td>85-95</td>
</tr>
<tr>
<td>Pb²⁺</td>
<td>Unspiked.</td>
<td>ND a</td>
<td>ND a</td>
</tr>
<tr>
<td>Spike recovery range, % (Spiking range: 20-300 µg l⁻¹).</td>
<td>91-102</td>
<td>94-103</td>
<td>89-100</td>
</tr>
<tr>
<td>Cd²⁺</td>
<td>Unspiked.</td>
<td>ND a</td>
<td>ND a</td>
</tr>
<tr>
<td>Spike recovery range, % (Spiking range: 20-150 µg l⁻¹).</td>
<td>89-101</td>
<td>85-103</td>
<td>81-96</td>
</tr>
<tr>
<td>Cu²⁺</td>
<td>Unspiked.</td>
<td>ND a</td>
<td>ND a</td>
</tr>
<tr>
<td>Spike recovery range, % (Spiking range: 20-300 µg l⁻¹).</td>
<td>89-99</td>
<td>97-103</td>
<td>81-95</td>
</tr>
<tr>
<td>Zn²⁺</td>
<td>Unspiked.</td>
<td>ND a</td>
<td>ND a</td>
</tr>
<tr>
<td>Spike recovery range, % (Spiking range: 20-200 µg l⁻¹).</td>
<td>85-98</td>
<td>86-101</td>
<td>81-94</td>
</tr>
</tbody>
</table>

Conclusion

Nitric acid treatment of multi-walled carbon nanotubes gave higher recoveries of metal ions than the non-oxidized sorbent (CNT-NO). It also gave higher recovery than the hydrogen peroxide treatment and the ammonium persulphate treatment of the carbon nanotubes. It is thought that the nitric acid treatment has two effects on carbon nanotubes: first, it generates new acidic groups on the surface of the carbon nanotubes that may be used for direct binding of metal ions at pH 5. Second, it opened the caps of the carbon nanotubes and thus may facilitate the capturing process of the precipitated metal hydroxides at pH 9. However, the recovery of metals at pH 9 was higher than that achieved at pH 5. It is thought that the effect of hydrogen peroxide treatment of carbon nanotubes was similar to nitric acid treatment in terms of increasing recovery at pH 9 and at pH 5 (except for Mn$^{2+}$ the recovery was not satisfactory with CNT-HP). Generally, the recovery achieved with CNT-NA sorbent was higher than that achieved with CNT-HP sorbent. Ammonium persulphate treatment of carbon nanotubes improved the recovery of some metal ions at pH 5 but not at pH 9.

Comparing the analytical performance of non-oxidized sorbent (CNT-NO) and CNT-NA revealed that the main difference between the two sorbents was in the limit of linearity, in which CNT-NA gave a wider linear range. It is also noted that the method sensitivity was higher when using CNT-NA and that lower limits of quantification were achieved with CNT-NA. Application of the optimum method using CNT-NA on real environmental waters gave satisfactory results and revealed that this method can be recommended for preconcentration and analysis of the targeted metal ions.

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