

Speciation of some trace elements in water samples after preconcentration on activated carbon by neutron activation analysis

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A new filtering column has been developed on the covalent attachment of chelating functionalities to simple, highly hydrophilic adsorbent material, which can then complex heavy metal ions irreversibly and targeted towards toxic metals removal. The capacity of the chemically modified sorbent (modified charcoal) materials used in this work was evaluated for the above mentioned heavy metal ions in the presence of iron ions and simulated water samples. The methods are based on preconcentrations of the elements of interest on activated carbon and zirconium loaded activated carbon using specific conditions of pH and oxidation states followed by a final determination by neutron activation analysis (NAA). It has been investigated that zirconium loaded activated carbon is able to adsorb As (V), Se (VI), Cr (VI) and Hg (II) at any pH while activated carbon is able to adsorb As (III), Se (IV), Cr (III) and Hg(I) at higher pH.

Introduction

The presence and fate of elements, especially the heavy metals, in natural and drinking waters in relatively high concentrations and their chronic toxicity have become priority areas in the chemistry of marine and fresh water ecosystems. Much interest has, therefore, been shown in the analysis of trace elements in water using among other techniques such as neutron activation analysis (NAA).¹ Preliminary concentration procedures are usually required in trace element analysis of water samples, since in various natural waters most of the heavy metals are present in low concentrations even in areas associated with particularly heavy metal pollution burdens. The European Union recently initiated the development of several (environmental science oriented) reference materials to be characterized for heavy, trace and rare earth elements. This process in other countries is under way.² With respect to the analysis of the carbon-based compounds, the analytical challenge is posed by the ultra-low impurity levels. In this work examples of the multi-element speciation by these advanced materials are reported and quantitatively determined by NAA.^{3–5} An indication is given of the sensitivities that can be attained under typical conditions.

Waters are enriched with metals in contact with minerals and soils. Water also can have extensive concentrations of metals in the surroundings of ore finding places. The main anthropogenic source of heavy metals are the waste waters from mining and treatment of ores, agricultural insecticides, sludge depositories and contamination of atmospheric water.⁶ This water is enriched by the oxidation of cations when acid ion is enriched and this acidic ion will dissolve the minerals in the surroundings.

Filtration is one of the unit processes used in the production of potable water or those generated during treatment processes. Adsorption with activated carbon has been one of the most useful techniques in water treatment. While in the past, activated carbon was predominantly used to remove odor and color producing molecules in water,⁷ recent experimental results have been reported for the removal of inorganic chemicals with it.⁸ Since multi pollutant systems encountered in water treatment contain both inorganic and organic, and inorganic can affect the adsorption of organic onto activated carbon, it is important to study their competitive adsorption. In this work, the competitive adsorption of inorganic pollutants as As, Se, Cr and Hg are studied.

Experimental

Preparation of activated carbon

In the first step, palm shells were cleaned of loose fibers and traces of kernel and then ground, washed and dried at 100 °C before sieving. As received, oil palm stones were crushed and sieved. Materials of grain size 1.4–2.0 mm were selected for use. For the preparation of high grade activated carbon pyrolysis of the pretreated oil palm kernel was performed in a quartz tube horizontal reactor, which was placed in a tube furnace (Thermolyne 21100). The furnace has programmable temperature control such as heating rate, pyrolysis temperature and retention time. About 100 g of raw materials was placed into the middle of the quartz tube, which was seated at the center of the tube furnace. 100% water vapor with flow rate of 100 ml·min⁻¹ was used as the inert gas flushing through the reactor, right from the beginning of the pyrolysis process. The experiments were carried out from room temperature to 400, 600 and

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800 °C. For retention times of 1 and 2 hours at each pyrolysis temperature and a heating rate of 40 °C·min⁻¹ was used.

Preparation of Zr-activated carbon

A fixed weight (g) of activated charcoal was put into of zirconyl nitrate solution and the suspension was stirred with a magnetic stirrer at room temperature for a certain time. The resulting material (Zr-AC) was filtered off, washed with water until free of nitrate and air-dried.

Preparation of soil particles

Red soils collected from a nearby clay deposit were first cleaned from hard rocks or stones and fibers, traces of other foreign particles and then ground, washed and dried at room temperature before sieving. The preparation of hard soil particle from the clay-like soil was performed in a ceramic basin reactor, which was placed in a tube furnace (Thermolyne 21100). About 500 g of raw soil was placed into the middle of the basin reactor, which was seated at the center of the tube furnace. The experiments were carried out from room temperature to 400 °C. For retention times of 4 hours at each operation temperature and a heating rate of 40 °C·min⁻¹ was used. As received, soil stone was crushed and sieved. Materials of grain size 0.2–0.5 mm were selected for use.

Chemicals

Owing to the high sensitivity of instruments, high-purity reagents have been used. In these methods all acids used were of ultra high-purity grade. Concentrated nitric acid (specific gravity 1.41-Merck) has been used to prepare HNO₃ (1+1) and nitric acid HNO₃ (1+9) solutions. The former and the later acid solutions consisted of 500 ml and 100 ml of conc. HNO₃, respectively, diluted to 1 liter with 400 ml of ASTM type-1 water. ASTM type-1 water has been used for the preparation of all solutions and dilutions. The stock solution was stored in Teflon bottles. The following procedures were used for preparing standard stock solutions. Certified reference materials soil sediments (Soil-7) and (SL-1) were supplied by the International Atomic Energy Agency (IAEA).

Preparation of stock solutions As(III), As(V), Cr(III), Cr(VI) Se(IV), Se(VI) Hg(I) and Hg(II)

The As(III) stock solution of 1000 µg·ml⁻¹ was prepared by dissolving 0.1320 g of arsenic trioxide (Allied Chemicals) in 25 ml deionized distilled water.

The solution was acidified with 4 ml of 1M HNO₃ (Merck) and diluted to 100 ml with deionized water. A stock solution of As(V) 1000 µg·ml⁻¹ was prepared by dissolving 0.4163 g of sodium arsenate (J. T. Baker & Co.) with 0.5 ml of conc. HNO₃ and diluted with deionized water up to the mark. Standard stock solution (1000 mg·l⁻¹) of Cr(III) was prepared by diluting Cr(NO₃)₃·9H₂O (Riedel-Haen AG Seelze-Hannover, Germany) while the standard stock solution (1000 mg·l⁻¹) of Cr(VI) was prepared by dissolving K₂Cr₂O₇ (Merck) in deionized water. Solutions were stored in acid washed polyethylene containers. About 0.1405 g of SeO₂ was dissolved in 20 ml ASTM type-1 water and diluted the solution up to 1000 ml with ASTM type-1 water for Se(IV) standard stock solution (1000 mg·l⁻¹) while the standard stock solution (1000 mg·l⁻¹) of Se(VI) was prepared by dissolving H₂SeO₄ (Merck). The stock solutions were stored in Teflon bottles. Mercury(II) chloride stock solution (1000 mg·l⁻¹) was prepared by dissolving (0.1354 g) mercury(II) chloride in 10 ml of nitric acid and diluted to 100 ml with water.

Separation of the As, Cr, Se and Hg species

The pH of the mixed standard solutions of As(III), Se(IV), Cr(III), and Hg(I) was adjusted to 9.0±0.2 with NH₃-NH₄Cl buffer solution and 1.0 ml of 0.1M FeCl₃ solution (about 5.6 mg Fe) was added. The precipitate that formed was allowed to coagulate for at least 20 minutes, after which 0.100 g of activated charcoal powder was added. The mixture was shaken and left to stand for a while before filtration. After filtration the loaded filters were air-dried at room temperature overnight.⁹

For the separation of As(V), Se(VI), Cr(VI) and Hg(II) the filtrate was poured into a second polyethylene-leaching bottle and the pH of the mixed standard solutions was adjusted to 3.9±0.2 with NaOH and HNO₃ solutions. Then Zr-AC (0.100 g) was added to the sample and after stirring, the mixture was left to stand for a while before filtration. Loaded filters were air-dried at room temperature overnight. Separation of As(V), Se(VI), Cr(VI) and Hg(II) and separation of As(V), Se(VI), Cr(VI) and Hg(II) were also performed in reversed order.⁹

Total inorganic As, Se, Cr and Hg separation in IAEA Soil-7 and SL-1 Sediment SRMs was performed similarly using aqueous solutions prepared after dissolving the materials. Normally about 1 g of the SRMs was carefully weighed into a Teflon PFA pressure decomposition vessel of a CEM Model MDS-81D microwave digester before adding between 5–10 ml of 70% HNO₃. Most samples can be digested within 2–2.5 minutes with controlled heating. In arsenic speciation,

samples were digested for 5 minutes at low heating (48 °C) at 30% power (190 W). For sediment samples intended for ICP-MS analysis, the cooled digested solutions were added with 5 ml of (30%) H₂O₂ until effervescence stopped.

The overall separation of the metal species using the filtering unit with multi-layer components (Fig. 1) was performed by passing the environmental water samples collected from specific sites through the unit. The filtrates before and after passing through the column were collected and analyzed accordingly using INAA and ICP-MS techniques.

Irradiations and counting

All irradiations have been carried out using the facilities of the Malaysian Institute for Nuclear Technology Research (MINT). About 0.1 g of the homogenized sample was weighed onto a 1 cm³ polyethylene vial and again weighed. The weight was recorded and the vial was heat-sealed. The sealed vial was placed in a polyethylene capsule and three sealed sub-samples were prepared for each sample. The reliability of the instrumental neutron activation analysis (INAA) was validated using the IAEA Soil-7 and SL-1 Sediment standard reference materials (SRM).

The SRMs used were prepared and packed in the same manner as the adsorbed carbon samples. Irradiations were performed on 1 ml of the final extraction solution in a neutron flux of $5 \cdot 10^{16} \text{ n} \cdot \text{m}^{-2} \cdot \text{s}^{-1}$ for 6 hours at 750 kW power from a Triga Mark II reactor at the Malaysian Institute for Nuclear Technology Research (MINT) followed by 2 to 20 days of cooling according to the radionuclides investigated. A large-volume coaxial HPGe detector with a resolution of 1.9 keV at 1332 keV ⁶⁰Co was used to count the 559 keV γ -rays of ⁷⁶As in the solid samples over a period of 1800–3600 seconds. Amplification and analysis of signals were done using an ADC ND 592 (Nuclear Data) analyzer connected to a ND 6000 (Nuclear Data) multi-channel analyzer. The calibration of the spectroscopy system was performed with sealed point sources namely ⁶⁰Co, ¹³⁷Cs and ¹³³Ba. The efficiency of the detector was experimentally measured using IAEA SL-1 sediment SRM.^{10–11} Arsenic was analyzed by using the 559.2 keV photopeak of ⁷⁶As, while mercury was analyzed via the 279.47 keV photopeak of ²⁰³Hg. The determination of mercury via the 279.47 keV photopeak of ²⁰³Hg is interfered by the 279.60 keV of ⁷⁵Se, hence, corrections have to be made for the photopeak contribution. Selenium was determined by using the 264.34 keV photopeak of ⁷⁵Se while chromium was measured using the 320.23 keV of ⁵¹Cr and zirconium via the 755.54 keV photopeak of ⁹⁵Zr.

Results and discussion

The nature and characteristics of the activated carbon (AC) and zirconium activated carbon (Zr-AC) prepared is described elsewhere and the substrate is used throughout this work. The assembly unit and the filtering column using the prepared AC and (Zr-AC) is shown in Fig. 1. Spiked and actual water samples were passed through this column at the rate determined by the natural flow under gravitational influence.

The advantage of this preconcentration methods is the elimination of interfering ²⁴Na, ⁸²Br and ³⁸Cl activities, usually encountered in the analysis of surface water and sea water for trace metals by neutron activation. Usually Na, Br and Cl are poorly adsorbed on Zr-AC and AC. Any traces of these ions can be almost completely removed by washing the adsorbent 5 to 6 times with deionized water. Secondly, the separation of the trace metals by this simple procedure is achieved in less than one hour. It can be carried out immediately after sample collection. Thirdly, any possible contamination of samples and more importantly loss of volatile elements are minimized. The aim of the neutron activation study is to investigate the absorption capacity of the activated carbon, modified activated carbon and soil particles. The adsorption capacities (%) of AC and Zr-AC at different pH values for water samples containing As, Cr, Se and Hg of different species were shown in the Table 1.

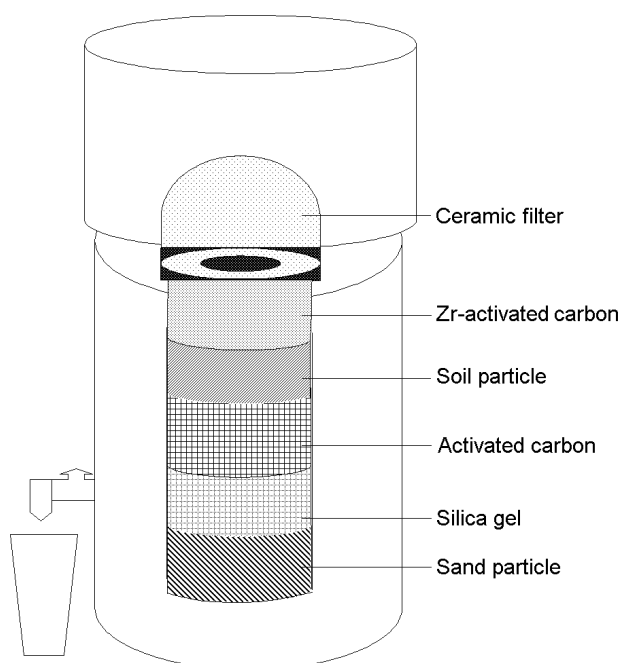


Fig. 1. The filter unit assembly showing the adsorbent components

Table 1. Adsorption capacities (in percent) of AC and Zr-AC at different pH values

| Element | Concentration, $\mu\text{g}\cdot\text{l}^{-1}$ | Adsorption capacity on AC, % (pH value) | | | | |
|---------------------------------|---|--|-------|-------|-------|-------|
| | | (3.0) | (5.0) | (7.0) | (8.0) | (9.0) |
| As(III) | 100 | 1.02 | 25.08 | 58.76 | 80.92 | 96.87 |
| Cr(III) | 100 | 0.0 | 24.66 | 64.99 | 82.02 | 98.32 |
| Se(IV) | 10 | 0.0 | 28.02 | 70.16 | 85.37 | 98.66 |
| Hg(I) | 10 | 0.52 | 31.29 | 75.76 | 89.54 | 99.33 |
| Adsorption capacity on Zr-AC, % | | | | | | |
| As(V) | 100 | 97.53 | 97.65 | 94.67 | 93.01 | 32.34 |
| Cr(VI) | 100 | 98.22 | 98.59 | 95.52 | 94.82 | 37.66 |
| Se(VI) | 10 | 99.10 | 98.78 | 96.06 | 95.12 | 28.92 |
| Hg(II) | 10 | 99.82 | 96.87 | 96.04 | 93.45 | 40.72 |

Table 2. Recovery of total As, Se, Cr, Hg and Zr content in standard reference materials

| Element | SRM (Soil-7), $\text{mg}\cdot\text{kg}^{-1}$ | | SRM (SL-1), $\text{mg}\cdot\text{kg}^{-1}$ | |
|---------|--|--------------------|--|-------------------|
| | Certified value | Obtained value | Certified value | Obtained value |
| As | 13.4 | 13.79 ± 0.76 | 27.5 ± 2.9 | 27.21 ± 4.71 |
| Se | 0.40-0.80 | 0.60 ± 0.20 | 2.90* | 1.53 ± 0.18 |
| Cr | 60.0 | 67.16 ± 3.44 | 104.0 ± 9.0 | 94.84 ± 2.49 |
| Hg | 0.04 | 0.047 ± 0.008 | 0.13* | 0.055 ± 0.01 |
| Zr | 185.0 | 170.36 ± 52.72 | 241.00* | 155.52 ± 12.6 |

* Information value in the sediment SL-1.

The accuracy and precision of the analysis as well as standard reference materials (SRM) certified values and obtained values are shown in Table 2. The obtained SRM values were calculated and compared with irradiated standard solution values. The analyzed values of As, Se, Cr, Hg and Zr for SRM Soil-7 showed good agreement in comparison to the certified values. The calculated values of As and Cr for SRM SL-1 also showed good agreement with the certified values, while Se, Hg and Zr did not show good agreement. In Table 2 it was found that the standard deviation value is reasonable, i.e., precision and accuracy is very good. The certified values of Se, Hg and Zr in the SRM SL-1 were not given and their mention is only for information.

When the polluted water samples were passed through the newly modified filtering column containing the Zr-AC, all species of toxic elements were adsorbed on AC and Zr-AC at different pH value range. Attempts were made in this work to prove that the species of As(III), Se(IV), Cr (III) and Hg(I), and As(V), Se(VI), Cr (VI) and Hg(II) were adsorbed on AC and modified Zr-AC, respectively, at different pH values. It was observed that the Zr-AC can adsorb As(V), Se(VI), Cr (VI) and Hg(II) species at all pH range, but unloaded AC carbon can only absorb As(III), Se(IV), Cr (III) and Hg(I) at higher pH range in the presence of Fe ions.¹²⁻¹⁴ The basic theory observed was that the "electron deficient ion or complex was interacted upon with the

electron rich ion or complexes" for the adsorption of different species of chromium. The same theory would be appropriately applicable for As(V), Se(VI) and Hg(II) to be adsorbed onto the Zr-loaded activated carbon or Zr-AC. For As(III) and Hg(I), adsorption on unloaded activated carbon (AC) occurred at higher pH values in the presence of iron ion.

The results from the adsorption experiment are presented in the Table 3. The metals As, Se, Cr and Hg were quantitatively removed from the spiked water through the developed filtering unit. In Table 3, the results show that the blank activated carbon contains Cr and Se only, other elements such as As, Hg and Zr are not present. Blank values were determined and subtracted from the same elements in the sample value to give the actual trace element concentrations. All of these elements were determined in the soil sample before and after use. It was observed from results in Table 3 that after filtration the soil particles have partially adsorbed As, Cr, Hg and Zr but some Se remained in the filtrate in relatively small amount. Selenium species were found to be totally absorbed by the AC and Zr-AC layers. It has been suggested that this activated carbon will be a good adsorbent for some heavy metals and their complexes. This may account for the quantitative recovery of As, Se, Cr, and Hg, by complexation with Zr-loaded activated carbon.

Table 3. The trace elements adsorption results on activated carbon, modified activated carbon and soil particles in environmental samples

| Element | Determination by NAA | | | Initial concentration of species, $\mu\text{g g}^{-1}$ | Blank activated carbon, $\mu\text{g g}^{-1}$ | Total concentration by ICP-MS, mg l^{-1} |
|---------|--------------------------|-----------------------------|----------------------------|--|--|---|
| | AC, $\mu\text{g g}^{-1}$ | Zr-AC, $\mu\text{g g}^{-1}$ | Soil, $\mu\text{g g}^{-1}$ | | | |
| As(III) | 10.40 \pm 1.43 | | | | nil | |
| As(V) | | 19.04 \pm 4.01 | 2.45 \pm 0.93 | 31.89 \pm 5.44 | | 0.72 \pm 0.04 |
| Cr(III) | 11.32 \pm 0.83 | | | | | |
| Cr(VI) | | 13.31 \pm 2.43 | 3.57 \pm 1.81 | 28.20 \pm 3.26 | 0.43 \pm 0.05 | 0.64 \pm 0.09 |
| | $\mu\text{g kg}^{-1}$ | $\mu\text{g kg}^{-1}$ | $\mu\text{g kg}^{-1}$ | $\mu\text{g kg}^{-1}$ | $\mu\text{g kg}^{-1}$ | $\mu\text{g kg}^{-1}$ |
| Se(IV) | 30.00 \pm 2.0 | | | | | |
| Se(VI) | | 115.00 \pm 23.0 | 0.0 | 510.00 \pm 65.0 | 0.02 \pm 0.01 | 11.77 \pm 1.0 |
| Hg(I) | 8.86 \pm 1.42 | | | | | |
| Hg(II) | | 29.89 \pm 3.45 | 31.54 \pm 4.6 | 70.29 \pm 6.10 | nil | |
| | 1.61 \pm 0.06 | | | | | |

The normal AC was not an efficient adsorbent for As(V), Se(VI), Cr(VI) and Hg(II). Mercury(I) is adsorbed on both the normal and loaded activated carbon. The adsorption of As(III), Cr(III), Hg(I) and Se(IV) was insignificant throughout the investigated pH range. At higher pH range most of the As, Se, Cr and Hg species were adsorbed well onto the activated carbon. Based on the same concept and hypothesis it can be implied that As(V), Se(VI) and Hg(II) were well adsorbed onto Zr-AC. Many researchers have proven that between 60–70% of the higher oxidation states of the trace metals were found in surface waters and the ratio of As(III)/As(V), Cr(III)/Cr(VI) and Hg(I)/Hg(II) is usually less than one.^{15–17} In Table 3 it was observed that the quantity of As, Se, Cr and Hg adsorbed by Zr-AC is greater than those absorbed by AC, and the ratio of AC adsorbed value to Zr-AC absorbed value is less than one. So, it has been suggested that Zr-AC adsorbed As(V), Cr(VI), Se(VI) and Hg(II) of higher oxidation state, and AC adsorbed As(III), Cr(III), Se(IV) and Hg(I) species.

Conclusions

Relatively cheap activated carbon can be readily prepared from agricultural waste and conveniently used as good adsorbents for some toxic heavy metals in aqueous form. The filtering column developed by assembling layers of AC and Zr-AC with soil particles improved its adsorption power towards As, Cr, Se, Cd, Pb and Hg significantly. This column was developed in order to adsorb the specific species of the above elements from water samples taken from the surface by filtration after making sure that the adsorbates were adsorbed on zirconium loaded activated carbon and activated carbon. The adsorbed amount of As, Se, Cr and Hg species onto the zirconium loaded activated carbon were 94.67% to 98.78% at pH level 5.0 to 7.0, respectively, while the adsorbed amount of the above elements onto activated carbon were found to be 24.66%

to 75.76%. Accordingly, the species adsorbed on Zr-AC were As(V), Se(VI), Cr(VI) and Hg(II) and, those on AC were As(III), Se(IV), Cr(III) and Hg(I).

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