Adsorption of some toxic elements from water samples on modified activated carbon, activated carbon and red soil using neutron activation analysis

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A simple and sensitive method for the determination of some metalloids and heavy metals in water samples is presented. The method is based on the preconcentration of the attachment of chelating functionalities with metalloids and toxic metals irreversibly and targeted towards toxic metals adsorbed on modified activated carbon, activated carbon and red soil particles at pH 3.0–9.0±0.2, followed by quantitative determination using instrumental neutron activation analysis (INAA), on the absorbers. Attachment results from attraction that may be physical, chemical, electrical, or a combination of all three. The efficient removal of metalloids and toxic metals, especially arsenic, chromium and mercury is anticipated. The adsorption capacity of the chemically modified activated carbon materials was evaluated for the above mentioned metalloid and toxic metal ions in the presence of iron ions and simulated water samples. Red soil particles containing iron was utilized in the control of oxidation-reduction reaction with metalloids and toxic metals. The preconcentration of the elements of interest on red soil particles, activated carbon and modified activated carbon at different depths, pH and oxidation states was investigated. The results obtained showed good agreement with certified values giving relative errors of less than 10%.

Introduction

Reliable measurements of dissolved trace metal concentrations are needed when the behavior of trace metals in surface waters is studied. However, obtaining such data in polluted surface water systems is very difficult, due to sample contamination during collection, handling, analysis[1,2] and with the detection limits of analytical instruments. Concern has been expressed that much of the trace element data for World Rivers published prior to the 1980s may be incorrect.[3–5]

Trace metals can exist in a number of physico-chemical forms or species in natural waters. These include free aquatic ionic forms, dissolved inorganic or organic complexes, complexes with colloidal or particulate matter (inorganic or organic), and complexes associated with biota. The speciation can have a major influence on the transport, behavior, bioavailability and toxicity of trace metals. It has been suggested that the manner in which chemicals partition among the dissolved, particulate and colloidal phases affects both of their chemical and physical behaviors in aquatic environments.[3,6] Thus all three phases need to be considered in aquatic environments studies. Free ionic forms of a number of trace elements (As, Cd, Cr, Cu, Pb, etc.) have been found to be considerably more toxic to aquatic biota than complexed, colloidal or particulate forms.[6] However, for elements such as Hg the methylated forms are more toxic than the ionic forms.[7] In many cases, bioavailability and toxicity of a trace metal are dependent on the chemical and physical form of the metal, which is affected by water chemistry (e.g., pH, temperature, salinity)[8] in addition to other factors.

In fresh water systems, organic matter plays an important role, through complex formation, in controlling the fraction of trace metals that is bioavailable.[9–12]

Some concentrations of trace elements in surface water are at $pg \cdot ml^{-1}$ level and their direct determination sometimes is not easy by atomic absorption spectroscopy (AAS) and inductively coupled plasma-mass spectrometry (ICP-MS). This necessitates the development of preconcentration for the separation of trace elements as a group from different matrices. Procedures generally followed for group separation and speciation of trace elements include: (1) electrical adsorption (exchange adsorption), (2) Van der Waals attraction and (3) chemical reaction (chemical adsorption).[13] In most cases, adsorption results from some combination of all three of these conditions, with physical adsorption, possibly enhanced by low solubility, playing the dominant role for many organic compounds. Activated carbon (AC) has been used as a collector for multi-element preconcentration in the analysis of natural water.[14] No exhaustive studies have been made on the preconcentration and speciation of trace elements from water using AC. Hence, separation and speciation of trace elements as a group from matrix elements for their determination at very low levels has received considerable attention.

If the AC participates in the reduction process, it cannot be considered as an inert species. In fact, some authors[15,16] have suggested that the stronger the interaction between the carbon and the metals species, the more favored will be the reduction process. One may then deduce that both the texture of the AC and the

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metal loading will affect the redox process. The main objective of this work was to evaluate the modification in porosity and adsorption capacity of the AC when impregnated with zirconium salt.

Adsorption is one of the reactions that decreases surface energy, which will be concentrated at the liquid-vapor interface, whereas materials that decrease interfacial energy will concentrate more in the liquid-solid interface.[17] Adsorption of some metal species in soils is more likely to occur at the solid-liquid interfaces. This type of adsorption can be distinguished as positive and negative adsorption. Positive adsorption relates to the concentration of the solute on the colloidal surfaces. It is also referred to as specific adsorption. The solute usually decreases surface tension. On the other hand, negative adsorption refers to the concentration of the solvent on the clay surface. The solute is then concentrated in the bulk solution, here the surface tension is decreased.

Few methods are available for the determination of trace elements at concentrations below $1\ \mu g \cdot l^{-1}$.[18,19] At this level, preconcentration by adsorption is mandatory to obtain the required sensitivity, preconcentration by adsorption on AC, modified AC and red soil was applied. All species of the trace elements were adsorbed on AC and modified AC under various conditions. The advantage of this method over others is the simplicity, which allows the preconcentration to be performed at any analytical laboratory and the high sensitivity of neutron activation analysis, which is used for the final determination. The aim of the neutron activation study was to investigate the adsorption capacity of the AC, modified AC and soil particles. If these materials really adsorbed the toxic elements such as As, Cr and Hg, then these could be exactly determined by neutron activation analysis (NAA).

Experimental

Preparation of standard solutions

All reagents were analytical grade and the water used was ultra pure grade deionized water. Polyethylene leaching bottles were used in the adsorption and coprecipitation procedures and all glassware were acid washed (10% HNO_3 overnight). Standard stock solution of Cr(VI) ($1000\ mg \cdot l^{-1}$) was prepared by dissolving $K_2Cr_2O_7$ (Merck) in deionized water. Mercury(II) chloride (Ajax Chemicals) stock solution ($1000\ mg \cdot l^{-1}$) was prepared by dissolving 0.1354 g mercury(II) chloride in 10 ml of HNO_3 (65%) (Merck) and diluted to 100 ml with water. The solution was stored in a refrigerator at 4 °C. A stock solution of As(V) ($1000\ \mu g \cdot ml^{-1}$) was prepared by dissolving 0.4163 g of sodium arsenate ($NaAsO_3$) (J. T. Baker & Co.) with 0.5 ml of conc. HNO_3 and diluted with deionized water

up to the mark. Solutions were stored in acid washed polyethylene containers. Zirconyl nitrate hydrate ($ZrO_7N_2 \cdot aq$), (Fluka) was used for the preparation of the granulated AC loaded with zirconium. Granulated AC (ultra pure grade activated carbon prepared in our lab) was used without further modification.[20]

Construction of filter system-1 and filter system-2

The proposed water purification filter units will be of good advantage due to their low cost and ease in handling. These filter units are anticipated to be capable of supplying hygienic and palatable water. The chemicals and materials used to fabricate the filter units are of local origin.[20]

Filter system-1 (Fig. 1):

1st layer: This layer contains high grade AC for the removal of Cr(III), As(III) and Hg(I) from the water.[20]

2nd layer: This layer contains a specially prepared AC. The modified AC was prepared by mixing zirconyl salts with AC at pH 7.0. Loading of AC with zirconium improves the adsorption capacity of Cr(VI), As(V) and Hg(II), which are present in the aqueous solution as anions over the whole pH range.[20] The function of this layer is to adsorb the above toxic elements from the water rapidly.

3rd layer: This layer is composed of silica sol which is highly effective as a coagulant aid. It can be prepared from various chemicals including sodium silicate, chlorine, sodium bicarbonate, sulfuric acid and carbon dioxide. Better results would be obtained if the injection time of the activated silica was increased. The function of this layer is to remove odor from the water.

4th layer: The last layer contains fine and blackish stone particles, the sizes of which range from 15–20 mesh and that are rich in silicates. The function of this layer is to retain foreign particles and supply CaO slightly. This layer contains limestone, which will react with bicarbonate (HCO_3^-) and finally reduce the alkalinity.

Filter system-2 (Fig. 2):

1st layer: Material and functions of this layer is similar to that of 2nd layer of FS-1.

2nd layer: This layer contains soil for the removal Cr(III), As(III), and Hg(I) from the water. Manganese dioxide (MnO_2) is insoluble in water, but in this layer it acts as an oxidizing agent in decolorizing the water.[20]

3rd layer: This layer is comprised of materials similar to the 1st layer of FS-1.

4th and 5th layer: The materials for the last two layers are similar to the 3rd and 4th layers of FS-1, respectively.

A ceramic primary filter system was set up onto the filtering columns in both FS-1 and FS-2. The function of this ceramic filter is to remove foreign particles and microorganisms, such as algae and fungi, from the raw water. A plastic or stainless steel screen of 200 to 300 mesh size was placed at the bottom of each layer to retain the particles.

Determination of the adsorption properties of FS-1 and FS-2

The adsorption properties of FS-1 and FS-2 were compared for their abilities to adsorb Cr, As and Hg in polluted surface waters according to the following steps. The constructed FS-1 and FS-2 were used in the adsorption study of toxic elements. Artificial polluted water samples were prepared by mixing 200 ppb As,

200 ppb Cr and 10 ppb Hg as total species into 2 liter of deionized water and these artificially polluted waters were eluted through by the FS-1 and FS-2 for 1–2 hours. Actual surface water samples collected from different locations were eluted through FS-1 and FS-2 for 10 days. Test filters were thoroughly washed using contaminant-free water, then rinsed with 20% HNO_3 prior to use. It was again systematically back-washed a minimum of three times with contaminant free water after the filtering process. The elemental concentrations of As, Cr and Hg in AC, Zr-AC and the soil layer were determined by instrumental neutron activation analysis (INAA). Three replicates of about 0.1 g taken at 1, 3 and 5 cm depth from each of the AC and Zr-AC layers were weighed and placed into polyethylene vials of 1 cm^3 capacity for the irradiation procedures.
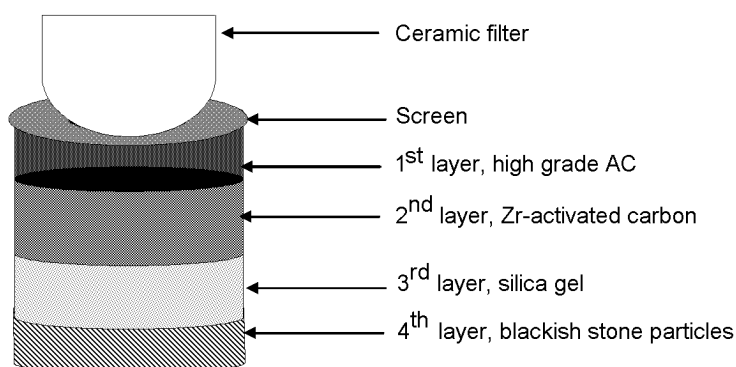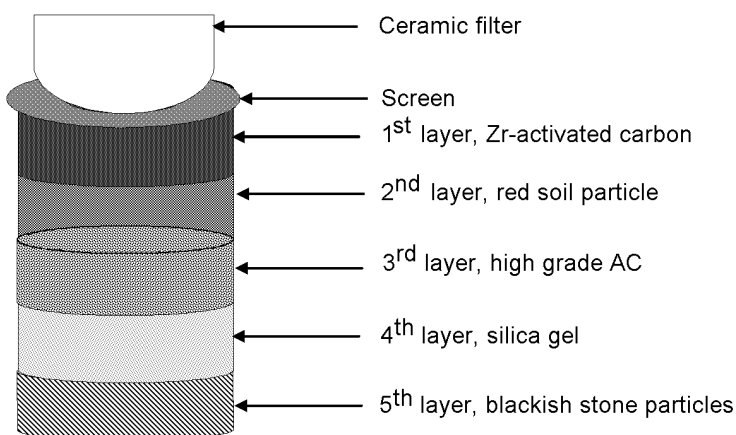

Fig. 1. Constructed filter unit FS-1

Fig. 2. Constructed filter unit FS-2

Irradiation and counting

All irradiations were carried out using the facilities of the Malaysian Institute for Nuclear Technology Research (MINT). About 0.1 g of the homogenized sample was weighed into a 1-ml 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 sealed together with three sub-samples prepared for each sample. The reliability of the INAA technique was validated using the International Atomic Energy Agency (IAEA) Soil-7 and SL-1 Sediment standard reference materials (SRMs). The IAEA samples were prepared and packed in the same manner as the adsorbent samples. Special care was taken in sealing the vials to prevent leakage during the irradiation step. Irradiations were also performed on 1 ml of the final extraction solution in a neutron flux of $4 \cdot 10^{16}$ n·m^{-2}·s^{-1} for 6 hours at 750 kW power from a Triga Mark II reactor at the MINT followed by between 2 to 20 days of cooling depending on the radionuclides of interest. A large-volume coaxial HPGe detector with a resolution of 1.9 keV at 1332 keV ^{60}Co was used to count the 559 keV γ-rays of ^{76}As in the solid samples over a period of 1800–3600 seconds. Amplification and analysis of signals were done using a Nuclear Data ADC ND 592 analyzer connected to a ND 6000 multichannel analyzer. The calibration of the spectroscopy system was performed with sealed point sources, namely ^{60}Co, ^{137}Cs and ^{133}Ba.

The γ-ray activities of the samples were measured by a high resolution gamma-spectrometer consisting of an Ortec HP Ge detector with a resolution of 1.9 keV at 1332 keV and a relative efficiency of 20%. The detector was connected to an Ortec 472A spectroscopy amplifier and a Nuclear Data ND 66 multichannel analyzer calibrated at 0.5 keV per channel. A dedicated PDP11 computer connected to the system was used in the identification and quantitation steps.

The determination of mercury via the 279.47 keV photopeak of ^{203}Hg was interfered by the 279.60 keV peak of ^{75}Se and corrections have to be made for the photopeak contribution. Arsenic was analyzed using the 559.2 keV photopeak of ^{76}As. Chromium was determined via the 320.23 keV photopeak of ^{51}Cr, while zirconium was analyzed via the 755.54 keV photopeak of ^{95}Zr. The precision and accuracy of the analytical technique of INAA for total As, Cr, Hg and Zr were evaluated by analyzing SRMs from IAEA Soil-7 and Soil-1 (SL-1).

Results and discussion

Sodium, bromine and chlorine are poorly adsorbed on Zr-AC and AC. Any traces of these ions can be almost completely removed by washing the adsorbent five to six times with deionized water.[21] The advantage of this preconcentration method is the elimination of interfering ^{24}Na, ^{82}Br and ^{38}Cl activities, usually encountered in the analysis of surface water samples for trace metals by neutron activation techniques.

The concentration of the standard samples were calculated using a relationship that takes into account the average total area of the peaks recorded and expressed as counts per second per gram (A_0, s^{-1}·g^{-1}) of As, Cr, and Hg as shown in Table 1. The concentrations in part per million (ppm) showed very good agreement for all three elements for total As, Cr and Hg concentration. Obtained SRM values were calculated and compared with the irradiated standard solution total area counts per second per gram (A_0, s^{-1}·g^{-1}) for As, Cr, and Hg. The accuracy and precision of the analysis as well as certified values and obtained values are shown in Table 2. The analyzed values of As, Cr and Hg for SRM Soil-7 showed good agreement when compared to the certified values from Soil-7. The calculated values of As and Cr in the SRM SL-1 also showed good agreement with the certified values, while Hg exhibited poor agreement.

Table 1. Calculated concentrations of As, Cr and Hg from the total area counts per second per gram in standard samples

Element	Actual concentration, μg·l^{-1}	Average concentration, μg·l^{-1}
As	10.00	10.03 ± 0.06
Cr	100.00	97.87 ± 12.10
Hg	5.00	5.19 ± 0.51

Table 2. Total As, Cr and Hg concentration in standard reference materials Soil-7 and SL-1

Element	SRM (Soil-7), μg·g^{-1}		SRM (SL-1), μg·g^{-1}	
	Certified value	Obtained value	Certified value	Obtained value
As	13.4	13.79 ± 0.76	27.5 ± 2.9	27.21 ± 4.71
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

*Informed value in the SRM only.

When the polluted water samples were passed through FS-1, all species of the toxic elements As, Cr and Hg were adsorbed on the AC and Zr-loaded or modified AC (Zr-AC) at different pH values between 5.09 and 6.51. The basic theory observes that the "electron deficient ion or complex interacted with electron rich ion or complexes" for the adsorption of different species of As, Cr and Hg. The theory would be appropriate to explain As(V), Cr(VI) and Hg(II) adsorbed on the Zr-AC.[22] However, As(III), Cr(III) and Hg(I) were adsorbed on AC at higher pH value in the presence of iron ions present in the red soil particles. In FS-1, as shown in Fig. 1, the first layer is AC followed by the second layer which is Zr-AC serving as the major functional layer. Using prepared standards, the concentrations of As, Cr and Hg in the filtrates were measured using ICP-MS and the retention performance of FS-1 and FS-2 were evaluated and were found to be very high as shown in Table 3.

Environmentally polluted water samples collected from different sites passing through FS-1 and FS-2 showed results (Table 4) of relatively good water quality and safe for drinking when compared with WHO water quality standards. The raw water and filtrates were analyzed by ICP-MS. As shown in Table 4, it was found that both the FS-1 and FS-2 were capable of adsorbing toxic elements to a significant level as reported in our previous work.[20] It was also found that the AC-Zr can adsorb higher oxidation states of such elements at all the pH range but AC can absorb species of lower oxidation states at higher pH value range in the presence of iron ions.[21–23] The results given in Table 5 indicated that the amount of As, Cr and Hg adsorbed on Zr-AC were relatively higher than those adsorbed on AC, and the calculated AC/Zr-AC ratio were 0.41, 0.36 and 0.17, respectively, for each element in FS-1. Hence, it was deduced that the adsorption capacity for AC-Zr is higher than AC for As, Cr, and Hg species. Many researchers have found that Zr-AC adsorbed species of higher oxidation states, such as As(V), Cr(VI) and Hg(II) while AC has the tendency to adsorb the lower oxidation states, such as As(III), Cr(III) and Hg(I).[21–25] The pH value of the filtrates obtained using the FS-1 were remarkably lower (<3.0), as shown in Table 6, and this low pH value is not permissible for drinking water.

Table 3. Retention performance of filter FS-1 and FS-2 based on concentrations in filtrates measured by ICP-MS

Element	Initial concentration, $\mu g \cdot l^{-1}$	FS-1		FS-2	
		Concentration in filtrate, $\mu g \cdot l^{-1}$	Retention, %	Concentration in filtrate, $\mu g \cdot l^{-1}$	Retention, %
As	200	2.46 ± 0.06	98.77	1.35 ± 0.03	99.33
Cr	200	6.52 ± 0.78	96.74	3.57 ± 0.08	98.22
Hg	10	ND	100.00	ND	100.00

Table 4. Concentrations of As, Cr and Hg in raw water samples before and after filtration using FS-1 and FS-2

Sample ID	As, $\mu g \cdot l^{-1}$		Cr, $\mu g \cdot l^{-1}$		Hg, $\mu g \cdot l^{-1}$	
	Before	After	Before	After	Before	After
FS-1						
S-1	1.23 ± 0.05	0.86 ± 0.05	3.29 ± 0.13	2.69 ± 0.30	1.21 ± 0.18	0.90 ± 0.04
S-2	3.55 ± 0.06	3.45 ± 0.09	1.61 ± 0.004	1.88 ± 0.17	1.59 ± 0.13	0.42 ± 0.03
S-3	2.49 ± 0.03	1.72 ± 0.03	1.56 ± 0.16	2.47 ± 0.04	0.83 ± 0.75	1.23 ± 0.09
S-4	11.42 ± 1.10	5.71 ± 0.18	2.54 ± 0.10	2.21 ± 0.25	0.44 ± 0.05	1.32 ± 0.07
S-5	0.94 ± 0.01	0.46 ± 0.26	1.78 ± 0.05	1.81 ± 0.05	1.42 ± 0.12	0.61 ± 0.06
S-6	1.35 ± 0.04	1.08 ± 0.31	0.53 ± 0.03	1.48 ± 0.03	1.37 ± 0.06	0.54 ± 0.03
S-7	1.46 ± 0.03	2.11 ± 0.03	1.81 ± 0.08	1.15 ± 0.07	1.84 ± 0.19	0.78 ± 0.04
S-8	1.38 ± 0.06	1.43 ± 0.11	2.10 ± 0.03	0.93 ± 0.07	0.40 ± 0.06	1.07 ± 0.05
S-9	2.09 ± 0.02	1.41 ± 0.03	1.27 ± 0.06	0.72 ± 0.07	0.89 ± 0.10	0.51 ± 0.04
S-10	11.07 ± 0.38	0.98 ± 0.04	2.45 ± 0.05	1.01 ± 0.01	1.64 ± 0.18	0.25 ± 0.02
S-11	28.73 ± 0.78	2.46 ± 0.06	27.25 ± 1.15	6.52 ± 0.78	0.64 ± 0.06	0.23 ± 0.03
FS-2						
S-1	1.23 ± 0.05	0.75 ± 0.01	3.29 ± 0.13	0.24 ± 0.45	1.21 ± 0.18	<0.01
S-2	3.55 ± 0.06	0.07 ± 0.03	1.61 ± 0.01	<0.01	1.59 ± 0.13	0.62 ± 0.01
S-3	2.49 ± 0.03	0.85 ± 0.01	1.56 ± 0.16	<0.01	0.83 ± 0.75	0.90 ± 0.02
S-4	11.42 ± 1.10	0.85 ± 0.03	2.54 ± 0.10	0.60 ± 0.04	0.44 ± 0.05	0.27 ± 0.01
S-5	0.94 ± 0.01	<0.01	1.78 ± 0.05	0.62 ± 0.11	1.42 ± 0.12	0.26 ± 0.02
S-6	1.35 ± 0.04	0.92 ± 0.03	0.53 ± 0.03	0.77 ± 0.06	1.37 ± 0.06	<0.01
S-7	1.46 ± 0.03	0.69 ± 0.02	1.81 ± 0.08	0.78 ± 0.13	1.84 ± 0.19	0.31 ± 0.01
S-8	1.38 ± 0.06	0.79 ± 0.01	2.30 ± 0.04	0.90 ± 0.15	0.40 ± 0.06	0.28 ± 0.01
S-9	2.09 ± 0.02	0.92 ± 0.01	1.27 ± 0.06	0.85 ± 0.17	0.89 ± 0.10	0.85 ± 0.04
S-10	11.07 ± 0.38	0.80 ± 0.01	2.35 ± 0.09	0.80 ± 0.17	1.64 ± 0.18	0.60 ± 0.01
S-11	28.73 ± 0.78	0.91 ± 0.03	27.25 ± 1.15	0.64 ± 0.23	0.64 ± 0.06	0.58 ± 0.07

Table 5. Retention concentrations of As, Cr and Hg in materials from FS-1 measured by NAA

Sample ID	Graduated depth, cm	As, $\mu g \cdot g^{-1}$	Cr, $\mu g \cdot g^{-1}$	Hg, $pg \cdot g^{-1}$
AC-Zr-1	1.00	50.97	27.17	233.09
AC-Zr-2	3.00	36.65	25.24	153.68
AC-Zr-3	5.00	32.50	20.62	140.09
AC-1	8.00	24.61	11.65	32.3
AC-2	10.00	15.03	9.63	32.01
AC-3	12.00	9.18	5.30	23.55

AC-Zr: Zirconium modified activated carbon; 1, 2, 3 denote layer depth where sample was taken.
AC: Activated carbon.

Table 6. pH readings of from raw water before and after filtration using FS-1 and FS-2 units

Sample location	Raw water	Filtrates using FS-1	Filtrates using FS-2
1	5.09	2.35	7.23
2	6.51	2.65	6.68
3	3.33	2.64	7.48
4	6.11	2.63	7.21
5	5.24	2.71	7.07
6	5.99	2.79	6.78

To solve the problem of getting filtrates low in pH, further rearrangement has been done in the major layers of the filtering components, hence, the FS-2 was proposed and it is shown in Fig. 2. In this system, rearrangement of the components comprised of Zr-AC as the first layer followed by soil particles in the second layer, AC in the third layer serves as the major functioning component and finally all lower layers were similar to the arrangement in FS-1. The same samples were passed through FS-2 and the retention concentrations of As, Cr and Hg in materials for FS-2 were given in Table 7. It was observed from the results obtained that all targeted elements were adsorbed properly with the pH values in the filtrate corrected within the range of 6.68–7.50 as shown in Table 6. Probable causes of the proper functioning of this filter column can be attributed to the followings: (a) the upper layer is Zr-AC and this layer is able to adsorb As(V), Cr(VI), and Hg(II) species over an inside pH range as reported by YUSOF et al.;[25] (b) if the eluted water contains the above species, then the second layer of soil particles will adsorb these species and at the same time

provides Fe, Ca, and Mg to the filtered water, hence increases the pH;[23] (c) the Fe^{3+} ions helped to flocculate As(III), Cr(III) and Hg(I), and (d) the AC could easily adsorb these species.[23,25]

This adsorption behavior can be explained by the formation of colloidally dispersed metal hydroxide such as arsenic and chromium hydroxide during neutralized pH.[21] This hydroxide is readily adsorbed on the AC at higher pH. In surface water pH (6.0–8.5) trivalent metals are hydrated complexes, which are probably converted quite slowly to hydroxide. This hypothesis is supported by the results from our experiment, as shown in Table 6, using AC at higher pH in the FS-2. In Table 7 it was found that higher concentrations of As, Cr and Hg could be adsorbed on Zr-AC compared to using AC only in FS-2 with the ratios of As, Cr and Hg adsorbed on AC/Zr-AC are 0.55, 0.85 and 0.30, respectively, as compared to 0.41, 0.36 and 0.17 using FS-1, respectively. Ratios obtained for AC/Zr-AC using FS-2 are apparently higher than AC/Zr-AC values calculated for the same respective layers than those obtained using FS-1. Therefore, it is clear that an oxidation-reduction reaction occurred in between the red soil layer, and after reduction these species gained electrons and, hence, easily transformed to the trivalent hydroxide. These are adsorbed on the AC layer and the concentrations of the lower oxidation state species are higher in FS-2 than those adsorbed by FS-1. Therefore, the FS-2 fulfilled all the requirements for drinking water. Quantitation of As, Cr and Hg in the red soil layer revealed that some of these elements were also partially retained as shown in Table 8.

Table 7. Retention concentrations of As, Cr and Hg in materials from FS-2

Sample ID	Graduated depth, cm	As, $\mu g \cdot g^{-1}$	Cr, $\mu g \cdot g^{-1}$	Hg, $pg \cdot g^{-1}$
AC-Zr-1	1.00	23.45	11.39	33.82
AC-Zr-2	3.00	18.08	12.50	31.10
AC-Zr-3	5.00	15.60	16.05	24.76
AC-1	8.00	11.77	11.90	9.96
AC-2	10.00	10.53	10.73	9.36
AC-3	12.00	8.92	Omitted	7.25

Table 8. Adsorbed concentration of As, Cr and Hg
on red soil particle from FS-2

Sample ID	As, $\mu g \cdot g^{-1}$	Cr, $\mu g \cdot g^{-1}$	Hg, $pg \cdot g^{-1}$
Soil	2.45 ± 0.93	3.57 ± 1.81	31.54 ± 4.35

Conclusions

The modified AC with zirconium is a promising adsorbent for the preconcentration of As(V), Cr(VI) and Hg(II) from aqueous solutions for the determination by INAA. Zr-AC significantly improved the adsorption capacity of carbon towards the specific species of As(V), Cr(VI) and Hg(II). When the pH of the sample solution was high (above 10) or low (less than 2), Zr-AC had no effect on the adsorption of specific species of As, Cr and Hg, while at high pH, greater than 7.0, AC would adsorb As(III), Cr(III) and Hg(I) species. Adsorption of arsenic, chromium and mercury specific species onto the Zr-AC is attributable to the reaction of these metals with Zr, rather than with activated carbon. If the eluted water contains the above (higher oxidation state) species, the second layer of soil particles would adsorb these and at the same time this soil layer will provide Fe, Ca, and Mg ions to the filtered water, contributing to the increase pH value of ≥6. Finally the iron (Fe^{3+}) helped to flocculate As(III), Cr(III), and Hg(I) from the aqueous samples.

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