

Reduction of arsenate and inorganic trivalent chromium mobility in soils

Summary of PhD dissertation

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I Research Background and Problem Statement

Chromium (Cr) and arsenic (As) contamination of natural water bodies and soil systems has caused serious environmental quality deterioration because of urbanization, industrialization and rapid population growth. Chromium and As pollution is caused by atmospheric deposition, agricultural chemical application, natural rock weathering, mineral mining, wood preservation, industrial activities among others. In particular, organoarsenic feed additives have veterinary benefits but the soluble forms of As species are excreted into the environment after arsenical compounds are administered to animals to improve development, promote growth, control parasites and enhance efficient feed utilization. These activities have caused widespread As and Cr soil contamination and destabilization of the ecosystem resulting in human health problems.

Unlike in aqueous systems, removal of heavy metal (HMs)/metalloids from soils is difficult to accomplish. The best available ways are to reduce Cr(VI) to Cr(III) coupled with other mechanisms to stabilize it in the soil system. Additionally, arsenite [iAs(III)] is not only more toxic, but may represent a greater carcinogenic hazard than iAs(V). Several conventional methods have been adopted for soil remediation, which include chemical precipitation, solidification, soil washing, chemical reduction, electrokinetics, and bioremediation, etc. Oftentimes, organic materials, which are readily available, are usually employed to accomplish metal/metalloids stabilization in soil systems. Moreover, functionalization of these organic materials is promising alternative to increase the efficacy of these organic materials for metal/metalloid remediation. Activated carbon prepared from *Arachis hypogea* shell as a biowaste, available in large quantities may be a promising candidate for mobility reduction of iAs(V) in acidic sandy soil and the suitability of natural brown coal in different grain sizes for Cr(III) mobility reduction in both acidic and carbonaceous sandy soils has not been extensively elaborated.

II Objectives

The objectives of the present thesis aimed at reduction of mobility of inorganic trivalent chromium and arsenate in soil systems. The specific objectives are listed as follows:

1. To study the reduction of inorganic Cr(III) contamination by immobilization using appropriate and inexpensive sorbent in acidic and calcareous sandy soils.

2. Determination of physico-chemical characteristics of lignite affecting Cr mobility to elucidate the Cr-lignite adsorption mechanism.
3. Assessment of Cr distribution on the water-soluble, carbonate bound and easily reducible fractions in the acidic and calcareous sandy soils as well as estimation of the phytoavailable fraction of Cr by applying appropriate leaching tests.
4. To find a cheap biowaste material readily available in large quantities, suitable for carbonization and activation by simple and cost-effective methods for mobility reduction of arsenate [iAs(V)] in acidic sandy soil.
5. Amendment of iAs(V) artificially contaminated soil with suitable activated carbon (AC) by investigating the immobilization rate.
6. Application of the carbonized and activated peanut shell biowaste material and its HNO₃, Celite® or Florisil® composites for reduction of iAs(V) mobility in acidic sandy soil.
7. To investigate the effect of oxalic acid (OA), a low-molecular weight organic acid in the enhancement of the immobilization rates as a result of further protonation of AC and iAs(V) ions by OA.
8. Elucidation of the binding mechanism of iAs(V) by the AC prepared from the peanut shell in aqueous phase and in soil.

III Materials and methods

Experiments were carried out with an acidic and an calcareous sandy soil, sampled from Nyírlugos (47°43'N, 22°00'E) and Órbottyán (47°40'N, 19°14'E), respectively each sieved to <2 mm.

For the immobilization experiments soil samples were artificially contaminated by Cr(III) or iAs(V) in a concentration 375 mg/kg and 15 mg/kg As respectively, using appropriate aliquots of Cr(NO₃)₃ or KH₂AsO₄ [iAs(V)] stock solutions. In some cases, a contamination level of 30 mg/kg iAs(V) was also applied.

In experiments aimed Cr(III) immobilization, the artificially contaminated acidic and basic soils were thoroughly mixed with lignite powder originating from the mines of Visonta (Hungary). To investigate the effect of particle size on the immobilization efficiency, the brown coal powder was size-fractionated in three particle ranges (i.e., <0.5 mm, 0.5–1.0 mm and 1.0–2.0 mm) by sieving. Then, each was added to the soil samples at a dose of 5% by weight. The incubation of samples under controlled temperature (kept at 21°C) and moisture

content (65% of field water capacity, monitored weekly) lasted for eight weeks. For the characterization of the porosity of the brown coal powder a Thermo Scientific Surfer gas adsorption porosimeter (Bremen, Germany) was used. The point of zero charge of lignite samples were determined by applying the pH drift method. Scanning electron microscopy studies were performed on a model Quanta 3D apparatus (FEI, USA) equipped with a secondary Everhart-Thornley detector and back-scattered electron detector together with silicon drift energy-dispersive detector.

For mobility reduction of iAs(V) contaminated soils, different types of ACs were mixed to the acidic sandy soil from Nyírlugos in 2.0 % by weight. These AC were produced from peanut (*Arachis hypogea*) shell after carbonization with concentrated sulphuric acid. Three types of composites were also prepared by addition concentrated nitric acid, or Celite or Florisil powders. (In case of Florisil® composite 5 % by weight AC content was also checked at a 30 mg/kg iAs(V) dosage.) An AC prepared by addition of oxalic acid was also produced to study the mobility reduction as a result of further protonation of resulting AC. The AC containing artificially contaminated soil samples were incubated for 4 weeks. For the characterization of the AC, Fourier-transform infrared (FT-IR) spectra were recorded in the attenuated total reflection (ATR) mode by means of a Varian 2000 instrument (Scimitar Series). The FT-IR spectrometer was fitted with a mercury cadmium telluride detector and a single reflection diamond ATR accessory (Golden Gate). Adsorption studies of AC and composite samples was also performed using the batch technique. About 0.05 g AC samples were mixed with 25 mL of solutions containing 50–800 mg/L iAs(V) at pH 5. The equilibrium concentration in the solid phase (q_e) was expressed as the mass of adsorbed As (mg) divided by the AC mass (g). Freundlich and Langmuir adsorption models were applied to study the adsorption mechanisms of As.

For the assessment of As or Cr distribution a fit-to-purpose BCR sequential soil extraction procedure was applied. Extraction of the water soluble and carbonaceous fraction was achieved together with 0.11 mol/L acetic acid solution. This step was followed by extraction of the fraction bound to amorphous oxides of Fe(III)/Mn(IV) with the assistance of 0.5 mol/L hydroxylamine-hydrochloride at pH=2. The samples were shaken for 16 h at 30 rpm by using an endover-end shaker (IKA® Works Inc., Staufen, Germany). After extraction, the supernatant was separated from the solid residue by centrifugation at 4500 rpm for 15 min (Hermle Labortechnik GmbH, Wehingen, Germany). Finally, microwave (MW)-assisted digestion of the leachate residues with *aqua regia* was applied to determine the remaining metal content after the two extraction steps.

For the estimation of the phytoavailable fraction of Cr(III) and iAs(V), the Lakanen and Ervio leaching procedure was applied using 0.02 mol/L EDTA solution of pH \approx 4.65. In this case the shaking time was 1h. And similarly to above mentioned procedure, after centrifugation the supernatant and the residue were separated.

The Cr/or As concentrations of the supernatant solutions were determined by Element 2 type sector field inductively coupled plasma mass spectrometer equipment (Thermo-Fisher Scientific, Bremen, Germany). In the case of Cr(III) treatment, chemical analysis was also performed by total-reflection X-ray fluorescence (TXRF) spectrometry (ATOMIKA Model TXRF 8030C spectrometer (ATOMIKA Instruments GmbH, Oberschleißheim, Germany)). According to the analysis, results the immobilization rates were calculated.

IV New results

By applying i) a fit-for-purpose BCR sequential soil extraction procedure consisting of leaching of Cr from the water-soluble and carbonatic as well as the easily reducible fractions with acetic acid and hydroxyl amine, respectively; and ii) leaching with EDTA for assessment of Cr phytoavailability of an acidic (pH = 5.0) as well as a calcareous soil (pH = 7.7) each artificially contaminated with 375 mg/kg inorganic Cr(III) and incubated for 8 weeks with 5% by weight lignite applied in three particle size ranges (<0.5; 0.5–1.0 and 1.0–2.0 mm), the following statements as new results can be made:

1. Since about 90% and 60% of the initial Cr(III) dose were immobilized by the calcareous and acidic soils *per se*, respectively, and taking into consideration pH-driven hydrolysis of Cr(III), soil pH is the main determining factor in the immobilization of this HM species. The point of zero charge measurements revealed that the surface of lignite is negatively charged above pH \approx 4.5 enhancing adsorption of Cr(III) ions, as well as its positively charged hydroxo complexes formed at slightly basic pH values (up to 9). However, application of lignite is unnecessary in the case of calcareous soils due to the low water solubility of these latter species.

2. Phytoavailable Cr fraction was about 10–25%. These low values might be attributed to kinetic hindrance of Cr(III)-EDTA complex formation. Since leaching with hydroxylamine can be considered to some extent as a phytoavailable test because several higher plants are able to uptake nutrients through root surface acidification often accompanied by H⁺-mediated reduction, the results obtained by hydroxylamine and EDTA leaching were compared. The

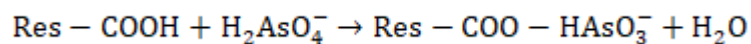
results obtained for Cr leaching by hydroxylamine confirmed those results obtained by leaching with EDTA the acidic sandy soils where application of lignite is also effective.

3. Lignite grain size applied in the range of <0.5–2.0 mm in the present study did not provide any considerable additional gain on immobilization rates of Cr(III).

4. Arsenic adsorption onto ACs from iAs(V) model solutions proved to be adequately fitted with the Freundlich isotherm and adsorption was almost linear. Moreover, approximately 20% of the total iAs(V) could be adsorbed. The acidic sandy soil *per se* could retain ≈15% of either 15 mg/kg or 30 mg/kg iAs(V), while in the presence of Florisil®-AC this ratio increased to 35% independently of the iAs(V) treatment dose.

5. The similar As immobilization rates obtained for the reference AC, HNO₃-and Florisil®-modified ACs indicate that, Florisil® has a role in the mechanical stabilization of the AC. Composite formation with silicate materials were confirmed by attenuated total-reflection Fourier-transform infrared spectroscopy (ATR-FTIR).

6. Adsorption of As to the AC is achieved by formation of a covalent bond between iAs(V) and O of the carboxylic functional group of the AC with simultaneous elimination of a water molecule and formation of a mixed acid anhydride according to the following equation:



Coordination of As towards C(=O)-O— was confirmed by ATR-FTIR spectra.

7. By soaking the acidic soil with oxalic acid (OA) solution, the As mobility reduction rate did not further increase. Therefore, previously reported protonation of iAs(V) and/or biowaste derived AC with further enhancement possibility for As immobilization in soil by OA did not take place.

SCI publications constituting the basis of the present dissertation

Anemana, T., Óvári, M., Szegedi, Á., Uzinger, N., Rékási, M., Tatár, E., Yao, J., Strelí, C., Záráy, G., Mihucz, V. G. (2019). Optimization of lignite particle size for stabilization of trivalent chromium in soils. *Soil and Sediment Contamination: An International Journal*, 1–20. DOI:10.1080/15320383.2019.1703100

Anemana, T., Óvári, M., Varga, M., Mihály, J., Uzinger, N., Rékási, M., Jun Yao, J., Tatár, E., Strelí, C., Záráy, G., Mihucz, V. G. (2019). Granular activated charcoal from peanut

(*Arachis hypogea*) shell as a new candidate for stabilization of arsenic in soil. *Microchemical Journal*, 149, 104030. DOI:10.1016/j.microc.2019.104030

Oral presentations constituting the basis of the present dissertation:

1. Anemana T, Makó A, Rékási M, Uzinger N, Óvári M, Tatár E, Záray G, Mihucz VG: Immobilization of arsenic and chromium by lignite in sandy soils. *XVI Hungarian – Italian Symposium on Spectrochemistry: Technological innovation for water science and sustainable aquatic biodiversity*, Budapest, 4-6 October 2018.
2. Anemana T, Rékási M, Uzinger N, Óvári M, Strelci C, Záray G, Mihucz VG: Granular Activated Charcoal from peanut (*Arachis hypogea*) shell as a new candidate for stabilization of arsenate in soil. Renewal Meeting of Hungarian Spectrochemical Association of Hungarian Chemical Society, 09 April 2019

Poster presentations constituting the basis of the present dissertation:

1. Anemana T, Rékási M, Uzinger N, Óvári M, Strelci C, Záray G, Mihucz VG: Study of immobilization of arsenic in sandy soils by lignite. *European Symposium on Atomic Spectrometry Colloquium Analytische Atomspektroskopie Anwendertreffen Plasmaspektrometrie - ESAS & CANAS 2018*, Berlin, 19–23 March 2018
2. Anemana T, Rékási M, Uzinger N, Óvári M, Strelci C, Záray G, Mihucz VG: Granular activated charcoal from peanut (*Arachis hypogea*) shell as a new candidate for stabilization of arsenate in soil. *XVI Hungarian – Italian Symposium on Spectrochemistry: Technological innovation for water science and sustainable aquatic biodiversity*, Budapest, 4-6 October 2018.
3. Anemana T, Óvári M, Strelci C, Záray G, Mihucz VG: Suitability of total-reflection X-ray fluorescence spectrometry for arsenic determination in soil leachates. *18th International Conference on TXRF Analysis and Related Methods (TXRF-2019)*, Girona (Spain) 25-28 June 2019.

Presentations not constituting the basis of the present dissertation:

1. Anemana T, Filotás D, Nagy L. Simultaneous determination of heavy metals in herbal tea samples by potentiometric stripping analysis and atomic absorption spectroscopy methods. *Műszaki Kémiai Napok 2017*, Visegrád, 11-16 June 2017.
2. Anemana T, Filotás D, Nagy L. Simultaneous detection of heavy metals in aqueous solutions by atomic absorption spectroscopy and potentiometric stripping analysis methods. *Műszaki Kémiai Napok 2017*, Veszprém, 25 -27 April 2017.

3. Anemana T, Filotás D, Nagy L. Simultaneous detection of heavy metals in aqueous solutions by Atomic Absorption Spectroscopy and potentiometric stripping analysis methods, 13th Carpathian Basin Conference for Environmental Science, Cluj Napoca, 5-8 April 2017.