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Water treatment residues as accumulators of oxoanions in soil. Sorption of arsenate and phosphate anions from an aqueous solution

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HIGHLIGHTS

- Fe- and Al-WTR showed a high affinity for P(V) and As(V) species at pH 4, 7 and 9.
- Fe-WTR showed a greater As(V) and P(V) sorption capacity compared to Al-WTR.
- The As(V) and P(V) sorption capacity decreased with increasing pH from 4.0 to 9.0.
- The main sorption mechanism of two anions was the formation of inner-sphere complexes.
- As(V) and P(V) desorption from both WTRs was minimal suggesting irreversible sorption.

ARTICLE INFO

ABSTRACT

Here we report a survey addressed to determine, at different pH values (pH 4.0, 7.0 and 9.0), the ability of two different water treatment residues, a Fe-based (Fe-WTR) and an Al-based (Al-WTR), to accumulate arsenate and phosphate anions from an aqueous solution and to define the mechanism which regulate the sorption of these anions. Fe-WTR showed a greater As(V) and P(V) sorption capacity respect to Al-WTR at all the pH values investigated, in particular at pH 4.0. The greater capacity of the Fe-WTR to accumulate phosphate at pH 4.0 seems to be linked to the higher content of manganese ions compared to Al-WTR, which can give rise, with phosphate ions, to the formation of $MnHPO_4$ precipitates. Sequential extraction of As(V)- or P(V)-WTRs suggested that the main mechanism governing the sorption of both two anions likely involve the formation of inner-sphere surface complexes [Fe/Al–O–As(P)]. Such a coordination mode was supported by the FT-IR spectra that exhibit well resolved band at $865\,cm^{-1}$ and $1040\,cm^{-1}$ attributable to $\nu(As–O)$ or $\nu(P–O)$ stretching vibration, respectively.

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1. Introduction

Arsenic (As) is classified as a carcinogenic by the International Agency for Research and Cancer (IARC) and it is considered among the most significant and dangerous pollutants. Arsenic, in its different inorganic and organic species, is present in most natural environments (soils, sediments, groundwaters, and surface waters) due to natural processes and anthropogenic activities [1,2]. Arsenate [As(V)] and arsenite [As(III)] are the main forms of As commonly found in soils, sediments and waters [3]. Arsenate generally predominates under oxidising conditions, whereas arsenite occurs when conditions become sufficiently reducing [4,5]. In soil pore water, at pH values between 4.0 and 9.5, arsenic can be mainly found as arsenate oxyanions ($H_2AsO_4^-$, $HAsO_4^{2-}$ and AsO_4^{3-}), as arsenious acid (H_3AsO_3) and arsenite ($H_2AsO_3^-$). Arsenate and arsenite can be sorbed by the soil mineral surfaces, especially by

iron and aluminum oxi–hydroxides, to which, therefore, has been attributed an important role in limiting arsenic toxicity in soil [3,6].

Chronic and acute poisoning by arsenic due to exposure to elevated concentrations has been reported worldwide [7]. In this regard many techniques have been proposed for the remediation of arsenic-polluted soils and waters, including physical, chemical and biological treatments [1]. Amongst chemical treatments, the in situ stabilisation of pollutant is an promising approach where an inorganic or organic sorbent is added to a contaminated soil in order to decrease the mobility of pollutants through sorption and/or co-precipitation reactions [1,8].

Various As sorbents have been tested to immobilize As in polluted soils and waters. In particular, granular-activated alumina [9], Fe/Al/Mn oxides and hydroxides [10,11], activated carbon [12], natural red earth [13], and some industrial by-products such as red mud [1,14,15], have been evaluated among the others.

Alternative low-cost and potentially effective sorbents for arsenic, are the drinking-water treatment residuals (WTRs), the waste material resulting from the treatment of surface, or groundwater with Al and Fe salts [16–18]. In the conventional

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coagulation–filtration treatment process, suspended solids, natural organic matter, dyes, contaminants, etc., are removed from the raw water supply by the addition of aluminum, iron or calcium salts as coagulants, resulting in the production of WTRs [19–22].

The effectiveness of the sorption reactions between WTRs and arsenate could be influenced by a number of chemical and physical parameters such as pH, redox potential, temperature, initial As concentration, ionic strength and, importantly, by the co-occurrence of other competing ions such as phosphate e.g. [18]. Similarities in the chemical nature of phosphate and arsenate suggest that WTRs would act as accumulators of both As(V) and P(V) [21]. Consequently, both anions could compete for the same sorption sites located mainly on Al/Fe oxi–hydroxides surfaces of WTRs [23,24]. The existence of such competition phenomena could affect the As mobility and bioavailability in soil and some recent studies seem to support this view. For example, Zhang and Selim [25] showed that the application of phosphorus fertilizer to agricultural soils can result in the release of As already sorbed by the soil matrix.

Another interesting question concerns the understanding of the different processes governing the sorption of anionic species by the WTRs surfaces. To the best of our knowledge, no report discriminating the different interaction processes (particularly adsorption and precipitation) between WTRs and arsenate/phosphate is currently available in literature. Similarly, no information is available on the contribution of the WTRs soluble fraction in such phenomena.

The objective of this paper was therefore to determine the ability of WTRs to accumulate arsenate and phosphate at different pH values (i.e. 4.0, 7.0 and 9.0), to discriminate the different interaction processes (i.e. adsorption and precipitation) between WTRs and arsenate/phosphate, and to evaluate the contribution of the WTRs soluble fraction on such phenomena. Besides, the mechanisms which regulate the sorption of both anions by these waste materials have been defined through sequential extraction and FT-IR spectroscopy.

2. Materials and methods

2.1. Samples description

An Al-based and a Fe-based WTR provided by the Abbanoa S.p.A. company (Italy) were used in this study. The Al-WTR was obtained from the drinking-water treatment plant in Truncu Reale, Sassari (Italy), where the raw water was treated with $Al_2(SO_4)_3$, while the Fe-WTR was provided by the Bidighinzu plant in Sassari (Italy), where $Fe_2(SO_4)_3$ is used as the coagulant.

The WTR samples were dried overnight at 105 °C, and subsequently finely ground and sieved to <0.02 mm. The pH and electric conductivity (EC) were determined in 1:2.5 ratio of WTR/distilled water. The specific surface area of the WTRs was determined by applying the BET model to the N_2 sorption results obtained from a Sorptomatic Carlo Erba. The details on the sample pre-treatment are reported in Castaldi et al. [14]. Total organic matter in WTRs was determined using the method of Walkley and Black previously described [26]. To determine the content of humic (HA) and fulvic (FA) acids the method reported by Ciavatta et al. [27] was used. The content of dissolved organic carbon (DOC) in Fe- and Al-WTRs was determined according to Brandstetter et al. [28].

Total N and P were determined by the Kjeldhal and ascorbic acid methods, respectively [29,30]. Available P were determined using the Olsen method [31]. The pH_{PZC} of WTRs was measured by Laser Doppler Velocimetry coupled with Photon Correlation Spectrometry using a Coulter Delsa 440 spectrometer equipped with a 5 mW He–Ne laser (632.8 nm).

The element composition of WTRs was determined by using Energy Dispersive X-ray (EDX) by JOEL model JSM-6480LV. X-ray diffraction (XRD) analysis of WTRs was carried out with a Rigaku D/MAX diffractometer (Cu $K\alpha$) equipped with a graphite monochromator in the diffracted beam. The pattern was collected in the 2θ range from 10° to 70°.

The total concentration of selected metals in Fe-WTR and Al-WTR was determined on dried WTRs (105 °C) after digestion with a mixture of nitric acid and hydrochloric acid (HNO_3/HCl, 1:3 ratio) in a microwave Milestone MLS 1200. The heavy metal concentrations were determined using a Perkin Elmer Analyst 600 flam atomic absorption spectrometer (FAAS) equipped with HGA graphite furnace. Oxalate-extractable Al, Fe, and others heavy metals were also determined using FAAS as described by Makris and Harris [20].

Each experiment was conducted in triplicate and mean values ± standard deviations are reported.

2.2. Sorption isotherms of arsenate and phosphate on WTRs at pH 4.0, 7.0 and 9.0

All chemicals were of analytical grade and used without further purification. Fe- and Al-WTRs samples were artificially and separately enriched with solutions containing increasing concentrations of $Na_2HAsO_4·7H_2O$ or $NaH_2PO_4·7H_2O$ to obtain sorption isotherms. Three batch experiments were prepared for Fe- and Al-WTRs at three pH values (4.0, 7.0 and 9.0) and at constant temperature (25 ± 1 °C). Polyethylene bottles containing 1.0 g of WTR were filled with 25 mL of arsenate or phosphate enriched solutions. Eleven different concentrations of $Na_2HAsO_4·7H_2O$ or $NaH_2PO_4·7H_2O$ varying from 0.025 to 3.0 mmol × 25 mL^{-1} were used to determine the sorption isotherms. A background electrolyte of 0.1 M NaCl was used as diluent for all batch experiments. The pH values (4.0, 7.0, and 9.0) of Fe- and Al-WTRs not-exchanged and of the mixtures WTR/polluting solution were adjusted with 0.01 M, 0.1 M or 1.0 M NaOH solutions. The mixtures (1:25 w/v ratio of WTR/arsenate or phosphate solution) were shaken for 24 h at constant temperature (25 ± 1 °C). After equilibrium, the samples were centrifuged at 8000 rpm for 10 min and filtered to completely separate the liquid and solid phases. An aliquot of the supernatant was taken and As(V) and P(V) measured by ionic chromatography by using an IonPac AS9-HC Analytical Column equipped with an IonPac AG9-HC Guard Column, 4 mm. Sodium carbonate (11 mM) was employed as the eluent at a flow rate of 1.0 mL min^{-1}. The sample loop was 10 μL.

Each point of the sorption isotherms (at the three pH values) was carried out on three independent samples and mean values ± standard deviations are reported.

2.3. Sorption kinetics of arsenate and phosphate on WTRs at pH 4.0, 7.0 and 9.0

For kinetic studies, polyethylene bottles containing 1.0 g of each WTR were filled with 25 mL of a solution containing 3.0 mmol of $Na_2HAsO_4·7H_2O$ or $NaH_2PO_4·7H_2O$ (the concentration of the last point of the isotherm).

At different times (0.083 h, 0.167 h, 0.25 h, 0.5 h, 1 h, 2 h, 3 h, 6 h, 15 h, 24 h) the samples were centrifuged at 8000 rpm for 10 min and filtered with 0.2 μm filters to separate the liquid and solid phases. An aliquot of the supernatant was taken and arsenate and phosphate were quantified by ionic chromatography as previously described.

Each point of the sorption kinetics (at the three pH values) was carried out on three independent samples and mean values ± standard deviations are reported.