Arsenic surface complexation behavior in aqueous systems onto Al substituted Ni, Co, Mn, and Cu based ferrite nano adsorbents

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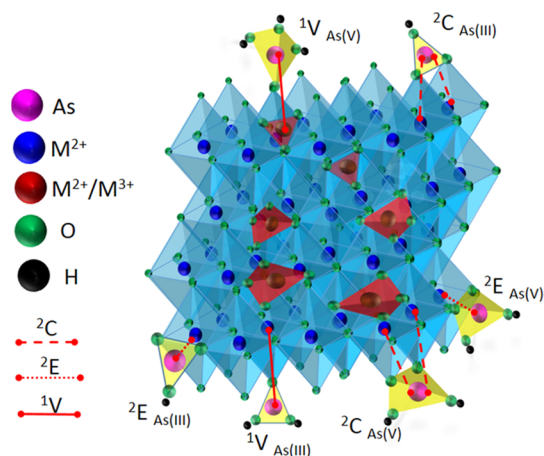
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GRAPHICAL ABSTRACT

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The present study is about surface complexation behavior of arsenic species adsorbed onto ternary metal oxide adsorbents (Ni-Al-Fe, Co-Al-Fe, Mn-Al-Fe, and Cu-Al-Fe). The analysis is carried out by X-ray absorption spectroscopy (XAS) tool. XANES ($\mu(E)$ vs. E) spectra close to the absorption edge (i.e., As K-edge) of all samples are observed along with the As(III) and As(V) standards. The first derivative of XANES for Ni-As(V), and Cu-As(V) samples agree with that of As(V) standards, respectively. Whereas, As(III) adsorbed adsorbent systems (i.e., Ni, Co, Mn, and Cu) are observed with mixed oxidation state of arsenic. A total of 65–85 % is observed with initial oxidation state (As(III) or As(V)), and remaining 15–35 % is observed with modified oxidation state (As(V) or As (III)) that explains the occurrence of possible charge transfer. EXAFS analysis shows the As-O bond distances in the range of 1.7–1.8 Å. The corresponding As-M bond distances are around 2.7, 3.2, and 3.6 Å which confirms the formation various edge sharing (^{2}E), and corner sharing (^{2}C, ^{1}V) surface complexes. Surface coverage is

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understood as an important parameter as bidentate attachments ([2]E, [2]C) are evident in As(III), and As(V), but monodentate attachments ([1]V) are only observed in As(V).

1. Introduction

Arsenic, ubiquitous trace metalloid normally exists in aquatic and soil environments, which is generally introduced from geogenic and anthropogenic sources [1–4]. It is one of the well-known aquatic contaminants with toxic and carcinogenic behavior. In natural aquatic systems it is mostly present in two inorganic forms, i.e., arsenite (As(III)), and arsenate (As(V)) [5–8]. As(III) systems are reported with their higher toxicity, and mobility behaviour compared to As(V) species [9–12]. WHO issued safety guidelines to keep the maximum acceptable limit of arsenic to 10 ppb in drinking water systems [13]. Adsorption is one of the best remediation techniques for mass scale application. Individual, binary, and doped metal oxides are few class of adsorbents reported for better arsenic remediation [14–18]. Zero valent iron (ZVI) based adsorbents were also observed for better As(III), As(V) retention and As(0) formation [19–23]. Redox reactions (e[−] transfer), ligand exchange, surface-complexation on to metal centers of various adsorbents are some of few important aspects in arsenic remediation process [24–32]. Surface complexation study using X-ray absorption spectroscopy (XAS) is a microscopic analysis which gives insight of geometries of adsorbed arsenic species onto the adsorbent [33–36]. The major geometries of surface complex structures are classified as (i) bidentate mononuclear edge sharing ([2]E), (ii) bidentate binuclear corner sharing ([2]C), (iii) monodentate mononuclear corner sharing ([1]V), and (iv) tridentate hexa-nuclear corner-sharing ([3]C) [37,38]. The corresponding geometries and interatomic bond distances are generally used as measure of bond strength in understanding the mineral structure, and mobility of arsenic surface complexes in the environment [39–54]. Different metal (e.g., Fe, Al, and Mn) based adsorbents were observed with arsenic remediation by means of various arsenic surface complex structures [33–47]. It was also mentioned in the literature that the relative significance of individual complex depends on various adsorption parameters (e.g., surface loading (or) surface coverage: μ mol. m^{-2}/ mg m^{-2}) [37].

Sherman et al. reported arsenate $((AsO_4)^{3-})$ surface complexes of [2]E and [2]C geometries near 2.85, and 3.26 Å onto hematite (α-Fe$_2$O$_3$), goethite (α-FeOOH), and lepidocrocite (γ-FeOOH) adsorbents [37]. An in-situ X-ray absorption fine structure spectroscopy study reported As(III) adsorption at goethite/water interface by bi-dentate binuclear complexes with As-Fe bond distance of 3.37 Å. Arai et al. observed As(III), and As(V) with inner sphere complexes with a bidentate binuclear configuration at the γ-Al$_2$O$_3$/water interface and the effect of pH, ionic strength in outer sphere complexes formation [38]. Different Al-based sorbents are observed with various As(V)-O, and As(V)-Al inner sphere structures in the range of 1.7, and 3.2 Å [42–47]. Arsenic sorption mechanism onto aluminum (Al) based adsorbents (e.g., γ-gibbsite) were reported with non-dissociative mechanism apart from the well-known Arrhenius acid-base mechanism [45]. Aluminum oxides (e.g., gibbsite) actively involved in arsenic retention over soil/aqueous interface due to their aluminol functional groups, which can work as possible oxy-anionic sinks [38]. Aluminum substitution affects the physicochemical parameters of ferrihydrites, mainly in solubility, stability, bio-availability and redox behavior [50–52].

Mixed oxide based adsorbents (e.g., magnetite) were reported with bidentate binuclear corner sharing ([2]C), and tridentate hexa-nuclear corner-sharing ([3]C) kind of complexes for As(V) and As(III) systems, respectively [39,53]. Coexistence of goethite, and siderite during mineral transformation were reported with better arsenic adsorption in oxic condition due to better As-Fe coordination in [2]C, and [1]V complexes [41]. In few recent studies combined 3d- transitional metal oxides (Fe and Mn binary oxide) were observed with oxidation assisted (i.e., As

(III) to As(V)) arsenic adsorption in forming As-M (M = Fe/Mn $\sim$ 3.22–3.24 Å) inner-sphere edge sharing and corner sharing complexes [53,54]. Adra et al. reported Al-substituted ferrihydrites for arsenic adsorption with As-Fe interatomic distances of $\sim$ 2.9, and 3.4 Å corresponding to [2]E, and [2]C type surface complexes [36,53,54]. It was also observed that incorporation of aluminum in Fe(III) based adsorbents for arsenic remediation improvised their stability over arsenic desorption by influencing the reductive dissolution behavior of iron centers [55]. Because the mobility, and toxicity of As(III) are reported greater than As(V), any redox based remediation along with the mitigation ability of the adsorbents should be provided due consideration. This warrants a detailed study on surface complexation behavior of arsenic species onto a ternary metal oxide adsorbent consisting of iron (Fe), and aluminum (Al) in presence of a redox active 3d-transitional metal element. In the present study, an attempt has been performed to understand the arsenic surface complexation behavior onto four different ternary metal oxide nano adsorbents of M-Al-Fe kind (M = Ni, Co, Mn, and Cu).

2. Experimental section

Chemicals such as Al(NO$_3$)$_3$·9H$_2$O [Merck, India], Fe(NO$_3$)$_3$·9H$_2$O [Qualigens Fine Chemicals, India], Ni(NO$_3$)$_2$·6H$_2$O [Loba Chemie, India], Co(NO$_3$)$_2$·6H$_2$O [Loba Chemie, India], MnCl$_2$.4H$_2$O [Loba Chemie, India], CuCl$_2$.2H$_2$O [Loba Chemie, India], and Liq. Ammonia [Qualigens Fine Chemicals] of laboratory grade (A.R) were procured and used as received. Different arsenic salts like sodium arsenite (NaAsO$_2$) for As(III) systems, sodium arsenate hepta hydrate (NaH$_2$AsO$_4$·7H$_2$O) for As(V) systems (S.D fine - chemicals Ltd, India) were used. HCl [Loba Chemie, India] and NaOH [Fisher Scientific, India] were used as titration mediums. All processes, and experiments were performed under normal atmosphere, and room temperature conditions using double distilled (DD) water medium. All four adsorbents (i.e., Ni-Al-Fe, Co-Al-Fe, Mn-Al-Fe, and Cu-Al-Fe) were synthesized following similar procedures as reported in the literature. The corresponding data on experimental conditions, and characterization techniques are provided in the supporting information.

2.1. X-ray absorption spectroscopy (XAS) analysis

XAS measurements of these samples at As *K*-edge have been performed in fluorescence mode at the Scanning EXAFS Beam line (BL-9) at the Indus-2 Synchrotron Source (2.5 GeV, 100 mA) at the Raja Ramanna Centre for Advanced Technology (RRCAT), Indore, India [56]. The beam line equipped with a double crystal monochromator (DCM) which works in the 4–25 KeV photon energy range with a resolution of 10^4 at 10 KeV. A 1.5 m horizontal pre-mirror with meridional cylindrical curvature is used prior to the DCM for collimation of the beam and higher harmonic rejection. The second crystal of the DCM is a saggital cylinder with radius of curvature in the range 1.28–12.91 meters, which provides horizontal focusing to the beam. For measurements in the fluorescence mode, the sample is placed at 45° to the incident X-ray beam and the fluorescence signal (I_f) is detected using a Si drift detector placed at 90° to the incident X-ray beam. An ionization chamber detector is used prior to the sample to measure the incident X ray flux (I_o) and the absorbance of the sample ($\mu = I_f / I_o$) is obtained as a function of energy by scanning the monochromator over the specified energy range. The EXAFS spectra of the samples at As *K*-edge were recorded in the energy range of 11,800–12,430 eV.

2.1.1. Arsenic K-edge

In order to take care of the oscillations in the absorption spectra, the