Arsenate uptake by Al nanoclusters and other Al-based sorbents during water treatment

Jasmin Mertens [a, b, *], Jérôme Rose [c, d], Bernhard Wehrli [a, b], Gerhard Furrer [a]

[a] Institute of Biogeochemistry and Pollutant Dynamics (IBP), ETH Zürich, Universitätstrasse 16, 8092 Zürich, Switzerland
[b] Eawag, Swiss Federal Institute of Aquatic Science and Technology, Überlandstrasse 133, 8600 Dübendorf, Switzerland
[c] CNRS, Aix-Marseille University, CEREGE, UMR 7330 (FR ECCOREV), 13545 Aix-en-provence, Cedex 4, France
[d] International Consortium for the Environmental Implications of Nanotechnology iCEINT, CNRS (France) — Duke University, NC, USA

A R T I C L E   I N F O

A B S T R A C T

In many parts of the world, arsenic from geogenic and anthropogenic sources deteriorates the quality of drinking water resources. Effective methods of arsenic removal include adsorption and coagulation with iron- and aluminum-based materials, of which polyaluminum chloride is widely employed as coagulant in water treatment due to its low cost and high efficiency. We compared the arsenic uptake capacity and the arsenic bonding sites of different Al-based sorbents, including Al nanoclusters, polyaluminum chloride, polyaluminum granulate, and gibbsite. Extended X-ray absorption fine structure (EXAFS) spectroscopy revealed that As(V) forms bidentate-binuclear complexes in interaction with all Al-based removal agents. The octahedral configuration of nanoclusters and the distribution of sorption sites remain the same in all types of removal agents consisting of nano-scale Al oxyhydroxide particles. The obtained distances for As(V)—O and As(V)—Al agreed with previously published data and were found to be 1.69 ± 0.02 Å and $3.17-3.21$ Å, respectively.

Our study suggests that As(V) binds to Al nanoclusters as strongly as to Al oxide surfaces. The As sorption capacity of Al nanoclusters was found to be very similar to that of Al clusters in a polyaluminum chloride. The most efficient Al-based sorbents for arsenic removal were Al nanoclusters, followed by polyaluminum granulate.

© 2015 Elsevier Ltd. All rights reserved.

1. Introduction

Groundwater and surface water contaminated by arsenic (As) poses a serious health risk to millions of people worldwide. More than 140 million people are exposed to elevated concentrations of As in drinking water (>10 μg/L; Ravenscroft et al., 2009). Thus, the efficient removal of As from drinking water sources is an important endeavor. Most common arsenic removal practices are based on adsorption, coagulation and precipitation with various iron (Fe)- or aluminum (Al)-based sorbents (e.g. activated alumina, hydrous ferric oxides) or coagulants (e.g. $AlCl_3$, polyaluminum chloride, alum and $FeCl_3$ salts) (Bratby, 2006; Chen et al., 2006). Coagulation followed by coprecipitation has been identified as one of the most efficient and cost-effective ex-situ water treatment technologies (EPA, 2000). Polymeric Fe- and Al-based coagulants, such as poly-aluminum chloride and polymeric ferric chloride, are more efficient than non-polymeric coagulating agents, as used in conventional water treatment (Fan et al., 2003). Arsenic sorption to aluminum minerals such as allophane, γ-Al_2O_3 and gibbsite revealed a maximum saturation capacity from 0.8 to 2.4 μmol m^{-2} (Arai et al., 2005, 2001; Ladeira et al., 2001). X-ray absorption spectroscopy (XAS) studies have shown that As(V) forms inner-sphere surface complexes with a bidentate-binuclear configuration on Al_2O_3 (Arai et al., 2001) and gibbsite (Ladeira et al., 2001) with As(V)—Al distances of 3.11—3.19 Å. Further XAS investigation of arsenic sorption by a drinking water treatment residual from $Al_2(SO_4)_3$-flocculation revealed a combination of inner-sphere bonding types with As(V)—Al distances of 2.47—3.14 Å. The large variation was explained by mixed surface geometries (Makris et al., 2009). Recently, a bidentate-binuclear configuration was confirmed for As sorption on amorphous $Al(OH)_3$ sludges (Kappen and Webb, 2013).

Nanoscale metal oxides have higher adsorption capacity and faster kinetics than their non-metal counterparts because of higher

---

* Corresponding author. Institute of Biogeochemistry and Pollutant Dynamics (IBP), ETH Zürich, Universitätstrasse 16, 8092 Zürich, Switzerland.
E-mail address: jasmin.mertens@env.ethz.ch (J. Mertens).

specific surface area, shorter intra-particle diffusion distance and larger number of surface reaction sites. Metal-based nanomaterials have received much attention due to their high removal potential, especially for arsenic removal (Qu et al., 2013; Auffan et al., 2009). The surface-specific As sorption capacity of crystallized nano-iron oxide is larger than that of amorphous ferrihydrite (13.6 and 2.4 $\mu mol/m^2$, respectively). This important difference was discussed as 'nano effect' (Auffan et al., 2008). Nano-scale Al oxyhydroxide particles with Keggin-type structures are supposed to be some of the most efficient removal agents for toxic metals (Casey, 2006; Abeysinghe et al., 2013). Al nanoclusters exhibit higher efficiency than Al salts during coagulation (Chen et al., 2006; Bottero et al., 1981) and promise higher surface-specific sorption capacity. The two main Al nanoparticles are Al_{13} ($AlO_4Al_{12}(OH)_{24}H_2O_{12}^{7+}$) and Al_{30} ($Al_2O_8Al_{28}(OH)_{56}(H_2O)_{26}^{18+}$) (Allouche et al., 2000; Rowsell and Nazar, 2000) with 1 nm width and 1 and 2 nm length, respectively. These Al nano complexes stand out due to their high charge (+7 for Al_{13} and +18 for Al_{30}) (Furrer et al., 1992; Casey et al., 2005) and large surface area (Bottero and Bersillon, 1988; Rakotonarivo et al., 1984). In the near-neutral and alkaline pH range the nanoclusters are subject to deprotonation and aggregation. In comparison to two hexagonal rings of a gibbsite layer with 12 terminal water molecules (Wehrli et al., 1990, Fig. 1a), the Al_{13} Keggin surface is formed by 12 Al octahedrons, each with one terminal water molecule (Fig. 1b). The polycation Al_{30} exhibits 28 surface sites: 24 are equal to those at the Al_{13} and those four octahedron, which are forming the linkage equatorial belt between the two Al_{13} clusters, exhibit six terminal water molecules (Fig. 1c). In a previous study (Mertens et al., 2012a) we showed that Al nanoclusters occur as the major Al fraction in polyaluminum chloride, and that Al_{30} remains the dominant species in solution and in precipitated sludge. The specific structure and small size of Al nanoclusters promise high binding capacity for sorption, making them efficient removal agents. A recent study about the adsorption process of copper on Al_{30} in the presence of disulfonate anions has shown opposite

trends in preferred adsorption sites (Abeysinghe et al., 2013). An-ions adsorb at the belt linkage while cations prefer the caps of Al_{30}, confirming results with perchlorate anions from Casey et al. (2005). The belt region is considered the area with highest deprotonation and therefore highest acidity of Al_{30}.

Despite their good removal properties and wide application in water treatment, the binding mechanisms and binding capacity of Al nanocluster-rich removal agents for the toxic arsenate ion are not well characterized. This is due to the fact that the analysis of aqueous Al clusters is a long-standing challenge because of poorly crystalline surface features and the high complexity of aqueous Al chemistry with a variety of species that can be formed, from monomeric to polymeric hydroxides, colloidal solutions, and pre-cipitates (Wang et al., 2013).

In this study we aimed at identifying the binding capacity as well as reactive sites and the molecular structure of As sorbed to Al nanoclusters. We compared the As removal efficiency of the four removal agents polyaluminum chloride ($PACl_{Al30}$), solid-state pol-yaluminum granulate (PAG), Al_{30} nanoclusters (Al_{30}), and gibbsite for the use in water treatment. X-ray absorption spectroscopy was used to identify the structure of As bonding in the sludge residuals and in the granulate. Finally, we address the implications for water treatment practices.

2. Materials and methods

2.1. Chemicals

All chemicals in this work were reagent grade from Sigma-−Aldrich or Merck. High-purity 18 MΩ water was used to prepare stock solutions. Arsenate solutions of 13.3 mM and 5.33 mM As were prepared by dissolving 1.04 g and 416.3 mg Na_2HAsO_4 in 250 ml volumetric flasks. The 5.33 mM solution was diluted 1:1 to achieve a final concentration of 2.66 mM. A 0.02 M $NaNO_3$ solution was prepared by dissolving 1.69 g $NaNO_3$ in 1 L ultrapure water.
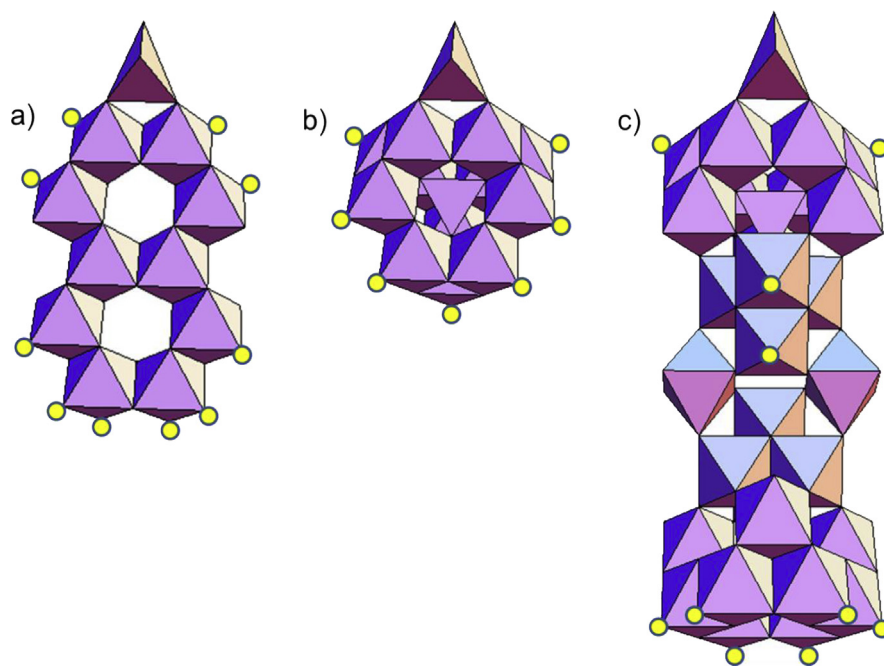

Fig. 1. The structure of aluminum surfaces and possible arsenic bonding sites depicted as yellow circles and one exemplary As tetrahedron on three different aluminum structures: (a) two hexa-coordinated rings of gibbsite (after Wehrli et al., 1990). (b) 12 octahedral surface sites of the polynuclear Al_{13} with one tetrahedral center (Furrer et al., 2002), (c) 28 octahedral surface sites of the nanocluster Al_{30} formed by 2 Al_{13} units linked by four octahedrons (after Casey et al., 2005). Note: only those terminal water ligands are marked that are best suited for the formation of binuclear complexes. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)