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

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Arsenate

Gibbsite

Structurally qualified pair of terminal water molecules for bidentate arsenate binding

Al_{30}

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

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24 EXAFS

Abstract

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 $1.69 \pm 0.02 \text{ \AA}$ and $3.17\text{-}3.21 \text{ \AA}$, 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.

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 ($> 10 \mu\text{g/L}$; 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 polyaluminum 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, $\gamma\text{-Al}_2\text{O}_3$ and gibbsite revealed a maximum saturation capacity from 0.8 to $2.4 \mu\text{mol m}^{-2}$ (Arai et al., 2005; Arai et al., 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

75 3.11-3.19 Å. Further XAS investigation of arsenic sorption by a
76 drinking water treatment residual from $\text{Al}_2(\text{SO}_4)_3$ -flocculation
77 revealed a combination of inner-sphere bonding types with
78 As(V)-Al distances of 2.47 – 3.14 Å. The large variation was
79 explained by mixed surface geometries (Makris et al., 2009).
80 Recently, a bidentate-binuclear configuration was confirmed
81 for As sorption on amorphous $\text{Al}(\text{OH})_3$ sludges (Kappen and
82 Webb, 2013).

83 Nanoscale metal oxides have higher adsorption capacity and
84 faster kinetics than their non-metal counterparts because of
85 higher specific surface area, shorter intra-particle diffusion
86 distance and larger number of surface reaction sites. Metal-
87 based nanomaterials have received much attention due to their
88 high removal potential, especially for arsenic removal (Qu et
89 al., 2013; Auffan et al., 2009). The surface-specific As sorption
90 capacity of crystallized nano-iron oxide is larger than that of
91 amorphous ferrihydrite (13.6 and 2.4 $\mu\text{mol}/\text{m}^2$, respectively).
92 This important difference was discussed as ‘nano effect’
93 (Auffan et al., 2008). Nano-scale Al oxyhydroxide particles
94 with Keggin-type structures are supposed to be some of the
95 most efficient removal agents for toxic metals (Casey, 2006;
96 Abeysinghe et al., 2013). Al nanoclusters exhibit higher
97 efficiency than Al salts during coagulation (Chen et al., 2006;
98 Bottero et al., 1981) and promise higher surface-specific
99 sorption capacity. The two main Al nanoparticles are Al_{13}

100 $(\text{AlO}_4\text{Al}_{12}(\text{OH})_{24}\text{H}_2\text{O}_{12}^{7+})$ and Al_{30}
 101 $(\text{Al}_2\text{O}_8\text{Al}_{28}(\text{OH})_{56}(\text{H}_2\text{O})_{26}^{18+})$ (Allouche et al., 2000; Rowsell
 102 and Nazar, 2000) with 1 nm width and 1 and 2 nm length,
 103 respectively. These Al nano complexes stand out due to their
 104 high charge (+7 for Al_{13} and +18 for Al_{30}) (Furrer et al., 1992,
 105 Casey et al., 2005) and large surface area (Bottero and
 106 Bersillon, 1988; Rakotonarivo et al., 1984). In the near-neutral
 107 and alkaline pH range the nanoclusters are subject to
 108 deprotonation and aggregation. In comparison to two hexagonal
 109 rings of a gibbsite layer with 12 terminal water molecules
 110 (Wehrli et al., 1990; Figure 1a), the Al_{13} Keggin surface is
 111 formed by 12 Al octahedrons, each with one terminal water
 112 molecule (Figure 1b). The polycation Al_{30} exhibits 28 surface
 113 sites: 24 are equal to those at the Al_{13} and those four
 114 octahedrons, which are forming the linkage equatorial belt
 115 between the two Al_{13} clusters, exhibit six terminal water
 116 molecules (Figure 1c). In a previous study (Mertens et al.,
 117 2012a) we showed that Al nanoclusters occur as the major Al
 118 fraction in polyaluminum chloride, and that Al_{30} remains the
 119 dominant species in solution and in precipitated sludge. The
 120 specific structure and small size of Al nanoclusters promise
 121 high binding capacity for sorption, making them efficient
 122 removal agents. A recent study about the adsorption process of
 123 copper on Al_{30} in the presence of disulfonate anions has shown
 124 opposite trends in preferred adsorption sites (Abeyasinghe et al.,

125 2013). Anions adsorb at the belt linkage while cations prefer
126 the caps of Al_{30} , confirming results with perchlorate anions
127 from Casey et al. (2005). The belt region is considered the area
128 with highest deprotonation and therefore highest acidity of
129 Al_{30} .
130 Despite their good removal properties and wide application in
131 water treatment, the binding mechanisms and binding capacity
132 of Al nanocluster-rich removal agents for the toxic arsenate ion
133 are not well characterized. This is due to the fact that the
134 analysis of aqueous Al clusters is a long-standing challenge
135 because of poorly crystalline surface features and the high
136 complexity of aqueous Al chemistry with a variety of species
137 that can be formed, from monomeric to polymeric hydroxides,
138 colloidal solutions, and precipitates (Wang et al., 2013).
139 In this study we aimed at identifying the binding capacity as
140 well as reactive sites and the molecular structure of As sorbed
141 to Al nanoclusters. We compared the As removal efficiency of
142 the four removal agents polyaluminum chloride ($\text{PACl}_{\text{Al}_{30}}$),
143 solid-state polyaluminum granulate (PAG), Al_{30} nanoclusters
144 (Al_{30}), and gibbsite for the use in water treatment. X-ray
145 absorption spectroscopy was used to identify the structure of
146 As bonding in the sludge residuals and in the granulate. Finally,
147 we address the implications for water treatment practices.

148 2. Materials and methods

149 2.1 Chemicals

150 All chemicals in this work were reagent grade from Sigma-
151 Aldrich or Merck. High-purity 18 M Ω water was used to
152 prepare stock solutions. Arsenate solutions of 13.3 mM and
153 5.33 mM As were prepared by dissolving 1.04 g and 416.3 mg
154 Na₂HAsO₄ in 250 ml volumetric flasks. The 5.33 mM solution
155 was diluted 1:1 to achieve a final concentration of 2.66 mM. A
156 0.02 M NaNO₃ solution was prepared by dissolving 1.69 g
157 NaNO₃ in 1 L ultrapure water.

158 *2.2 Al-based removal agents*

159 The removal of As occurs via different pathways. Four types of
160 Al-based materials and their adequate methods to remove
161 arsenic were investigated. Al₃₀ solution with an Al(tot)
162 concentration of 0.1 M was prepared by aging an Al₁₃ solution
163 of 7.8 mM for 11 years at room temperature (Casey et al.,
164 2001). The final pH of the solution was 4.5 and ²⁷Al NMR
165 confirmed the content of 99% Al₃₀ nanocluster and 1% Al³⁺
166 (Casey et al., 2001).

167 One of the purposes of this work was to compare the efficiency
168 of pure Al₃₀ solutions with commercially available
169 polyaluminum chloride. Polyaluminum chloride solution
170 (PACl) with Al(tot) concentration of 0.15 M was obtained by
171 dissolving 14.64 g of the Al salt Locron-S[®] (Clariant) in 500 ml
172 deionized water. Ferron measurements of this solution at pH 5
173 revealed Al₃₀, Al₁₃ and Al³⁺ shares of 74 %, 25.4 %, and 0.6 %,
174 respectively (Mertens et al., 2012a). This agent will be called

175 $\text{PACl}_{\text{Al30}}$ in this document. Solid-state ^{27}Al MAS NMR
176 revealed that Al nanoclusters remain the dominant Al species in
177 the sludge precipitated at pH 7 (Mertens et al., 2012a).
178 Polyaluminum granulate (PAG) with a size of 1-3 mm and
179 surface area of $35 \pm 1 \text{ m}^2 \text{ g}^{-1}$ was generated from a coagulation
180 process by neutralizing the acidic $\text{PACl}_{\text{Al30}}$ solutions to pH 7
181 (Mertens et al., 2012b). For the removal of chloride, four
182 repetitive washing cycles of $\text{PACl}_{\text{Al30}}$ solutions consisted of
183 aggregation, centrifugation, and washing with high purity
184 water. Precipitated material was air-dried for 5 days and
185 compressed. In order to compare our Al_{30} -rich reagents to
186 previously investigated, natural materials, we also used the
187 mineral gibbsite. A gibbsite suspension with $\text{Al}(\text{tot})$
188 concentration of 0.77 M $\text{Al}(\text{III})$ was prepared by the sol-gel
189 route via hydrolysis of Al nitrate up to pH 6 and aging of the
190 formed gel for three weeks at pH 4 (Jolivet et al., 2000).

191 *2.3 Removal experiments*

192 Two adsorption experiments were performed. The first was to
193 obtain adsorption isotherms for the two sorbents polyaluminum
194 chloride and polyaluminum granulate. The second was to
195 achieve single-point adsorption data for all four Al-based
196 sorbents with the same method. The As-loaded samples
197 obtained from the second experiments were examined by XAS
198 analyses.

199 As adsorption experiments with $\text{PACl}_{\text{Al30}}$ or PAG were

performed by mixing different amounts of 13.3 mM Na_2HAsO_4 solution with a $\text{PACl}_{\text{Al30}}$ solution of 0.255 mM $\text{Al}(\text{tot})$ or with 0.5 g PAG in synthetic water with an alkalinity of 8 mM in 50 ml sterile polypropylene tubes. The chemical composition of synthetic water was derived from field studies and contained 0.6 mmol L^{-1} MgCl_2 , 8 mmol L^{-1} NaHCO_3 , 1 mmol L^{-1} CaCO_3 (Mertens et al., 2012a). The pH was adjusted to $\text{pH } 7.5 \pm 0.2$ with 0.1 mol L^{-1} NaOH . The sorption isotherm was obtained by varying the initial As concentration from 0.3 $\mu\text{mol L}^{-1}$ to 4 mmol L^{-1} . The tubes with $\text{PACl}_{\text{Al30}}$ were shaken horizontally at 150 rpm for 30 min and the formed aggregates were allowed to settle for 5 hours. Batches containing PAG were shaken horizontally at 150 rpm for 20 hours to reach equilibrium. The different reaction times between the coagulant $\text{PACl}_{\text{Al30}}$ and the granulate were allowed to assure best reaction kinetics: 20 h for maximum As uptake by PAG (Mertens et al., 2012b), 30 minutes or less for maximum As removal by $\text{PACl}_{\text{Al30}}$ (Mertens et al., 2012a). The supernatant solution was analyzed for total As concentrations by inductively coupled plasma-mass spectrometry (ICP-MS, Agilent 7500cx). ICP-MS was required for accurate As measurements at the low end of the isotherms. EXAFS samples were prepared by adding the amount of 13.3 or 2.66 mM As(V) solutions needed to yield initial As concentrations of 0.13 or 0.67 mM to 0.01 M NaNO_3 electrolyte solution in a 50 ml polyethylene tube. The removal

225 process was started by adding Al_{30} , $\text{PACl}_{\text{Al}30}$ or gibbsite
 226 solutions to yield initial $\text{Al}(\text{tot})$ concentration of 75 mM. For
 227 As removal with PAG a solution with an ionic strength of 10
 228 mM, and an arsenic concentration of 0.26 mM was prepared by
 229 mixing 25 ml of 0.02 M NaNO_3 , 20 ml of ultrapure water and 5
 230 ml of arsenic stock solution with $[\text{As}] = 2.66 \text{ mM}$ in a 50 ml
 231 polyethylene tube. Subsequently, 0.5 g PAG was added. The
 232 pH of all solutions was adjusted to 7.5 ± 0.2 with 0.1 M NaOH
 233 at room temperature ($22\text{--}25^\circ\text{C}$). The solutions with gibbsite,
 234 Al_{30} and $\text{PACl}_{\text{Al}30}$ solutions were shaken horizontally during 30
 235 min, and centrifuged for 30 min at 80'000 rpm. The PAG
 236 sample was shaken horizontally for 20 hrs. The supernatant
 237 solutions were replaced by 50 ml 0.01 M NaNO_3 for rinsing,
 238 shaken during 30 min and centrifuged at 80'000 rpm for 30 min
 239 (gibbsite, Al_{30} , $\text{PACl}_{\text{Al}30}$), or shaken for 20 hours (PAG). The
 240 supernatant solutions were removed and dissolved As
 241 concentrations were measured by inductively coupled plasma-
 242 optical emission spectrometry (ICP-OES, Vista-MPX CCD
 243 Simultaneous, Varian), and the remaining precipitate was
 244 freeze-dried. As-loaded PAG was air-dried at room temperature
 245 for 3 days.

246 2.4 X-ray absorption spectroscopy

247 The As-loaded precipitates and granulates were mixed in a 1:5
 248 ratio with polyvinylpyrrolidone (PVP), and pressed to 20 mm
 249 pellets. XAS spectra of an As(V) solution (0.53 M Na_2HAsO_4)

were collected as As(V) reference. As K-edge (11.867 eV) X-ray absorption near-edge structure (XANES) and extended X-ray absorption fine structure (EXAFS) data were recorded in fluorescence detection mode on the SAMBA beamline at the French national synchrotron facility (SOLEIL; Belin et al., 2005), using an Au foil for internal energy calibration. All data were recorded at 77 K using a liquid N₂ cryostat. The beamline operated with a Si(220) monochromator, a beam of 2.75 GeV and a current of 400 mA. Multiple scans (3 to 9) were collected for each sample. Sample spectra were first energy calibrated, based on the inflection point of the Au reference foil. The determination of the E_0 was performed using a second-degree derivative of the spectra obtained from the Au foil (Au LIII-edge: 11.919 eV). Subsequently, spectra were background corrected using a two-polynomial fit, and data were merged and normalized using the ATHENA program (Ravel and Newville, 2001). The FEFF6 code (Newville, 2001) was used to calculate theoretical amplitude and phase shift functions for As-O and As-Al backscatters for single and multiple scattering (MS) paths. MS paths were calculated on a symmetric AsO₄ tetrahedron model with all As-O distances of 1.69 Å and all O-As-O angles of 110°. During fitting the values for the distances r of the As-O and As-Al shells as well as for As-O-O and As-O-As-O MS paths were allowed to vary.

3. Results and discussion

275 3.1 Surface area

276 The surface properties of coagulants and adsorbents are
 277 important for the removal of contaminating compounds from
 278 the aqueous phase. In the cases of polyaluminum chloride and
 279 Al_{30} solutions, an accurate measure of the surface area is
 280 difficult to achieve, because Al nanoclusters aggregate
 281 depending on pH and concentration. Here, we propose an
 282 approximation of how to approach this problem. Coagulation of
 283 Al nanoclusters in a polyaluminum solution was observed to
 284 start at pH 5 and to increase until the pH of zero charge (pH_{PZC})
 285 of 6.7 was reached (Furrer et al, 1992, Casey et al, 2005).
 286 Based on the size of Al_{30} ($1 \text{ nm} \times 1 \text{ nm} \times 2 \text{ nm}$) and a
 287 rectangular shape, the geometric surface area was calculated as
 288 $2550 \text{ m}^2 \text{ g}^{-1}$. This value implies that single Al_{30} clusters interact
 289 at each of their surface sites with the solution. This is an
 290 unrealistic case, particularly above pH 7, where strong
 291 aggregation and sedimentation are taking place. The BET
 292 surface area of $\text{PACl}_{\text{Al}_{30}}$, settled at pH 7 after four washing
 293 cycles extracting chloride from Al surfaces, yielded to $13.7 \pm$
 294 $0.2 \text{ m}^2 \text{ g}^{-1}$. This result is unexpectedly low for the small Al
 295 entities in solution, but can be explained by the aggregation at
 296 pH 7 and solidification during the processes of settling and
 297 centrifugation, by which the flocs agglomerated into a white gel
 298 paste with low porosity. Between these two extreme cases the
 299 surface area needs to be approximated in the aqueous phase.

300 Rakotonarivo et al. (1984) calculated the specific surface area
 301 of aluminum hydroxide gels at pH 6.5 and 7.5 at different $[\text{OH}]$
 302 $[\text{Al}]^{-1}$ ratios (0, 2, 2.5) by using the relationship of the
 303 molecular area of long-chain alkylsulfonates, the Avogadro
 304 number (N_A) and the adsorbed quantity of alkylsulfonates
 305 (Q_{max}) taken at sorption plateaus from adsorption isotherm data.
 306 Resulting surface areas ranged between 540 and 1210 $\text{m}^2 \text{g}^{-1}$,
 307 and decreased with increasing pH and $[\text{OH}] [\text{Al}]^{-1}$ ratio. The
 308 solution composition which matched our experiments most
 309 closely provided a value of 540 $\text{m}^2 \text{g}^{-1}$ for pH 7.5 and $[\text{OH}]$
 310 $[\text{Al}]^{-1}$ ratio of 2.5. As organic substances are known to have
 311 very high sorption affinity for metal oxide surfaces (Bauer and
 312 Blodau, 2006), the surface area after Rakotonarivo et al. (1984)
 313 was employed further in this work to calculate surface loading
 314 for the polyaluminum chloride and the Al_{130} sample.

315 3.2 *As(V) surface coverage*

316 In order to compare the arsenic surface coverage for different
 317 Al sorbents employed in this study, the amount of removed
 318 arsenic was related to the surface area. The adsorbed As
 319 concentrations on $\text{PACl}_{\text{Al}130}$ were calculated for the three
 320 discussed surface areas (Table 1). The Langmuir equation was
 321 used considering that a sorption maximum had been reached.
 322 The goodness of fit indicated by the nonlinear correlation
 323 coefficient R^2 was 0.97 for the $\text{PACl}_{\text{Al}130}$ data. The maximum
 324 adsorbed As(V) quantity ranged from 2.3 $\mu\text{mol m}^{-2}$ when

325 assuming single Al_{30} clusters to $170 \mu\text{mol m}^{-2}$ when related to
 326 the measured BET surface area of $13.7 \text{ m}^2 \text{ g}^{-1}$ (Figure 2, dashed
 327 lines for lower and upper boundary). The latter was just above
 328 the absolute theoretical coverage maximum ($160 \mu\text{mol m}^{-2}$),
 329 assuming a maximum of 100 As atoms per nm^2 . This
 330 unrealistically high value is another indication that the surface
 331 area measured for the dried precipitate is not representative for
 332 aqueous Al nanoclusters. The As(V) uptake capacity per area
 333 using $540 \text{ m}^2 \text{ g}^{-1}$ for the surface of $\text{PACl}_{\text{Al}_{30}}$ was reached at 11
 334 $\mu\text{mol m}^{-2}$, about 80% higher than for granulate from the same
 335 polyaluminum material (Figure 2), and threefold compared to
 336 gibbsite (Table 1).

337 3.3 Surface coverage for EXAFS samples

338 The removal of As(V) by Al nanoclusters, whether as
 339 nanoclusters in suspension or as main components of
 340 polyaluminum chloride or granulate, was compared to As(V)
 341 sorption to gibbsite, which is well described in the literature
 342 (Ladeira et al., 2001; Banning, 2005). The loaded $\text{PACl}_{\text{Al}_{30}}$
 343 samples used in EXAFS analyses contained 0.12 and 0.61 μmol
 344 m^{-2} (Table 2). These results accounted for 2% and 10% of the
 345 maximum sorption capacity of $540 \text{ m}^2 \text{ g}^{-1}$ listed in Table 1, and
 346 were named PAClAs_2 and PAClAs_{10} , respectively. The Al_{30}
 347 sample, which was exposed to the same initial As(V)
 348 concentration than the sample PAClAs_{10} (0.66 mM) showed a
 349 similar surface coverage with $0.57 \mu\text{mol m}^{-2}$ (Table 2),

350 indicating that Al_{30} solutions do not enhance As uptake
 351 efficiency compared to $\text{PACl}_{\text{Al}_{30}}$. PAG surface coverage was
 352 slightly higher with $0.73 \mu\text{mol m}^{-2}$. For gibbsite, initial As(V)
 353 concentrations of $0.133 \text{ mmol L}^{-1}$ and $0.667 \text{ mmol L}^{-1}$ resulted
 354 in 1.7 and $4.9 \mu\text{mol As m}^{-2}$, using the calculated surface area of
 355 $37 \text{ m}^2 \text{ g}^{-1}$ (Section 1.2, Page S6, Supplementary information).
 356 Because As(V) concentrations in solution decreased by only
 357 50%, the value of $4.9 \mu\text{mol m}^{-2}$ (Table 2) was assumed to be
 358 close to the maximum uptake capacity of gibbsite. Hence, all
 359 nanocluster-based materials exhibit a higher uptake capacity
 360 than gibbsite.

361 3.4 EXAFS spectroscopy

362 EXAFS spectroscopy was used to discern the atomic
 363 environment of As(V). For all samples, the energy height and
 364 position in the XANES range of the As K-edge XAS spectra at
 365 11878 eV corresponded to the sharp edge of the As(V)
 366 oxidation state represented by the As(V) reference (data not
 367 shown). In general, the EXAFS oscillations of all materials
 368 based on Al nanoclusters showed the same frequency than the
 369 gibbsite samples, indicating similar atomic structures.
 370 However, PACl samples showed a slight difference in
 371 amplitude for two different As concentrations (Figure 3a). The
 372 Fourier transformation of the EXAFS signal yielded
 373 information on the interatomic distances, and showed 3-4 peaks
 374 for all prepared samples (Figure 3b). The peak at $1.3 \text{ \AA}$

(distance uncorrected for phase shift) was attributed to the As-O shell, and the 2-3 small peaks at 1.9-3 Å (uncorrected) corresponded to the As-Al shell and multiple scattering of the photoelectron between the oxygen atoms surrounding the arsenic atom.

For the gibbsite sample, the first and second shells were isolated, back-transformed, and fitted in order to obtain the optimized fit parameters of atomic distance and structural disorder for each shell. The first coordination shell was simulated with one shell of 4 oxygen atoms surrounding arsenic. The fitting yielded an atomic distance of 1.69 Å and a Debye-Waller factor of 0.002-0.004 Å² for low and high arsenic concentrations (Table 3), in accordance with the tetrahedral structure of As(V). The second neighboring shell was fitted by comparing the backscattering amplitude for As(V)-Al, As-O-O, As-O-As-O, and for a combination of all paths. The model results showed that two Al atoms surround the As atom at distance $R = 3.15\text{-}3.18$ Å (Table 3), which corresponds to the findings of Ladeira et al. (2001).

Since the oscillations showed some sub-structure, we tested whether the Al path was an important part of the fit, and if the multiple scattering (MS) paths are needed for an adequate interpretation of the fit. To verify the influence of the Al path, the two shells of the gibbsite spectrum were fitted by a model with the As-O and the MS paths, with and without including

the Al path. The two model outputs were subtracted from each other and the difference was compared to the noise level of the spectrum. The noise level was calculated using the back-Fourier transformed signal for all distances higher than $r = 6 \text{ \AA}$. The obtained residual of the As-Al fit was significantly higher than the noise (Figure 4), and therefore a substantial part of the fitting.

In previous studies, triangular As-O-O MS was included to improve the quality of the fit of the second shell (Kappen and Webb, 2013). In the present study of As on gibbsite, we considered all three types of 3- and 4-leg MS within the As-O tetrahedron, and compared it to the model with Al as a second test if the presence of Al improves the fit. The sequential additions of the MS paths lead to a decrease of the R-factor (normalized sum of squared residuals), and the fit with Al was marginally better than the fit without the Al path (Supporting Information, Table S1). Statistically, the direct data evaluation of the inclusion of MS paths did not show significant improvement. However, in both modeling approaches the As-Al distance were very similar for the same samples, and the results for the As-Al distance can therefore be considered as robust.

After Fourier transformation (Figure 3b), the raw data of the Al₃₀-based sorbents were fitted using the multiple scattering paths MS 1 and MS 3 based on the verified model derived from

the structure of gibbsite, with slight modifications to achieve the best fitting parameters. This gibbsite model was applied due to the similarity of the binding sites (Figure 1) and the closely related EXAFS spectra (Figure 3).

No major differences in atomic distances were found between the Al_{30} -based sorbents and gibbsite. However, the Debye-Waller factors for the MS paths varied between 0.001 and 0.009, inferring differences in the structural disorder of the multi-scattering pathways of the photoelectron (Figure 5, Table S2). These results suggest that the atomic environment of As(V) adsorbed to Al nanocluster-based removal materials is very similar to the structure of As(V) adsorbed to gibbsite, and corresponds to an inner-sphere bidentate-binuclear configuration. These results confirm the EXAFS findings of Kappen and Webb (2013) for amorphous aluminum hydroxide sludges. Additionally, our EXAFS study reveals that the octahedral configuration of nanoclusters and distribution of sorption sites will remain the same in all types of removal agents consisting of nano-scale Al oxyhydroxide particles with Keggin-type structures.

Applying this binding geometry with the corresponding distances to the chemical structure of Al_{13} and Al_{30} , it is apparent that As can only be adsorbed to the nearest-neighbored terminal water ligands of neighboring Al octahedra (Figure 6), and that this coordination geometry corresponds to

the same as already postulated for gibbsite. On single Al_{13} and Al_{30} clusters, 6 and 8 of these preferred sites are available, respectively (compare Figures 1b and 1c). Hence, the theoretical adsorption ratio of As to Al is 0.46 and 0.27 for Al_{13} and Al_{30} , respectively. For $PACl_{Al30}$ at pH 7.5, Mertens et al. (2012a) found a molar ratio of 0.2 As/Al. These results adduce evidence that most sorption sites of Al_{30} remain available for arsenic sorption also during coagulation and flocculation processes of Al nanoclusters. The inner-sphere adsorption reaction of As(V) to Al_{30} during treatment of drinking water in a near-neutral pH range can be derived from our adsorption site distribution as

if $pH > 6.7$ with $HAsO_4^{2-}$ as the dominant arsenate species, and the surface-specific charge of the Al_{30} polycation close to zero (Casey et al., 2005; Mertens et al., 2012a). At excess $HAsO_4^{2-}$ the only formed dominant complex is $[Al_{30}(AsOOH)_6]^{12+}$.

4. Conclusions and implications for water treatment

All tested Al nano surfaces represent robust sorbents of which As(V) is not released readily, because arsenate was directly bound in a bidentate-binuclear configuration to all the investigated Al nanocluster sorbents. By employing extended X-ray absorption fine structure we were able to show that

472 arsenic forms inner-sphere surface complexes with Al
473 nanoclusters with the same structural configuration but higher
474 density as gibbsite. Our results suggest further that (1) Al
475 nanoclusters lost half of the sorption sites in a compacted
476 polyaluminum granulate of 1-3 mm diameter compared to the
477 Al_{30} coagulant in suspension. Further investigations could
478 optimize the availability of sorption in granulated nanocluster
479 material as this product can be more easily separated from the
480 aqueous phase than colloidal suspensions. Polyaluminum
481 granulate remains a strong candidate for As removal as it
482 achieved higher As surface coverage than activated alumina or
483 microscale minerals, such as gibbsite, and allophane. (2) The
484 reactivity of an Al_{30} solution and Al_{30} -rich polyaluminum
485 chloride was found to be very similar. Therefore, the
486 economically interesting application of $\text{PACl}_{\text{Al}_{30}}$ with high
487 share of Al_{30} particles is a better option for As removal than
488 pure Al_{30} solutions. However, solid-liquid separation remains
489 more challenging compared to granulate material.

490 **Supporting Information.** Methods for transmission electron
491 microscopy (TEM) and TEM image of gibbsite suspension,
492 surface area calculation for the gibbsite samples, results of
493 multiple scattering pathways on the EXAFS fit.

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Tables

Table 1: As(V) adsorption efficiency of the Al-based sorbents used in this work compared to previously reported data

Al sorbent	Size	Surface area	As(V) surface coverage			Reference
			$\mu\text{mol/g}$	$\mu\text{mol/m}^2$	As/nm^2	
Gibbsite	< 500	45.0	33.1	0.73	0.44	Banning (2005)
Gibbsite	n.a.	13.5	33.1	2.45	1.50	Ladeira et al. (2001)
Amorphous $\text{Al}(\text{OH})_3$	< 500	42.9	38.0	0.87	0.53	Banning (2005)
Allophane	3×10^{-3}	370 ± 1.5	352	0.95	0.57	Arai et al. (2005)
Activated Alumina	6×10^{-3}	115	133	1.15	0.69	Lin and Wu (2001)
$\gamma\text{-Al}_2\text{O}_3$	n.a.	90.1	126	1.40	0.84	Arai et al. (2001)
MIL-53(Al)	n.a.	920	1409	1.53	0.91	Li et al. (2014)
$\text{PACl}_{\text{Al}_{130}}$	n.a.	13.7 ^a	2360	172.00	104.00	This work
		540 ^b	5870	10.9	6.55	
		894 ^c	5290	5.92	3.56	
Al_{30}	2×10^{-3}	2550 ^d	5750	2.25	1.36	This work
Gibbsite	0.1	37.0*	182	3.85 ^e	2.32	
PAG	$10^3 - 3 \times 10^3 \zeta$	$35.0 \pm 1.0 \zeta$	210	6.01	3.62	This work

n.a.: not available

^a measured on dried $\text{PACl}_{\text{Al}_{130}}$ powder by BET

^b from Rakotonarivo et al. (1984)

^c calculated after equation 10 from Rakotonarivo et al (1984) with Q_0 from As(V) adsorption isotherms for the added amount Al_{tot} (in g)

^d calculated for Al_{30} entities of the dimension 1 nm x 2 nm

^e The surface area after Banning et al.²⁷ was used

* Calculated (see S2, Supporting Information)

ζ from Mertens et al. (2012b)

Table 2: Sample codes and summary of As(V) adsorption data for EXAFS samples

Sample code ¹⁾	Al sorbent material	[As]initial	As adsorption		Surface coverage	
		mmol/L	%	$\mu\text{mol/g}$	$\mu\text{mol/m}^2$	%
Al ₃₀ As10	Al ₃₀	0.667	93.2	311.0	0.57	~ 10.0
PAClAs2 ²⁾	PACl _{Al30}	0.133	97.6	64.9	0.12	2.0
PAClAs10 ²⁾	PACl _{Al30}	0.667	99.9	330.0	0.61	10.7
GibAs35 ³⁾	Gibbsite	0.133	99.3	64.0	1.73	35.2
GibAs100 ³⁾	Gibbsite	0.667	53.9	182.0	4.92	~100
PAGAs20	Polyaluminum granulate	0.267	95.6	25.5	0.73	20.8

¹⁾ The number behind As indicates the As surface coverage in %

²⁾ "PACl" in the sample code is the abbreviation for the sorbent material polyaluminum chloride with high amount of Al nanoclusters

³⁾ "Gib" was used as abbreviation for gibbsite as the sorbent material

Table 3: Summary of the EXAFS modeling results

Sample ¹⁾	Atomic shell	N±20%	R (Å)*	E ₀ (eV)	σ ² (Å ²)*
GibAs40	As-O	4.0	1.69 ± 0.02	6.0	0.0029 ± 0.0008
	As-O-O ^{MS}	12.0	3.20 ± 0.10	5.0	0.0069 ± 0.0018
	As-O-As-O ^{MS}	12.0	3.49 ± 0.10	5.5	0.001 ± 0.0005
	As-Al	1.8*	3.17 ± 0.02	4.2	0.008 ± 0.0060
GibAs100	As-O	4.0	1.69 ± 0.02	6.0	0.0028 ± 0.0004
	As-O-O ^{MS}	12.0	3.23 ± 0.13	6.4	0.009 ± 0.00013
	As-O-As-O ^{MS}	12.0	3.49 ± 0.10	7.5	0.009 ± 0.00013
	As-Al	1.9*	3.19 ± 0.04	5.0	0.0091 ± 0.0037
Al ₃₀ As10	As-O	3.8	1.69 ± 0.01	5.5	0.0021 ± 0.0004
	As-O-O ^{MS}	12.0	3.11 ± 0.01	5.5	0.009 ± 0.0001
	As-O-As-O ^{MS}	12.0	3.49 ± 0.10	6.4	0.0017 ± 0.0018
	As-Al	1.8*	3.20 ± 0.05	5.0	0.0069 ± 0.0027
PAClAs2	As-O	4.0	1.68 ± 0.01	6.0	0.0025 ± 0.0004
	As-O-O ^{MS}	12.0	3.20 ± 0.10	4.0	0.0089 ± 0.00003
	As-O-As-O ^{MS}	12.0	3.49 ± 0.10	5.0	0.0089 ± 0.00003
	As-Al	2.0*	3.18 ± 0.04	6.0	0.009 ± 0.00003
PAClAs10	As-O	4.0	1.69 ± 0.01	6.6	0.0021 ± 0.0004
	As-O-O ^{MS}	12.0	3.15 ± 0.05	4.5	0.004 ± 0.001
	As-O-As-O ^{MS}	12.0	3.49 ± 0.10	4.2	0.001 ± 0.0003
	As-Al	2.0*	3.21 ± 0.06	7.0	0.0086 ± 0.0051
PAGAs20	As-O	4.0	1.68 ± 0.005	6.2	0.0017 ± 0.0009
	As-O-O ^{MS}	12.0	3.20 ± 0.10	4.0	0.0089 ± 0.00019
	As-O-As-O ^{MS}	12.0	3.49 ± 0.10	4.0	0.009 ± 0.00016
	As-Al	2.3*	3.18 ± 0.03	6.0	0.0076 ± 0.0058

¹⁾ for sample codes see Table 2.

N: coordination number, R: interatomic distance, σ²: Debye-Waller factor (disorder parameter), E₀: threshold energy, As-O-O^{MS} and As-O-As-O^{MS}: Multiple scattering paths

* allowed to vary during the fit

Figure 1

Figure 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.

Figure 2

Figure 2: Adsorption of As(V) per surface area for $PACl_{Al30}$ and PAG at initial pH 7.5 using the best proposed surface area after Rakotonarivo et al. (1984). Symbols represent experimental data and solid lines represent Langmuir models for $PACl_{Al30}$ ($R^2 = 0.97$) and for PAG ($R^2 = 0.94$). The two dashed lines represent the upper (factor 15.7 higher) and lower (factor 4.7 lower) boundary for $PACl_{Al30}$ data using the surface area from BET analysis ($13.5 \text{ m}^2/\text{g}$) and geometrical calculations ($2550 \text{ m}^2/\text{g}$), respectively.

Figure 3

Figure 3: (a) k^2 - weighted normalized χ functions, and (b) Fourier transformed arsenic K-edge χ functions for As(V) adsorbed on gibbsite and the five Al nanocluster – derived materials listed in Table 2.

Figure 4

Figure 4: Back-transformed EXAFS spectrum of the Al-subtracted gibbsite model and the noise level. The difference in models with and without the Al shell is above the noise signal.

Figure 5

Figure 5: Fit results (dashed green lines) on the back-transformed EXAFS data (solid black lines) for As(V) adsorbed on gibbsite, Al₃₀ nanoparticles, polyaluminum chloride with high Al nanoparticles share, and polyaluminum granulate. The fit range in k-space started at 3.3 Å⁻¹ and extended to the end (13 Å⁻¹) of the available data range.

Figure 6

Figure 6: Structural diagram of polyaluminum oxides and the binuclear linkage between the arsenate tetrahedron and two $\text{Al}(\text{O})_6$ octahedra.

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

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Highlights:

- Various nanoscale aluminum agents for arsenic removal from water are compared
- Sequence of removal efficiency: Al nanoclusters > poly-Al granulate > gibbsite
- Al_{30} and polyaluminum chloride in solution show similar removal efficiencies
- High saturation capacity of Al nanoparticles is quantified by adsorption isotherms