



Characteristics and components of poly-aluminum chloride coagulants that enhance arsenate removal by coagulation: Detailed analysis of aluminum species



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ABSTRACT

We evaluated 51 poly-aluminum chloride (PACl) coagulants to determine the coagulant characteristics that were responsible for effective arsenate removal from contaminated river water by means of experiments involving coagulation, settling, and microfiltration. Some of the high-basicity PACls exhibited high arsenate removal percentages, particularly under alkaline conditions, and we investigated various relevant properties and characteristics of these high-basicity PACls. Effective arsenate removal was correlated with the content of polymeric and colloidal aluminum species (Al_b and Al_c) in the PACls but was not well correlated with colloid charge or zeta potential. Multiple regression analysis revealed that a portion of Al_b and Al_c, which reacted with the ferron reagent during the period from 30 min to 3 h, that is, the (Al_{30min-3h}) fraction, had the highest arsenate sorption capacity, followed by a colloidal aluminum fraction (Al_{>3h}), which reacted with ferron at a time of >3 h. The Al_{30min-3h} fraction was stable, and its arsenate sorption capacity did not decrease markedly with increasing pH. The Al_{30min-3h} fraction did not correspond to the Keggin-type e-Al₁₃ polycation or the δ-Al₃₀ polycation; it is likely to be an aluminum polymer that is unobservable by ²⁷Al NMR spectroscopy. Our results suggest that PACls with a high proportion of the Al_{30min-3h} fraction should be used for enhanced arsenate removal by coagulation. A high content of the e-Al₁₃ polycation or the δ-Al₃₀ polycation was not indispensable for effective arsenate removal.

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1. Introduction

Arsenic, a carcinogenic metalloid, in drinking water sources is usually removed by means of coagulation with aluminum salts followed by sedimentation or filtration or both (Chen et al., 2002; Choong et al., 2007; Edwards, 1994; Gregor, 2001; Kartinen and Martin, 1995; McNeill and Edwards, 1995; Scott et al., 1995). If the arsenic is in the form of arsenite, As(III), which has little affinity for aluminum hydroxide formed from the aluminum salts during the coagulation process (Hering et al., 1997), oxidation to arsenate, As(V), prior to coagulation-settling-filtration is generally necessary for effective removal (Ghurye and Clifford, 2004).

Enhancing coagulation by optimizing the coagulant dose

effectively improves arsenic removal (Cheng et al., 1994). Adjusting the coagulation pH to approximately 6.5 is important because the efficiency of arsenate removal has been found to be maximized in the pH range of 6–7 (Bilici Baskan and Pala, 2010). Coagulants other than aluminum salts have been tested in attempts to improve arsenic removal. In some studies, ferric coagulants have been shown to be as effective as aluminum sulfate on a molar basis because iron flocs and aluminum flocs have the same adsorption capacity (Edwards, 1994; McNeill and Edwards, 1997). In contrast, other studies have shown that ferric coagulants have higher adsorption capacity than alum (Lakshmanan et al., 2008). Electrocoagulation has also been studied. For example, electrocoagulation with steel and iron electrodes effectively removes arsenate (Balasubramanian et al., 2009; Balasubramanian and Madhavan, 2001). However, electrocoagulation is inferior to conventional coagulation (Lakshmanan et al., 2010; Ratna Kumar et al., 2004). However, in situations in which the decrease in pH caused by the

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use of a high dose of coagulant during the coagulation process increases the solubility, and thus the removal efficiency, of arsenate compounds, electrocoagulation may be preferable to conventional coagulation (Lacasa et al., 2013).

Poly-aluminum chloride (PACl) is effective for controlling arsenate concentration than the above-mentioned coagulants because PACl removes more arsenate than do conventional coagulants, such as aluminum sulfate and chloride, at both acidic and alkaline pH, as well as at neutral pH (Fan et al., 2003). On the basis of a recent comparison between one alum and two PACls, Hu et al. (2012) proposed that the reasons for the superiority of PACls are that the e-Al₁₃ polycation (Keggin-type e-Al₁₃ polycation, [AlO₄Al₁₂(OH)₂₄(H₂O)₁₂]⁷⁺) is the active species responsible for arsenate removal by aluminum coagulants and that the e-Al₁₃ polycation that is preformed in PACl is stable during coagulation and is present at high levels even during coagulation under acidic and alkaline conditions. However, the commercially available PACls that are in practical use for arsenate removal do not necessarily contain large amounts of the e-Al₁₃ polycation (Fan et al., 2003; Kimura et al., 2013; Yan et al., 2007), but, in practice, PACls are better at arsenate removal than alum. Mertens et al. (2012) reported that PACls with a high content of the δ-Al₃₀ polycation (specifically, the Keggin-type δ-Al₃₀ polycation, [Al₃₀O₈(OH)₅₆(H₂O)₂₄]¹⁸⁺) have a higher removal efficiency than PACls with a low δ-Al₃₀ polycation content. Finally, higher arsenate removal by PACl than by conventional coagulants may be attributed to the e-Al₁₃ polycation, the δ-Al₃₀ polycation, or both. However, these findings were obtained by comparing a few PACls with a limited variety of characteristics. Therefore, the aluminum species in PACls that is most effective for arsenate removal remains unknown. In addition, whether or not the e-Al₁₃ polycation, the δ-Al₃₀ polycation, or both are indispensable species for arsenate removal remains to be determined.

The pH range that is optimal for arsenate removal (pH 6–7) is also optimal for in situ formation of the e-Al₁₃ polycation during coagulation with alum (Hu et al., 2012; Lin et al., 2008; Wang et al., 2004; Yan et al., 2008). If arsenate could be removed by coagulation at a nonoptimized pH, such as pH > 7.5, this would be beneficial because the pH increase to control corrosion in water distribution networks would not be required. It would also be beneficial for small treatment facilities that have difficulty attaining the optimal pH because such facilities have limited access to the required expertise. In this study, we prepared and tested 51 PACls with various characteristics to investigate the aluminum species responsible for arsenate removal and to identify PACls that can readily control arsenic concentration even when the coagulation pH is ≥ 7.5.

2. Materials and methods

2.1. Preparation and characterization of coagulants

We prepared 14 aluminum-based coagulants for the first set of coagulation experiments (Table 1S). The PACls were given unique designations in which the first number indicates percent basicity, “s” indicates “sulfated,” “t” indicates a commercial PACl coagulant or a trial PACl product obtained from Taki Chemical Co. (Kakogawa, Japan), and the final number (1) indicates that the coagulant was used in the first set of coagulation experiments. For the second set of coagulation experiments, we prepared an additional 20 coagulants, 16 of which were analyzed by ²⁷Al NMR spectroscopy (Table 2S). An additional 17 coagulants were prepared specifically for NMR analysis and were also used in supplemental coagulation experiments (Table 3S). The preparation of the coagulants is described in Supplementary Material. The distributions of the

aluminum species in the coagulants were analyzed by means of ferron colorimetry (Jia et al., 2004; Wang et al., 2004), and the aluminum species in the coagulants were characterized by ²⁷Al NMR spectroscopy (Chen et al., 2006, 2007; Gao et al., 2005). The charge densities of the aluminum species in the coagulants were determined with a colloid titrator (Hiranuma Sangyo Co., Ibaraki, Japan). The zeta potentials of aluminum hydrolysis products were determined with an electrophoretic light-scattering spectrophotometer (Zetasizer Nano ZS, 532-nm green laser; Malvern Instruments, Malvern, Worcestershire, UK). The measurement procedures are described in detail in Supplementary Material.

2.2. Water samples

In the first and second sets of coagulation experiments, we used mainly Toyohira River samples (collected at 42°57'57"N, 141°16'06"E), which contained arsenate and a trace amount of arsenite; the arsenic concentrations in the water used for the two sets of experiments were 15.8 and 21.0 μg/L, respectively. Water from the Kotonai River (collected at 43°30'44"N, 144°37'18"E) was also used in the first set of coagulation experiments, and the arsenic concentration in this water was 11.2 μg/L. For supplementary coagulation experiment, we collected Toyohira River water collected at the above-described site and mixed it with Toyohira River water collected at a site further upstream (42°57'55"N, 141°9'45"E) in proportions such that the arsenic concentration in the mixture was the same as that in the Toyohira River water used for the second set of coagulation experiments (21.0 μg/L). The dissolved organic carbon (DOC) concentrations in all the water samples were ≤1.0 mg/L (Table 4S), and thus the effect of DOC on arsenate removal during coagulation was assumed to be small (Zhang et al., 2012). Before being used in the jar tests, water samples were pretreated with a small amount of chlorine (0.15 mg-Cl₂/L) to oxidize traces of arsenite (present at a concentration of ~0.5 μg/L) to arsenate; therefore, all the arsenic in the test water samples was in the form of arsenate.

2.3. Jar tests

Jar tests were performed with a jar test apparatus at room temperature (~20 °C) as follows. Each raw water sample was transferred to a 1-L square plastic beaker, a predetermined volume of 0.1 N HCl or 0.1 N NaOH was added to bring the final coagulation pH to the target value, and a coagulant was injected into the water. The mixture was stirred rapidly for 1 min ($G = 190 \text{ s}^{-1}$, 136 rpm), slowly for 10 min (19 s^{-1} , 29 rpm), and then allowed to stand for 1 h so that the generated aluminum floc particles would settle. Sample of the supernatant were taken from the beaker for the measurement of coagulation pH and turbidity. A portion of the sample was filtered through a 0.45-μm polytetrafluoroethylene microfilter (DISMIC-25HP; Toyo Roshi Kaisha, Tokyo), and the arsenic and aluminum concentrations in the filtrate were determined by means of inductively coupled plasma mass spectrometry (HP-7700, Agilent Technologies) after the addition of nitric acid. The rationale for the selection of the microfilter is described in Supplementary Material including Fig. 1S. The filtrate was also analyzed for DOC (Sievers 900 TOC Analyzer, GE Analytical Instruments, Boulder, CO, USA) and ultraviolet absorbance at 260 nm (UV-1700, Shimadzu Co.).

3. Results and discussion

3.1. Arsenate removal in jar tests

First, we conducted jar tests with 14 PACls and evaluated

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