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Aggregating ability of ferric chloride in the presence of phosphate ligand

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ABSTRACT

Complexing anions such as phosphate or silicate play an ambivalent role in the performance of hydrolyzing metal coagulants: On one hand, they significantly interfere with the hydrolytic pathway of conventional iron or aluminum coagulants, the associated destabilization mechanism remaining rather elusive; on the other hand, they have been shown to be key ingredients in the formulation of innovative coagulant solutions exhibiting improved removal efficiency, their action mechanism at the molecular scale being presently poorly understood. In this paper, we explore the effect of small additions of phosphate ligand on the chemical coagulation of silica nanoparticles with ferric chloride. Transmission Electron Microscopy-Energy Dispersed X-ray Spectroscopy (TEM-EDXS) combined with Extended X-ray absorption Fine Structure Spectroscopy (EXAFS) at the Fe K-edge are used to provide an insight into the nature of coagulant species, whereas jar-tests, laser diffraction, Small Angle X-ray Scattering (SAXS), and electrophoretic mobility, are used to investigate the aggregation dynamics of silica particles in the presence of phosphate ligand. We show that, in spite of a slight increase in the consumption of iron coagulant, the addition of phosphate significantly improves the formation of silica aggregates provided that the elemental Fe/P ratio remains above 7. Such effects originate from both a large increase in the overall number of coagulant species, the binding of a phosphate ligand terminating the growth of polymeric chains of edge-sharing Fe octahedra, and a change in the nature of the coagulant species that evolves with the Fe/P ratio, small polycations built-up from Fe-oligomers linked by phosphate tetrahedra being eventually formed. Those non-equilibrium nanosize Fe-P coagulant species assemble the silica nanoparticles to form hetero-aggregates whose structure is consistent with a Diffusion-Limited Cluster Aggregation mechanism.

Keywords: Coagulant species, coagulation, aggregation, phosphate anions, EXAFS,
Ferric chloride.

1. INTRODUCTION

Identifying the exact aggregation mechanisms when using aluminum or iron-based coagulants is crucial in drinking water and wastewater treatment operations. Until now, the classical destabilization mechanisms reported in the literature, *i.e.* charge neutralization with iron or aluminum hydrolysis products in the acidic pH range and enmeshment within an abundant mass of amorphous precipitate at basic pH (Duan and Gregory 2003; Yu et al. 2015), have not been clearly linked to usual aggregation descriptors such as floc size or floc growth rate. As a result, day-to-day operations, such as readjusting the optimal coagulant concentration following a change in raw water quality, remain mainly based on empirical guidelines (El Samrani et al. 2008). The primary reason for such limitations originates from the complex interplay between the various physico-chemical parameters that underlie coagulation of raw water: when added to water, the iron or aluminum salt hydrolyses to yield hydrolysis products; this lowers the pH of the treated water, which subsequently modifies the charge of the colloidal matter and the organization of the natural organic matter during the course of aggregation (Sieliechi et al. 2008; Chen et al. 2018). In addition, the presence of complexing anions may significantly alter the hydrolytic pathway of the coagulant (Rose et al., 1996; Rose et al., 1997; Vilgé-Ritter et al. 1999, Doelsch et al. 2000; Doelsch et al. 2003), and hence the nature of hydrolysis products responsible for aggregation (El Samrani et al.

2004; 2006). Preformed coagulant species such as Al_{13} polycations have also been shown to depolymerize upon association with colloidal matter present in the raw water (Lartiges et al. 1997; Masion et al. 2000).

This paper attempts to decipher the intricate relationships between simple aggregation descriptors and the nature of coagulant species formed in the particular case of silica nanoparticles aggregated with ferric chloride in the presence of phosphate ligands at pH 7.5. Ferric chloride is a hydrolyzing metal salt commonly used in drinking water treatment for turbidity removal and in wastewater treatment for phosphate elimination (Sieliechi et al. 2008; Hauduc et al. 2015). In view of the selected pH and range of phosphate concentrations the present study is more relevant to wastewater treatment than drinking water treatment (El Samrani et al. 2004; Houhou et al. 2009). However, our investigation may also open new lines of research on the synthesis of innovative inorganic coagulants, enhanced aggregation efficiency being observed with iron-based coagulants prepolymerized in the presence of PO_4^{3-} and SiO_4^{4-} ligands (Wang et al. 2000; Chen et al. 2015).

The aggregation of silica nanoparticles was followed by turbidity removal, electrophoretic mobility of aggregates, kinetics of floc growth and maximum floc size reached during aggregation using laser diffraction, and floc structure at the semi-local scale using SAXS. The nature of Fe-P hydrolysis products was investigated by EXAFS at the Fe K-edge combined with TEM-EDXS. EXAFS probes the average local atomic environment around the Fe atoms and provides the numbers, types, and interatomic distances to neighboring atoms, whereas TEM-EDXS enables the determination of average Fe/P elemental ratio of aggregates. We show that, even though the presence of phosphate complexing ligand involves a slight additional consumption in coagulant, floc growth and turbidity removal can be optimized with an appropriate addition of phosphate ligand.

2. EXPERIMENTAL SECTION

2.1 Sample preparation. The suspensions of silica nanoparticles were prepared from the dilution of Ludox HS40 colloidal silica (Sigma-Aldrich) to 500 mg/L using a 4×10^{-3} mol/L NaHCO_3 solution to provide an ionic strength buffer (Lartiges et al., 1997). Ludox HS40 silica nanoparticles are almost spherical in shape with an average diameter of 14 nm (Axelos et al., 1989). An aliquot of phosphate solution taken from a 0.1 mol/L $\text{Na}_2\text{HPO}_4 \cdot 2\text{H}_2\text{O}$ stock solution was then added to the silica suspension before adjusting the pH of the suspension to 7.5 by dropwise addition of dilute HCl.

A commercial unhydrolyzed ferric chloride solution (Arkema), 38 % wt in FeCl_3 and 1.4 in density, was used as coagulant. The aggregation experiments were conducted in a 1L reactor equipped with 4 plexiglas baffles and a rectangular paddle placed at one-third of the reactor height from the bottom (Lartiges et al. 1997). The coagulant was added under agitation as a pure solution with a micropipette (Eppendorf) and stirring was maintained at 100 rpm (average velocity gradient G of 135 s^{-1}) for 40 minutes. The coagulated suspension was then allowed to settle for 24h in graduated Imhoff cones. Such settling time is unusually long for a jar-test but is required to compare, for a given amount of added phosphate, the settling of aggregates formed in the presence and in the absence of silica nanoparticles. It is also worth noting that the drop in pH after ferric chloride addition was less than 1 in the range of coagulant concentrations investigated.

2.2 Aggregates characterization. After 24h of settling, 50 mL of supernatant were collected from about 25 mm below the free surface with a syringe. The residual turbidity of supernatant was measured with a Hach XR ratio turbidimeter, and 30mL of supernatant were filtered on a

0.2 μm pore size cellulose acetate membrane (Machery-Nagel) for analysis of dissolved Fe, Si and P (ICP-AES - Jobin-Yvon 70 type B model).

The electrophoretic mobility of aggregates was determined using a Zetaphoremeter III (Sephy/CAD) equipped with a CCD camera to track the trajectories of aggregates under a constant direct-current electric field (800 V/m). 1 mL of settled sediment was re-dispersed in the corresponding supernatant before being pumped to the measurement cell. About 100 measurements of aggregate mobility were carried out for a given coagulant/phosphate concentration.

The size distribution of aggregates was measured on-line using a laser diffraction particle size analyzer (Malvern Mastersizer) in the 1.2-600 μm size range. The aggregated suspension was continuously withdrawn from the bottom of the reactor, passed through the analyzer beam with a peristaltic pump located downstream the measurement cell (flow rate of 55 mL/min), before being recycled to the reactor. Previous experiments, conducted with shear-sensitive aggregates under similar operating conditions, showed that the relative variations in aggregate size measured by the laser sizer were closely related to the changes in agitation conditions inside the reactor rather than to shearing in the transport tubing (Chaignon et al. 2002). Aggregate size measurements were averaged for 1 second and taken every 3 seconds to ensure a complete renewal of the measurement cell. The volume size distributions thus obtained are monomodal, self-similar during aggregate growth, and hence, the aggregation dynamics can be represented by the temporal evolution of mean aggregate diameter D_{50} . As already shown in previous studies (Chaignon et al. 2002; Sieliechi et al. 2016), D_{50} grows linearly with time to reach a maximum diameter $D_{50\text{max}}$; the slope of the straight portion of the curve defines the aggregation rate.

2.3 Sediment characterization. Small-Angle X-ray Scattering (SAXS) experiments were performed using freshly settled aggregates on the D22 beamline at LURE synchrotron facility (Orsay-France). The detector was positioned at 2.52 m from the sample. The collected data covered the Q-range from $2.5 \cdot 10^{-3}$ to 10^{-1} \AA^{-1} with $Q = 4\pi\sin(\theta)/\lambda$ in which Q is the magnitude of the scattering vector, 2θ the scattering angle, and λ the wavelength of X-rays (1.49 Å). Such range of Q-values does not cover the Guinier regime of silica aggregates obtained in this study but allows studying the fractal regime below 1 µm. The intensity scattered by the aggregates can be expressed as: $I(Q) = K I_0(Q) G(Q)$ where K is a constant, $I_0(Q)$ the intensity scattered by a single silica particle, and G(Q) an interference function related to the particle arrangement within the aggregate. When the aggregates are fractal, G(Q) can be approximated by $G(Q) \sim Q^{-D_f}$ in the $[1/L - 1/R_0]$ Q range where D_f is the fractal dimension of aggregates, L the characteristic length of aggregates, and R_0 the size of elementary particles (Ramsay and Booth, 1983).

The sediment was freeze-dried before observation with a Philips CM20 Transmission Electron Microscope equipped with an Energy Dispersive X-ray Spectrometer (EDAX). The powder was dispersed by sonication in ethanol and a drop of suspension was then evaporated on a carbon-coated copper grid. After calibration of the Energy Dispersive X-ray Spectrometer with a Phosphosiderite standard ($\text{FePO}_4 \cdot \text{H}_2\text{O}$), the Fe/P elemental ratio of aggregates was determined from about 50 EDX spectra collected at random locations using a 70 nm probe size and a 30 s counting time acquisition.

EXAFS experiments were performed on the D42 beamline at LURE synchrotron facility. The freeze-dried sediment was prepared as pellets using microcrystalline cellulose. The X-ray absorption spectra were recorded in transmission mode at room temperature around the Fe K-edge from 7000 to 8100 eV with 2 eV steps and 2 seconds collecting time. EXAFS data reduction was performed according to a standard procedure previously described

(Manceau and Calas, 1986). A Kaiser window ($3.5\text{-}14.7 \text{ \AA}^{-1}$) was used for deriving Fourier transforms from EXAFS spectra (Bonnin et al., 1985). The Radial Functions (RDF) thus obtained are not corrected for phase shifts, which leads to peaks shifted down by about 0.3 \AA compared with crystallographic distances. Fitting was essentially carried out on the second coordination shell, on the backfiltered $k^3\chi(k)$ curves in the $[2.1\text{-}3.5] \text{ \AA}$ range. Theoretical phase and amplitude functions were used to obtain the number of neighbors in the shell around the absorbing Fe atom and the radial distances, as well as the Debye-Waller factors (s). The electron mean free path ($G = k/\lambda$) and the energy shift (DE) were respectively fixed at 0.82 \AA^{-2} and 5 eV .

3. RESULTS

3.1 Destabilization of silica nanoparticles with ferric chloride in the presence of phosphate ligand. Typical curves of residual turbidity as a function of ferric chloride concentration in the presence of various amounts of phosphate are shown in figure 1a. The curves exhibit similar profiles characteristic of a nanoparticle suspension increasingly aggregated by the addition of coagulant (Sieliechi et al. 2008): at low ferric chloride concentration, the turbidity of the supernatant steadily increases as small non-settleable aggregates of increasing size are formed. After reaching a maximum, the residual turbidity steeply decreases with further coagulant addition when settling aggregates are obtained. A rapid build-up in sediment volume is then observed in that concentration range (figure 1b). The minimum ferric chloride concentration that determines the highest level of turbidity reduction defines the optimal coagulant dose $[\text{Fe}]_{\text{opt}}$.

The presence of phosphate ligand has two main effects: (i) the maximal residual turbidity is lowered upon addition of low P levels and then increases with further addition of

P; (ii) the residual turbidity curve is stretched towards higher coagulant concentrations, or in other terms, the addition of P to the silica suspension increases $[\text{Fe}]_{\text{Opt}}$. Actually, as illustrated in figure 2a, $[\text{Fe}]_{\text{Opt}}$ becomes proportional to the phosphate content of the suspension above a P concentration of 0.5 mmol/L, *i.e.* a Fe/P molar ratio less than 2, regardless of silica concentration. As the removal of P and silica nanoparticles occurs simultaneously when settleable aggregates are formed (fig. 2b), it is clear that all the components – silica nanoparticles, phosphate, and iron coagulant – participate together in the aggregation process.

To further investigate the aggregation behavior of silica nanoparticles at low phosphate concentrations, a series of experiments were conducted with increasing phosphate concentrations and a fixed amount of ferric chloride (figure 3). The coagulant concentration selected (0.36 mmol/L, *i.e.* close to the maximum of residual turbidity in the absence of phosphate ligand – see fig. 1a) helps exacerbating the sensitivity to phosphate additions; further underdosing, or on the contrary iron concentrations in the optimal dosing range, would reduce the range of turbidity variation. For an iron concentration equal to 0.36 mmol/L, the addition of small amounts of phosphate ligand linearly decreases the level of residual turbidity from an initial high level of about 27 NTU to reach a minimum of 12 NTU for a Fe/P molar ratio of about 7, before slightly re-increasing; on the other hand, the sediment volume increases and reaches a maximum that is slightly shifted to higher Fe/P ratios (*i.e.* lower phosphate concentrations) before returning to zero (figure 3). According to figure 1a, it can be expected that the residual turbidity will decrease again at higher phosphate concentration.

3.2 Characterization of aggregates. That a small addition of phosphate ligand improves the removal of silica nanoparticles with ferric chloride implies a significant change of aggregate properties. Figure 4a shows typical temporal evolutions of the mean aggregate diameter D_{50}

for various added P concentrations and an iron coagulant concentration of 0.36 mmol/L. Both the aggregation rate and the maximum mean aggregate diameter are inferred from these curves. Figure 4b presents the corresponding evolution of aggregation rate and maximum mean aggregate diameter ($D_{50\max}$) with phosphate concentration. Like residual turbidity and sediment volume, both the aggregation rate and the $D_{50\max}$ drastically vary with small phosphate additions: the aggregation rate steeply increases from initially non-measurable values to reach a 50 $\mu\text{m}/\text{min}$ growth at a Fe/P molar ratio of about 14 and then gradually returns to zero; $D_{50\max}$ also increases from an initial value lower than the measuring range of the particle sizer to reach a maximum mean aggregate diameter of about 110 μm at a Fe/P ratio of 7, and then drops to submicron sizes at higher phosphate concentrations.

An elemental ratio Fe/P in the [7-8] range is also a threshold value for the structure of aggregates. The SAXS curves, shown in figure 5a as a Log-Log plot of the scattering intensity versus the scattering vector, are characterized by a linear portion that identifies the fractal region in the [$6 \cdot 10^{-3} - 4 \cdot 10^{-2} \text{ \AA}^{-1}$] Q range, followed by a cross-over at higher Q that corresponds to the scattering of silica nanoparticles of radius 7 nm. The fractal dimension D_f obtained from the slope of the scattering factor remains close to 1.72 for small additions of phosphate ligand (figure 5b). However, above a Fe/P of 7, D_f exhibits a step increase to an average value of 1.83. On the other hand, the electrophoretic mobility of aggregates, varying between -2.95 and -3.05 $\mu\text{m}\cdot\text{s}^{-1}/\text{V}\cdot\text{cm}^{-1}$, remains almost constant in the range of P concentration investigated (fig. 6). The diameter of Ludox silica nanoparticles (14 nm) is well below the lower size limit of particles (about 0.2 μm) that can be followed from the image analysis system of a Zetaphoremeter III. However, it is expected that the electrophoretic mobility of pristine silica particles is lower than -3 $\mu\text{m}\cdot\text{s}^{-1}/\text{V}\cdot\text{cm}^{-1}$ since such value was reported for Ludox HS particles in a suspension of same ionic strength as ours but at pH 6 (Fatombi et al. 2013).

248

249 **3.3 Nature of coagulant species.** EDX microanalysis provides a first approach to the nature
250 of hydrolysis products that trigger the aggregation of silica nanoparticles (figure 7). The
251 histograms of Fe/P atomic ratios measured on the freeze-dried sediments obtained for a given
252 ferric chloride concentration and increasing phosphate concentrations reveal that, at low
253 phosphate concentration, *i.e.* $\text{Fe/P} \geq 10$, the Fe/P atomic ratios are rather uniformly distributed
254 across the 2-10 range. At higher phosphate concentrations, *i.e.* $(\text{Fe/P} \leq 8)$, the width of Fe/P
255 distributions becomes narrower and a maximum around 4-5 clearly emerges. This suggests
256 that well-defined coagulant species, formed from the complexation of hydrolyzed Fe and
257 phosphate ligands, are developing with increasing phosphate concentration.

258 EXAFS curves and k^3 -weighted Fourier transforms of EXAFS oscillations into R-
259 space are reported in figure 8. The first peak of the Fourier transform, or radial distribution
260 function RDF, is centered at 1.5 Å and represents the first coordination shell around iron
261 atoms. This first shell is composed of 6 oxygen atoms with a Fe-O bond length close to 2 Å,
262 which is consistent with previous X-ray absorption studies (Bottero et al. 1994; Zhu et al.
263 2013; Collins et al. 2016). The second peak, centered at 2.7-2.8 Å, is of greater interest since
264 it reflects the average degree of iron polymerization. In our case, three kinds of atoms, Fe, P,
265 and Si, can be expected in the second coordination shell of iron atom. $K^3\chi(k)$ curves reveal a
266 small oscillation centered at 7.5 Å^{-1} typical of heavy atoms, and hence a Fe contribution in the
267 second shell, that sharply decreases with increasing phosphate concentration. In parallel, the
268 intensity of the second peak of the Fourier Transform gradually decreases.

269 The fitting results are reported in Table 1 and figure 9. In the absence of phosphate
270 addition, *i.e.* $\text{P/Fe} = 0$, two iron neighbors sub-shells are necessary for fitting. The distances
271 thus obtained, 3.04 and 3.14 Å, identify edge-sharing Fe-O octahedra (Bottero et al., 1994;
272 Doelsch et al. 2000; Collins et al. 2016). The fitting can be slightly improved by the addition

of a third shell assigned to a Fe-Si contribution. Si being a lighter atom in comparison with Fe, its contribution as a backscatterer in the EXAFS oscillations can be argued. In particular, the number of Si neighbors is rather inaccurate.

Upon the addition of $[P] = 0.008$ mmol/L to the silica suspension, *i.e.* $Fe/P = 45$, the EXAFS curve is fitted with two sub-shells of Fe-Fe edge-sharing bonding and a supplementary shell of iron atoms linked by double corner sharing (Figure 10B). Further increase in phosphate significantly decreases the number of iron neighbors sharing edges from $2.5 (\pm 0.5)$ to $1.5 (\pm 0.5)$ ($N_1 + N_2$ in table 1), the Fe-Fe distance varying from 2.98 to $3.04 \text{ \AA} (\pm 0.1 \text{ \AA})$ for the first sub-shell and from 3.13 to $3.15 \text{ \AA} (\pm 0.1 \text{ \AA})$ for the second sub-shell. The contribution of double corner sharing Fe-Fe bonding could not be evidenced, which implies a limited hydrolysis of iron species. Above a P addition of 0.008 mmol/L, the curve fitting is mainly performed using edge-sharing Fe-Fe bonding, corner-sharing Fe-P bonding, and in the case of $Fe/P=6.4$ and $Fe/P=5.8$, with corner-sharing Fe-Fe bonding. The values of Fe-Fe bond length (3.56 and 3.58 \AA respectively for $Fe/P=6.4$ and $Fe/P=5.8$) may identify the presence of double corner-sharing trimers (figure 10B) or Fe_2P complexes (figure 10E). Actually, the latter geometry should be favored, as phosphate neighbors are needed for an appropriate fitting.

The structural parameters inferred from curve-fitting analysis reveal that the presence of phosphate ligand decreases the number of iron neighbors, *i.e.* a decrease of Fe-Fe bonds, and leads to a contribution of phosphorus atoms in the second coordination shell of Fe. The number of phosphate neighbors is highly variable from one sample to another, but it should be noted that those numbers are rather inaccurate and are only given to evidence the presence of Fe-P bonds. In contrast, the values of Fe-P bond length, between 3.26 and 3.34 \AA , are unambiguously assigned to the formation of single-corner sharing complexes (see Figure 10D, E and F). For Fe/P ratios lower than 18, the phosphate ligand substitution for Fe does

not prevent the formation of Fe-dimers and Fe-trimers, the number of neighbors (subshells 1 and 2) remaining above 1. Nevertheless, the presence of phosphate certainly changes the size of iron polymer chains, but, as the curve fitting was performed in the [2.5-3.8] Å distance range, no information can be inferred about the chain size and the semi-local structure of iron octahedra aggregates.

4. DISCUSSION

4.1 Nature of coagulant species in the system ferric chloride/phosphate/silica nanoparticles.

Most of the information available in the literature on iron (III) hydrolysis has been acquired in the context of solutions of high Fe concentration (decimolar to molar) slowly hydrolyzed from acidic conditions (Tchoubar et al. 1991; Bottero et al. 1994; Rose et al. 1996; 1997; Doelsch et al. 2000; 2003, Collins et al. 2016). Thus, depending on the hydrolysis ratio OH/Fe, dilution and ageing, the hydrolysis of ferric chloride solutions typically yields monomers, corner-sharing dimers, edge-sharing dimers, double-corner trimers, polycations and aggregates of those polycations, that eventually form akaganeite (β -FeOOH) upon ageing (Murphy et al. 1976; Tchoubar et al., 1991; Manceau and Drits 1993; Bottero et al., 1994). In the presence of organic or inorganic complexing ligands, the speciation diagrams of iron-base solutions are drastically modified. Most often, when a sufficient amount of complexing ligands has been added (*e.g.* phosphate anions, small organic acids, dissolved organic matter), the hydrolysis of ferric chloride is hindered to the dimer stage (Rose et al., 1996; Rose et al., 1997; Vilgé-Ritter et al. 1999, Doelsch et al. 2000). In the case of silicate and sulfate ligands, EXAFS at the Fe K-edge and SAXS experiments revealed the presence of edge- and corner-

sharing Fe shells that led to the formation of three-dimensional molecular clusters (Doelsch et al. 2000; Doelsch et al. 2003; Zhu et al. 2012; Collins et al. 2016).

In contrast, natural raw waters and wastewaters relevant to this study generally show neutral or slightly alkaline pH conditions before being treated with ferric chloride concentrations in the millimolar range or less (El Samrani et al. 2004; Caravelli et al. 2010). The rapid hydrolysis of ferric chloride that results from such conditions (Pham et al. 2006) modifies the classical polymerization pathway. In particular, the formation of the double corner-sharing Fe trimer (fig. 10B) can only be evidenced for a Fe/P ratio of 45. Instead, polymeric chains of edge-sharing Fe octaedra, equivalent to those obtained from molecular dynamics simulations (Zhang et al. 2015) occur in solution.

In the presence of increasing phosphate concentration, the complexation dynamics becomes gradually dominant over the kinetics of iron (III) hydrolysis. The number of iron neighbors sharing edges decreases, which can be interpreted as the termination of the active chains growth whenever a phosphate ligand binds on the end of a Fe polymer chain. An increased number of oligomeric structures, and hence an increased number of coagulant species, is then formed from edge-sharing Fe dimers/trimers/oligomers linked by a phosphate tetrahedra (fig. 10). Single corner-sharing Fe octahedra, identified at Fe/P ratios of 6.4 and 5.8, may also participate in the bridging of oligomeric Fe-P chains (Rose et al. 1996). Below a Fe/P molar ratio of 7, the excess phosphate binding on iron dimers/trimers should decrease the charge of coagulant species and/or promote the growth of oligomeric structures through phosphate bridging (fig. 10). Therefore, both the number and efficiency of coagulant species decrease for a Fe/P less than 7. In summary, if the strong affinity of iron (III) for phosphate lowers the degree of polymerization of iron coagulant (Rose et al. 1996; Rose et al. 1997; El Samrani et al. 2004), it also increases at first the number of coagulant species and improves

the aggregation of silica nanoparticles. Further addition of phosphate ligand ($\text{Fe/P} \leq 7$) becomes detrimental for aggregation.

To evidence a possible effect of silica nanoparticles on the nature of coagulant species is not straightforward. The detection of Si neighbors using EXAFS at the Fe K-edge is rather difficult because of the large difference in atomic number between Si and Fe. Including a Si shell improves the spectral fitting only in the absence of phosphate. It has been shown that the polymerization of iron (III) is inhibited for Fe/Si molar ratios in the 1 to 4 range (Doelsch et al. 2000). In our case, the number of silanol groups per unit surface area of silica that may interact with the Fe hydrolyzed products, is about 4.6 nm^{-2} (Zhuravlev 2000). Using a specific surface area of $220 \text{ m}^2/\text{g}$ for the Ludox HS nanoparticles, we calculate a Fe/Si molar ratio of 0.42. Actually, both steric hindrance and charge repulsion between the positive coagulant species attached on the surface of silica nanoparticles should further decrease this ratio. Therefore, the effect of the silica surface on iron hydrolysis is expected to be considerably less than that of phosphate ligand, even though the association of polymeric chains of edge-sharing Fe octahedra with the silica nanoparticles may also inhibit the chain growth.

4.2 Aggregation mechanism of silica nanoparticles in the system $\text{FeCl}_3/\text{PO}_4$.

It is especially interesting that the nature of hydrolysis products, and hence the type of coagulant species that bind the silica nanoparticles, significantly changes with the relative concentrations of iron coagulant and phosphate ligand. Such feature has not been addressed in previous physicochemical models for phosphorus removal in which only equilibrium species such as FeHPO_4^+ , $\text{FeH}_2\text{PO}_4^{2+}$ or $\text{Fe}(\text{OH})_3$ have been considered (Smith et al. 2008; Caravelli et al. 2010; Hauduc et al. 2015). Our study reveals that Fe dimers, through the formation of complexes such as $\text{Fe}_2(\text{HPO}_4)(\text{OH})(\text{H}_2\text{O})_8^{3+}$ and $\text{Fe}_4(\text{PO}_4)(\text{OH})_2(\text{H}_2\text{O})_{16}^{7+}$, play a significant role during phosphate removal, those transient species nevertheless leading to the

thermodynamically favored $\text{Fe}(\text{PO}_4)(\text{H}_2\text{O})_5$ complex at longer times (Lente et al. 2000; Lente and Fabian 2002). That the ionic background of the raw water may interfere with the hydrolytic pathway of aluminum or iron coagulants is also overlooked in traditional destabilization mechanisms (Duan and Gregory 2003). Yet, in continental surface waters, the average contents in silica, sulfate, phosphate and chloride anions (Meybeck and Helmer 1989) are in sufficient amounts to modify the polymerization of hydrolyzing metal salts (El Samrani et al. 2006).

It is nevertheless rather difficult to precisely elucidate, for a given Fe/P ratio, both the number and various types of coagulant species. EXAFS and even more TEM-EDXS, only provide an average description of the hydrolysis products present in the bulk solution. If iron oligomers linked by a phosphate tetrahedron may lead to polycations such as $\text{Fe}_4(\text{PO}_4)(\text{OH})_2(\text{H}_2\text{O})_{16}^{7+}$, those highly charged species do not account by themselves for the destabilization of silica nanoparticles. Under the conditions of pH and ionic strength used in this study, the surface charge density of Ludox nanoparticles is about $-1.6 \mu\text{C}/\text{cm}^2$ (Bolt 1957; Allison 2009). This corresponds to 61 negatively charged $-\text{SiO}^-$ groups per silica particle. In that case, the number of polycations of charge $7+$ necessary to neutralize the silica surface would be less than 10. As a 500 mg/L Ludox HS suspension corresponds to a $1.58 \cdot 10^{17}$ particles per liter, a Fe concentration of $9.4 \mu\text{mol}/\text{L}$ should then be theoretically sufficient to achieve the neutralization of silica nanoparticles. The latter concentration is two orders of magnitude less than the actual coagulant concentration used. Therefore, the coagulant species present in suspension are certainly a mix of weakly positive hydrolyzed products comprising on the average about 4-5 Fe atoms for one P atom.

As the SAXS curves do not reveal any increase in the radius of elementary particles with P addition, the size of coagulant species is expected to remain in the lower nanometer range. In that context, a sweep-flocculation mechanism, characterized by the formation of an

abundant precipitate enmeshing the silica nanoparticles, seems rather unlikely especially in the underdosing range. Moreover, the examination of TEM micrographs does not reveal the presence of an abundant hydroxide precipitate (See Fig. S2 in Supporting Information). A simple charge neutralization mechanism can also be argued since the electrophoretic mobility of silica aggregates is negative. However, a hetero-aggregation process involving negative silica particles attached by positive nanosize coagulant species may reconcile all the observations. In that framework, a local charge neutralization within the aggregate is sufficient to ensure the build-up of aggregates, the negative electrophoretic mobility being explained by the terminal attachment of partially neutralized and still negative silica particles in excess at the outer part of aggregates. The linear decrease in residual turbidity and the concomitant increase in aggregate size observed with increasing phosphate concentration when using an underdose of iron coagulant (figures 3 and 4b), are also consistent with a hetero-aggregation framework. Indeed, when mixing large and small oppositely charged particles, previous research has shown that, below the destabilization threshold, the number of hetero-aggregates obtained decreases linearly with the relative number of large and small particles (Dumont et al. 1990). In our case, a small addition of phosphate ligand determines an increase in the overall number of nanosize coagulant species, and hence promotes the growth of larger aggregates thus improving their settleability.

Although limited to less than a decade in Q , an estimate of about 1.7 for the fractal exponent of silica aggregates is consistent with a diffusion-limited cluster aggregation (DLCA) (Meakin 1988). Such DLCA regime can be argued because the aggregates are formed in a stirred vessel. The relative importance of shear aggregation to Brownian diffusion can be assessed using the Péclet number $Pe = 6\pi\eta Gd_0^3/kT$ in which η is the dynamic viscosity of the suspension ($\eta = 1.07 \cdot 10^{-6} \text{ m}^2\text{s}^{-1}$), G the average velocity gradient ($G = 135 \text{ s}^{-1}$), d_0 the radius of silica particles ($d_0 = 7 \text{ nm}$), k the Boltzmann constant and T the absolute temperature

(Frappier et al. 2010). In the early stage of aggregation, Pe is about $2 \cdot 10^{-7}$ which suggests that Brownian aggregation is largely predominant over shear aggregation and governs the aggregate structure investigated by SAXS. For micron size aggregates, the two aggregation modes become equivalent.

The slightly higher D_f value of 1.83 obtained below a Fe/P ratio of 7 can also be explained by the same DLCA aggregation regime provided that some reorganization of aggregates is allowed (Meakin and Julien, 1988). Wu et al. (2013) have recently shown that thermal restructuring may drive an increase in the fractal dimension of DLCA aggregates that is more pronounced with a decrease in the radius of primary particles. For silica nanoparticles having a radius of 7 nm, a D_f value of about 1.9 can be expected if the bonds between primary particles are weak (Wu et al. 2013). Accordingly, this suggests that the bonds formed from the coagulant species between the silica particles are strong and even rigid above a Fe/P of 7, and that some restructuring of aggregates occurs below a Fe/P of 7 because of the slightly different nature of coagulant species that leads to a lower binding energy between the particles.

5. CONCLUSIONS

The aggregation of silica nanoparticles with ferric chloride was studied in the presence of small amounts of phosphate ligand. The characteristics of aggregates formed were described using a combination of techniques, *i.e.* laser granulometry, turbidity measurements, SAXS, TEM-EDXS microanalysis and EXAFS at the Fe K-edge. We found that the addition of phosphate dramatically modifies the nature of hydrolysis products without changing the aggregation mechanism. The phosphate ligands terminate the polymerization of Fe-octahedra chains to lead to an increasing number of Fe-oligomers bridged by phosphate tetrahedra. An

elemental ratio Fe/P of about 7 appears optimal for the production of efficient positively charged coagulant species. The SAXS results indicate that the size of those coagulant species remains in the nanoscale range and reveal that a Diffusion Limited Cluster Aggregation governs the structure of aggregates in the early stage of aggregation.

The prevalence of non-equilibrium Fe-P species formed in the course of chemical coagulation of silica particles suggests that thermodynamic approaches of phosphorus removal with iron or aluminum coagulants are not of much use. Instead, the relative contents in hydrolyzing metal coagulant and in complexing anions in the raw water to be treated, coupled with a partial charge model (Jolivet 2019), might be better suited for describing the coagulant species likely to be formed. Our results demonstrate the usefulness of coupling microscopic and spectroscopic approaches to clear up the nature of active coagulant species and to properly understand coagulation mechanism.

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