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1 **Aggregating ability of ferric chloride in the presence of**
2 **phosphate ligand**

3
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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.

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

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56 **1. INTRODUCTION**

57

58 Identifying the exact aggregation mechanisms when using aluminum or iron-based
59 coagulants is crucial in drinking water and wastewater treatment operations. Until now, the
60 classical destabilization mechanisms reported in the literature, *i.e.* charge neutralization with
61 iron or aluminum hydrolysis products in the acidic pH range and enmeshment within an
62 abundant mass of amorphous precipitate at basic pH (Duan and Gregory 2003; Yu et al.
63 2015), have not been clearly linked to usual aggregation descriptors such as floc size or floc
64 growth rate. As a result, day-to-day operations, such as readjusting the optimal coagulant
65 concentration following a change in raw water quality, remain mainly based on empirical
66 guidelines (El Samrani et al. 2008). The primary reason for such limitations originates from
67 the complex interplay between the various physico-chemical parameters that underlie
68 coagulation of raw water: when added to water, the iron or aluminum salt hydrolyses to yield
69 hydrolysis products; this lowers the pH of the treated water, which subsequently modifies the
70 charge of the colloidal matter and the organization of the natural organic matter during the
71 course of aggregation (Sieliuchi et al. 2008; Chen et al. 2018). In addition, the presence of
72 complexing anions may significantly alter the hydrolytic pathway of the coagulant (Rose et
73 al., 1996; Rose et al., 1997; Vilg -Ritter et al.1999, Doelsch et al. 2000; Doelsch et al. 2003),
74 and hence the nature of hydrolysis products responsible for aggregation (El Samrani et al.

75 2004; 2006). Preformed coagulant species such as Al_{13} polycations have also been shown to
76 depolymerize upon association with colloidal matter present in the raw water (Lartiges et al.
77 1997; Masion et al. 2000).

78 This paper attempts to decipher the intricate relationships between simple aggregation
79 descriptors and the nature of coagulant species formed in the particular case of silica
80 nanoparticles aggregated with ferric chloride in the presence of phosphate ligands at pH 7.5.
81 Ferric chloride is a hydrolyzing metal salt commonly used in drinking water treatment for
82 turbidity removal and in wastewater treatment for phosphate elimination (Sieliechi et al.
83 2008; Hauduc et al. 2015). In view of the selected pH and range of phosphate concentrations
84 the present study is more relevant to wastewater treatment than drinking water treatment (El
85 Samrani et al. 2004; Houhou et al. 2009). However, our investigation may also open new
86 lines of research on the synthesis of innovative inorganic coagulants, enhanced aggregation
87 efficiency being observed with iron-based coagulants prepolymerized in the presence of PO_4^{3-}
88 and SiO_4^{4-} ligands (Wang et al. 2000; Chen et al. 2015).

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

99

100 2. EXPERIMENTAL SECTION

101

102 **2.1 Sample preparation.** The suspensions of silica nanoparticles were prepared from the
103 dilution of Ludox HS40 colloidal silica (Sigma-Aldrich) to 500 mg/L using a $4 \cdot 10^{-3}$ mol/L
104 NaHCO_3 solution to provide an ionic strength buffer (Lartiges et al., 1997). Ludox HS40
105 silica nanoparticles are almost spherical in shape with an average diameter of 14 nm (Axelos
106 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
107 solution was then added to the silica suspension before adjusting the pH of the suspension to
108 7.5 by dropwise addition of dilute HCl.

109 A commercial unhydrolyzed ferric chloride solution (Arkema), 38 % wt in FeCl_3 and
110 1.4 in density, was used as coagulant. The aggregation experiments were conducted in a 1L
111 reactor equipped with 4 plexiglas baffles and a rectangular paddle placed at one-third of the
112 reactor height from the bottom (Lartiges et al. 1997). The coagulant was added under
113 agitation as a pure solution with a micropipette (Eppendorf) and stirring was maintained at
114 100 rpm (average velocity gradient G of 135 s^{-1}) for 40 minutes. The coagulated suspension
115 was then allowed to settle for 24h in graduated Imhoff cones. Such settling time is unusually
116 long for a jar-test but is required to compare, for a given amount of added phosphate, the
117 settling of aggregates formed in the presence and in the absence of silica nanoparticles. It is
118 also worth noting that the drop in pH after ferric chloride addition was less than 1 in the range
119 of coagulant concentrations investigated.

120

121 **2.2 Aggregates characterization.** After 24h of settling, 50 mL of supernatant were collected
122 from about 25 mm below the free surface with a syringe. The residual turbidity of supernatant
123 was measured with a Hach XR ratio turbidimeter, and 30mL of supernatant were filtered on a

124 0.2 μm pore size cellulose acetate membrane (Machery-Nagel) for analysis of dissolved Fe, Si
125 and P (ICP-AES - Jobin-Yvon 70 type B model).

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

132 The size distribution of aggregates was measured on-line using a laser diffraction
133 particle size analyzer (Malvern Mastersizer) in the 1.2-600 μm size range. The aggregated
134 suspension was continuously withdrawn from the bottom of the reactor, passed through the
135 analyzer beam with a peristaltic pump located downstream the measurement cell (flow rate of
136 55 mL/min), before being recycled to the reactor. Previous experiments, conducted with
137 shear-sensitive aggregates under similar operating conditions, showed that the relative
138 variations in aggregate size measured by the laser sizer were closely related to the changes in
139 agitation conditions inside the reactor rather than to shearing in the transport tubing
140 (Chaignon et al. 2002). Aggregate size measurements were averaged for 1 second and taken
141 every 3 seconds to ensure a complete renewal of the measurement cell. The volume size
142 distributions thus obtained are monomodal, self-similar during aggregate growth, and hence,
143 the aggregation dynamics can be represented by the temporal evolution of mean aggregate
144 diameter D_{50} . As already shown in previous studies (Chaignon et al. 2002; Sieliechi et al.
145 2016), D_{50} grows linearly with time to reach a maximum diameter $D_{50\text{max}}$; the slope of the
146 straight portion of the curve defines the aggregation rate.

147

148 **2.3 Sediment characterization.** Small-Angle X-ray Scattering (SAXS) experiments were
149 performed using freshly settled aggregates on the D22 beamline at LURE synchrotron facility
150 (Orsay-France). The detector was positioned at 2.52 m from the sample. The collected data
151 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
152 magnitude of the scattering vector, 2θ the scattering angle, and λ the wavelength of X-rays
153 (1.49 Å). Such range of Q-values does not cover the Guinier regime of silica aggregates
154 obtained in this study but allows studying the fractal regime below 1 μm. The intensity
155 scattered by the aggregates can be expressed as: $I(Q) = K I_0(Q) G(Q)$ where K is a constant,
156 $I_0(Q)$ the intensity scattered by a single silica particle, and G(Q) an interference function
157 related to the particle arrangement within the aggregate. When the aggregates are fractal,
158 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
159 dimension of aggregates, L the characteristic length of aggregates, and R_0 the size of
160 elementary particles (Ramsay and Booth, 1983).

161 The sediment was freeze-dried before observation with a Philips CM20 Transmission
162 Electron Microscope equipped with an Energy Dispersive X-ray Spectrometer (EDAX). The
163 powder was dispersed by sonication in ethanol and a drop of suspension was then evaporated
164 on a carbon-coated copper grid. After calibration of the Energy Dispersive X-ray
165 Spectrometer with a Phosphosiderite standard (FePO_4 , H_2O), the Fe/P elemental ratio of
166 aggregates was determined from about 50 EDX spectra collected at random locations using a
167 70 nm probe size and a 30 s counting time acquisition.

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

173 (Manceau and Calas, 1986). A Kaiser window ($3.5-14.7 \text{ \AA}^{-1}$) was used for deriving Fourier
174 transforms from EXAFS spectra (Bonnin et al., 1985). The Radial Functions (RDF) thus
175 obtained are not corrected for phase shifts, which leads to peaks shifted down by about 0.3 \AA
176 compared with crystallographic distances. Fitting was essentially carried out on the second
177 coordination shell, on the backfiltered $k^3\chi(k)$ curves in the $[2.1-3.5] \text{ \AA}$ range. Theoretical
178 phase and amplitude functions were used to obtain the number of neighbors in the shell
179 around the absorbing Fe atom and the radial distances, as well as the Debye-Waller factors
180 (s). The electron mean free path ($G= k/\lambda$) and the energy shift (DE) were respectively fixed at
181 0.82 \AA^{-2} and 5 eV .

182

183 **3. RESULTS**

184

185 ***3.1 Destabilization of silica nanoparticles with ferric chloride in the presence of phosphate***
186 ***ligand.*** Typical curves of residual turbidity as a function of ferric chloride concentration in
187 the presence of various amounts of phosphate are shown in figure 1a. The curves exhibit
188 similar profiles characteristic of a nanoparticle suspension increasingly aggregated by the
189 addition of coagulant (Sieliechi et al. 2008): at low ferric chloride concentration, the turbidity
190 of the supernatant steadily increases as small non-settleable aggregates of increasing size are
191 formed. After reaching a maximum, the residual turbidity steeply decreases with further
192 coagulant addition when settling aggregates are obtained. A rapid build-up in sediment
193 volume is then observed in that concentration range (figure 1b). The minimum ferric chloride
194 concentration that determines the highest level of turbidity reduction defines the optimal
195 coagulant dose $[\text{Fe}]_{\text{opt}}$.

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

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

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

219

220 **3.2 Characterization of aggregates.** That a small addition of phosphate ligand improves the
221 removal of silica nanoparticles with ferric chloride implies a significant change of aggregate
222 properties. Figure 4a shows typical temporal evolutions of the mean aggregate diameter D_{50}

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

233 An elemental ratio Fe/P in the [7-8] range is also a threshold value for the structure of
234 aggregates. The SAXS curves, shown in figure 5a as a Log-Log plot of the scattering intensity
235 versus the scattering vector, are characterized by a linear portion that identifies the fractal
236 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
237 corresponds to the scattering of silica nanoparticles of radius 7 nm. The fractal dimension D_f
238 obtained from the slope of the scattering factor remains close to 1.72 for small additions of
239 phosphate ligand (figure 5b). However, above a Fe/P of 7, D_f exhibits a step increase to an
240 average value of 1.83. On the other hand, the electrophoretic mobility of aggregates, varying
241 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
242 concentration investigated (fig. 6). The diameter of Ludox silica nanoparticles (14 nm) is well
243 below the lower size limit of particles (about 0.2 μm) that can be followed from the image
244 analysis system of a Zetaphoremeter III. However, it is expected that the electrophoretic
245 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
246 reported for Ludox HS particles in a suspension of same ionic strength as ours but at pH 6
247 (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 \AA^{-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

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

276 Upon the addition of $[P] = 0.008$ mmol/L to the silica suspension, *i.e.* $Fe/P = 45$, the
277 EXAFS curve is fitted with two sub-shells of Fe-Fe edge-sharing bonding and a
278 supplementary shell of iron atoms linked by double corner sharing (Figure 10B). Further
279 increase in phosphate significantly decreases the number of iron neighbors sharing edges
280 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
281 $3.04 \text{ \AA} (\pm 0.1 \text{ \AA})$ for the first sub-shell and from 3.13 to $3.15 \text{ \AA} (\pm 0.1 \text{ \AA})$ for the second sub-
282 shell. The contribution of double corner sharing Fe-Fe bonding could not be evidenced, which
283 implies a limited hydrolysis of iron species. Above a P addition of 0.008 mmol/L, the curve
284 fitting is mainly performed using edge-sharing Fe-Fe bonding, corner-sharing Fe-P bonding,
285 and in the case of $Fe/P=6.4$ and $Fe/P=5.8$, with corner-sharing Fe-Fe bonding. The values of
286 Fe-Fe bond length (3.56 and 3.58 \AA respectively for $Fe/P=6.4$ and $Fe/P=5.8$) may identify the
287 presence of double corner-sharing trimers (figure 10B) or Fe_2P complexes (figure 10E).
288 Actually, the latter geometry should be favored, as phosphate neighbors are needed for an
289 appropriate fitting.

290 The structural parameters inferred from curve-fitting analysis reveal that the presence
291 of phosphate ligand decreases the number of iron neighbors, *i.e.* a decrease of Fe-Fe bonds,
292 and leads to a contribution of phosphorus atoms in the second coordination shell of Fe. The
293 number of phosphate neighbors is highly variable from one sample to another, but it should
294 be noted that those numbers are rather inaccurate and are only given to evidence the presence
295 of Fe-P bonds. In contrast, the values of Fe-P bond length, between 3.26 and 3.34 \AA , are
296 unambiguously assigned to the formation of single-corner sharing complexes (see Figure
297 10D, E and F). For Fe/P ratios lower than 18, the phosphate ligand substitution for Fe does

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

303

304 **4. DISCUSSION**

305

306 **4.1 Nature of coagulant species in the system ferric chloride/phosphate/silica** 307 **nanoparticles.**

308 Most of the information available in the literature on iron (III) hydrolysis has been acquired in
309 the context of solutions of high Fe concentration (decimolar to molar) slowly hydrolyzed
310 from acidic conditions (Tchoubar et al. 1991; Bottero et al. 1994; Rose et al. 1996; 1997;
311 Doelsch et al. 2000; 2003, Collins et al. 2016). Thus, depending on the hydrolysis ratio
312 OH/Fe, dilution and ageing, the hydrolysis of ferric chloride solutions typically yields
313 monomers, corner-sharing dimers, edge-sharing dimers, double-corner trimers, polycations
314 and aggregates of those polycations, that eventually form akaganeite (β -FeOOH) upon ageing
315 (Murphy et al. 1976; Tchoubar et al., 1991; Manceau and Drits 1993; Bottero et al., 1994). In
316 the presence of organic or inorganic complexing ligands, the speciation diagrams of iron-base
317 solutions are drastically modified. Most often, when a sufficient amount of complexing
318 ligands has been added (*e.g.* phosphate anions, small organic acids, dissolved organic matter),
319 the hydrolysis of ferric chloride is hindered to the dimer stage (Rose et al., 1996; Rose et al.,
320 1997; Vilg -Ritter et al.1999, Doelsch et al. 2000). In the case of silicate and sulfate ligands,
321 EXAFS at the Fe K-edge and SAXS experiments revealed the presence of edge- and corner-

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

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

332 In the presence of increasing phosphate concentration, the complexation dynamics
333 becomes gradually dominant over the kinetics of iron (III) hydrolysis. The number of iron
334 neighbors sharing edges decreases, which can be interpreted as the termination of the active
335 chains growth whenever a phosphate ligand binds on the end of a Fe polymer chain. An
336 increased number of oligomeric structures, and hence an increased number of coagulant
337 species, is then formed from edge-sharing Fe dimers/trimers/oligomers linked by a phosphate
338 tetrahedra (fig. 10). Single corner-sharing Fe octahedra, identified at Fe/P ratios of 6.4 and
339 5.8, may also participate in the bridging of oligomeric Fe-P chains (Rose et al. 1996). Below a
340 Fe/P molar ratio of 7, the excess phosphate binding on iron dimers/trimers should decrease
341 the charge of coagulant species and/or promote the growth of oligomeric structures through
342 phosphate bridging (fig. 10). Therefore, both the number and efficiency of coagulant species
343 decrease for a Fe/P less than 7. In summary, if the strong affinity of iron (III) for phosphate
344 lowers the degree of polymerization of iron coagulant (Rose et al. 1996; Rose et al. 1997; El
345 Samrani et al. 2004), it also increases at first the number of coagulant species and improves

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

348 To evidence a possible effect of silica nanoparticles on the nature of coagulant species
349 is not straightforward. The detection of Si neighbors using EXAFS at the Fe K-edge is rather
350 difficult because of the large difference in atomic number between Si and Fe. Including a Si
351 shell improves the spectral fitting only in the absence of phosphate. It has been shown that the
352 polymerization of iron (III) is inhibited for Fe/Si molar ratios in the 1 to 4 range (Doelsch et
353 al. 2000). In our case, the number of silanol groups per unit surface area of silica that may
354 interact with the Fe hydrolyzed products, is about 4.6 nm^{-2} (Zhuravlev 2000). Using a specific
355 surface area of $220 \text{ m}^2/\text{g}$ for the Ludox HS nanoparticles, we calculate a Fe/Si molar ratio of
356 0.42. Actually, both steric hindrance and charge repulsion between the positive coagulant
357 species attached on the surface of silica nanoparticles should further decrease this ratio.
358 Therefore, the effect of the silica surface on iron hydrolysis is expected to be considerably
359 less than that of phosphate ligand, even though the association of polymeric chains of edge-
360 sharing Fe octahedra with the silica nanoparticles may also inhibit the chain growth.

361

362 **4.2 Aggregation mechanism of silica nanoparticles in the system $\text{FeCl}_3/\text{PO}_4$.**

363 It is especially interesting that the nature of hydrolysis products, and hence the type of
364 coagulant species that bind the silica nanoparticles, significantly changes with the relative
365 concentrations of iron coagulant and phosphate ligand. Such feature has not been addressed in
366 previous physicochemical models for phosphorus removal in which only equilibrium species
367 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
368 et al. 2010; Hauduc et al. 2015). Our study reveals that Fe dimers, through the formation of
369 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
370 role during phosphate removal, those transient species nevertheless leading to the

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

378 It is nevertheless rather difficult to precisely elucidate, for a given Fe/P ratio, both the
379 number and various types of coagulant species. EXAFS and even more TEM-EDXS, only
380 provide an average description of the hydrolysis products present in the bulk solution. If iron
381 oligomers linked by a phosphate tetrahedron may lead to polycations such as
382 $\text{Fe}_4(\text{PO}_4)(\text{OH})_2(\text{H}_2\text{O})_{16}^{7+}$, those highly charged species do not account by themselves for the
383 destabilization of silica nanoparticles. Under the conditions of pH and ionic strength used in
384 this study, the surface charge density of Ludox nanoparticles is about $-1.6 \mu\text{C}/\text{cm}^{-2}$ (Bolt
385 1957; Allison 2009). This corresponds to 61 negatively charged $-\text{SiO}^-$ groups per silica
386 particle. In that case, the number of polycations of charge $7+$ necessary to neutralize the silica
387 surface would be less than 10. As a 500 mg/L Ludox HS suspension corresponds to a 1.58
388 10^{17} particles per liter, a Fe concentration of $9.4 \mu\text{mol}/\text{L}$ should then be theoretically
389 sufficient to achieve the neutralization of silica nanoparticles. The latter concentration is two
390 orders of magnitude less than the actual coagulant concentration used. Therefore, the
391 coagulant species present in suspension are certainly a mix of weakly positive hydrolyzed
392 products comprising on the average about 4-5 Fe atoms for one P atom.

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

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

414 Although limited to less than a decade in Q , an estimate of about 1.7 for the fractal
415 exponent of silica aggregates is consistent with a diffusion-limited cluster aggregation
416 (DLCA) (Meakin 1988). Such DLCA regime can be argued because the aggregates are
417 formed in a stirred vessel. The relative importance of shear aggregation to Brownian diffusion
418 can be assessed using the Péclet number $Pe = 6\pi\eta Gd_0^3/kT$ in which η is the dynamic viscosity of
419 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
420 radius of silica particles ($d_0 = 7 \text{ nm}$), k the Boltzmann constant and T the absolute temperature

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

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

436

437 **5. CONCLUSIONS**

438

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

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

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

458

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462

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