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Influence of particle properties on iron flocculation

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Abstract

In this study the importance of charge interactions during flocculation of Fe^{3+} in the presence of particles and anions/cations at various pH values was investigated. $SiO_{2,(s)}$ and $ZnO_{(s)}$ were dosed as particles to promote charge interactions and/or serve as nucleus to accelerate floc formation. In the pH range 6-9, $SiO_{2,(s)}$ is negatively charged, while $ZnO_{(s)}$ carries a positive charge. Ca^{2+} and HPO_4^{2-} were selected to investigate charge interactions in the water phase.

A significant delay in floc growth due to charge repulsion between negatively charged iron species was observed at pH_{ini} 9. For positively charged species at pH_{ini} 6, a delay in floc growth was observed as well, but to a lesser degree. These effects could be neutralized by either dosing (positively charged) $ZnO_{(s)}$ or Ca^{2+} at pH_{ini} 9, or (negatively charged) $SiO_{2,(s)}$ at pH_{ini} 6.

The addition of phosphate did not hinder floc growth at pH_{ini} 6. While phosphate completely inhibited floc growth at pH_{ini} 7-9 in the presence of negatively charged $SiO_{2,(s)}$, the presence of positively charged $ZnO_{(s)}$ partly neutralized the detrimental influence of phosphate on floc growth. Similarly, dosing Ca^{2+} partly neutralized the effect of phosphate.

Keywords: iron flocculation; particles; charge interaction

1. Introduction

Iron chemistry is an important aspect of water treatment, where it is either added to promote removal of organic matter, heavy metals and colloidal material, or where removal of iron itself is the main goal. In the pH range 6-8, which it typical for groundwater, iron is mainly present as Fe^{2+} (Jolivet *et al.* 2004). When groundwater is aerated, Fe^{2+} oxidizes to Fe^{3+}, where the rate of oxidation increases for increasing pH values and stabilizes at a plateau rate at pH > 8 (Morgan & Lahav 2007). The oxidized Fe^{3+} ion readily hydrolyses into $Fe(OH)^{2+}$, $Fe(OH)_2^+$, $Fe(OH)_{3,(aq)}$ or $Fe(OH)_4^-$, depending on the pH. When comparing Fe^{3+} hydrolysis product speciation using hydrolysis constants from different authors, the trend seems to be that either (i) the positively charged $Fe(OH)_2^+$ dominates at pH 7, the negatively charged $Fe(OH)_4^-$ dominates at pH 9, and pH 8 is a mixture of these, and of neutral $Fe(OH)_3$ (Liu & Millero 1999; Pham *et al.* 2006 ; Stefansson 2007), or (ii) the neutral $Fe(OH)_3$ dominates at each of these pH values (Flynn 1984; Millero & Pierrot 2007). When comparing the values for the hydrolysis constants (Supporting information S 1), it is notable that the values for $Fe(OH)_2^+$ and $Fe(OH)_4^-$ are reasonably close, which would imply that their actual concentrations are similar for all authors. Whether the concentrations of $Fe(OH)_{3,(aq)}$ are in comparison high (references (Flynn 1984; Millero & Pierrot 2007)) or low (references (Liu & Millero 1999; Pham *et al.* 2006 ; Stefansson 2007)) could essentially be related to the specific membrane pore size used by the authors to separate the "dissolved" iron fraction from the solid fraction.

The Fe^{3+} hydrolysis products will form larger complexes by binding via olation (Fe-OH-Fe) or oxolation (Fe-O-Fe) (Jolivet *et al.* 2004), forming nuclei and eventually growing into iron flocs. After fast hydrolysis of Fe^{3+}, amorphous 2-line ferrihydrite is formed (Schwertmann & Cornell 1991).

Addition of particles allows for more control of iron flocculation, as these particles may act as nucleus for floc growth (Hove *et al.* 2009). In practical applications, the purpose of adding particles is often to increase the density of the iron flocs, which sediment more rapidly and have lower water content, and/or to accelerate floc formation (Desjardins *et al.* 2002; Gan *et al.* 2005; Gottfried *et al.* 2008; Hove *et al.* 2009; Zhou *et al.* 2012) . In the synthesis of iron oxide nanoparticles, addition of particles (seed-mediated growth) allowed for production of more monodisperse particles (Huang *et al.* 2009). While the addition of particles has proven to be beneficial, there have been limited attempts to identify the responsible mechanisms. Our aim is to investigate the importance of charge interactions during flocculation of Fe^{3+} in the presence of particles.

Particles with a negative surface charge (SiO_2; pH_{pzc} 2-3) and positive surface charge (ZnO; pH_{pzc} 9.2) were selected, in order to assess the importance of charge attraction or – repulsion for charged iron hydrolysis products at pH 6, 7, 8 and 9. Fe^{3+} hydrolysis products should be mainly positively charged at pH 6, 7 ($Fe(OH)_2^+$), negatively charged at pH 9 ($Fe(OH)_4^-$), or a mixture of these, together with $Fe(OH)_{3,\,(aq)}$ could be present at pH 8. In addition, the influence of the bivalent cations (Ca^{2+}) and anions (HPO_4^{2-}) under these experimental conditions was assessed. The influence of HPO_4^{2-} and Ca^{2+} on iron flocculation at pH 7 has received considerable attention (Chattelier *et al.* 2004; Voegelin *et al.* 2009; Kaegi *et al.* 2010; Voegelin *et al.* 2013; Senn *et al.* 2015). The research presented in this manuscript extends on this, by broadening the pH range beyond pH 7 and thereby gaining more variety in the charge of iron hydrolysis products, and by adding particle surface with either a positive or negative surface charge.

2. Materials and methods

2.1 Chemicals and stock solutions

ZnO (>99,0%), $FeCl_3{*}6H_2O$, $CaCl_2$, $NaHCO_3$, Na_2HPO_4 were obtained from Sigma Aldrich (p.a. grade). The SiO_2 originated from Mol, Belgium, and was obtained from Sibelco as M32 size fraction (0.18-0.35 mm, D_{50} 0.26 mm). It was ground for 60 seconds with a ring grinder (HSM100, Herzog) before use in the experiments. All stock solutions were prepared in demineralized (demi) water (Aquadem installation, Veolia, 0.09 µS/cm). The Fe^{3+} solution was acidified to pH 2 to prevent flocculation. The stock solutions were dosed to obtain concentrations of 2 mg/l Fe, 150 mg/l HCO_3^-, 40 mg/l Ca^{2+} or 1 mg/l HPO_4^{2-}. HCO_3^- was dosed to all solutions to serve as pH buffer. The pH was adjusted with HCl or NaOH to its required value.

2.2 Particle size distribution of SiO_2 and ZnO

The particle volume distribution of ZnO and ground SiO_2 were measured with a Mastersizer 2000 (Malvern), coupled with a hydro 2000mu wet sample dispersion unit. This dispersion was obtained by mechanical mixing, no additional dispersants were added.

The particle volume distribution of SiO_2 and ZnO can be found in the supporting information (S 2) Particle counts and surface area were calculated from this data by assuming spherical particles. A fixed amount of particle surface of 0.15 m^2/l was dosed for either SiO_2 or ZnO.

2.3 Zeta potential

Zeta potential was measured with Zetacompact (CAD instruments), using 8.54 V/cm direct current, under the conditions (pH, conductivity) relevant in our experiments. These measurements confirmed the negative zeta potential of SiO_2 (supporting information S 3). ZnO, on the other hand, showed a positive zeta potential in MilliQ water, but a negative surface potential in the presence of HCO_3^-, indicating that HCO_3^- adsorption might have resulted in charge reversal (Degen & Kosec 1999; Sedlak & Janusz 2008).

2.4 Jar tests

Jar tests were executed on a JLT6 flocculation tester (Velp scientifica), using 1 L of solution in baffled 2 L jars. In all cases, mixing was at a constant 120 rpm, and experiments were carried out at room temperature (around 18 °C). pH values were adjusted to 6, 7, 8 or 9, and either 0.33 g/l SiO_2 or 0.35 g/l ZnO or no particles were dosed. ZnO powder dispersed poorly, and dispersion was aided by using a turrax mixer (T45N, IKA Werk) at 47,5% capacity for 5 seconds.
When SiO_2 or ZnO particles were added, a sample was taken before iron addition, and the particle size distribution was analysed with a particle counter (HIAC Royco model 9703, Pacific scientific), where the measuring principle is based on laser obscuration. Here, 5 ml of solution was scooped from the jar and diluted in 100 ml demineralized water. This dilution may have led to floc destabilisation due to the decrease in ionic strength. The mixing rate of the particle counter sample was set to approximate the mixing rate used in the jars, and the mixing duration was kept to a minimum in an attempt to minimize floc breakage or further flocculation during analysis.
Abstractions of 10 ml were done twice and were analysed by the particle counter. The results of these consecutive analyses were close, with a standard deviation less than 1% for the total amount of particles and the calculated particle volume. This indicates that further particle breakage or flocculation during analysis was limited.
Every sample measurement was followed by a rinsing step with demineralized water. Samples were taken 1, 3, 15 and 30 minutes after iron dosage. At the same time intervals, 5 ml of solution was filtered over a 0.45 µm polyethersulphone syringe filter and the total Fe concentration of the filtrate was measured. This was done photometrically (Nova spectroquant, Merck), where iron is reduced to Fe^{2+} in thioglycolate medium and forms red-violet complexes with triazide (Fe analysis kit 1.14761.0001, Merck). The 0.45 µm filter is used to arbitrarily differentiate “dissolved” from “solid” iron in this study. This is no absolute definition, since solid iron particles can be formed that are smaller than 0.45 µm.

When no particles were added, the formed iron flocs could not be readily detected by the particle counter, as the measured particle counts were much lower. In these experiments, samples were filtered over a series of syringe filters (0.2/0.45/0.8 µm (nylon); 10/20 µm (polypropylene), mdi membrane technologies) and the remaining iron concentration was determined after 1, 3, 15 and 30 minutes. The pH values were only initially corrected to pH 6, 7, 8 or 9 before iron dosing, and not adjusted afterwards. These values are referred to as “pH_{ini}” in this manuscript. Typical pH variation during the experiments is shown in S 4.

3. Results and discussion

3.1 No addition of particles

The size of iron oxide flocs when no particles were added was indirectly determined by filtering the sample from the jar test over a series of syringe filters in the range of 0.2 – 20 µm, and measuring the iron concentration in the filtrate. A decrease in iron concentrations in the filtrate indicates that iron flocs have grown to a diameter that is larger than the syringe pore size.

Floc growth after adding 2 mg/l Fe^{3+} is represented by the remaining iron concentration in the filtrate of a 0.2, 0.45, 0.8, 10 and 20 µm filter in Figure 1. For the filters < 0.8 µm, iron concentrations in the filtrate were below the detection limit after 3 minutes, except at pH_{ini} 9.

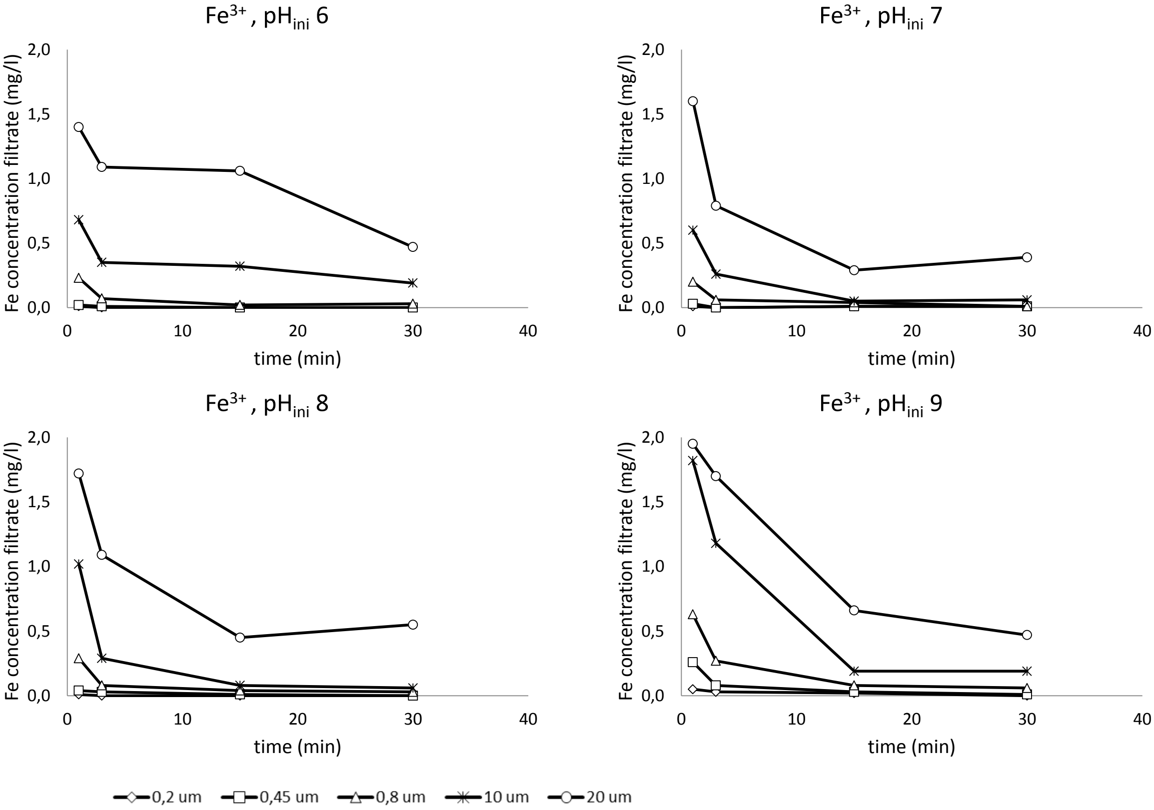

Figure 1: Fe^{3+} removal after filtration with 0.2 – 20 µm syringe filters at initial pH_{ini} 6, 7, 8 and 9 in buffered demi water (150 mg/l HCO_3^-) at 120 rpm. Initial concentration 2 mg/l Fe^{3+}.

Charge attraction and rapid growth is expected around the point of net zero charge. Figure 1 shows rather similar Fe^{3+} concentrations for pH_{ini} 7 and 8, which suggests that the point of net zero charge of the iron flocs could have been in-between pH_{ini} 7 and 8. This is plausible, as the datasets of both Stefansson (2007) and Liu and Millero (1999) show their lowest iron oxide solubility at pH 7-7.5 at an ionic strength of 0.01 M, and Schwertmann and Cornell state that the net zero charge of iron oxides is typically within a broad pH range of 7-8 (Schwertmann & Cornell 1991).

At both extremes of the pH range, pH_{ini} 6 and 9, floc growth was delayed. At pH_{ini} 9, the initial floc growth in 0-15 minutes was delayed, while at pH_{ini} 6, the initial floc growth seems relatively comparable to pH_{ini} 7 and 8, but was delayed after 3 minutes. Pham et al (2006) found asymmetry in ferric iron flocculation rates at pH 6 and 9 as well, and proposes different responsible mechanisms; at pH 6, the rate of H_2O-OH^- exchange is mainly responsible for delayed floc growth, while charge repulsion between negatively charged $Fe(OH)_4^-$ hydrolysis products delays floc growth at pH 9 (Pham *et al.* 2006).

3.2 Addition of SiO_2 and ZnO particles

When particles were added, floc growth was followed by measuring the particle size distribution. To compare the floc growth in the presence and absence of particles, the volume increase of flocs > 20 µm is presented. This can be compared with the removed Fe fraction by the 20 µm syringe filter in the experiments without particles (Figure 1 and Figure 2, inverse trend). In addition, the amount of Fe that is removed after filtration over a 0.45 µm syringe filter was determined. These results can be found in the supporting information S 6-8 and typically match with the trends that are found with the particle counter.

Floc growth after adding 2 mg/l Fe^{3+} and addition of SiO_2 or ZnO at pH_{ini} 6-9 is presented in Figure 2. The results of baseline experiments, where particle agglomeration was followed without addition of Fe are shown as a dotted line. While the same amount of Fe was used in all experiments, the volume of flocs > 20 µm was considerably larger in the presence of ZnO as compared to SiO_2, which may indicate that flocs with lower density were formed in the presence of ZnO.

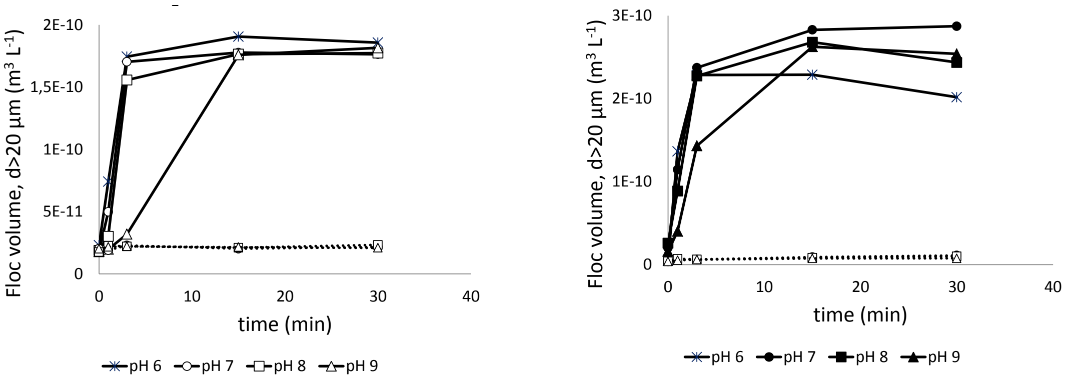

Figure 2: Influence of pH on floc growth (d>20 µm) with 0.15 m^2/l of SiO_2 (left), and ZnO (right). Buffered demi water (150 mg/l HCO_3^-), 120 RPM, 2 mg/l Fe^{3+}. Dotted lines: baseline experiments (SiO_2 or ZnO without Fe dose)

For pH_{ini} 6-8, the addition of SiO_2 resulted in rapidly reaching a “plateau” value for the floc volume within 3 minutes (Figure 2, left), which was faster than the trends observed when no particles were dosed. The general trends observed for ZnO were more comparable with the case where no particles were present, where “plateau” values were reached after about 15 minutes.

Expected charge interactions between particles and iron species are summarized in Table 1, based on the premise of electrostatic attraction between unlike charges, and – repulsion between like charges. Due to its negative surface charge, SiO_2 should promote floc growth at pH_{ini} 6, and delay it at pH_{ini} 9, while For ZnO, the opposite effect is expected. Charge attraction for SiO_2 at pH_{ini} 6, and ZnO at pH_{ini} 9 seemed to indeed occur; for SiO_2, the highest floc volume was found at pH_{ini} 6, while the experiments where no particles were added indicate a delay in floc growth at this pH value. At pH_{ini} 9, floc growth was excellent for ZnO, with both rapid floc volume increase (Figure 2, right) and virtually complete Fe removal after 0.45 µm filtration at all time intervals (S 6). This would also indicate that the negatively charged $Fe(OH)_4^-$ is able to interact with the (positively charged) ZnO surface, and is able to replace the HCO_3^- which is suggested to be present at the ZnO surface, as discussed in paragraph 2.3 based on zeta potential measurements.

Charge repulsion was less obvious. At pH_{ini} 9, floc growth was clearly delayed at SiO_2, although the effect of charge repulsion by the SiO_2 surface cannot be separated from the charge repulsion between negatively charged iron species in the water phase. For ZnO the lowest volume increase after 15-30 minutes is found at pH_{ini} 6. The initial floc growth at pH_{ini} 6 during 1-3 minutes does not seem to be delayed at all, but the resulting floc was fragile and was breaking up due to shear forces created by mixing at 120 rpm.

Table 1: Overview charge interactions particle-Fe at pH 6, 7, 8, 9. Positive Fe or particle charge is represented by "+". Negative Fe or particle charge is represented by "-".

		SiO_2	ZnO
pH_{ini} 6	Charge Fe^{3+} species	+	+
	Particle charge	-	+
	Fe-Fe interaction	Repulsion Fe-Fe	Repulsion Fe-Fe
	Fe-particle interaction	Attraction Fe-SiO_2	Repulsion Fe-ZnO
pH_{ini} 7 pH_{ini} 8	Charge Fe^{3+} species	+/-	+/-
	Particle charge	-	+
	Fe-Fe interaction	Attraction Fe-Fe	Attraction Fe-Fe
	Fe-particle interaction	Both attraction/repulsion	Both attraction/repulsion
pH_{ini} 9	Charge Fe^{3+} species	-	-
	Particle charge	-	+
	Fe-Fe interaction	Repulsion Fe-Fe	Repulsion Fe-Fe
	Fe-particle interaction	Repulsion Fe-SiO_2	Attraction Fe-ZnO

3.3 Addition of SiO_2, ZnO - Influence of Ca^{2+} and HPO_4^{2-}

The experimental results when Ca^{2+} or HPO_4^{2-} were dosed in the presence of ZnO and SiO_2 are shown in Figure 3.

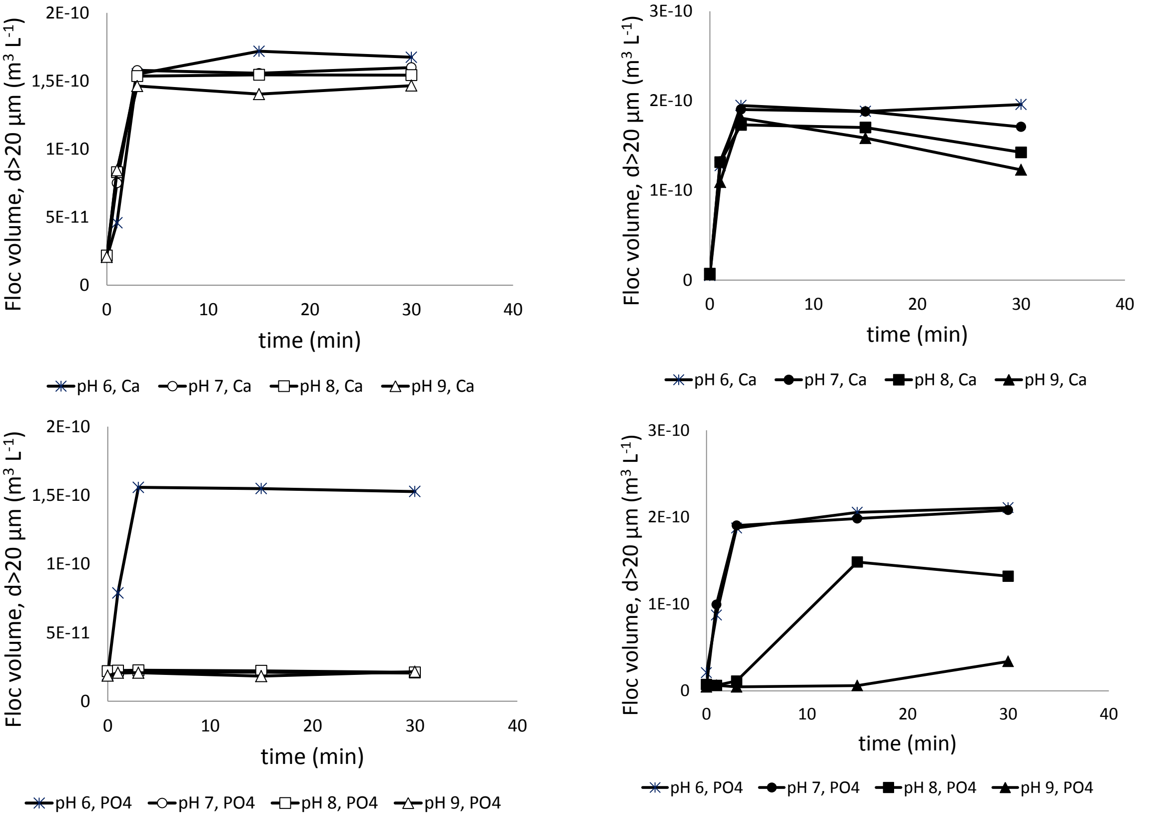

Figure 3: Influence of pH and HPO_4^{2-} (lower graphs) or Ca^{2+} (upper graphs) dosage on floc growth (d>20 µm) in the presence of SiO_2 (left graphs) or ZnO (right graphs). Buffered demi water (150 mg/l HCO_3^-), 40 mg/l Ca^{2+}, 120 RPM, 2 mg/l Fe^{3+}

Floc growth in the presence of Ca^{2+} and SiO_2 was rapid at all initial pH values (Figure 3, left). The delay which was observed at pH_{ini} 9 in the absence of Ca^{2+} (Figure 2) was neutralized, which may confirm charge bridge formation of Ca^{2+} between SiO_2 and $Fe(OH)_4^-$ and/or $Fe(OH)_4^-$ molecules in the water phase. Alternatively or additionally, electrostatic repulsion can be lowered due to increased charge shielding, since addition of $CaCl_2$ increases the ionic strength.

Addition of HPO_4^{2-} completely stopped flocculation at pH_{ini} 7-9, but did not affect flocculation at pH_{ini} 6. Based on expected charge interactions (Table 2), there are two factors that can explain why flocculation was effective at pH_{ini} 6 in the presence of HPO_4^{2-} ; (i) phosphate bridges two positively charged $Fe(OH)_2^+$ iron species in the water phase, and (ii) phosphate is mostly present in its monovalent form, $H_2PO_4^-$ at pH 6, rather than its divalent form, HPO_4^{2-} at pH 7-9. Formation of (strongly) negatively charged Fe-P species is less likely at pH_{ini} 6.

For ZnO, Ca^{2+} was expected to have no (charge-related) influence at pH_{ini} 6 (table 2), and the floc volume increase was indeed roughly similar to ZnO in the absence of Ca^{2+}. At increasing pH values, the floc volume after 30 minutes became gradually less (Figure 3, right). While Ca^{2+} did not affect the initial floc growth during 0-3 minutes, it did seem to affect the floc stability, creating flocs that were more easily broken up by shear at higher pH values, as compared to when no Ca^{2+} was present. This difference was not observed for SiO_2, where the created flocs are stable. Since floc stability for ZnO in the presence of Ca^{2+} decreases at higher pH values, and $Fe(OH)_4^-$ becomes increasingly more dominant at higher pH values, it is possible that (charge) interaction between $Fe(OH)_4^-$ and Ca^{2+} reduces the interaction between $Fe(OH)_4^-$ and positively charged ZnO surface, leading to weaker floc structures.

In contrast to SiO_2, HPO_4^{2-} did not completely stop iron flocculation at pH_{ini} 7 – 9; Fe removal after 0.45 µm filtration was initially lower, but still >85% Fe was removed after 3 minutes at these pH values (S 8). This indicates that the presence of positively-charged ZnO surface can partly reverse the detrimental influence of HPO_4^{2-} on iron flocculation. Similarly, addition of Ca^{2+} partly neutralized this detrimental influence of HPO_4^{2-} as shown in S 9, which is in accordance with existing literature (Voegelin *et al.* 2009; Kaegi *et al.* 2010; Senn *et al.* 2015).

Table 2: Overview charge interactions particle-Fe-Ca^{2+} at pH 6, 9. Positive Fe or particle charge is represented by "+". Negative Fe or particle charge is represented by "-".

		SiO_2	ZnO
pH_{ini} 6	Charge Fe^{3+} species	+	+
	Particle charge	-	+
	Fe-particle interaction	Attraction Fe-SiO_2	Repulsion Fe-ZnO
	Ca^{2+} competition and charge bridging	Competition with Fe (+) for SiO_2 surface	
	HPO_4^{2-} competition and charge bridging	Fe-Fe bridging	Fe-Fe bridging Fe-ZnO bridging
pH_{ini} 9	Charge Fe^{3+} species	-	-
	Particle charge	-	+
	Fe-particle interaction	Repulsion Fe-SiO_2	Attraction Fe-ZnO
	Ca^{2+} competition and charge bridging	Fe-Fe bridging Fe-SiO_2 bridging	Fe-Fe bridging
	HPO_4^{2-} competition and charge bridging		Competition with Fe (-) for ZnO surface

4. Conclusions

The aim of this research was to investigate the importance of charge interactions during flocculation of Fe^{2+} and Fe^{3+} in the presence of particles, anions and cations at different pH values.

A significant delay in floc growth due to charge repulsion between negatively iron species was observed at pH_{ini} 9 when only Fe^{3+} was dosed. For positively charged species at pH_{ini} 6, a delay in floc growth was observed as well, but to a lesser degree. These effects could be neutralized by either dosing (positively charged) $ZnO_{(s)}$ or Ca^{2+} at pH_{ini} 9, or (negatively charged) $SiO_{2,(s)}$ at pH_{ini} 6. The addition of phosphate did not hinder floc growth at pH_{ini} 6. While phosphate completely inhibited floc growth at pH_{ini} 7-9 in the presence of negatively charged $SiO_{2,(s)}$, the presence of positively charged $ZnO_{(s)}$ partly neutralized the detrimental influence of phosphate on floc growth. Similarly, dosing Ca^{2+} partly neutralized the effect of phosphate.

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Supporting information

S 1: Hydrolysis constants for Fe^{3+}

$$[Fe^{3+}] \rightarrow [Fe(OH)^{2+}] + [H^+] \qquad \beta_1 = \frac{[Fe(OH)^{2+}] \cdot [H^+]}{[Fe^{3+}]}$$

$$[Fe^{3+}] \rightarrow [Fe(OH)_2^+] + \ 2\,[H^+] \qquad \beta_2 = \frac{[Fe(OH)_2^+] \cdot [H^+]^2}{[Fe^{3+}]}$$

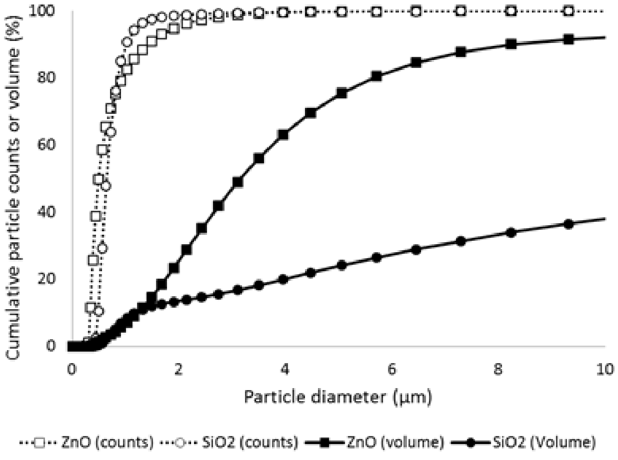
$$[Fe^{3+}] \rightarrow [Fe(OH)_3] + \ 3\,[H^+] \qquad \beta_3 = \frac{[Fe(OH)_3] \cdot [H^+]^3}{[Fe^{3+}]}$$

$$[Fe^{3+}] \rightarrow [Fe(OH)_4^-] + \ 4\,[H^+] \qquad \beta_4 = \frac{[Fe(OH)_4^-] \cdot [H^+]^4}{[Fe^{3+}]}$$

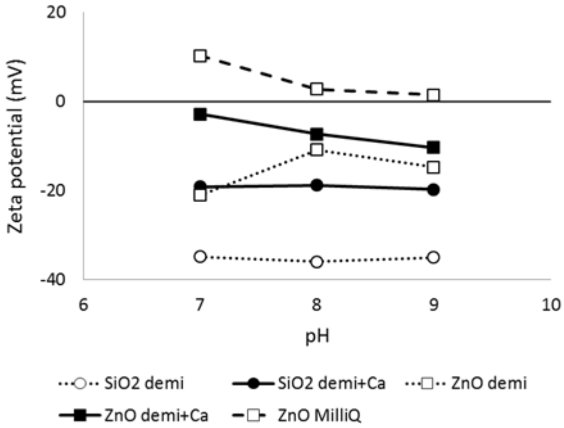
Log β_1	Log β_2	Log β_3	Log β_4	Reference
-2.1	-6.3	-14.3	-22.3	Liu e.a. 1999
-2.19	-5.8	-14.3	-21.7	Stefansson 2007
-2.13	-6.1	-14.3	-22.2	Pham e.a. 2006
-2.18	-6.9	-13.0	-22.3	Millero, Pierrot 2007
-2.25	-6.0	-12.1	-22.1	Flynn 1984*

*Hydrolysis constants obtained by curve-fitting the original data

S 2 : Cumulative volume distribution SiO$_2$, ZnO



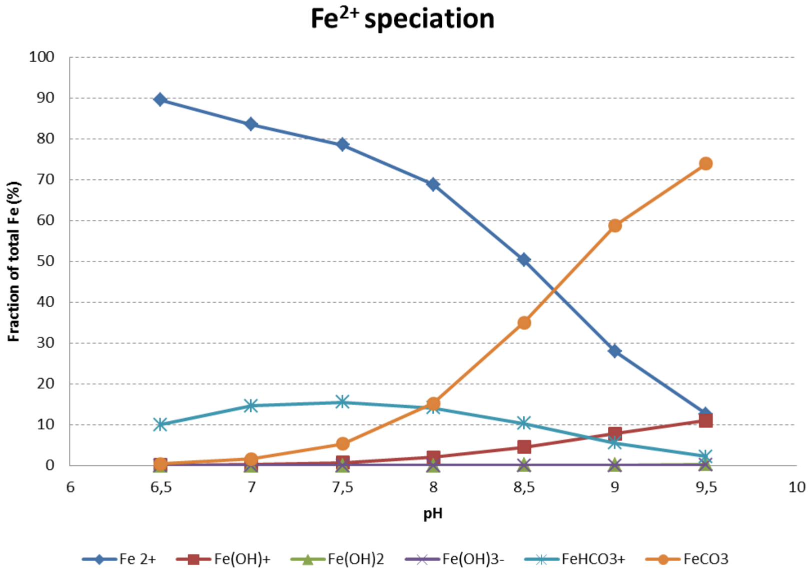
S 3 : Zeta potential of SiO_2 and ZnO in buffered demi water with/without Ca^{2+}



S 4 : pH variation during jar test experiments

	Fe^{2+}			Fe^{3+}			
Time (min)	pH	pH	pH	pH	pH	pH	pH
0	7,06	8,07	9,05	6,04	7,05	8,05	9,02
0,5	6,88	7,58	8,62	5,91	6,93	7,50	8,47
30	7,31	7,98	8,56	6,48	7,36	7,82	8,32

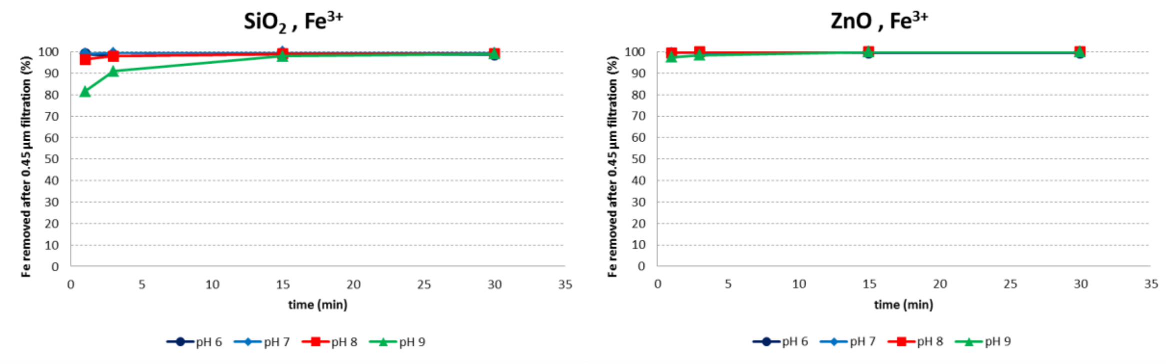
S 5: Calculated Fe^{2+} speciation (PHREEQCi, version 3.3.8-11728, wateq4f database)



Parameter	value	
pe	-3,4	(Eh: -0,2 V)
T	25 °C	
Fe	0,035 mmol/l	(2 mg/l)
C	2,46 mmol/l	(150 mg/l HCO_3^-)

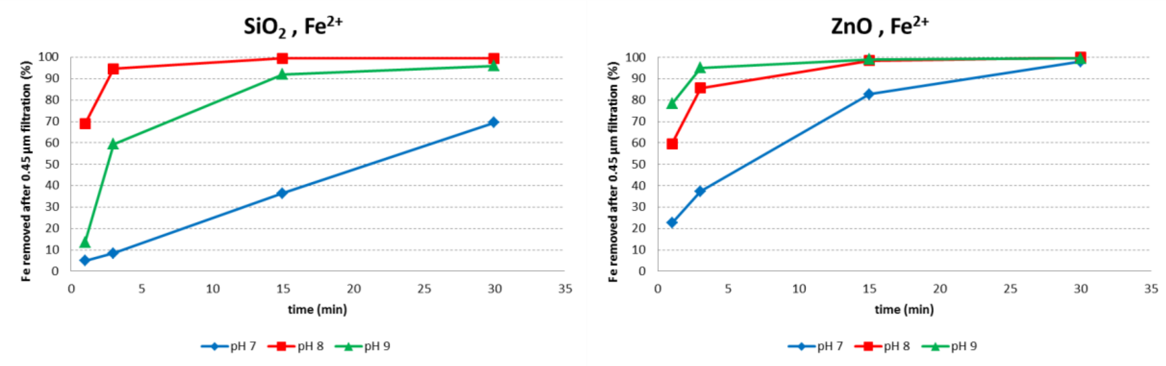
S 6: Fe^{3+} removed after filtration over 0,45 µm PES filter.

SiO_2 or ZnO dosed, 2 mg/l Fe^{3+}, pH 6/7/8/9, buffered demi water (150 mg/l HCO_3^-), 120 rpm



S 7: Fe^{2+} removed after filtration over 0,45 µm PES filter.

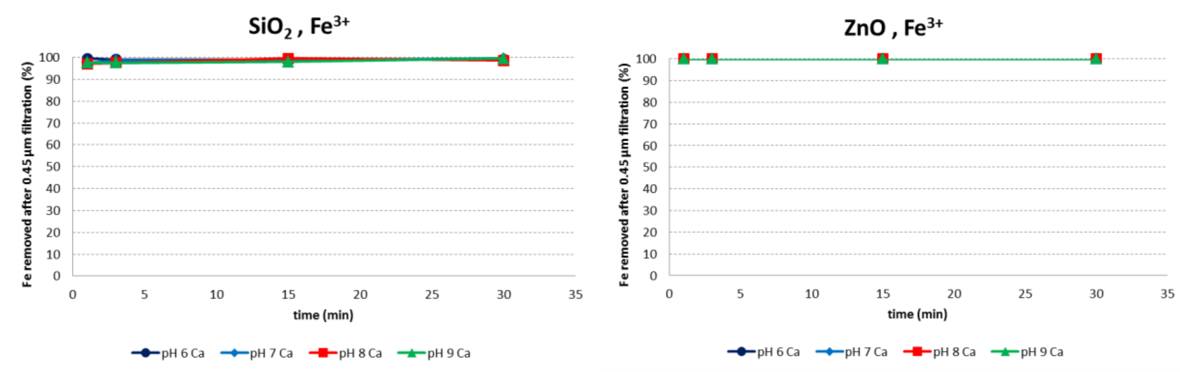
SiO_2 or ZnO dosed, 2 mg/l Fe^{2+}, pH 7/8/9, buffered demi water (150 mg/l HCO_3^-), 120 rpm

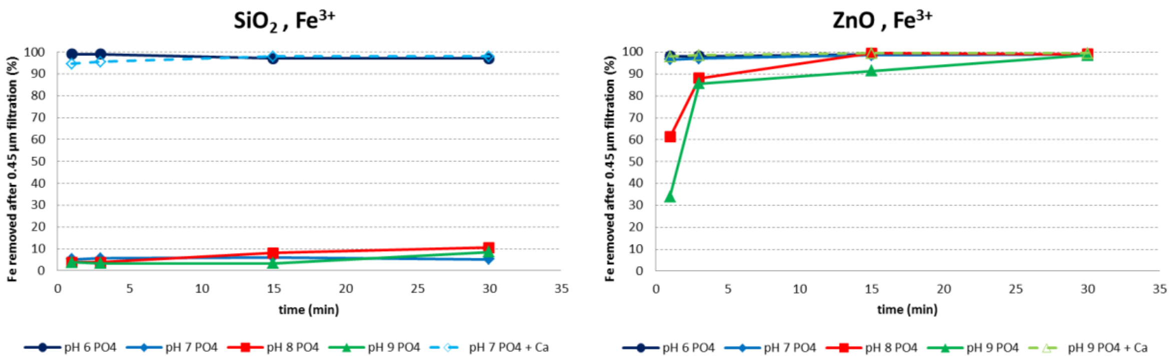


S 8: Fe^{3+} removed after filtration over 0,45 µm PES filter.

SiO_2 or ZnO dosed, 2 mg/l Fe^{3+}, pH 6/7/8/9, buffered demi water (150 mg/l HCO_3^-), 120 rpm

with 1 mg/l HPO_4^{2-} and/or 40 mg/l Ca^{2+}





S 9: influence of simultaneous dosage of HPO_4^{2-} and Ca^{2+}