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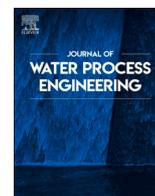
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Investigating the parameters influencing floc formation

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ABSTRACT

Flocculation, as the formation of insoluble organo-metallic complexes, has been studied considerably in the field of soil science, as it emerges e.g. from podzolization where a soil layer with reduced permeability is created; but also in the field of water treatment, as a means to remove natural organic matter (NOM). It is based on the process where positively charged metal species – Aluminium (Al), Iron (Fe) and Zirconium (Zr) in this study – react with the negatively charged surface of dissolved organic matter (DOM) and precipitate to form flocs. Since pH affects the surface charge of the organic matter (OM) particles and the form in which the coagulants are present in solution, controlling physico-chemical parameters, such as the pH, would significantly improve the flocculation process and help to enhance the efficiency of water purification strategies and soil permeability reduction from a geo-engineering perspective. It was shown that (1) there are ideal intervals in terms of metal to Carbon ratio (Me/C), in which the coagulants should be added to cover the surface of the DOM particles and these vary with metal type and pH; (2) at pH = 1, the OM forms flocs only with protons when mixed with Al, while with Fe some, and with Zr all, metal is associated with the solid phase; (3) Zr generally forms larger flocs than Al and Fe, even at acidic pH = 1, but also at higher concentrations; and (4) as the Me/C increases, the floc size does as well.

1. Introduction

In the environment, flocculation naturally occurs in podzols, where natural organic matter (NOM) and mineral leaching results in the formation of a soil layer with reduced permeability [1]. Therefore, studies have been done recently, to evaluate the possibility of using podzolization-derived approaches to reduce soil permeability [2] and decontaminate water [3].

Designer-flocs can be used to clog soil pores and reduce the soil permeability to control the water flow, e.g. for dyke stabilisation. It is comparable to microbially induced calcite precipitation (MICP) but it is more efficient in reducing soil permeability than mineral crystals, as they can cover the pore entrance instead of just filling them up [4]. Also, less mass of metal-OM flocs is needed to achieve the same permeability reduction.

Although historically, coagulation has been employed in water treatment processes to decrease turbidity and colour, and remove pathogens [5], it is now also used to remove natural (NOM), dissolved (DOM) and particulate organic matter, for which the optimal conditions are not necessarily the same. The coagulation process is used to

destabilise the NOM suspension by coating its negatively charged surface with positively charged species [6].

Usually, the removal of NOM can be achieved by coagulating with hydrolysed metal species, such as Aluminium (Al) or Iron (Fe). The NOM either complexes with the metal ions (e.g. Al^{3+} and Fe^{3+} ; *charge neutralisation*), adsorbs onto metal hydroxides (e.g. $Al(OH)_3$ and $Fe(OH)_3$; *sweep flocculation*) or co-precipitates with the hydroxides [7].

Generally, coagulation is performed in two stages: first the coagulant is rapidly mixed, then the flocculation is enhanced by slow mixing. Through coagulation, the naturally occurring particles and macromolecules are destabilised; during flocculation, the aggregation of destabilised particles is being promoted, micro-flocs bind together and the larger flocs that are formed can subsequently be removed by sedimentation and/or filtration [8,9].

However, the exact processes of flocculation as they occur in podzolization – where metals (Al and Fe) are mobilised by DOM, precipitate and clog the soil pores [10] – are still not fully understood because they depend on a complex interplay of soil physical and chemical parameters, e.g. pH and soil composition [1,11]. This is hindering an optimal application in water treatment as well as a building-

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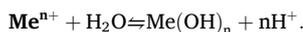
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with-nature engineering tool aimed at reducing soil permeability.

Coagulation is a complex process where the repulsive potential of the electrical double layers of colloids is reduced in a way that micro-particles can be produced. These collide with each other and form larger structures – also called **flocs** – in the flocculation process [5]. There are different ways to form flocs: through charge neutralisation, sweep flocculation or bridging; and which process dominates depends on a few initial conditions: the pH, the type of coagulant and its concentration.

At low pH, the metal species (Me) are present in solution in their free cationic form as hydrolysis products [12]:



The cationic metal can then react with the anionic dissolved organic matter (DOM; see Fig. 1) and form insoluble particles [13]. Charge-neutralised species are often preferred, as they can easily form again: broken flocs can re-grow to their original size before breakage, e.g. through stirring [14].

For monomeric Al based coagulants, charge neutralisation (CN) produces different floc characteristics, including floc growth speed and size, than sweep flocculation does (see mechanism below). In a previous study [15] it was also shown that CN performs more efficiently than sweep flocculation (SF) in terms of DOM removal and filterability, and achieves improved turbidity removal.

At higher pH, the metal species are present in solution also as hydroxides:



When these metal salts are added to water at a sufficiently high concentration to cause the precipitation of amorphous metal hydroxides, the colloidal particles are enmeshed in the flocs ([16]; see Fig. 2). But in this scenario, the amorphous hydroxide precipitate can also incorporate impurities [12], and they appear to be less stable than flocs formed through CN or bridging (see mechanism below).

In the two previous coagulation processes, monomeric metal species were used, but metallic polymer chains can also form flocs. The destabilization by bridging – which is a special case of CN – occurs when segments of polymer chains absorb on more than one particle, thereby linking particles together (see Fig. 3; [17,18]). The aggregates formed through bridging appear to be significantly more resistant to breakage, than the flocs formed with simple cations or salts [16,19].

The advantages of organic polymeric coagulants – such as PFAC-PD, which is a composite inorganic-organic flocculant that combines Al^{3+} and Fe^{3+} – are a higher molecular weight, a lower pH dependence and an increased aggregation capacity; but they also come with high costs [20,21].

As mentioned above, a broad range of initial conditions can alter flocculation: depending on the charge and therefore the form in which the coagulant is present in solution, either CN or SF is the dominant

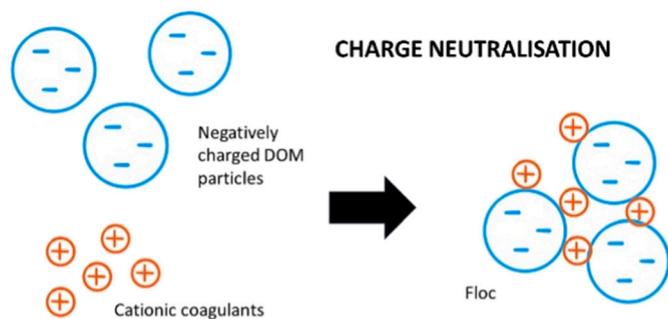


Fig. 1. Charge neutralisation is a flocculation process in which the coagulants are present in their cationic form and react with the negatively charged DOM particles to form flocs.

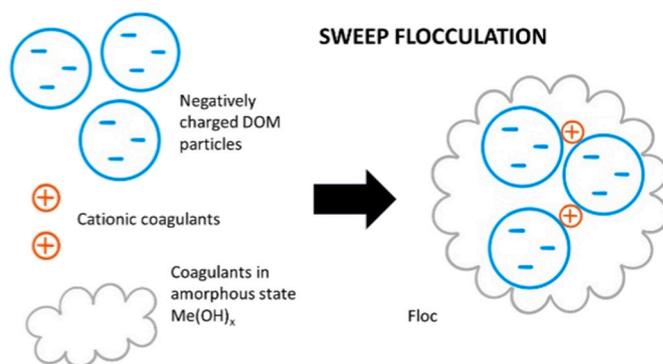


Fig. 2. Through sweep flocculation, flocs are formed through the binding process of cationic coagulants and negatively charged DOM particles, but also enmeshing of the coagulants in their amorphous state.

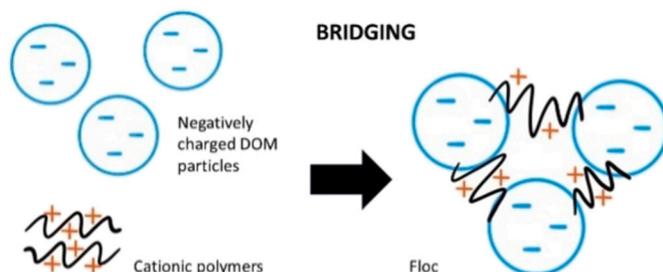


Fig. 3. Bridging is a flocculation process in which the chain-like cationic coagulants form bridges between the negatively charged particles.

process; if the coagulant is a polymer, flocs are formed through a bridging mechanism. In this study the focus will be on CN and SF, as the main parameter leading to bridging is evidently the use of a polymeric coagulant and does not risk to lead to the two other mechanisms.

For these flocculation processes the variables of interest are the choice of coagulant type, the pH and the dosage of both reagents, which will be referred to as the molar metal to Carbon ratio (Me/C). Previous research [22] has also shown, that the stirring strength and time affect the floc structure and properties, but flocs formed under CN are capable of fully recovering after breakage [23].

The choice of coagulant used for flocculation is important, as it is established that some metal species form stronger bonds with DOM than others [24]. Given the large number of variable charge sites on NOM, the charge of the mononuclear species also attracts interest. For example, some scientists have started to look into Zirconium (Zr) as it results in significantly larger flocs [5] and it has an increased positive charge, compared to Al and Fe.

Another study [25] reported that floc properties – e.g. for recalcitrant NOM removal – also significantly improved with larger and stronger flocs, as they indicate a greater resistance to breakage. The median floc sizes for Al, Fe and Zr were 450 μm , 710 μm and 930 μm respectively. They also showed through bench and pilot scale experiments, that Zr out-performed Al and Fe in both DOM removal and residual floc formation for trihalomethane (THM).

For each metal species, the pH of the solution is essential, as it indicates in which form the coagulant is present [26]. Previous research [12] gives the distribution of hydrolysis products in equilibrium with amorphous hydroxides for Al and Fe. These mole fractions, based on the pH value for each coagulant, were calculated using the solubility constant K . Based on the solubility product obtained from literature ($\log K = -62.46 \pm 0.10$; [27]), it has been possible to recreate the same distribution curve for Zr and therefore, predict in which form the coagulant is present in solution (see fig. S1 in the *Supplementary Information*).

Evidently, the concentration of coagulant in comparison to the DOM concentration is significant, as it has an influence on the surface charge of the DOM. In this paper, the concentrations of both the metals and DOM are therefore referred to as a metal to Carbon (Me/C) ratio: it is the combination of both molar concentrations of the metal (Al, Fe or Zr) and Carbon (from the DOM) in solution. With a low Me/C, the surface of the DOM particles is negatively charged and partly neutralised by mono-valent Potassium (K; coming from the type of DOM that was used) or Hydrogen ions. At higher Me/C, the multi-valent metal coagulants combine with the DOM's negatively charged functional groups [11].

Previous research [4] has shown, that 0.06 is a critical value for the Me/C, as above it the Al-DOM complexes that precipitate are insoluble. This point is often reached on purpose in water treatment techniques and is called an enhanced coagulation (EnhCoag) process. In order to gain more efficient NOM removal, an excess dose of coagulant (more than what is needed for the baseline coagulation) is used together with changes in pH [5].

While we know which parameters influence flocculation, it is still unclear how the interplay of the different parameters (coagulant type, pH and Me/C) leads to the occurrence of the various precipitation mechanisms under different circumstances. Therefore, we must unravel the complex mechanisms controlling flocculation, which are fundamental for the optimisation of water treatment applications, or soil settings, where we are likely to encounter less constrained physico-chemical conditions. The goal of this work is to study the interactions between Al, Fe and Zr with DOM to form flocs. Through titrating each stock solution in a controlled manner, modelling the chemical speciation of the inorganic solutions, analysing the residual supernatant and employing electronic light scattering on the flocs, we strove to disentangle the processes controlling both the charge neutralisation and the sweep flocculation mechanisms.

2. Material and methods

2.1. Stock solutions

2.1.1. Dissolved organic matter (DOM)

In order to create the flocs in the laboratory, an easily accessible commercial fertilizer – HUMIN-P775 (which contains K) from *Humintech*, Germany – has been used, as it has a high density of carboxyl groups, which result in a high number of Me-DOM precipitates [7,28] and is suitable for geo-engineering studies [29].

The stock solution was prepared by dissolving the OM in MilliQ water, shaking it for 24 h and centrifuging it at high-speed (10,000 G) for 20 min. After that it was filtered through cellulose filters with a 0.45 µm pore size. The end concentration of this DOM solution was 0.16 molL⁻¹.

2.1.2. Coagulants

Three metallic coagulants have been chosen for these series of experiments: Al, Fe and Zr. Al and Fe can naturally be found in soils, such as Podzols, where they form Al/Fe-DOM precipitates and Zr is used in the water cleaning industry [25].

In our experiments, charge neutralisation and sweep flocculation were investigated. Therefore, Al chloride (AlCl₃·6H₂O), Fe chloride (FeCl₃·6H₂O) and Zr oxychloride (ZrOCl₂·8H₂O) – from *Merck*, Germany – were used to prepare the stock solutions, because the metals are present in their free cationic state in solution: +III for Al and Fe, and +IV for Zr. The stock solutions were prepared by dissolving a certain amount of each coagulant in water, at a concentration of 0.01 molL⁻¹.

2.2. MINTEQ

We applied Visual MINTEQ version 3.1, which is based on the original MINTEQA2 model (<https://vminteq.com/>; [30]) to model the pH-dependent inorganic solution speciation of Al, Fe and Zr. Visual

MINTEQ is a chemical speciation model [31], which can calculate the speciation of inorganic ions and complexes in natural waters, but also estimate the binding of ions to hydroxide surfaces and OM, using complexation models, such as NICA-Donnan [28,32].

Here it has been used to calculate the species distribution of the coagulants (Al, Fe and Zr) in water, and to estimate the amount that would bind to the DOM at 3 pH values, in which the proportion of the cationic form of each coagulants is expected to decrease and the proportion of hydroxides to increase. Zr-DOM interactions were not considered because speciation parameters for Zr are not included in the NICA-Donnan database (this is also why there are no saturation indexes for Zr in the *Supplementary Information*).

2.3. Titrations

In order to evaluate the interaction between the coagulants and the DOM, and the influence both the pH and the Me/C have, two sets of titrations were done. First, the coagulants – each Al, Fe and Zr in three different set-ups – were titrated into the DOM solution, which increases the Me/C. Second, the DOM solution has been separately titrated into each coagulant, which decreases the Me/C. In both scenarios, the pH has been measured throughout the whole titration and replicated three times.

The titrations were done using a graduated burette and a beaker on a magnetic shaker. Because of the avid stirring, flocs could not be formed during this experiment, but they usually do within a couple of minutes depending on the conditions [33], when the solution is left still, as the coagulants immediately attach to the available groups on the DOM.

2.4. Analysis on supernatant

Based on the results of the previous titrations, four pH (unchanged, 6, 4.5 and 1) and six Me/C (0.01, 0.02, 0.03, 0.04, 0.05 and 0.06) values were chosen to prepare 24 combinations for each of the coagulants. These Me/C values are critical points on the titration curves, where precipitation starts, is happening, and has happened for each of the coagulants. The pH values were chosen as realistic conditions for acidic soils (pH = 4.5; [34,35]), but also extreme conditions in which the coagulants would be present in different forms, i.e. as cations at pH = 1 and hydroxides at pH = 6 respectively, and the unchanged pH is used as a reference for the way the samples would have reacted, if we hadn't interfered with the solutions (see pH values in *Table S1* of the *Supplementary Information*). The solutions were mixed to the desired Me/C using the stock solutions, and then acidified using HCl or the pH was increased using NaOH.

An Inductively Coupled Plasma analyser with Optical Emission Spectrometer (ICP-OES; *Perkin Elmer*, Singapore) was used to measure the residual coagulant concentration in the supernatant – following [13] – and the Total Organic Carbon (TOC) analysis (*Elementar Analysensysteme GmbH*, Germany) measured the residual C from the DOM [36,37].

2.5. Analysis on flocs

Using the same solutions as for the previous experiment, here the flocs' size and surface charge were analysed. The size was measured with the Dynamic Light Scattering (DLS) method, and the zeta potential using the mixed-mode measurement-phase analysis light scattering (M3-PALS) technique on a Malvern Zetasizer Ultra device using the ZS XPLORER v1.2.0.91 software. The measurements were performed in disposable folded capillary cells DTS1070 with gold-coated electrodes designed for the combination of particle size and zeta potential measurements. Each zeta potential measurement was performed 5 times for each sample and each of these runs consisted of a maximum of 30 sub-runs. The DLS size measurements were conducted 5 times in back scattering detection angle at 174.7°, because this yielded the best data

for measuring different size groups in the suspension of this capillary cell compared to other or multiple detection angles.

The zeta potential, which reflects an average of the surface charge of a particle, can indicate which flocculation mechanism is dominant [38]. It is also important to measure the zeta potential of the DOM in reference conditions, as the surface heterogeneity of particles can create anomalies in the measurements [39].

3. Results

3.1. Modelling metal-DOM interactions with MINTEQ

3.1.1. Speciation modelling without DOM present

In this first scenario, the aim was to visualise how much of the inorganic ions (Al, Fe and Zr) are still present in cationic form at low pH values (0.5; 1; 2; 3; 4). All three coagulants have been taken in their free phase in water (Al^{3+} , Fe^{3+} and Zr^{4+}), and the part that is missing in the species distribution is the sum of all various dissolved hydroxylated species each coagulant can be present in, such as $\text{Al}(\text{OH})_2^+$ for example (see Fig. 4).

Based on these results, it is possible to predict which precipitation mechanism is favourable: rather charge neutralisation when the coagulants are in cationic form or sweep flocculation, when they are in dissolved hydroxyl complex form.

The model predicts that Al is mainly present in cationic form up until pH = 4, which coincides with previous findings [12]. Fe is predominantly present as Fe (III) up to pH = 2, until it drastically decreases to < 20 % at pH = 3. Zr on the other hand, is not to be found in its free ionic state, unless the pH is lower than 1.

3.1.2. Speciation modelling with DOM present

After modelling the species distribution for each coagulant in water, the specie distribution has been combined with a NICA-Donnan DOM phase in order to visualise the proportion of the metals that can potentially bind to the DOM, and the speciation in solution. Each of the three graphs per coagulant (Al and Fe only) shows the distribution between the cations, the hydroxides and the metals bound to the DOM for six Me/C values at three different pHs.

The species distributions do not always add up to a 100 %, as the Al or Fe is sometimes modelled to still be bound to chloride (Cl^-), which is

not relevant here and therefore left out (< 2 %). The Al-DOM and Fe-DOM fractions include flocs formed through CN and SF, therefore the charges are not indicated.

At pH = 1, Al is modelled to be mainly present in its cationic form: 80 % at Me/C = 0.01 to 95 % at 0.06 (see Fig. 5a). But as the pH increases, most of the Al is bound to DOM (see Figs. 5b and c), until no cations are left but some hydroxides form: 10 % at pH = 4.5 and 23 % at pH = 6 both for Me/C = 0.06.

Fe shows a roughly similar trend (see Figs. 5d, e and f) as Al, but with much less Fe(III) in solution to start with: 1 % at Me/C = 0.01 to 51 % at 0.06; and none left at pH = 4.5 or 6 for any Me/C. Similarly to Al, Fe starts appearing in its amorphous state, although its amount decreases: 15 % at pH = 4.5 and 12 % at pH = 6 both for Me/C = 0.06.

3.2. Titrations

As mentioned before, the following titrations (see Fig. 6) have been done to evaluate the influence of the coagulant dose – in other words the Me/C – on the pH. The initial pH values were 9.41 ± 0.34 for the DOM and 3.99 ± 0.54 , 2.80 ± 0.63 and 2.68 ± 0.62 for Al, Fe and Zr respectively.

Fig. 6a represents three replicates for each coagulant titrated into the DOM solution. Therefore, all curves started at a pH above 9, which is the pH of the DOM stock solution, with no addition of coagulant yet, so a Me/C = 0. The pH rapidly declined, as the coagulant stock solutions are very acidic, and stabilised at the pH of the coagulant's stock solution at a Me/C of approximately 0.05 for Al and Fe and 0.08 for Zr. The Zr curve also had a second inflection point at Me/C = 0.04 that was not present or to a much lower extent in the curves of the two other metals.

Fig. 6b shows the titrations done the other way around: the DOM solution was titrated into Al, Fe and Zr solutions respectively. This explains why none of the curves reach Me/C = 0. The goal of this experiment is to see, whether the same reactions can be obtained, if the solutions were mixed in any chosen order, which is crucial information not only to unravel underlying processes, but also for an eventual geo-engineering application. The gaps between the dots are different as it is difficult to reach the same doses experimentally, but overall a similar pH is reached at similar Me/C ratios, when titrated one direction or the other. The overall trends for each coagulant are alike, although some offsets in the inflection points of the curves are observed, depending on the direction of titration (Fig. 6a versus b).

3.3. Supernatant analyses

3.3.1. Residual Al, Fe and Zr

On Fig. 7a the residual Al at pH = 1 increased gradually, as the Me/C increased. The trends were almost the same for pH = 6 and unchanged pH, and similar but at lower concentration for pH = 4.5: the Al concentration increased to 3 mmol L^{-1} at Me/C = 0.02, but then gradually decreased to approximately 0.6 mmol L^{-1} at 0.05, and subsequently decreased to almost none left for pH = 6, although it increased again for pH = 4.5 and unchanged pH. After that the concentration in the supernatant started decreasing even though the added dose was increasing.

The residual Fe (see Fig. 7b) also showed an almost linear increase in molar Fe concentration as the coagulant was added, but lower than Al pH = 1. At pH = 4.5 and unchanged the residual Fe started decreasing after Me/C = 0.02 as the Me/C increases. The same happened at pH = 6, but starting at Me/C = 0.03 and with higher concentrations of residual Fe.

In contrast, the Zr concentrations were low or below detection limit at pH = 1 (see Fig. 7c), as there were no residues measured until Me/C = 0.04. At pH = 4.5, 6 and unchanged the Zr concentration increased until Me/C = 0.02 or 0.03 but then decreased with increasing Me/C.

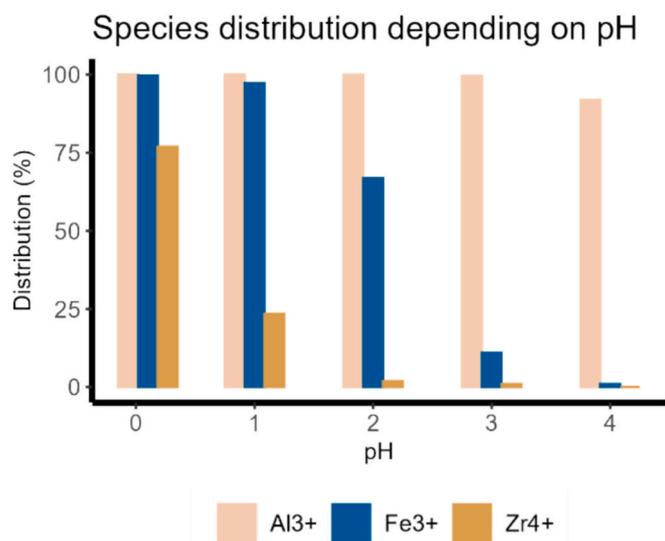


Fig. 4. Species distribution, as modelled with Visual MINTEQ, depicting percentage of metal coagulant present in free cationic state (Al^{3+} , Fe^{3+} and Zr^{4+}). The remainder of the metal is then present in hydrolysed states, including both ionic and precipitated state.

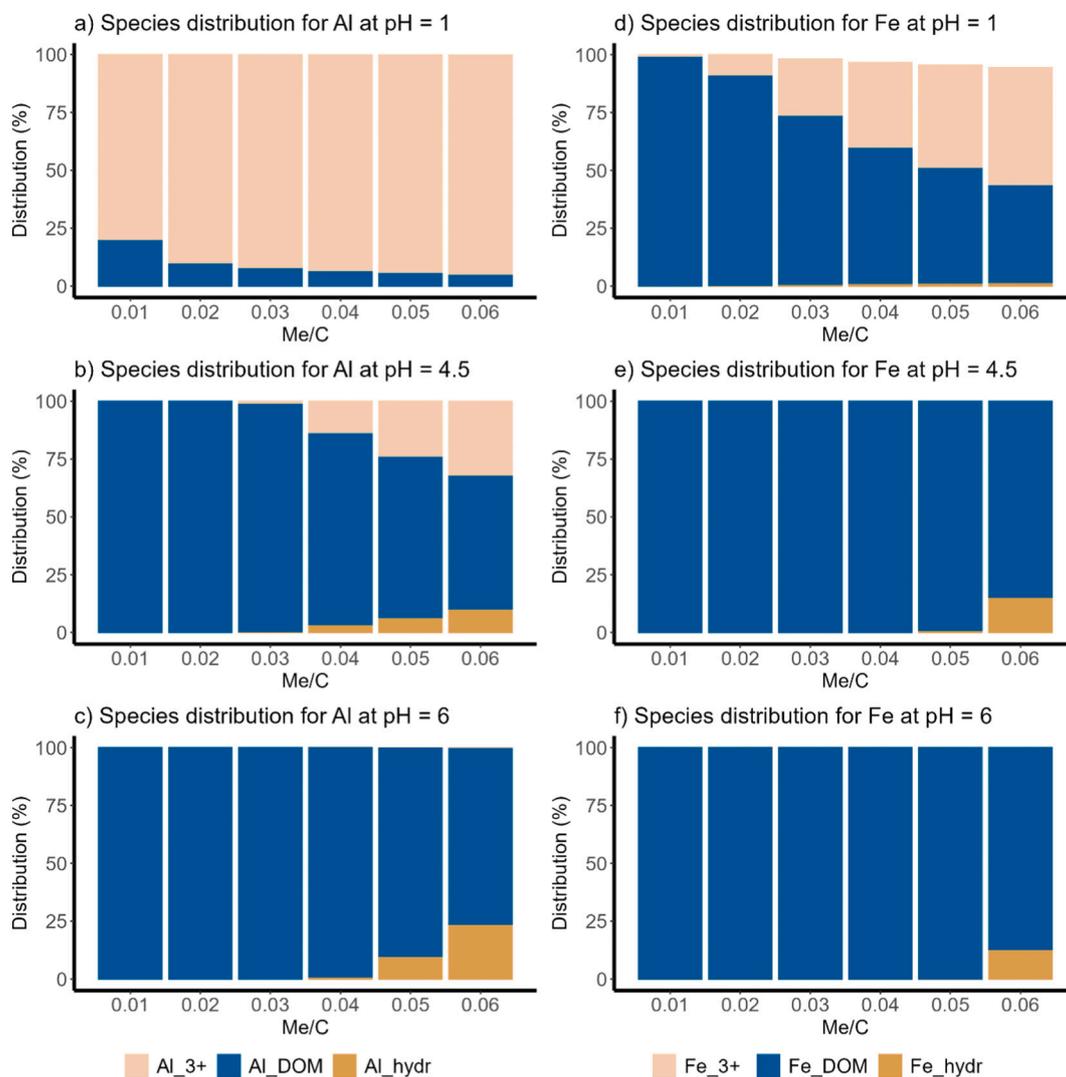


Fig. 5. These three species distributions, calculated with Visual MINTEQ, show the proportion of Al (a, b and c) and Fe (d, e and f) that either stays in its cationic form (Al³⁺ or Fe³⁺), binds with the DOM or precipitates as a hydroxide at pH = 1, 4.5 and 6.

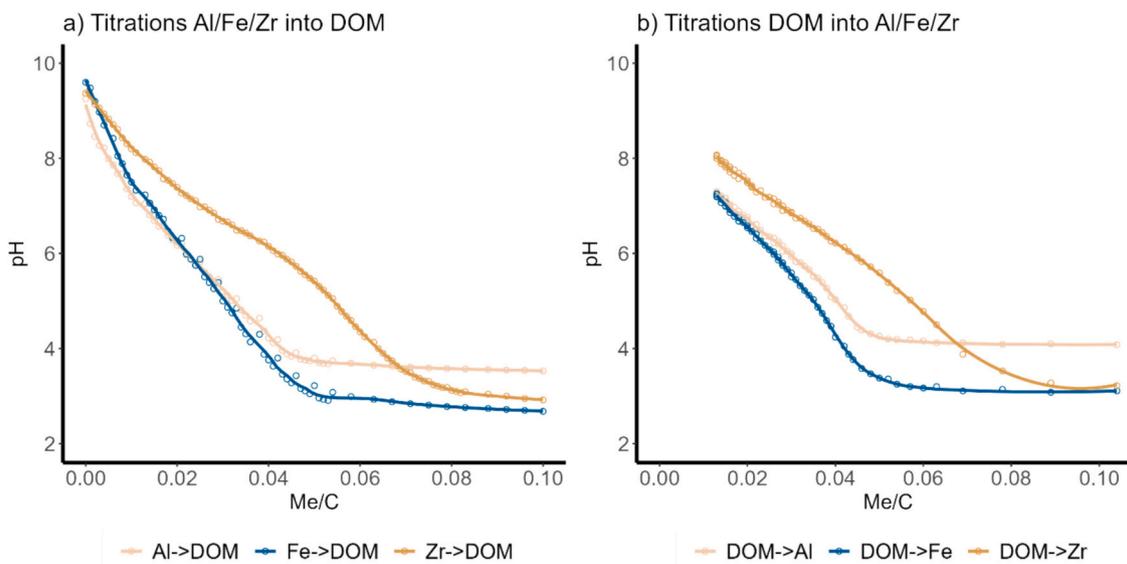


Fig. 6. Variations in pH as a function of increasing Me/C for Al, Fe and Zr; in Fig. 6a the metals were titrated into the DOM solution and in 6b DOM was titrated into the Me solutions. The hollow circles represent measurement points and the line is a loess smoothed fit curve.

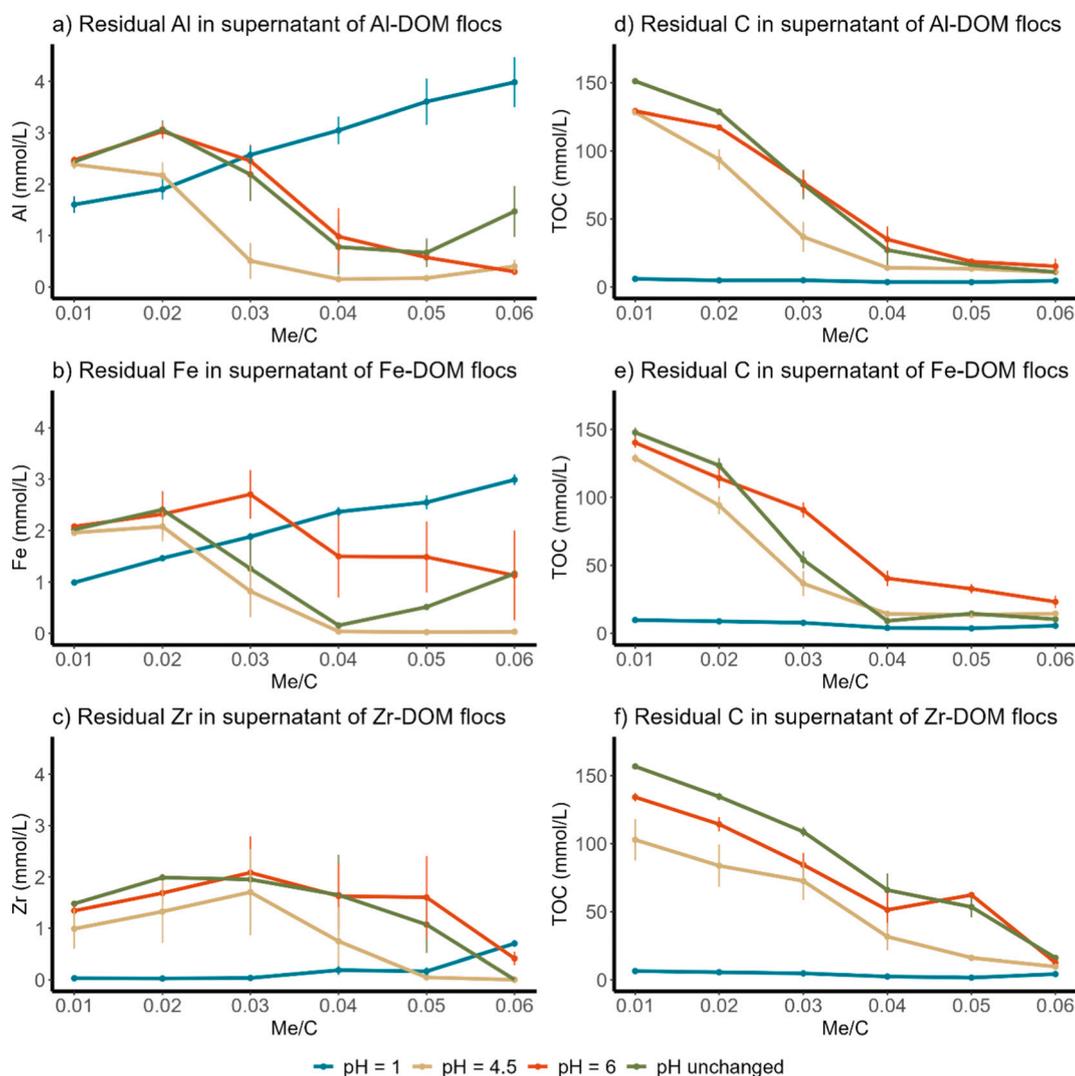


Fig. 7. Residual Al (a), Fe (b) and Zr (c) concentrations and residual C concentrations (d, e and f; TOC: Total Organic Carbon) in the supernatant of the floc solutions. The error bars indicate the standard error of the mean. (The pH values of the “pH unchanged” data set can be found in the *Supplementary Information*.)

3.3.2. Residual C

Fig. 7d, e and f display the residual C concentration in the supernatant of the floc solutions, which translates to the amount of DOM that has not reacted with the coagulant and is left in solution.

All three coagulants showed very similar trends. For pH = 4.5, 6 and unchanged pH, the residual C concentration starts at 150 mmol L⁻¹ and diminishes until it is below 25 mmol L⁻¹, which indicates that as the amount of coagulant increases, a larger proportion of the DOM can react with it and ultimately settles as freshly formed flocs. On the other hand, at pH = 1 the C concentration never exceeds 10 mmol L⁻¹. This is explained by the choice of DOM, which was a commercial humic acid, and humic acid is operationally defined as insoluble at pH = 1 [40].

3.4. Analyses of flocs

Analyses of the properties of the precipitated flocs (see Fig. 8) give us insight on the impact of pH and Me/C on the floc size and surface charge [38].

3.4.1. Size

As shown in Fig. 8a, b and c, overall the size of the flocs increased as the Me/C increased for all three coagulants. For Al, at pH = 6 the flocs slowly reached a size of approximately 2100 nm at the highest Me/C. At pH = 4.5 and unchanged the flocs formed a diameter of about 7500 nm,

and at pH = 1 the size varied between 2400 and 4000 nm.

For Fe, the floc diameter stayed below 500 nm until Me/C = 0.03, but then drastically increased at an unchanged pH until 13,000 nm at Me/C = 0.06, up until 5700 nm at pH = 4.5 and stayed lower than 900 nm at pH = 6. At pH = 1 the floc size decreases from 7000 nm at Me/C = 0.01 to 3600 nm at 0.06.

For Zr, the floc diameter stayed below 400 nm until Me/C = 0.04, but did not increase much more until Me/C = 0.06: 3900 nm for pH = 4.5, 3500 nm for 6 and 6000 nm at an unchanged pH. At pH = 1 the diameter of the Zr-DOM flocs increased from 6500 nm at Me/C = 0.01, to 12000 nm at 0.03, and decreased again to 6000 nm at 0.06. Table 1 shows the size and zeta potential measurements of the DOM particles for the different stock solutions, without any metal solution added (Me/C = 0).

3.4.2. Zeta potential

Fig. 8d, e and f present the global zeta potential of the particles over the course of the experiment. If the absolute zeta potential is less than ±30 mV, then the particle is considered less stable [41–44] and more prone to aggregation due to less strong repulsive forces around it, which won't preserve the particle from collisions that can lead to uniting with other particles and hence, forming a larger aggregate [39]. The zeta potential of the reference DOM solution was at -62.5 ± 3.9 mV, which explains why each of the curves started at a strong negative value for a Me/C of 0.01.

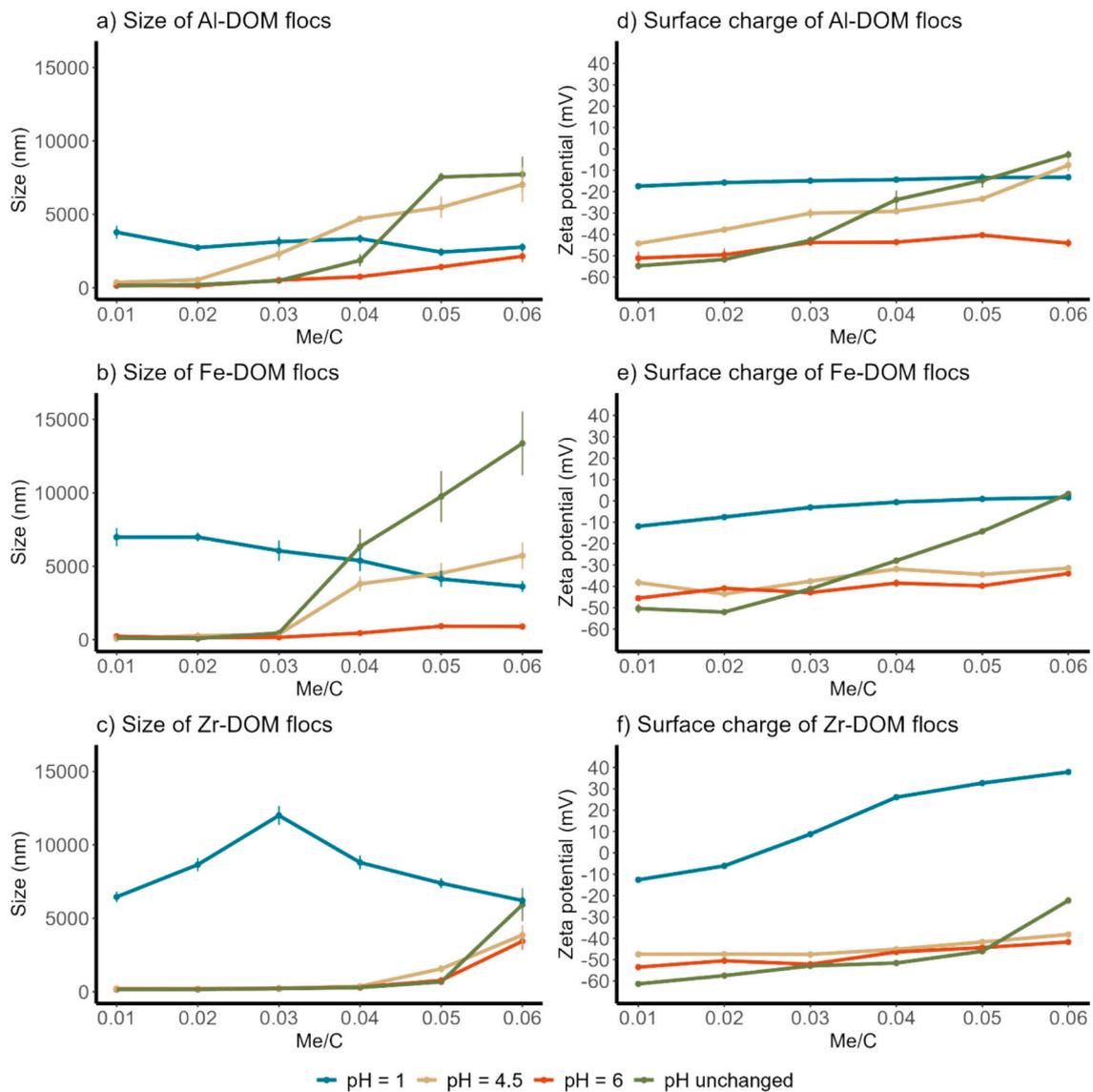


Fig. 8. Size (a, b and c) and surface charge (d, e and f) measurements of the Al-, Fe- and Zr-DOM flocs. The error bars indicate the standard error of the mean. (The pH values of the “pH unchanged” data set can be found in the *Supplementary Information*.)

Table 1

Size and surface charge of DOM particles in pH-(un)-adjusted stock solutions as references. (* At pH = 1 DOM coagulates with H^+ and settles in its solid phase.)

	Size	Zeta potential
pH unchanged	190 ± 6 nm	-62 ± 4 mV
pH = 6	223 ± 12 nm	-52 ± 2 mV
pH = 4.5	148 ± 31 nm	-48 ± 5 mV
pH = 1	2239 ± 343 nm*	-22 ± 1 mV

In Fig. 8d, all zeta potentials were negative for Al, but at pH = 1 the curve was mostly steady within -18 and -13 mV, because the surface charge of the DOM is neutralised by H^+ and the DOM is present as a flocc. At pH = 6 the curve slightly increased but stayed between -52 and -40 mV. At pH = 4.5 and unchanged, the zeta potential increases (i.e. becomes less negative) as the Me/C increased, respectively starting from -45 and -55 mV at Me/C = 0.01 and getting to -7 and -2 mV at 0.06.

The Fe-DOM flocs showed similar trends for each pH (see Fig. 8e), with a slow increase for pH = 1, as the positive values are reached at Me/C = 0.03 and continued to increase until 2 mV. At pH = 4.5 and 6 the zeta potentials intertwined at Me/C = 0.02 but respectively increased

from -39 to -31 mV and from -46 to -33 mV. The surface charge at unchanged pH increased linearly from -52 at Me/C = 0.02 to 3 mV at Me/C = 0.06.

The almost linear increase in surface charge at pH = 1 was even steeper for Zr on the Fig. 8f, as it started at -13 mV and reached 38 mV at Me/C = 0.06, which is the highest positive value reached for all coagulants and is outside of the stability range. All other curves stayed at a low negative value over all ratios, with just one steep increase for the unchanged pH at Me/C = 0.06 to -22 mV.

4. Discussion

Flocs are formed through a precipitation process performed in two steps: first, the solution is rapidly mixed to destabilise the particles, and then during flocculation, the solution is slowly mixed, so that the coagulants (Al, Fe or Zr) can bind with the DOM and form precipitates, which subsequently collide with each other and form larger structures [5,8]. This process is used in water treatment, where excess coagulant is being added so that the flocs can settle and be filtered out to remove NOM [6,7], but also to reduce soil permeability by clogging soil pores [4].

However, there are various flocculation processes, that are influenced by different parameters, such as CN and SF that are pH-dependent, and bridging that is due to polymeric coagulants. This study has aimed to understand the influence of the choice of coagulants, the pH and the Me/C on the efficiency of the two flocculation processes CN and SF.

As the pH defines the coagulants' charge [12], certain hypotheses were formed: (1) there must be an optimum range for the Me/C, in which flocs start to form but the coagulant is not yet added in excess; (2) if we tried to form flocs in extreme acidic conditions, we must be able to form them through CN for all coagulants; (3) as Zr is a heavier element than Al and Fe, with a higher positive charge, it must have a different behaviour as well; and (4) if the flocculation process is pH dependent, then the floc size must be too.

4.1. Precipitation and excess of coagulant

The increase in coagulant concentrations that can first be observed in the supernatant analysis (see Fig. 7) indicates, that the Me/C is initially too low to make flocculation possible. The pH being very high at the beginning of the titrations because of the DOM stock solutions, suggests that hydrolysis does not take place, but that the ion is immediately absorbed onto the DOM regardless of the metal type. Both titration methods (see Fig. 6) show that hydrolysis can only take place after the charge on the flocs has been completely neutralised or at high background pH. The pH is high because the affinity between H^+ and DOM is stronger than K^+ : upon dissolving the K-DOM, K^+ is exchanged for H^+ and HO^- remains in solution, compensating the charge of the released K^+ . By adding the coagulant at relatively high concentrations compared to the available H^+ in solution, two processes will simultaneously reduce the pH: by adding H^+ with the coagulant in an unbuffered system and by exchanging H^+ for the coagulant. This process continues until the surface charge of the DOM is completely neutralised.

Moreover, the titration experiment has also shown that the floc suspensions stabilise when the flocs have precipitated and the DOM can no longer bond with the coagulants, which are therefore added in excess and are influencing the solutions' pH to their stock solutions' pH. We therefore assume, for $pH > 1$, that the flocs are fully formed by a Me/C of 0.05–0.06 for Al and Fe – which coincides with literature [4] – and 0.08 to 0.09 for Zr. Therefore, any addition of coagulant would be excessive. Yet at unchanged pH, coagulant concentration starts increasing again at Me/C = 0.05 for Al and Me/C = 0.04 for Fe, which suggests that more coagulant can bound to the DOM, when the pH is altered.

For water treatment plants it is interesting to use the coagulant doses in excess, to make sure all DOM has precipitated with it and settled, which makes filtration easier. But in soil science, the goal is to form flocs of a certain size and strength, and to limit the costs and any environmental hazard, as excess coagulant would pollute.

4.2. At $pH = 1$, CN by protons and not metal coagulants

As mentioned above, in unconstrained experiments where the coagulant is added to a solution containing DOM, the titration curves settle at the coagulants' stock solution pH. They therefore never reached $pH = 1$, which is an extreme scenario, using the current stock solutions. This means that CN never naturally occurs for Zr and is minimal for Fe in the environment, based on the results gotten from the Visual MINTEQ model (see Figs. 4 and 5). The solutions need to be artificially acidified to get the coagulants in their cationic form, which contrastingly leads the DOM to precipitate and settle if the solution is not mixed [40].

The results of the supernatant analysis in the following experiment imply that Al and Fe have not bound to DOM at $pH = 1$ – which cannot be confirmed nor denied by the TOC analysis (see Figs. 7d, e and f) – and therefore suggest that CN occurs by H^+ and cannot be reached this way by the coagulants. In contrast with the other pH curves, the zeta potential measurements (see Figs. 8d, e and f) for $pH = 1$ do not show low

negative values at Me/C = 0.01 to resemble the DOM surface charge, but have a particle surface charge within -20 and -10 mV and rather little variations over all measurements. For Zr – and a little for Fe – the zeta potential increases though, which is probably related to their strong positive charges and increase the average measured value.

Due to changes in human activities, the composition of NOM and DOM can change – in particular phenolic and carboxylic groups, to which the coagulants bind [26] – and therefore influence the precipitation behaviour in nature.

4.3. Different behaviour for Zr

In opposition with the previous findings, Zr appears to react with DOM at $pH = 1$. But given that CN was expected at an acidic pH and the model showed that Zr basically does not exist in cationic form, it might be, that Zr hydroxides present at such low pH enmesh the DOM particles, which Al and Fe cannot do, as Visual MINTEQ shows. Overall, we only see SF as a process for Zr.

Although the titrations indicate an excess in Al and Fe above a Me/C of 0.05–0.06, Zr-DOM appear to form from Me/C = 0.03 on, and Zr is not excessively added throughout the other experiments. While Zr does not appear in cationic form, its 4 valence electrons make it possible for the Zr hydroxides to be charged positively and this explains the high zeta potential at $pH = 1$, but also the low negative surface charge at the other pH values, because most flocs have not formed yet.

4.4. Floc size is pH dependent

The general trend for the size measurements is an increase from when the Me/C is sufficiently high to support flocculation. For Al, the measured flocs increase in size from the lowest Me/C (see Fig. 8a). For Fe, flocs start forming at Me/C = 0.03, but form the biggest flocs with a diameter of 13,000 nm on average at $pH = 4.5$ (see Fig. 8b). The Zr-DOM flocs only start to form at a Me/C of 0.04–0.05 (see Fig. 8c), but based on the titration results (see Fig. 6), the flocculation process goes above Me/C = 0.06 for Zr, and would probably form even bigger flocs than Fe at Me/C = 0.09.

The fact the Fe – and Zr – form the largest flocs, supports the hypothesis, that SF forms bigger flocs than CN, as mainly hydroxides are present for these coagulants at pH values of 4.5, 6 or even unchanged pH (see degrees of supersaturation in Tables S2 and S3).

The scenario is very different at $pH = 1$: at Me/C = 0.01 the particle sizes are already relatively high, which supports the conclusion, that no flocs were formed with the coagulants and only the H-DOM floc sizes were measured. Although the size measurements slowly decrease for Al and Fe, it increases for Zr until Me/C = 0.03 and then decreases again to reach the same size at 0.06 than at 0.01. The increase may suggest flocculation of Zr-DOM, but then a similar decrease than for Al and Fe, as excess coagulant is added.

5. Conclusion

The goal of this study has been to understand the major influence pH has on the various processes that lead to floc formation. Although CN was expected to be the main flocculation process at very acidic pH, as the coagulants are present in their cationic form, this could not be proven, as the DOM used in these experiments precipitates and settles at $pH = 1$; except for Zr, with which it reacts. Yet the modelling exercise has shown that Zr almost never occurs in its cationic form, and therefore it is flocs formed through SF that were measured.

At higher pH, flocs start forming at a Me/C of approximately 0.02 for Al and Fe, and 0.03–0.04 for Zr. The flocs have then fully formed and the coagulants are added in excess above a Me/C of 0.05–0.06 for Al and Fe, and 0.08–0.09 for Zr. The flocs' diameter becomes larger, as the Me/C increases, until excess is reached.

These experiments have also shown, that altering the pH of the floc

solutions gives the possibility to control the flocculation processes. Using this, precipitation can be delayed and floc size can be modified, which is a useful tool for geo-engineering purposes.

CRedit authorship contribution statement

Edith J.S. Eder: Writing – original draft, Methodology, Investigation, Data curation, Conceptualization. **Alemeh Karami:** Writing – original draft, Investigation, Data curation. **Timo J. Heimovaara:** Writing – review & editing, Supervision. **Mariëtte Wolthers:** Writing – review & editing, Supervision. **Boris Jansen:** Writing – review & editing, Supervision, Conceptualization.

Declaration of competing interest

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: Edith Eder reports financial support was provided by Institute for Biodiversity and Ecosystem Dynamics (IBED). Edith Eder reports financial support was provided by TAUW. Edith Eder reports financial support was provided by Heijmans. If there are other authors, they declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.jwpe.2025.107126>.

Data availability

Data will be made available on request.

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