Sulfate precipitation treatment for NOM-rich ion exchange brines

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Ion exchange (IEX) resins can remove natural organic matter (NOM) from drinking water sources. However, the IEX system produces a waste brine rich of sodium, chloride, NOM and sulfate. The treatment of the waste brine aims to recover a clean solution rich of sodium chloride, that can be reused to regenerate IEX resin. Previous research showed that ceramic nanofiltration partially removes NOM from the waste brine, but sulfate removal requires additional treatment. Sulfate removal by chemical precipitation was previously studied either on brines with low NOM concentrations or water with low concentrations of NOM and salts. The current work focussed on sulfate removal from NOM-rich brines by chemical dosing of (1) BaCl₂ resulting in precipitation of barite (BaSO₄), and (2) CaCl₂, Ca(OH)₂ and NaAlO₂, resulting in precipitation of calcium sulfate and, subsequently, ettringite (Ca₆Al₂(SO₄)₃(OH)₁₂). Additionally, the effect of NOM on SO₄²⁻ removal was studied. Modelling and batch experiments were conducted with IEX and synthetic brines within the typical ion strength range of 0.1 to 1 M. With doses of 2.2 g of BaCl₂ per g of initial sulfate, BaSO₄ precipitation removed more than 83 percent of sulfate, resulting in final concentrations below 0.4 g/L even in the presence of NOM. However, NOM inhibited the precipitation of calcium sulfate and, subsequently, ettringite. With doses of 1.3 g of CaCl₂, 0.5-0.7 g of Ca(OH)₂ and 0.4-0.6 g of NaAlO₂ per g of initial sulfate, calcium sulfate and ettringite precipitation removed between 8 and 95 percent of sulfate from NOM-rich brines, resulting in final concentrations between 0.8 and 2 g/L. As a reference, NOM-free brines required doses of 1.3 g of CaCl₂, 0.2-0.7 g of Ca(OH)₂ and 0.1-0.6 g of NaAlO₂ per g of initial sulfate for 89 to 99 percent of sulfate removal, resulting in final concentrations of 0.2 g/L. The inhibition might be attributed to covering of crystal sites by NOM molecules, and to NOM coagulation with aluminum.

1. Introduction

Anion exchange (IEX) can effectively remove negatively charged natural organic matter (NOM) during drinking water treatment [1]. In IEX processes, resins are reused after cleaning with an electrolyte regenerant solution. In IEX for NOM removal, the regenerant solution is usually NaCl [2-4]. The regenerant solution is then reused several times before disposal, which increases the concentrations of NOM and anions, like sulfate (SO₄²⁻) [3-5]. The composition of spent IEX brines depends on the quality of the water to be treated, the affinity of negatively charged components with the resin, and the specific IEX system operation. Spent IEX brines obtained by four pilot and full-scale installations had concentrations between 0.04 and 1.6 g/L of dissolved organic carbon (DOC), and concentrations of chloride (Cl⁻) and SO₄²⁻ in a broad range of 2.6 to 19.1 g/L and 0.3 to 24.3 g/L, respectively

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lower temperatures and NaCl concentrations than anhydrite. Gypsum was found to precipitate below 25 °C and with NaCl concentrations below 4 M at 25 °C [11], and is therefore potentially relevant for treatment of IEX spent regenerant, that has NaCl concentrations below 2 M [2–4]. A disadvantage of gypsum is its high solubility product, i.e. a log Ksp of −4.31 at 25 °C [12], and, thus, the required low SO$_4^{2−}$ concentrations cannot be reached. BaSO$_4$ has a much lower solubility product, i.e. a log Ksp of −9.96 at 25 °C [12], but it requires the dosage of toxic BaCl$_2$. An alternative is ettringite precipitation. Ettringite is stable at high alkaline conditions, with an optimum pH close to 12 [13], and its solubility product is low, i.e. log Ksp of −44.91 at 25 °C [14]. SO$_4^{2−}$ removal from brines by ettringite precipitation has been frequently studied, mostly subsequent to calcium sulfate precipitation [15–19]. Generally, very low concentrations of SO$_4^{2−}$ could be obtained by chemical precipitation. However, to the authors’ knowledge, brines with high NOM concentrations were not studied before.

Based on other applications, some NOM interference on chemical precipitation could be expected. NOM and polynucleic acid, which is a synthetic surrogate of the fulvic fraction of humic substances [20], for instance, has been found to inhibit chemical precipitation in studies for water recycling in cooling towers [21,22]. In addition, Banz and Luthi [21] found that NOM of wastewater origin inhibited calcium sulfate precipitation, which was attributed to complexation of Ca$_{2+}$ and NOM. However, NOM and salts concentrations in cooling tower water are much lower than in spent IEX brine and different mechanisms might be involved.

In the present study we therefore studied chemical precipitation as an alternative to remove SO$_4^{2−}$ from NOM-rich spent IEX brines. In particular, the focus was on the performances of BaSO$_4$ precipitation, and the combination of calcium sulfate and ettringite precipitation to obtain low concentrations of SO$_4^{2−}$ . The impact of NOM on chemical precipitation in brines and the mechanisms involved were also investigated. We studied spent and synthetic brines with varying NOM, sodium (Na$^+$), Cl$^−$ and SO$_4^{2−}$ concentrations within the typical ion strength range of 0.1 to 1 M, by means of laboratory experiments and modelling.

2. Materials and methods

2.1. Analyses for NOM and ions’ concentrations

NOM was measured as dissolved organic carbon (DOC) by a total organic carbon analyser (TOC-VPCH, Shimadzu, Japan) after filtration of the sample. For some of the analyses, the Cl$^−$ and SO$_4^{2−}$ concentrations were determined by ionic chromatography using an ion-exchange column (A Supp 150/4.0, Metrohm AG, Switzerland). Other experiments required direct measurement results for SO$_4^{2−}$. Therefore, test cell kits (NOVA 60 Spectroquant, Merck, Germany; or LCK 311/153 with spectrophotometer DR 3900, Hach, Germany) were used. For both DOC and anion measurements, the samples were filtered with 0.45 µm filters and diluted when needed.

2.2. Brines

2.2.1. Preparation of synthetic brines

For the synthetic brines, Na$_2$SO$_4$ and NaCl were weighted and dissolved in demineralized water. The pre-set anion concentrations divided the synthetic brines into two groups: (1) low concentration brines, in the range of 0.2 to 5 gCl$^−$/L and 0.2 to 2 gSO$_4^{2−}$/L; and (2) high concentration brines, in range of 9 to 18 gCl$^−$/L and 8 to 16 gSO$_4^{2−}$/L. In addition, for the synthetic brines with NOM, concentrated NOM (HumVi, Vitens) was added to obtain concentrations of 0.5 and 2 gDOC/L. The NOM of HumVi has groundwater origins and was recovered from spent IEX regenerant brine. HumVi was also used and described in previous research [10,23].

2.2.2. Characterisation of spent IEX brine

A spent IEX brine was provided by a drinking water facility in Sweden (Sweden brine). This facility piloted suspended ion exchange (SIX®), as described by Galjaard and Koreman [24]. The NOM of the brines was characterized using liquid chromatography-organic carbon detection (LC-OCD), according to the procedure from Huber et al. [25]. LC-OCD gave the chromatographic fractionation of organic carbon (CDOC), being the sum of the concentrations of five NOM fractions. In decreasing size, the fractions are biopolymers (BP), humic substances (HS), building blocks (BB), low molecular weight acids (LMWα) and neutrals (LMWn) [25].

2.3. Precipitation experiments

Sweden brine and the synthetic brines of Table 1 were tested in duplicate for BaSO$_4$ precipitation. Samples for NOM and anion measurements were taken before and after precipitation. First, 150 mL of brine in a plastic container was stirred on a magnetic plate (speed 9%, Labinco, the Netherlands). The acidity (measured by Multi 3630 with SenTix 940 electrode, WTW, Germany) was adjusted to pH 8 by adding 0.1 M NaOH, to the brines. While stirring, BaCl$_2$·2H$_2$O dissolved in ultrapure water, was added in the BaSO$_4$ moles proportion of 1:1, considering the pre-set SO$_4^{2−}$ concentration of the synthetic brines and the initial SO$_4^{2−}$ concentration measured in the Sweden brine. After the BaCl$_2$·2H$_2$O was added, the brines were mixed for 30 min, and the precipitate was allowed to settle for another 30 min. The supernatant was then filtered to collect the samples to be analysed, according to Section 2.1.

Sweden brine and the synthetic brines of Table 2 were tested for calcium sulfate precipitation and subsequent ettringite precipitation, similar to the work of Almasri et al. [15]. All the experiments were in duplicate. Samples for NOM and anion measurements were taken before calcium sulfate precipitation, and before and after ettringite precipitation. For the calcium precipitation, 150 mL of brine in a plastic container was stirred on a magnetic plate (at 9% speed, Labinco, the Netherlands). While stirring, CaCl$_2$ was added in the CaSO$_4$ moles proportion of 1:1, considering the pre-set SO$_4^{2−}$ concentration of the synthetic brines and the initial SO$_4^{2−}$ concentration of the Sweden brine. The plastic container was closed directly after the addition of CaCl$_2$, and the stirring continued for 2 h. The pH before the addition of CaCl$_2$ and after precipitation was 7.6 ± 1.2 and 8.3 ± 0.7 (average ± standard deviation), respectively. The solid content in the plastic container after calcium sulfate precipitation was separated using gravity glass fibre filters. The supernatant was then filtered to collect the samples to be analysed, according to Section 2.1. For the subsequent ettringite precipitation, 115 mL of the filtered brine was again stirred on the magnetic plate. While stirring, NaAlO$_2$ and Ca(OH)$_2$ were added as solids in the Al:SO$_4$ and CaSO$_4$ moles proportion of 0.67:1 and 1:1, respectively, considering the concentration of the brines after gravity filtration. Afterwards, the stirring continued for 2 h. The supernatant was then filtered to collect the samples to be analysed, according to Section 2.1. The pH before the addition of NaAlO$_2$ and Ca(OH)$_2$ and after precipitation, was 8.2 ± 0.6 and 11.8 ± 0.1 (average ± standard deviation), respectively. The final

### Table 1

| Brine              | Ionic strength, IS | Cl$^−$ (g/L) | SO$_4^{2−}$ (g/L) | NOM (gDOC/L) |
|--------------------|--------------------|--------------|------------------|--------------|
| 1. 0gNOM/L-low IS | 0.1                | 1.8          | 1.6              | 0            |
| 2. 0gNOM/L-mid IS | 0.5                | 9            | 8                | 0            |
| 3. 0gNOM/L-high IS| 1                  | 18           | 16               | 0            |
| 4. Sweden brine    | −0.2               | 5            | 2                | 0.5          |
pH was in the range for ettringite formation according to Almasri et al. [15] without further adjustment, except for Sweden brine. For Sweden brine, the pH before ettringite precipitation was increased from 8.1 to 11.9 with addition of 1 M NaOH. The chemicals used for the precipitation experiments have a purity ≥ 93 percent.

2.4. PhreeqC model

The results of the precipitation experiments of the synthetic brines without NOM were compared to the results modelled with PhreeqC, a geochemical modelling software. Solutions with high salinity can be modelled using the Pitzer database, as an alternative for the default PhreeqC database [26]. The PhreeqC script for calcium and ettringite precipitation was validated using the data from Almasri et al. [15]. According to the reasoning in Chapter 1, the calcium sulfate precipitate in the model was gypsum. Our scripts of the models and their validation are presented in the Supplementary Information.

3. Results and discussion

3.1. Brines characteristics

The NOM in the Sweden brine and in the synthetic brines consisted mostly of HS and BB (Table 3), because these fractions are preferentially removed by IEX from natural water [27–30].

3.2. Modelling of sulfate precipitation with BaSO₄, calcium sulfate and ettringite

The scripts for the PhreeqC model, and the procedure of its validation are presented in the Supplementary Information. Model simulations are shown in Figs. 1–3, including the validation points of BaSO₄ and calcium sulfate precipitation. The model shows that, in Na₂SO₄ solutions with an ionic strength of 0.1 to 1 M, SO₄²⁻ precipitation with calcium sulfate depends on the initial SO₄²⁻ concentration (Fig. 1). The low SO₄²⁻ removal at low ionic strength is explained by the relatively high solubility product of calcium sulfate, that puts a theoretical limit on the achievable minimum concentration of SO₄²⁻ to 1.5 g/L [31]. In the same SO₄²⁻ range, precipitation with BaSO₄ and ettringite, that have low solubility products, only depends on stoichiometry (Figs. 2 and 3).

Table 2 Pre-set concentrations of synthetic brines tested for calcium sulfate and subsequent ettringite precipitation experiments.

| Brine                        | Ionic strength, IS (M) | Cl⁻ (g/L) | SO₄²⁻ (g/L) | NOM (gDOC/L) |
|------------------------------|------------------------|-----------|-------------|--------------|
| 0gNOM/L-low IS               | 0.2                    | 5         | 2           | 0            |
| 0gNOM/L-high IS              | 1                      | 18        | 16          | 0            |
| 0.5gNOM/L-high IS            | 1                      | 18        | 16          | 0.5          |
| IS                           | 0                      | 10        | 10          | 0            |
| 2gNOM/L-high IS              | 1                      | 18        | 16          | 2            |
| Sweden brine                 | ~0.2                   | 5         | 2           | 0.5          |

Table 3 LC-OCD fractionation of NOM in HumVi (used for the synthetic brines), NOM in the Sweden brine, given as carbon percentage of the CDOC.

| NOM sample | Biopolymers | Humic Substances | Building Blocks | Low molecular weight neutrals <350 Da | Low molecular weight acids <350 Da |
|------------|-------------|------------------|-----------------|--------------------------------------|----------------------------------|
|            | >=20,000 Da | -1000 Da 300-500 Da |                |                                      |                                  |
| HumVi      | 0.0%        | 88.7%            | 6.8%            | 4.5%                                 | 0.0%                             |
| Sweden brine | 0.3%   | 74.7%            | 16.0%           | 9.0%                                 | 0.0%                             |
the synthetic brines without NOM was above 98 percent, resulting in SO\textsubscript{4}\textsuperscript{2-} concentrations below 0.2 g/L (Table 4). Table 4 includes the SO\textsubscript{4}\textsuperscript{2-} concentration of Sweden brine before and after precipitation with BaSO\textsubscript{4}, and for the modelled brine without NOM as a reference. The SO\textsubscript{4}\textsuperscript{2-} of Sweden brine decreased by 84 percent, from 2 to 0.3 g/L, showing that the presence of NOM slightly inhibited BaSO\textsubscript{4} precipitation, probably attributed to the antiscalant properties of NOM [32,33]. During BaSO\textsubscript{4} precipitation of Sweden brine, also NOM was removed by 23 percent, which could be a potential problem in case NOM recovery is desired.

Another application issue is linked to the toxicity of barium. The toxicity is linked to its chemical form [42]. In particular, barium salts with low solubility, such as BaSO\textsubscript{4}, are generally considered less dangerous than free Ba\textsuperscript{2+} and readily soluble barium salts. Therefore, residual Ba\textsuperscript{2+} in the treated brine should be measured. The EPA drinking water standard for barium from 2002 was 2 mg/L [43]. However, ecotoxicity studies derived lower limits for environmental quality standards [44]. In the Netherlands, the maximum concentration of Ba\textsuperscript{2+} in surface water intended for drinking water production is 200 µg/L [45].

### 3.4. SO\textsubscript{4}\textsuperscript{2-} removal and effect of NOM during calcium sulfate and ettringite precipitation

Calcium sulfate and subsequent ettringite precipitation without NOM, removed 89 to 99 percent of SO\textsubscript{4}\textsuperscript{2-}, resulting in a final SO\textsubscript{4}\textsuperscript{2-} concentration of 0.2 g/L for synthetic brines of both low and high initial SO\textsubscript{4}\textsuperscript{2-} concentrations (1.8 to 14.8 g SO\textsubscript{4}\textsuperscript{2-}/L, with ionic strength between 0.2 and 1 M). However, the presence of NOM affected the precipitation (Figs. 4 and 5).

At low initial SO\textsubscript{4}\textsuperscript{2-} concentration (Fig. 4), calcium sulfate precipitation removed only <7 percent of SO\textsubscript{4}\textsuperscript{2-} for both synthetic brine without NOM and Sweden brine, due to high solubility of calcium sulfate (see Section 3.2). However, NOM in Sweden brine inhibited the subsequent ettringite precipitation, resulting in an overall SO\textsubscript{4}\textsuperscript{2-} removal of only 7.5 percent and a final SO\textsubscript{4}\textsuperscript{2-} concentration of 1.7 g/L.

At high initial SO\textsubscript{4}\textsuperscript{2-} concentration (Fig. 5), calcium sulfate precipitation removed 75 percent of SO\textsubscript{4}\textsuperscript{2-} from the synthetic brine without NOM. However, calcium sulfate precipitation was inhibited by NOM, and the average removed SO\textsubscript{4}\textsuperscript{2-} dropped to 35 and 6 percent in the synthetic brines with 0.5 and 2 gDOC/L, respectively. Similar to the case of BaSO\textsubscript{4}, inhibition of calcium sulfate precipitation by NOM was attributed to the antiscalant properties of NOM [34,35]. Due to the fact that calcium sulfate precipitation only removed 3 to 4 percent of NOM from the synthetic brines, SO\textsubscript{4}\textsuperscript{2-} removal by subsequent ettringite precipitation was inhibited by NOM as well. The dose of chemicals for ettringite precipitation was dependent on the remaining SO\textsubscript{4}\textsuperscript{2-} concentration after calcium sulfate precipitation. Therefore, considerably more NaAlO\textsubscript{2} and Ca(OH)\textsubscript{2} were dosed in the NOM-rich synthetic brines than in the brine without NOM (Fig. 5). Nevertheless, the overall SO\textsubscript{4}\textsuperscript{2-} removal was between 86 and 95 percent, although the final SO\textsubscript{4}\textsuperscript{2-} concentrations for the NOM-rich synthetic brines were still above 0.8 g/L.

The overall NOM removal from the NOM-rich brines was between 23 and 67 percent (Table 5). The calcium sulfate precipitation step only removed between 3 and 11 percent of NOM. The ettringite precipitation step removed 14 percent of the residual NOM from Sweden brine with low initial SO\textsubscript{4}\textsuperscript{2-}, and between 51 and 65 percent of the residual NOM from the two NOM-rich synthetic brines with high initial SO\textsubscript{4}\textsuperscript{2-}, likely due to coagulation of NOM by NaAlO\textsubscript{2} [36,37].

Table 4 summarises the initial NOM/sulfate ratio of the brines, the

| Brine for BaSO\textsubscript{4} precipitation | Ionic strength, IS (M) | Initial SO\textsubscript{4}\textsuperscript{2-} (g/L) | Final SO\textsubscript{4}\textsuperscript{2-} (g/L) | Initial NOM (gDOC/L) | Final NOM (gDOC/L) |
|---------------------------------------------|------------------------|-------------|-------------|---------------------|---------------------|
| 0 gNOM/L-low IS                             | 0.1                    | 1.34        | <0.01       | 0                   | –                   |
| 0 gNOM/L-mid IS                             | 0.5                    | 7.86        | <0.01       | 0                   | –                   |
| 0 gNOM/L-high IS                            | 1                      | 14.50       | 0.19 ± 0.02* | 0                   | –                   |
| Sweden brine                                | −0.2                   | 2.02        | 0.33 ± 0.05* | 0.44 ± 0.34        | 0.01 ± 0.03         |
| Model-low IS                                | 0.2                    | 2.00        | 0.00        | 0                   | –                   |

*aaverage ± standard deviation of duplicate measurement.

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**Fig. 4.** SO\textsubscript{4}\textsuperscript{2-} concentration before and after CaSO\textsubscript{4} and subsequent ettringite precipitation of brines at low ionic strength: NOM-rich Sweden brine, and synthetic brine without NOM. The doses of chemicals are 2.2 g/L of CaSO\textsubscript{4} for the intermediate calcium sulfate precipitation step, and 1.3 to 1.4 g/L of Ca(OH)\textsubscript{2} and 1.1 to 1.2 g/L of NaAlO\textsubscript{2} for the final ettringite precipitation step. A Phreeqc model calculation of the brine without NOM is included.

**Fig. 5.** SO\textsubscript{4}\textsuperscript{2-} concentration before and after CaSO\textsubscript{4} and ettringite precipitation of synthetic brines at high ionic strength (1 M) and different NOM concentrations. For the intermediate calcium sulfate precipitation step, the dosed CaCl\textsubscript{2} was 20 g/L for all brines. For the final ettringite step, Ca(OH)\textsubscript{2} and NaAlO\textsubscript{2} were dosed. For the 2 gDOC/L brine, the dose was 11 g Ca(OH)\textsubscript{2}/L and 9 g NaAlO\textsubscript{2}/L. For the 0.5 gDOC/L brine, the dose was 8 g Ca(OH)\textsubscript{2}/L and 6 g NaAlO\textsubscript{2}/L. For the 0 gDOC/L brine, the dose was 3 g Ca(OH)\textsubscript{2}/L and 2 g NaAlO\textsubscript{2}/L. A Phreeqc model calculation of the brine without NOM is included.

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[Table 4]

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*Table 4 summarises the initial NOM/sulfate ratio of the brines, the
percentage of removal and chemicals dosed per initial sulfate concentration (specific dose). Calcium sulfate and subsequent ettringite precipitation is the most suitable for NOM-free brines with high ionic strengths, as indicated by the relatively low specific dose of chemicals and high SO\textsuperscript{4-} removal. However, brines with low ionic strength required a relatively high specific dose of Ca(OH)\textsubscript{2} and NaAlO\textsubscript{2}.

When applied to NOM-rich brines, calcium sulfate and subsequent ettringite precipitation removed hardly any SO\textsuperscript{4-} at high initial NOM/sulfate ratio, or required a relatively high dose of chemicals.

The potential effect of the initial NOM/sulfate ratio in practice was to see in our experience with additional spent IEX brines. The percentage of sulfate removed was higher in brines with less NOM and higher initial sulfate concentration than Sweden brine (Supplementary Information), indicating that calcium sulfate and ettringite precipitation were more suitable for IEX brines with low initial NOM/sulfate ratio.

The inhibition of precipitation of Ca\textsuperscript{2+} or SO\textsuperscript{4-} crystals caused by NOM and organic acids could be attributed to Ca\textsuperscript{2+} complexation or covering of nucleation and growth crystal sites [33,35,38-40].

Table 5 shows that the Ca\textsuperscript{2+} that can potentially be consumed by complexation was negligible compared to the available Ca\textsuperscript{2+}, i.e. below 10 percent. Therefore, similar to the experiments of Lee et al. [35], covering of crystal site by NOM molecules is suggested as precipitation inhibition mechanism during our experiments. PhreeqC models the interaction between NOM and ions is modelled as complexation and the antiscalent properties of NOM are not considered. Therefore, PhreeqC could not be used to model the NOM-rich brines of our experiments.

An application issue is linked to the purity of the chemical used for the precipitation of the sulfate salts. Natural limestone (calcium carbonate) contains magnesium in case of dolomitization [46], and therefore, Mg\textsuperscript{2+} ions can be present as impurity in the produced CaCl\textsubscript{2}. In our experiments, CaCl\textsubscript{2} had high purity, but the presence of Mg\textsuperscript{2+} should be checked in application. Previous studies showed that Mg\textsuperscript{2+} can maintain SO4\textsuperscript{2-} in the soluble form Mg(SO\textsubscript{4})\textsubscript{2} [47,48].

### 4. Conclusions

Chemical precipitation of SO\textsubscript{4}\textsuperscript{2-} to BaSO\textsubscript{4}, calcium sulfate and ettringite (Ca\textsubscript{6}Al\textsubscript{2}(SO\textsubscript{4})\textsubscript{3}(OH)\textsubscript{12}) was studied for brines with varying NOM and ionic strengths, and initial concentrations between 2 and 16 gSO\textsubscript{4}\textsuperscript{2-}/L. Sulfate removal with BaSO\textsubscript{4} precipitation was above 98 percent for NOM-free brines, and 84 percent for the NOM-rich spent IEX brine. This resulted in final concentrations below 0.4 g SO\textsubscript{4}\textsuperscript{2-}/L, even in the presence of NOM. In addition, 23 percent of NOM was removed from the spent IEX brine, which could decrease the potential for NOM recovery. For application, the residual concentration of dissolved barium, that is toxic, should also be investigated.

At low initial SO\textsubscript{4}\textsuperscript{2-} concentration, calcium sulfate and subsequent ettringite precipitation removed overall 89 percent of SO\textsubscript{4}\textsuperscript{2-} from the NOM-free brine, resulting in a final concentration of 0.2 g SO\textsubscript{4}\textsuperscript{2-}/L. However, the calcium sulfate precipitation step was limited by its high solubility, and the subsequent ettringite precipitation step required a relatively high dose of NaAlO\textsubscript{2} and Ca(OH)\textsubscript{2}. In the NOM-rich spent IEX brine, hardly any removal of SO\textsubscript{4}\textsuperscript{2-} was observed at low initial SO\textsubscript{4}\textsuperscript{2-} concentration.

At high initial SO\textsubscript{4}\textsuperscript{2-} concentration, inhibition of calcium sulfate and subsequent ettringite precipitation by NOM was observed as well. Without NOM, the overall SO\textsubscript{4}\textsuperscript{2-} removal was 99 percent, resulting in a final concentration of 0.2 g SO\textsubscript{4}\textsuperscript{2-}/L. When NOM was present, SO\textsubscript{4}\textsuperscript{2-} removal was between 86 and 95 percent, with final concentrations above 0.8 g SO\textsubscript{4}\textsuperscript{2-}/L, even with a relatively high dosage of chemicals for the ettringite precipitation. The inhibition might be attributed to covering of crystal sites by NOM molecules, and to NOM coagulation with aluminium.

**CRediT authorship contribution statement**

Irene Caltran: Conceptualization, Methodology, Data curation, Writing - original draft. Floriana Ayumurti Kukuh: Conceptualization,
Declarations of Competing Interest

The authors 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 A. Supplementary material

Supplementary data to this article can be found online at https://doi.org/10.1016/j.seppur.2021.118669.

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Separation and Purification Technology 269 (2021) 118669

I. Caltran et al.
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