Investigations on the filtration of natural aquatic suspensions supported by dosing small amounts of Fe(III)-salts ($\beta_{Fe} \leq 0.1 \text{ mg L}^{-1}$): mode of action and basic design criteria


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Abstract Improved removal of particles during the treatment of natural aquatic suspensions has been achieved by pre-ozonation and the addition of small quantities of iron salts ($\beta_{Fe} \leq 0.1 \text{ mg L}^{-1}$; Fe(III)-assisted filtration) followed by rapid filtration. As shown by investigations on a large-scale installation at Lake Constance Water Supply, this procedure reliably reduces suspended solids by at least 2–3 powers of ten in long-term use. However, the high efficacy of Fe(III)-assisted filtration cannot be explained on the basis of known coagulation mechanisms (like adsorption-charge neutralization, co-precipitation). Instead, the essential step was found to be the conditioning of the filter medium by coating it with colloids containing Fe(OH)$_3$, and this "Fe coating" process occurs only in the presence of alkaline earths (especially Ca$^{2+}$). According to further experiments, the enhanced solid-liquid separation was ultimately traced to chemical interactions such as the formation of calcium-organic association structures between the iron hydroxides and other solids. For design of Fe(III)-assisted filtration steps, finally, a $\beta_{Ca}/DOC$ ratio above 40 mg mg$^{-1}$ and pre-oxidation with ozone dosages not exceeding 2 mg O$_3$/mg DOC was recommended.

Keywords Alkaline earths; Fe(III)-assisted filtration; filter media conditioning; mechanism; particle removal

Introduction Along with disinfection, the removal of particulate matter (and thus of microorganisms as well) is one of the most important steps in the purification of natural aquatic suspensions. The available methods include the use of membrane filtration units and/or the addition of coagulants before mechanical solid-liquid separation. Techniques of this sort can substantially increase the degree of particle retention, and thus further reduce the probability that pathogenic protozoa (e.g. Cryptosporidium parvum or Giardia lamblia) will reach the consumer through the drinking water. However, economic and environmental factors also need to be taken into consideration when choosing a suitable method. At this point, the addition of even small quantities of Fe(III) salts ($\beta_{Fe} \leq 0.1 \text{ mg L}^{-1}$; "Fe(III)-assisted filtration") together with preliminary ozone treatment ($\beta_{O_3} = 1.0 \text{ mg L}^{-1}$) proved to be extremely effective. This was shown during recent studies into the optimization of rapid filtration, e.g. of soil filtrate from River Ruhr (Ontyd et al., 1999) or from Lake Constance water (Winzenbacher et al., 1999), where inorganic and organic particles > 1 µm were reliably reduced by about 2–3 orders of magnitude. Since this result can only be partly explained by well known coagulation theories the overall objective of this work was to study the mode of action of the employed purification process. The specific goal was to evaluate selected...
engineering/environmental parameters (coagulant dosing conditions, pre-oxidation regime, water hardness) with the aim to establish a series of design criteria which could be brought in for case-specific prediction of the applicability of Fe(III)-assisted filtration steps.

**Background**

The term “coagulation” covers the processes by which new particulates are produced and/or by which the surface properties of existing particulates are changed so that these particles are able to form aggregates. This leads to a change in the effectiveness of the removal of solids in subsequent purification steps. The most commonly used (inorganic) coagulants are Fe$^{3+}$ and Al$^{3+}$ salts, which are applied at concentrations between 0.6 and 80 mg L$^{-1}$ (Johnson and Amirtharajah, 1983; Petrusevski *et al*., 1995; Mouchet and Bonnélye, 1998). The essential mechanisms known to be involved in coagulation by multivalent metal ions in natural aquatic systems are two destabilization processes: adsorption-charge neutralization and sweep coagulation. In adsorptive charge neutralization the normally negative surface potential of natural suspended matter is modified by the adsorption of positively charged metal hydroxide complexes, reducing electrostatic repulsion between the particles to such an extent that the solids can touch each other or adhere to the reactor wall, whereas sweep coagulation involves the formation of voluminous hydroxide precipitates which incorporate the natural particles (Johnson and Amirtharajah, 1983).

Important factors which influence the coagulation process, and thus the efficacy of particle separation, are different engineering parameters (e.g. filter velocity or energy input) and the nature of the raw water. For example, the presence of natural organic matter (NOM) can have substantial (pH-dependent) effects on the intensity of coagulation (Jekel, 1994). Particularly, below a certain $\beta_{\text{coagulant/DOC}}$ ratio there may be massive disturbances due to formation of (genuinely) dissolved metal-NOM complexes or to extensive specific surface complexation of organic substances on freshly precipitated metal hydroxides. The latter gives rise to electrosteric stabilization (Amirbahman and Olson, 1995) of very fine colloidal precipitation products, which are not adequately retained in a subsequent filtration step and which therefore increase residual coagulant levels in the filtrate. Another parameter is the level of the divalent hardness formers, as they have the ability to bind coordinatively to the carboxyl and OH$^{-}$ groups of humic substances, metal oxides/hydroxides, and clay minerals (Jekel, 1994). This complex-forming potential of alkaline earth ions can thus help counteract inactivation of the coagulant by NOM, especially in alkaline medium (Petrusevski *et al*., 1995).

**Material and methods**

**Continuous filtration tests**

In order to identify the procedure-specific peculiarities and the relevant boundary conditions of Fe(III)-assisted filtration both a semi-technical pilot plant ($Q_{\text{max}} = 2.4$ m$^3$/h) and a small-scale test system ($Q_{\text{max}} = 0.06$ m$^3$/h) were applied. Raw water from Lake Constance (Table 1) was extracted from a depth of 60 m and was first passed through microstrainers (nominal mesh size: 15 µm) to remove larger algae and the remains of plankton. The subsequent ozone treatment was carried out in a spray tower with a counter-current of a mixture of ozone and oxygen. A reaction path taking at least 2 hrs to pass through was followed by a rapid filtration with outlet speeds of 8.5 (pilot plant) and 6.9 m h$^{-1}$ (small-scale test system), respectively. The filter material was pumice (upper layer at pilot plant only; grain size: 1.2–1.8 mm) and quartz sand (grain size: 0.3–0.7 mm at pilot scale and 0.4–0.8 mm at small scale). Both systems were operated as an “in-line filtration” where Fe(III) solution was added directly into the filter inlet pipe (residence time in the excess head: 12–26 min).
Different levels of alkaline earths were tested at the small-scale test system. As shown in Figure 1 this “stepwise softening” was realized using first a 15 L bead bed of the strongly acidic ion exchanger (Na form), which was operated as a fluidized bed. The exact level of water hardness required for the particular filtration test was then re-adjusted by the addition of CaCl₂ or MgCl₂ solution.

**Measurement techniques**

The analyses necessary to determine the chemical and physical parameters of water quality (iron, calcium, SAC₂₅₄, ozone, etc.) were carried out on the basis of appropriate DIN, ISO, or CEN standards. Filtration efficacy was characterized by determination of the particle count and size distribution (dₚ = 1–116 µm) using a laser-optic particle counter (Schick, 2000). The effective surface potential of the dispersed solids was determined by measuring the electrophoretic mobility using a zeta-potential meter (Winzenbacher et al., 1999). Scanning electron micrographs from the surface of the quartz sand collector were also recorded, and thereby, it was possible to carry out an energy-dispersive X-ray...
microanalysis (EDX) of the sample surface (detection limit: about 8–500 µg/g of solid for all elements with an atomic number > 4, except Au and Pd).

Results and discussion

The effects of Fe(III) addition on the surface properties of dispersed solids and collectors

According to earlier studies (Winzenbacher et al., 1999) the increased particle removal at Fe concentrations \( \leq 0.1 \text{ mg L}^{-1} \) – achieved in spite of a very low \( \beta_{\text{Fe}}/\text{DOC} \) ratio of approximately 0.08 mg mg\(^{-1}\) – would not have been anticipated on the basis of sweep coagulation or classical adsorption-charge neutralization. Instead, the addition of small quantities of Fe(III) to Lake Constance water led to a mixed population of natural particles and colloids containing Fe hydroxide whose sizes were estimated at 100–800 nm. The colloid particles formed were partly coated with organic material and showed a great tendency to deposit on the surfaces of the filter grains. Consequently, it can be assumed that a process which resembles the conditioning of the filtration medium is the decisive step in the improvement of particle removal. For example, the massive deposition of hydroxide colloids could increase the roughness of the collectors and thus improve the physical capture of particles, though reduced flow-related resuspension of particles already in contact with grains of filter material due to stronger chemical interactions is also conceivable. It was therefore consequent to investigate these possibilities with the aid of scanning electron microscopy (SEM).

Figure 2 shows micrographs of samples of quartz sand taken from the upper 10 cm of the filter bed during the filtration phase. The sand grains from a filter operated conventionally show a clearly structured surface with small sharp-edged elevations which provides roughness. By contrast, collectors from a filter operated with the addition of low amounts of iron(III) salts (\( \beta_{\text{Fe}} = 0.1 \text{ mg L}^{-1} \)) could be seen to have a coating with an irregular structure. EDX analysis (data not shown) confirmed that these deposits contain Fe. It was also found that the iron-hydroxide-rich zones always contained calcium as well, although significant retention of calcium did not occur during the filtration process. A semi-quantitative evaluation of the elementary composition of the coating gave a \( c_{\text{Fe}}/c_{\text{Ca}} \) mole ratio of about 3.5. Consequently, the colloidal iron on the grains of filter material seems to have accumulated in association with traces of calcium.

The small quantity of Fe(III) added thus actually does bring about a change to the surface of the sand grains, apparently causing increased deposition of suspended matter in the presence of organic substances and calcium ions. Since, however, the surface structure of the “Fe coating” did not display a substantial increase in roughness, it seems that it is not so much improved particle capture as improved adhesion resulting from chemical or physical interactions which is important.

Figure 2. Scanning electron micrograph of the surface of (a) quartz sand from a filter operated conventionally and (b) quartz sand from a filter operated with continuous Fe addition (\( \beta_{\text{Fe}} = 0.1 \text{ mg L}^{-1} \))
Study of selected process parameters

Impact of energy input during the mixing phase on filtration efficacy (pilot plant). Low mixing intensity during addition of anorganic metal(III)-salts which undergo hydrolysis in a split second could lead to local fluctuations of the pH value, resulting in a heterogenic mixture of different metal species (monomers, oligomers, polymers and amorphous precipitates, metal-NOM complexes, etc.). Thus, the efficacy of coagulant – when based on homogenous species distribution – could be impaired (Kawamura, 1996). In order to judge the relevance of this aspect in the present case the energy input at the dosing point should be varied by adjusting different stirrer velocities. The experiments demonstrated, however, only negligible influence of the energy dissipation regime on the achievable filtrate quality (data not shown). Consequently, energy input during the mixing phase seems to have nearly no or inferior significance on the effectiveness of Fe(III)-assisted filtration.

Impact of pre-oxidation on Fe(III)-assisted filtration efficacy (pilot plant). To study the role of ozonation in the Fe(III)-assisted filtration step, first of all the applied ozone concentration was varied. Thereby, the ozone dosage proved to be a very sensitive parameter for the maximal achievable filtration efficacy (Figure 3). An ozone addition between 1.5 and 2.5 mg L\(^{-1}\) (e.g. about 1.25–2 mg O\(_3\)/mg DOC) resulted in optimum particle removal (approximately 99.5%). Under these conditions a low iron concentration of even 0.05 mg L\(^{-1}\) (< 1 µmol L\(^{-1}\)) was enough to achieve such high removal rates that were nearly independent of seasonal changes in raw water quality. An overfeeding of ozone (β\(_{O_3} ≥ 3\) mg L\(^{-1}\)), however, re-decreased the solid-liquid separation efficiency as compared to the optimum. Supplemental analyses of surface charge properties of dispersed matter (natural turbidity and precipitated colloids containing Fe hydroxide) indicated a continuous shift towards more negative values with an increase in ozone dosage.

The observed effects should mainly be due to the specifically high selective reactions of ozone with dissolved and adsorbed organic macromolecules, respectively. We assume that the oxidation of NOM with β\(_{O_3} < 3\) mg L\(^{-1}\) leads to a break-up of a steric hindering adsorption layer (Schick, 2000) and to the destabilization of both natural particles and in-situ formed ferric containing colloids. However, the application of ozone also resulted in an introduction of acidic functional (polar) groups in adsorbed/adsorbable NOM and thus repulsion forces between the natural particles, the precipitated colloidal ferric hydroxides, and the filter grains were enhanced. If finally, the surface potential exceeds a critical value
(here: \(|\xi| \geq -20 \text{ mV at } \beta_{\text{Fe}} \geq 3 \text{ mg L}^{-1}\), see Figure 3) an electrostatic restabilization will occur. Therefore, the Fe(III)-assisted filtration could not profit best from pre-ozonation when ozone is used in an extensive manner.

Further tests were carried out focusing on another type of pre-oxidation process, namely the PEROXONE process. Therefore, \(\text{H}_2\text{O}_2\) was dosed immediately before ozonation in order to generate OH• radicals which have an “enhanced” oxidation potential (while on the other hand, the ozone-specific selective reactions with NOM were suppressed). It showed that the application of PEROXONE led to a deteriorated filtrate quality as compared to the findings after proper pre-ozonation. In particular, the efficiency of Fe(III)-assisted filtration decreased with increasing mole ratio \(\text{H}_2\text{O}_2:\text{O}_3\) (data not shown). Unlike ozone-specific interactions, radical reaction mechanisms thus seem to be of inferior significance with regard to an improvement of the particle separation.

Impact of alkaline earth cations on Fe(III)-assisted filtration efficacy (small-scale test system). Assuming that \(\text{Ca}^{2+}\) was involved in the Fe(III)-assisted filtration process (see SEM-EDX analyses), other experiments were designed to investigate the influence of alkaline earth ions on the particle removal rate. Actually, the small-scale investigations showed that both the nature and quantity of the alkaline earths present and their reactions with natural organic matter (NOM) had substantial effects on filter efficacy \(\eta_p\). Only 15\% of the suspended matter in softened Lake Constance water was removed despite the addition of Fe \((\beta_{\text{Fe}} = 0.1 \text{ mg L}^{-1})\), and there was a high residual iron content in the filtrate (94\% of the quantity added). The retention of iron and particulate matter rose again with increasing \(\text{Ca}^{2+}\) concentration (up to \(\eta_p = 85\%\) at \(c_{\text{Ca}} = 1.4 \text{ mmol L}^{-1}\), see Figure 4). In comparison, the addition of \(\text{MgCl}_2\) to softened water also increased the removal of particulate matter, but the highest efficacy, at \(c_{\text{Mg}} = 1.4 \text{ mmol L}^{-1}\), was only 75\%. Ozone treatment of water of various degrees of hardness before Fe(III)-assisted filtration (specific ozone dose: 0.8 mg \(\text{O}_3\) per mg DOC) only made an improvement to \(\eta_p\) at the highest calcium levels – analogous to those of Lake Constance water. By contrast, at lower \(\text{Ca}^{2+}\) concentrations (< 1 mmol L\(^{-1}\)) or when \(\text{Mg}^{2+}\) ions alone were used to harden the water, ozone treatment led to a deterioration in filtration efficiency. In unfavourable cases the oxidation of organic material in the water had such adverse effects on the removal of suspended matter that retention was less than 50\% of that achieved in non-ozonized samples.

Figure 4 The influence of calcium on the efficiency of Fe-assisted filtration \((\beta_{\text{Fe}} = 0.1 \text{ mg L}^{-1}; \text{small-scale test unit})\) in the water had such adverse effects on the removal of suspended matter that retention was less than 50\% of that achieved in non-ozonized samples.
Electrophoretically determined potential values demonstrated an ion-selective reduction in the negative surface charge with increasing Ca\textsuperscript{2+} or Mg\textsuperscript{2+} concentration (measurement time: approximately 30 min after Fe addition, $\beta_{\text{Fe}} = 0.1 \text{ mg L}^{-1}$; data not shown). Thereby, even small quantities of calcium (< 0.2–0.4 mmol L\textsuperscript{-1}) were sufficient to bring about a large shift in the potential in the direction of neutrality. In comparison, compensation of the negative charge on the particles by divalent cations was less pronounced after ozone treatment ($\beta_{\text{O}_3} = \text{approximately 1.0 mg L}^{-1}$) of the softened water samples. In these samples the specific direct reaction of ozone with NOM (introduction of functional groups, cleavage of macromolecules) could, therefore, have led to such negative charge densities on solid surfaces (natural particles, Fe(OH)\textsubscript{3} colloids, filter collectors) that an ozone-induced deterioration of $\eta_p$ occurred because of high electrostatic repulsion.

This relationship between particle charge and the concentration of alkaline earths suggests at first sight that ion-specific charge screening is a central prerequisite for successful particle removal. However, electrostatic effects alone cannot be responsible for the increase in efficiency of the Fe(III)-assisted filtration following the addition of Ca\textsuperscript{2+}/Mg\textsuperscript{2+}. This was made clear by a quantitative comparison of the measured $\zeta$-values and the corresponding filter efficacy at different levels of hardness. At most, there was a correlation between particle charge and filter efficacy at low calcium concentrations (up to approximately 0.4 mmol L\textsuperscript{-1}), and there was no correlation after the addition of larger quantities of Ca\textsuperscript{2+}. The large increase in filter efficacy in hard water – especially above the observed threshold Ca\textsuperscript{2+} concentration of 0.4 mmol L\textsuperscript{-1} (compare Figure 4 again) – must, therefore, relate to other chemical processes (e.g. formation of Ca\textsuperscript{2+}-NOM associations).

**Summary and conclusions**

- The fundamental mechanism of Fe(III)-assisted filtration can be described in outline as follows: Following the addition of a small quantity of Fe(III) salts, colloidal iron hydroxide ($d_p = \text{approximately 100–800 nm}$) is formed and, due to its strong surface affinity, largely deposited on the filter collectors (formation of an “Fe coat”). The filter medium conditioned in this way gives improved retention of the suspended material laden with natural organic matter in water from Lake Constance. The individual effects which are probably involved are hardness-associated electrostatic effects (charge

<table>
<thead>
<tr>
<th>Process parameter</th>
<th>Influence on filter efficacy</th>
<th>Recommended value**</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH value</td>
<td>$\uparrow$</td>
<td>close to precipitation optimum</td>
</tr>
<tr>
<td>Energy input (Shear value G)</td>
<td>$\uparrow$</td>
<td>$G \geq \text{approx. 200 . . . 400 s}^{-1}$</td>
</tr>
<tr>
<td>Collector diameter $d_K$</td>
<td>$\uparrow$</td>
<td>$0.4 . . . 0.7 \text{ mm (max. 1.25 mm; depends on filter medium)}$</td>
</tr>
<tr>
<td>Collector roughness $R_K$</td>
<td>$\uparrow$</td>
<td>$&gt; \text{approx. 2 } \mu\text{m}$</td>
</tr>
<tr>
<td>Retention time (excess head)</td>
<td>$\uparrow$</td>
<td>$t \geq \text{approx. 12 min}$</td>
</tr>
<tr>
<td>Filter velocity $v_F$</td>
<td>$\uparrow$</td>
<td>$\leq \text{20 . . . 25 m h}^{-1}$</td>
</tr>
<tr>
<td>Calcium $\beta_{\text{Ca}}$</td>
<td>$\uparrow$</td>
<td>$\beta_{\text{Ca/DOC}} \geq 40 \text{ mg mg}^{-1}$</td>
</tr>
<tr>
<td>Zeta-potential $\zeta$</td>
<td>$\uparrow$</td>
<td>$&gt; \text{approx. -20 mV}$</td>
</tr>
<tr>
<td>Oxidation</td>
<td>$\uparrow$</td>
<td>Pre-ozonation, $</td>
</tr>
</tbody>
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$\uparrow$: increase of parameter value
$\uparrow$: positive
$\uparrow$: negative
$\uparrow$: largely insignificant
$\uparrow$: shift towards zero

** according to this work and further experiences (see text)
screening) and chemical interactions (like Ca\(^{2+}\)-NOM bridging) between the collectors, the Fe hydroxides, and the natural particles.

- **Necessary pre-requisites for successful application of Fe(III)-assisted filtration are:** the presence of alkaline earths (a \(\beta_{\text{Ca}}/\text{DOC} \) ratio of at least 35–40 mg\( \cdot \)mg\(^{-1}\) is recommended, especially for ozonated water), maximum specific ozone dosages of approximately 2 mg O\(_3\) per mg DOC, and a suitable engineering design of the filtration procedure (not discussed here).

- **Energy input** (relevant for homogenous interference of coagulant) is not a dominating key factor.

- Both higher ozone concentrations and combined application of H\(_2\)O\(_2\) and O\(_3\) (PEROX-ONE) result in a lower filtrate quality compared to the optimum.

A brief summary of the essential design criteria based on the findings in this work and further experiences (Ontyd et al., 1999; Winzenbacher, 2000) is finally given in Table 2.

**References**


