Removal of ferric hydroxide by flotation with micro and nanobubbles

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Abstract

This work presents results on the removal of Fe\(^{3+}\) ions as precipitates and nanoparticles of Fe(OH)\(_3\) at pH 7 by nanobubbles (NBs) and by dissolved air flotation (DAF), a process which combines microbubbles (MBs) and NBs. DAF is a very well-known technology in the treatment of water and wastewaters. Studies were conducted at low and high levels of saturation pressures (P\(_{sat}\) of 2 and 4 bar) and with “isolated” (single) NBs. The latter were generated at 2.5 bar, after their separation from the MBs. Best results were obtained with flotation at 2 bar, when the concentration of MBs was low and NBs very high. The removal efficiency was 99% of the feed iron content (30 mg L\(^{-1}\)), and the treated water had a residual total iron concentration of 0.3 mg L\(^{-1}\) and a turbidity of 0.6 NTU (95% reduction). The flotation at 4 bar (mostly by MBs) was faster (0.07 cm s\(^{-1}\)) due to the high lifting power of the MBs but left a higher residual total iron content of 1.7 mg L\(^{-1}\). The flotation with isolated NBs (>10\(^8\) bubbles mL\(^{-1}\)) attained 91% iron removal due to “floatation” following NBs entrapment and the decrease of the relative density of the aggregates. Flotation of the nanoparticles with NBs was also studied and showed a removal efficiency of about 68%, considered high, for this difficult-to-separate system. All mechanisms involved were discussed in terms of physical, chemical and interfacial phenomena. It is believed that the combination of NBs and MBs has an excellent potential for future separation of particles, including nanoparticles, and will help to broaden applications in removing specific target pollutants from waters and wastewaters.

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1. Introduction

In the dissolved air flotation (DAF) process, the formation of microbubbles (MBs) and nanobubbles (NBs) is the result of the hydrodynamic cavitation of air-saturated water at high pressures due to a sudden drop in pressure in the narrowing of a nozzle or flow constrictor that increases the velocity of the flow, providing bubble nucleation. DAF has been studied for many years, focusing on the removal efficiency as a function of operating parameters and particle-bubble adhesion phenomena [18–20]. The flotation of the precipitates (Fe(OH)\(_3\)) is a very fast and efficient process and has been employed for more than 70 years as an adsorbent of toxic ions and serves as a contaminant carrier in water treatment [21–23]. The precipitates are formed following ion hydration, nucleation, and growth to generate nanoparticles (sub-micron), colloids and spongy-light and open assemblies (aggregates). These species undergo constant restructuring, passing from one species to another with formation kinetics very dependent on feed iron concentration [24–26].

The main difference between these bubbles is that MBs rise fairly rapidly in water (0.1–0.2 cm s\(^{-1}\)), whereas NBs remain stable for months, do not rise and their movement is caused by Brownian motion [7–9]. The mechanisms that make NBs stable have not yet been fully elucidated and constitute an open and quite intriguing topic in academia [10–13]. Thus, the interaction mechanisms between these bubbles and the particle system are different and sometimes synergic, with the NBs assisting flotation by MBs [14–17].

The removal of metal hydroxides and notably ferric hydroxide by flotation has been studied for years, focusing on the removal efficiency as a function of operating parameters and particle-bubble adhesion phenomena [18–20]. The flotation of the precipitates (Fe(OH)\(_3\)) is a very fast and efficient process and has been employed for more than 70 years as an adsorbent of toxic ions and serves as a contaminant carrier in water treatment [21–23]. The precipitates are formed following ion hydration, nucleation, and growth to generate nanoparticles (sub-micron), colloids and spongy-light and open assemblies (aggregates). These species undergo constant restructuring, passing from one species to another with formation kinetics very dependent on feed iron concentration [24–26].
Yet, the role of NBs in DAF, assisting the action of MBs and the mechanisms involved, have not been fully studied and constitutes one of the main objectives of this work. This paper is a continuation of a series on the properties, features and role of NBs in flotation, showing results for the removal of Fe\(^{3+}\) ions as precipitates and nanoparticles of Fe(OH)\(_3\). The main mechanisms involved in the action of NBs in DAF that assist the action of the MBs were also evaluated.

2. Experimental

2.1. Materials and reagents

Solutions containing iron ions were prepared in deionized (DI) water using analytical-grade iron (III) chloride hexahydrate (FeCl\(_3\)-6H\(_2\)O) (99% of purity) from Merck (Germany).

The DI water correspond to treated tap water using an ultrapurification system, which consisted of a reverse-osmosis cartridge and modules of ion-exchange resins and activated carbon, at room temperature (23 °C ± 1). This DI water had a conductivity of 3 μS cm\(^{-1}\) and a surface tension of 72.5 ± 0.1 mN m\(^{-1}\), at pH 5.5.

Solutions of 0.1 M NaOH (Merck) were employed for the pH adjustments.

2.2. Methods

The experiments were carried out using a system consisting of a saturation vessel made of PVC (2.5 L, h = 400 mm, diameter = 110 mm, equipped with manometer, a relief valve and two needle valves). A glass column I (2 L, h = 250 mm, diameter = 100 mm) was employed to separate the NBs from the MBs, a glass column II (2 L, h = 250 mm, diameter = 100 mm) for the precipitation/flotation procedures and a mechanical stirrer (Fisatom\(^{b}\) - model 713D) (Fig. 1).

Bubbles were formed by reducing the pressure of DI water that was pre-saturated with air at various saturation pressures (P\(_{sat}\)) for 30 min in the vessel. The supersaturated water was forced through a needle valve (Parker\(^{c}\), N400), and MBs and NBs were generated and injected into the glass column. The NBs were separated from the MBs using the procedure described by Calgaroto et al. [5,15] and Azevedo et al. [7]. The glass column I had two inputs at the base: one entry receiving the depressurized flow (MBs and NBs) and another connected to the precipitation/flotation column II to inject the isolated NBs. In the studies of MBs together with NBs, column I was not used.

Solutions (1 L) containing different Fe\(^{3+}\) ion concentrations ([Fe\(^{3+}\)] = 5–30 mg L\(^{-1}\)) were prepared. For the precipitation of Fe(OH)\(_3\), the pH of the solution was adjusted to 7 in glass column II with pre-established volumes of NaOH solution (1%) under agitation of 120 rpm for approximately 5 min.

2.2.1. Characterization of the Fe(OH)\(_3\) nanoparticles

The Fe(OH)\(_3\) nanoparticles were characterized in terms of their particle size distribution and concentration by a nanoparticle tracking analysis (NTA) instrument (ZetaView\(^{b}\) Particle Metrix, Germany) and optical micrographs. Samples of 100 mL with iron precipitates were collected in glass flasks for these analyses. As the Fe(OH)\(_3\) precipitates in a broad size distribution, suspensions were previously filtered, to separate the coarser species to obtain the nanoparticles dispersions. Filtration employed syringes (5 mL) and syringe filters with cellulose acetate hydrophilic membranes (porosity = 1.2 μm).

Optical micrographs were taken using an optical microscope (Olympus\(^{b}\), model BX41, Hicksville, NY, USA) with a backlight and an objective magnification of 1000x that was coupled to a high-performance microscope digital camera (Olympus\(^{b}\) - DP73 – 17 megapixel resolution). Samples of 100 mL were collected from glass column II at two different process stages: i. After the precipitation (from the base of the column) and ii. After 5 min of flotation (P\(_{sat}\) = 2 bar). The latter samples were collected carefully from the supernatant of column II with a glass syringe (5 mL) for visualization in the optical microscope.

A blank settling test was conducted in an Imhoff cone to evaluate whether the precipitates settle totally, remain disperse or present self-flotation. Experiments were done under similar conditions as in flotation, i.e. ([Fe\(^{3+}\)]\(_{feed}\) = 30 mg L\(^{-1}\)) and 5 min.

2.2.2. Flotation with MBs and NBs

The removal of Fe(OH)\(_3\) by flotation was performed by depressurizing 150 mL of air-saturated water at pH 7 or by the injection of aqueous dispersions of isolated NBs (150 mL), using P\(_{sat}\) = 2.5 bar and pH 7 and after MBs separation in the glass column I.

After the flotation, samples were collected at different time intervals from the base of glass column II in polyethylene flasks. These aliquots were preserved in a Styrofoam box for the analysis of the turbidity and total residual iron. The turbidity was measured in a Hach\(^{b}\) turbidimeter (model 2100 N) using the nephelometric method. The total iron ion content in all the samples was measured using an atomic absorption spectrophotometer (AAS) (PG Instruments\(^{b}\) - model AA990F) with an air-acetylene flame.

To measure the initial concentration of total iron, samples of the initial solution were collected. The total iron removal efficiency was calculated by Eq. (1), and all experiments were performed in duplicate.

Efficiency (%) = \[100 - \frac{(C_f \times F) \times 100}{C_0}\]  

where \(C_f\) = final concentration of total iron (mg L\(^{-1}\)); \(F\) = dilution factor (1.23); and \(C_0\) = initial concentration of total iron (mg L\(^{-1}\)).

The flotation kinetics of Fe(OH)\(_3\) was evaluated using two levels of P\(_{sat}\) (2 and 4 bar) by collecting samples of the treated water at flotation time intervals between 30 s and 5 min for a total iron analysis. The rising times and flotation rates in these different conditions were determined by monitoring the time required for the flotation of all the Fe(OH)\(_3\) precipitates visible in solution.

![Fig. 1. Experimental setup for the flotation of iron hydroxide precipitates: (1) saturator vessel; (2) glass column I - MBs - NBs separation; (3) glass column II with mechanical stirrer - precipitation/flotation.](image-url)
2.2.3. Fe(OH)₃ nanoparticle flotation

To evaluate the removal of the Fe(OH)₃ nanoparticles, studies were performed with the same feed concentration of 30 mg L⁻¹. After precipitation at pH 7, the samples (100 mL) were collected in glass beakers and, to separate the nanoparticles, by filtration using 5 mL glass syringes and syringe filters as discussed above. These filtered samples were analysed, and the measured values corresponded to the total iron content in the form of Fe(OH)₃ nanoparticles.

**Table 1**
Characterization (size and concentration) of nanoparticles formed in the precipitation of iron hydroxide.

<table>
<thead>
<tr>
<th>Feed iron concentration (standard deviation), mg L⁻¹</th>
<th>Nanoparticles concentration (standard deviation), Nanoparticles mL⁻¹</th>
<th>Mean numeric diameter of nanoparticles (standard deviation), nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>5.4 (0.2)</td>
<td>5.5 × 10⁷ (2.9 × 10⁹)</td>
<td>215 (22)</td>
</tr>
<tr>
<td>9.8 (0.3)</td>
<td>7.8 × 10⁷ (2.1 × 10⁹)</td>
<td>210 (14)</td>
</tr>
<tr>
<td>15.2 (0.6)</td>
<td>8.6 × 10⁷ (2.5 × 10⁹)</td>
<td>209 (15)</td>
</tr>
<tr>
<td>29.8 (0.4)</td>
<td>1.9 × 10⁸ (6.4 × 10⁹)</td>
<td>194 (21)</td>
</tr>
</tbody>
</table>

**Fig. 2.** Photographs of different stages of Fe(OH)₃ precipitation, before and after flotation with MBs and NBs: (a) Precipitation; (b) Injection of MBs and NBs; (c) Flotation at 30 s; (d) Flotation at 1 min; (e) Flotation at 5 min; (f) Floated precipitates and treated water. Conditions: [Fe³⁺]ₐ₀ = 30 mg L⁻¹; pH 7; saturation time = 30 min.

**Fig. 3.** Size distribution of Fe(OH)₃ nanoparticles. Conditions: [Fe³⁺]ₐ₀ = 30 mg L⁻¹; pH = 7; samples filtered in 1.2 μm membranes before NTA analysis.

**Fig. 4.** Settling of Fe(OH)₃ precipitates in an Imhoff cone after 5 min. Conditions: [Fe³⁺]ₐ₀ = 30 mg L⁻¹; pH = 7.
3. Results and discussion

3.1. Iron hydroxide characterization

Iron species form hydrolysis products (precipitates) by the reactions shown in Eqs. (2)–(5) [27,28]. In these systems, the species are in equilibrium, depending on the medium pH and the initial concentration. Based on the hydrolysis reaction constants of the iron ions and the solubility constant of the precipitated hydroxide, the diagram of species shows the molar fractions of the various hydrolysis products soluble in equilibrium with the amorphous and hydrophilic precipitate [27,28]. Accordingly, the predominant hydrolysed iron species, at pH 7, are:

\[
\text{Fe}^{3+} + \text{OH}^- \rightleftharpoons \text{Fe}(	ext{OH})^{2+} \tag{2}
\]

\[
\text{Fe}(	ext{OH})^{2+} + \text{OH}^- \rightleftharpoons \text{Fe}(	ext{OH})_2^+ + \text{OH}^- \tag{3}
\]

\[
\text{Fe}(	ext{OH})_2^+ + \text{OH}^- \rightleftharpoons \text{Fe}(	ext{OH})_3 \tag{4}
\]

\[
\text{Fe}(	ext{OH})_3^+ + \text{OH}^- \rightleftharpoons \text{Fe}(	ext{OH})_4^- \tag{5}
\]

The insoluble species are actually mixtures of sub-micron (nanoparticles) and macroscopic precipitates, either colloidal or soft–light assemblies (herein named aggregates). Some of the precipitates break apart under micro-turbulence and for this reason, the particle size analysis above the nanoscale by dynamic laser diffraction techniques is erratic and thus was not possible in this work.

Fig. 2 shows photographs of the formed precipitates between at different stages of the Fe(OH)₃ precipitation and flotation. The images show that they are yellow-reddish and some aggregates are fairly spongy and open. The concentration of all insoluble species (nano, colloidal or aggregates) of Fe(OH)₃ increase with the initial iron ion content.
The nanoparticles, after coarser precipitates separation by membrane filtration, presented volumetric average diameters between 194 and 215 nm varying the initial concentrations of iron ions (Table 1). Their size distribution, with an initial iron concentration between 194 and 215 nm varying the initial concentrations of iron ions (Table 1). Their size distribution, with an initial iron concentration of 30 mg L\(^{-1}\) is shown in Fig. 3. There are no previous reports in the literature on the concentration of these nanoparticles being measured by NTA; they have only been visualized by transmission electron microscopy (TEM) [23]. These authors reported that the nanoparticles of a mixture of iron oxides and amine precipitates were broken by the rising movement of the MBs [15]. Azevedo et al. [7], in this range of Psat, the concentration of MBs is low [29], and the concentration of NBs is high (3 \times 10^8 NB mL\(^{-1}\)). Under these conditions, with a Psat of 2 bar, the residual turbidity of the solution was less than 1 NTU and the residual total iron concentration was 0.3 mg L\(^{-1}\).

The high concentration of MBs at a high Psat and their rapid upward movement causes micro turbulence and a partial rupture of the formed precipitates. Then, the low residence time of these MBs in the flotation cell reduces separation efficiency of bigger precipitates and aggregates (colloids and soft-light assemblies), increasing the residual iron concentration. Similar results were obtained by our group for the removal of organic colloidal precipitates with decyl-ether-amines at pH 10.5. In that work, the light amine precipitates were broken by the rising movement of the MBs [15].

Table 2 shows that the mean uprising velocity of the iron precipitates was 0.07 and 0.13 cm s\(^{-1}\) for Psat values of 2 and 4 bar, respectively. Because this rapid rise of the MBs the time available for the bubble/precipitate interaction is lower when using a higher Psat.

More, these results appear to explain the role of the NBs, which do not have lifting power whatsoever. NBs interact with the particles and cause "floatation" (flotation without lifting power). NBs interact with the particles and cause "floatation" (flotation without lifting power). This entrainment leads to a reduction of the specific density of the solids and cause "floatation" (flotation without lifting power). Fig. 6 shows microphotographs of the Fe(OH)\(_3\) precipitates and the NBs entrapped inside them.

Table 3 shows that for the low concentrations of Fe\(^{3+}\) ions (\(\leq 15\) mg L\(^{-1}\)), the difference between the removal efficiencies, at different Psat values, is even more pronounced with a higher removal at the lower Psat, when the concentration of NBs is higher [7]. Due to the chemical equilibrium of the precipitation reactions (Eqs. (2)–(5)), at low iron feed concentrations the precipitates became smaller, decreasing the flotation efficiency (higher residual concentration of iron ions). Under these conditions the operating mechanisms, namely the entrainment mechanism of NBs and the entrainment by MBs (flotation at Psat values of 2 and 4 bar) were probably less pronounced.

Fig. 7 shows that the flotation kinetics is quite fast for Psat values of 2 and 4 bar, and after 30 s of flotation, the removal efficiency is already above 90% for both pressures. For flotation times of up to

---

### Table 3

<table>
<thead>
<tr>
<th>Feed iron ions concentration (standard deviation), mg L(^{-1})</th>
<th>Removal efficiencies (standard deviation), %</th>
<th>Residual concentration of iron ions (standard deviation), mg L(^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>Psat = 2 bar</td>
<td>Psat = 4 bar</td>
<td>Psat = 2 bar</td>
</tr>
<tr>
<td>5.5 (0.1)</td>
<td>64 (1.7)</td>
<td>65 (1.9)</td>
</tr>
<tr>
<td>9.6 (0.3)</td>
<td>77 (2.7)</td>
<td>65 (1.9)</td>
</tr>
<tr>
<td>15.7 (0.7)</td>
<td>99 (0.1)</td>
<td>84 (0.3)</td>
</tr>
<tr>
<td>29 (0.5)</td>
<td>99 (0.01)</td>
<td>94 (0.3)</td>
</tr>
</tbody>
</table>

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### Table 4

<table>
<thead>
<tr>
<th>Psat = 2 bar</th>
<th>Psat = 4 bar</th>
</tr>
</thead>
<tbody>
<tr>
<td>Feed iron concentration as NPs, mg L(^{-1})</td>
<td>Final iron concentration as NPs, mg L(^{-1})</td>
</tr>
<tr>
<td>0.479 (0.13)</td>
<td>0.127 (0.05)</td>
</tr>
</tbody>
</table>
Table 5
Efficiency of iron ion removal by flotation with isolated NBs. Effect of the feed concentration of iron ions. Conditions: pH 7; NBs generated at \( P_{\text{sat}} = 2.5 \) bar; Flotation time = 10 min.

<table>
<thead>
<tr>
<th>Feed iron ions concentration (standard deviation), mg L(^{-1})</th>
<th>Removal efficiencies (standard deviation), %</th>
<th>Residual concentration of iron ions (standard deviation), mg L(^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>5.6 (0.06)</td>
<td>5.2 (9)</td>
<td>5.4 (0.1)</td>
</tr>
<tr>
<td>9.5 (0.02)</td>
<td>66 (1.7)</td>
<td>3.6 (0.4)</td>
</tr>
<tr>
<td>14.9 (0.14)</td>
<td>76 (1.1)</td>
<td>3.5 (0.2)</td>
</tr>
<tr>
<td>30.1 (0.17)</td>
<td>91 (3)</td>
<td>2.7 (0.9)</td>
</tr>
</tbody>
</table>

Table 6
Removal of Fe(OH)\(_3\) nanoparticles by flotation with isolated NBs (generated at \( P_{\text{sat}} = 2 \) bar). Average results (standard deviation) of triplicate trials. Conditions: \( [\text{Fe}^{3+}]_{\text{feed}} = 30 \) mg L\(^{-1}\); pH 7; [nanoparticles] = total iron concentration in samples filtered on 1.2 \( \mu \)m membranes; flotation time = 10 min.

<table>
<thead>
<tr>
<th>Feed iron concentration as NPs, mg L(^{-1})</th>
<th>Final iron concentration as NPs, mg L(^{-1})</th>
<th>Removal of NPs, efficiency (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.475 (0.07)</td>
<td>0.144 (0.02)</td>
<td>68 (4)</td>
</tr>
</tbody>
</table>

60 s, the removal efficiency is higher at high pressure, which is attributed mainly to the higher uprising velocity of the MBs. After this period, it is observed that the iron removal is always superior with the use of a \( P_{\text{sat}} \) of 2 bar due to the longer time available for the entrapment of NBs. The equilibrium condition was attained at \( \sim 120 \) s of flotation. Similar results of flotation were published elsewhere [31], using the same pH for the precipitation of iron hydroxide, and using a \( P_{\text{sat}} \) of 4 bar.

3.3. Flotation of nanoparticles of Fe(OH)\(_3\)

The results on the removal of the Fe(OH)\(_3\) nanoparticles by NBs and MBs are shown in Table 4. These data validated the results earlier discussed (Fig. 5 and Table 3), with higher removal at 2 bar, when the NB/MB ratio is high, due to the longer residence times of the NBs and the nano size of the particles. Herein, the MBs rise rapidly, do not attach to the nano-species, and their flotation capacity becomes very low. Conversely, the NBs appear to adhere to and entrap the nanoparticles decreasing the density of the smallest units formed upon Fe(OH)\(_3\) precipitation [17].

3.4. Flotation of Fe(OH)\(_3\) precipitates by isolated NBs

Table 5 shows results for the removal of precipitates by isolated NBs as a function of the feed iron concentration and 10 min of flotation (longer than in Table 3). Results again show better efficiencies for the higher concentrations, probably because the formation of larger particles favours the entrapment of the NBs. Thus, at low feed iron concentration, whereby the amount of insoluble species is low, the removal efficiencies greatly decreased to less than 66% (for initial concentrations lower than 10 mg L\(^{-1}\)).

3.5. Flotation of Fe(OH)\(_3\) nanoparticles by isolated NBs

The separation of nanoparticles by NBs was studied and results are presented in Table 6. As expected the values were <68%, but due to the high dilution of the nanoparticles, the removal may be considered fairly high and should compare to filtration as an example. This appears to be one of the first results of the separation of nanoparticles by nanobubbles!

Summarizing, it is believed that the separation of Fe(OH)\(_3\) precipitated species, by MBs and NBs occurs by the following phenomena:

i. Entrapment of NBs inside the precipitates, decreasing their relative density and relative weight;
ii. Partial aggregation of these aerated precipitates;
iii. Entrapment of MBs inside the precipitates and entrainment of aggregates and precipitates by MBs.

These mechanisms of interactions between the bubbles and precipitates have been observed in other systems in studies published by our group [15].

Mechanism “i” was validated by flotation experiments of Fe(OH)\(_3\) precipitates and nanoparticles with isolated NBs, as shown in Tables 5 and 6. Herein, the flotation of the Fe(OH)\(_3\) precipitates was observed to be slower (10 min flotation) compared to the separation by MBs (5 min). This is the first report on the flotation of Fe(OH)\(_3\) precipitates with isolated NBs.

4. Conclusions

The flotation of colloidal precipitates and nanoparticles of Fe(OH)\(_3\) with micro (MBs) and nanobubbles (NBs) was studied. The separation of the solids from water was higher than 99%, leaving less than 1 mg L\(^{-1}\) of total residual iron, using the \( P_{\text{sat}} \) of 2 bar. The use of a higher \( P_{\text{sat}} \) (4 bar) decreased the removal efficiencies due to the high concentration of MBs and their high rising velocities, which caused breakage of some of the precipitates. It was discovered that flotation with isolated NBs is also effective in the removal of Fe(OH)\(_3\) colloidal precipitates and nanoparticles (66–91%), especially with Fe\(^{3+}\) feed content \( \geq 10 \) mg L\(^{-1}\). The separation of nanoparticles of Fe(OH)\(_3\) by NBs and their role in flotation of precipitates was demonstrated for the first time in the literature. The NBs interact with Fe(OH)\(_3\) mainly through an entrapment phenomenon, decreasing their relative density and assisting in flotation with MBs.

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