A Different View ofRemoving Iron and Manganese Complexes by Using Dissolved Air Flotation

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Abstract This work used dissolved air flotation (DAF) together with chemical oxidation as an option to promote iron and manganese organic complexes removal. The conjugated process was carried out by adding ferric chloride as coagulant and chlorine as oxidant where three different strategies were investigated. The main focus was to verify the iron organic and manganese complexes removal through the adjusting of the oxidation/coagulation processes aiming DAF stage. Some preliminary essays demonstrated that only oxidation was capable to promote the Mn precipitation but not the Fe organic compounds. Most of the organic metal compounds were removed by simply DAF (88% for iron and 60% for manganese). However, a low dosage of oxidant (2.6 mg/L of chlorine) was necessary. The DAF was an attractive alternative for iron organic compounds removal, demanding low dosages of chemicals in pH values (6.0) lower than the recommended ones (pH ≥7.5 for iron and pH ≥8.5 for manganese). The application of oxidant together with the coagulant during the rapid mix was the best alternative to promote the removal of color, turbidity, iron and manganese (residuals of <2CU; 0.71 NTU; 0.40 mgFe/L and 0.10 mgMn/L). In all cases no THM concentrations above 32µg/L was detected.

Keywords: Dissolved-Air flotation, Drinking water treatment and Organic Compounds of Iron and Manganese

Introduction

The assessment of efficient removal methods for organic compounds of iron and manganese has been extremely necessary. The appearance of iron and manganese forms in the drinking water treatment field is quite common and the occurrence of these metals is closely associated with color and taste, incrustation in pump lines and staining sanitary devices. When these metals are present in deep wells the removal is often very simple, yet when the source contains natural organic matter (NOM) the removal becomes more difficult. Some articles report iron and manganese removal by using different strategies and methods (Wong (1984); Michalokos et al. (1987); Aziz & Smith (1992) among others) but there was a lack of studies on the optimization of the coagulation process aiming the solid/liquid separation by DAF.

Iron and manganese are easily associated with organic matter forming colored compounds which are very stable. In this case, the associated costs to promote an adequate removal, by using sedimentation step, is high since the organic complexes demand high dosages of oxidant and coagulant in a high pH value so that the precipitated forms can be subsequently removed in sedimentation units. Knocke et. al. (1991) presented the results of an investigation to quantify the kinetics of iron and manganese oxidation by potassium permanganate and chlorine dioxide. The oxidation of Fe(II) and Mn(II) was very fast in the absence of organic matter. However, the reduction of iron could not reach 10% of removal when the organic compounds of iron were present even applying high dosages of oxidant (up
to 10 times of the stoichiometric amount). Thus, the authors affirm that an efficient removal of complexed Fe(II) must rely on processes that can remove NOM.

Most of the times the treatment system that applies oxidative process for iron and manganese removal in sources containing organic matter use sedimentation as a stage preceding filtration. In these cases, high dosages of coagulant and oxidant with high pH values are required so that the produced flocs can present an adequate sedimentation velocity. On the other hand, the Dissolved Air Flotation (DAF) process is a recognized alternative to remove NOM where the efficiency is much better when compared to sedimentation besides using low dosages of coagulant and working with a loading rate around 5 times bigger (Reali & Marchetto, 2001). So, the main aim of this work was the investigation of iron and manganese removal in colored water by adjusting the coagulation for the DAF process. The oxidation process was also investigated as an isolated step and as a conjugated process by adding chlorine in three different strategies described in the next item.

Methods

All the essays were carried out in a dissolved air flotation batch unit called Flotatest. The water was prepared by adding a commercial humic substance (Aldrich), caulin (Fluka), iron (Fe$^{3+}$) and manganese (Mn$^{2+}$) in a deep well water. The investigation was divided in three different stages as illustrated in Figure 1. First of all, oxidation essays were conducted by adding different dosages of chlorine followed by filtration in a 0.45µm medium pore size (1st stage). In this stage, a quenching agent was added in the end of each essay to terminate the oxidative process. Later, the coagulation/flocculation essays were carried out applying different dosages of ferric chloride (from 0 to 35mg/L) in different pH values (ranging from 5.8 to 7.9) for five flotation velocities (5, 12, 18, 25 and 30cm/min). In these essays, called 2nd stage, the oxidant was added (2.6 mg/L) in two different moments: i) in the rapid mix together with the coagulant (2nd stage-a) and ii) 5 minutes before the rapid mix (2nd stage-b).

In the 3rd stage, chlorine was added after the DAF process followed by filtration using filter paper (Whatmann 40). Finally, the dosages of oxidants were varied (from 1.3 to 4.0mg/L) in all the three different alternatives investigated.

The operational conditions along all the essays were kept constant as recommended by Dombroski (1996), apud Reali & Campos (2002): Rapid mixture: velocity gradient: 800s$^{-1}$, time: 20 sec.; Flocculation: velocity gradient: 60 s$^{-1}$, time: 20 min; Dissolved air flotation: recirculation: 10%(v/v), saturation pressure: 450±10 kPa.

Brief Description of the utilized equipment

The lab-scale dissolved air flotation equipment (Flotatest) was well described by Reali & Campos (1995). The installation is composed of four flotation vessels which work in parallel with the saturation chamber operating in intermittent flow (batch). After rapid mixing, with pH correction and coagulant addition, the flocculation step starts by turning on each agitator. After the adopted flocculation time, the needle valves that control the flow of the saturation chamber are opened and the batch flotation takes place.

Analysis

All the analysis referring to turbidity, apparent color, iron and manganese were performed following The Standard Methods for the Examination of Water and Wastewater 20th edition.
In order to verify the influence of the organic matter at the determination of iron and manganese all samples were divided on digested (D) and non-digested (ND) aliquots.

Figure 1: Scheme illustrating the strategies adopted during the essays

Experimental Results and Discussion

General aspects

Figure 3 presents, as an example, some of the results referring to the coagulation/flocculation essays when no chlorine was added.

Figure 3: Some results of flotation curves concerning apparent color with ferric chloride dose of 15 and 30 mg/L (Co: raw water apparent color; C: apparent color after DAF; $D_{FeCl_3}$: ferric chloride dose where $1mgFe^{3+}/L=4.84mgFeCl_3/L$; $D_{Cl_2}$: chlorine dosage; V: flotation velocity) Conditions of the essays: Rapid mixture: velocity gradient: 800 s$^{-1}$, time: 20 sec.; Flocculation: velocity gradient: 60 s$^{-1}$, time: 20 min; Dissolved air flotation: recirculation: 10% (v/v), saturation pressure: 450±10 kPa

In these essays, the behavior of the flotation efficiency when pH values and flotation velocity were varied can be observed. These curves give an idea about the ascension velocity of the flocs obtained in different coagulation and flotation conditions. It is interesting to mention...
that, although there were good conditions in both cases, the curves in Figure 1.2 ($D_{FeCl3}=30\text{mg/L}$) have a tendency to be near to the V axis. This occurs when the pair pH versus coagulation dosage is more adequate to the flotation conditions than the other pairs. The best dosage for the coagulation step ($30\text{mg/L versus pH 6.8}$) was confirmed by duplicate experiments. However, this situation was not confirmed when the oxidant was applied together with the coagulant during the rapid mix, as discussed subsequently (2nd stage-a).

1st Stage essays

The results concerning the oxidation essays (1st Stage) are shown in Table 1:

<table>
<thead>
<tr>
<th>Oxidant dosages (mg/L)</th>
<th>Fe residual (mg/L) (D/ND) [%R]</th>
<th>Mn residual (mg/L) (D/ND) [%R]</th>
<th>Apparent color (uPtCo) [%R]</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.6</td>
<td>(0.82/&lt;0.003*) [76.5]</td>
<td>(0.14/0.12) [44.0]</td>
<td>19 [87.3]</td>
</tr>
<tr>
<td>5.3</td>
<td>(0.45/&lt;0.003*) [87.1]</td>
<td>(0.11/0.07) [56.0]</td>
<td>15 [90.0]</td>
</tr>
<tr>
<td>16.0</td>
<td>(0.40/&lt;0.003*) [88.5]</td>
<td>(0.02/0.01) [92.0]</td>
<td>18 [88.0]</td>
</tr>
<tr>
<td>32.0</td>
<td>(0.36/&lt;0.003*) [89.7]</td>
<td>(0.02/0.01) [92.0]</td>
<td>18 [88.0]</td>
</tr>
</tbody>
</table>

Referring to iron and manganese residuals, it can be observed that their correspondent efficiencies really present improvement when the oxidant dosage was increased. However, the manganese forms were easily precipitated comparing to the iron forms. Even when high dosages of chlorine were applied the iron residual detected in the digested aliquot was pretty high. This gave an indication that the organic iron forms were present as small colloids and/or as dissolved forms. On the other hand, the iron in non-digested aliquots presented a non-detected residual in all cases indicating that all free forms of iron were precipitated. This behavior cannot be observed regarding the manganese residuals, when both digested and non-digested aliquots presented very close residuals. In water free of organic matter the manganese removal is far more difficult than the iron forms but, when the organic matter is presented the compounds of iron are more stable than the manganese compounds and consequently, more difficult to be removed. A possible explanation is that iron and organic matter form stronger complexes than manganese does, as observed to Snoeyink (1980).

Regarding the values of apparent color, it can be observed that there was not a direct relationship between color and iron residuals. The apparent color residuals were almost constant during all 1st Stage essays while the iron residuals varied from 0.82 to 0.36 mg/L.

In general terms, the 1st stage results showed that the chlorine itself was not enough to promote the precipitation of the iron organic complexes (after filtration in 0.45µm medium pore size), even when high dosages of oxidant ($32\text{mg/L that corresponds to 12 times the required stoichiometric dosage}$) were applied. This fact emphasizes that coagulation can be an important step when removing iron organic complexes.
2nd Stage essays

Figure 4 presents the best results referring to the 2nd Stage essays. The oxidant dosage of 2.6 mg/L was adopted in all cases when DAF was applied.

![Figure 4: Residual values of color, turbidity, total iron and manganese after applying DAF together with chemical oxidation with chlorine in two different strategies: a) oxidant applied during the rapid mix and b) oxidant applied 5 minutes before the rapid mix (DFeCl₃: ferric chloride dosage where 1mgFe⁺³/L=4.84mgFeCl₃/L). Raw water characteristics: pH=7.5; turbidity=15±01 (NTU); Apparent color=150±10 (CU=υPtCo); Total Iron=3.5mg/L; Total Manganese=0.25mg/L; Humic acid=5mg/L; Temperature=20±01(ºC); Time of oxidation=20 minutes for 2nd Stage-a and 25 minutes for 2nd Stage-b. Conditions of the essays: Rapid mixture: velocity gradient: 800s⁻¹, time: 20 sec.; Flocculation: velocity gradient: 60s⁻¹, time: 20 min; Dissolved air flotation: recirculation: 10%(v/v); saturation pressure: 450±10 kPa; flotation velocity: 12cm/min.]

Regarding Figure 4, it can be noted that the apparent color residuals were far lower when the oxidant was applied together with the coagulant in the rapid mix. By any reason, the longer oxidation produced worse color removal by DAF. Referring to the metal residuals, it can be observed that the values in both cases (2nd Stage a and b) were very similar. The lowest metals residuals were detected when applying ferric chloride dosage of 15 mg/L. Therefore it can be said that the coagulant application influences in the iron residual. To conclude, it can be asserted that the chlorine application permits an increase in the dissolved air flotation efficiency even when the optimal coagulant dosage (DFeCl₃=30mg/L showed in Figure 3) was decreased to 15mg/L.

3rd Stage essays

Figure 5 presents the results referring to the application of chlorine after clarification by DAF but before filtration. In these essays the oxidation time of 10 minutes was adopted as a representative time for filtration in a hypothetic rapid filter.
Figure 5: Results regarding the DAF process followed by oxidation before the filtration step. The results where “after DAF” appears indicate the application of DAF without any oxidant dosage. ($D_{FeCl_3}$: ferric chloride dosage where 1mgFe$^{3+}$/L=4.84mgFeCl$_3$/L). Raw water characteristics: pH=7.5; turbidity=15±01(NTU); Apparent color=150±10(CU=PtCo); Total Iron=3.5mg/L; Total Manganese=0.25mg/L; Humic acid=5mg/L; Temperature=20±01(ºC); Time of oxidation=10minutes. Conditions of the essays: Rapid mixture: velocity gradient: 800s$^{-1}$, time: 20 sec.; Flocculation: velocity gradient: 60 s$^{-1}$, time: 20 min; Dissolved air flotation: recirculation: 10%(v/v); saturation pressure: 450±10 kPa; flotation velocity: 12cm/min

In these essays chlorine was added only after DAF and before filtration. So, the residuals indicated by “after DAF” were obtained through the coagulation/flocculation followed by DAF without chlorine. Figure 5 showed that lowest manganese residuals were achieved after oxidation followed by filtration but iron organic forms were reasonably removed (around 85%) by the coagulation/flocculation step followed by flotation. Table 2 present some results where no oxidant was added hence it can be verified the efficiency after DAF and after filtration for a ferric chloride dosage of 30mg/L.

Table 2: Results concerning the DAF essays ($D_{FeCl_3}$=30mg/L and $D_{Cl_2}$=0mg/L) followed by filtration in 8µm membrane medium pore size (Whatmann 40)

<table>
<thead>
<tr>
<th>Coagulation pH</th>
<th>Fe (mg/L) (D/ND) [%R]</th>
<th>Mn (mg/L) (D/ND) [%R]</th>
<th>Fe (mg/L) (D/ND) [%R]</th>
<th>Mn (mg/L) (D/ND) [%R]</th>
</tr>
</thead>
<tbody>
<tr>
<td>6.8±0.1</td>
<td>(0.46/0.35)[86.8]</td>
<td>(0.26/0.19)[0.0]</td>
<td>(0.19/nd)[94.5]</td>
<td>(0.23/0.17)[8.0]</td>
</tr>
<tr>
<td></td>
<td>(0.53/0.30)[84.8]</td>
<td>(0.23/0.17)[8.0]</td>
<td>(0.27/nd)[92.3]</td>
<td>(0.25/0.17)[0.0]</td>
</tr>
</tbody>
</table>

Raw water characteristics: pH=7.5; turbidity=15±01(NTU); Apparent color=150±10(PtCo); Total Iron=3.5mg/L; Total Manganese=0.25mg/L; Humic acid=5mg/L; Temperature=20±01(ºC) ($D_{FeCl_3}$: ferric chloride dosage; D: digested aliquots; ND: non-digested aliquots; [%R]: percentage of removal of the total metals)

Regarding Table 2, a high removal efficiency of iron after DAF (>84%) and after filtration (>90%) without any oxidant dosage can be observed. However, manganese was practically not removed. This indicates that a low dosage of oxidant was necessary to efficiently promote Fe and Mn removal.
Referring to Figure 4 and 5 it can be observed that the essays where the oxidant was added together with the coagulant in the rapid mix presented a better group of results. Although the iron residual was not the lowest comparing to other alternatives, all considered removals (apparent color, turbidity and metals) were far more efficient.

Table 3 presents the results where oxidant dosages were varied for the three investigated alternatives for a fixed dosage of coagulant ($D_{FeCl3}$ 30mg/L).

Table 3: Results concerning the DAF essays together with oxidation in different dosages of chlorine followed by filtration in 8µm membrane medium pore size ($D_{FeCl3}$: 30mg/L; flotation velocity: 12cm/min)

<table>
<thead>
<tr>
<th>$D_{Cl2}$ (mg/L)</th>
<th>$T_{oxid}$ (min.)</th>
<th>pH coag</th>
<th>Fe (mg/L) D/ND [%R]</th>
<th>Mn (mg/L) D/ND [%R]</th>
<th>Fe (mg/L) D/ND [%R]</th>
<th>Mn (mg/L) D/ND [%R]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.3</td>
<td>20</td>
<td>5.8 ±0.1</td>
<td>0.73 ±0.19 [79.1]</td>
<td>0.16 ±0.10 [36.0]</td>
<td>nd/nd</td>
<td>nd/nd</td>
</tr>
<tr>
<td>2.6</td>
<td></td>
<td></td>
<td>0.33 ±0.06 [90.5]</td>
<td>0.11 ±0.08 [56.0]</td>
<td>nd/nd</td>
<td>nd/nd</td>
</tr>
<tr>
<td>4.0</td>
<td></td>
<td></td>
<td>0.43 ±0.04 [87.2]</td>
<td>0.15 ±0.14 [40.0]</td>
<td>nd/nd</td>
<td>nd/nd</td>
</tr>
</tbody>
</table>

Results referring to 2nd Stage-a

<table>
<thead>
<tr>
<th>$D_{Cl2}$ (mg/L)</th>
<th>$T_{oxid}$ (min.)</th>
<th>pH coag</th>
<th>Fe (mg/L) D/ND [%R]</th>
<th>Mn (mg/L) D/ND [%R]</th>
<th>Fe (mg/L) D/ND [%R]</th>
<th>Mn (mg/L) D/ND [%R]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.3</td>
<td>25</td>
<td>6.8 ±0.1</td>
<td>0.36 ±0.05 [89.7]</td>
<td>0.16 ±0.18 [36.0]</td>
<td>nd/nd</td>
<td>nd/nd</td>
</tr>
<tr>
<td>2.6</td>
<td></td>
<td></td>
<td>0.24 ±0.07 [93.1]</td>
<td>0.11 ±0.06 [56.0]</td>
<td>nd/nd</td>
<td>nd/nd</td>
</tr>
<tr>
<td>4.0</td>
<td></td>
<td></td>
<td>0.22 ±0.12 [93.7]</td>
<td>0.09 ±0.09 [64.0]</td>
<td>nd/nd</td>
<td>nd/nd</td>
</tr>
</tbody>
</table>

Results referring to 2nd Stage-b

<table>
<thead>
<tr>
<th>$D_{Cl2}$ (mg/L)</th>
<th>$T_{oxid}$ (min.)</th>
<th>pH coag</th>
<th>Fe (mg/L) D/ND [%R]</th>
<th>Mn (mg/L) D/ND [%R]</th>
<th>Fe (mg/L) D/ND [%R]</th>
<th>Mn (mg/L) D/ND [%R]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.3</td>
<td></td>
<td></td>
<td>0.49 ±0.24 [86.0]</td>
<td>0.30 ±0.09 [91.4]</td>
<td>0.03 ±0.01 [88.0]</td>
<td></td>
</tr>
<tr>
<td>2.6</td>
<td></td>
<td></td>
<td>0.46 ±0.35 [86.8]</td>
<td>0.26 ±0.19 [94.2]</td>
<td>0.03 ±0.01 [88.0]</td>
<td></td>
</tr>
<tr>
<td>4.0</td>
<td></td>
<td></td>
<td>0.53 ±0.30 [84.8]</td>
<td>0.23 ±0.17 [80.0]</td>
<td>0.01 ±0.01 [96.0]</td>
<td></td>
</tr>
</tbody>
</table>

Results referring to 3rd Stage

Raw water characteristics: pH=7.5; Turbidity=15±01(NTU); Apparent color=150±10(CU=uPtCo); Total Iron=3.5mg/L; Total Manganese=0.25mg/L; Humic acid=5mg/L; Temperature=20±01(ºC) ($D_{FeCl3}$ : ferric chloride dosage; $D_{Cl2}$ : chlorine dosage; $T_{oxid}$ : time interval between the oxidant addition and DAF (2nd Stage) or filtration (3rd Stage); pHcoag.: pH of coagulation; What.40: Whatmann40 paper filter (8µm); D: digested aliquots; ND: non-digested aliquots; [%R]: percentage of removal of the total metals; a: oxidant added after DAF and before filtration; b: residuals of metals not detected by the analytic method)

In all essays the removal of the metals occurred in a lower pH values than the suggested ones (>7.5 and >8.5 for iron and manganese, in that order) and in a lower dosages of oxidant. The total iron removal was higher than 80% (<0.73mg/L of residual) even when no oxidant was added. The essays involving the pre-oxidation alternative (2nd Stage-b) present the lowest iron residual yet the oxidation time was higher than the others (25minutes).

Comparing the results of Table 2 and 3, it can be clearly observed that the addition of a low dosage of oxidant produce better results for manganese but the total iron residuals were practically the same with or without oxidant after filtration. This probably occurs because iron forms more stable complexes than manganese does so the efficient removal of organic iron compounds must concern the optimization of solid/liquid separation processes.

Some Trihalomethanes (THMs) analyses during the best conditions for oxidant dosage of 2.6 mg/L were conducted. The biggest THM formation occurred when pre-oxidation was applied. However, even in this case, the THM concentration did not exceed 32µg/L. This fact might have two main explanations: i) DAF process was efficient enough to remove THM precursor and/or an eventually formed THM, and ii) iron complexes inhibit THM formation.
In general terms, the article showed that the dissolved air flotation without any oxidant dosage was able to remove most of the organic iron compounds (around 88% of removal efficiency) suggesting that organic compounds of iron could be removed through adjusting the chemical coagulation when DAF was applied as the clarification technique for solid/liquid separation. However, when the DAF was used together with chemical oxidation the results were even better for both the iron and the manganese removal (removal >90% and around 60%, respectively) in pH values lower than the recommended ones. The application of oxidant in the rapid mix moment presented the best group of results. In this case, the residuals of metals were not detected after the filtration using filter paper (8 µm pore size).

The application of adjusted dosages of coagulant for the DAF process together with low dosages of chlorine constitute an attractive alternative to promote both the clarification and the organic iron, or manganese, compounds removal of this kind of water.

Conclusions

- As expected, the iron organic compounds were harder to precipitate than the free forms even when high dosages of chlorine were applied;
- Manganese was easier to remove by oxidation/precipitation than the iron organics;
- The dissolved air flotation was an attractive alternative to promote the removal of iron organic compounds even without oxidant, however the association of DAF and chemical oxidation (in a low dosage) presents better results (<0.73mgFe/L);
- DAF together with chlorine (2.6mg/L) added in the rapid mix (1st Stage essays for DFeCl3=30mg/L) presents the best treatment alternative (0.33mgFe/L;0.16mgMn/L);
- THM concentration was not expressive in all investigated strategies but an alternative oxidant is recommended to reduce the associated risk of THM formation.

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