Influence of the apparent molecular size of humic substances on the efficiency of coagulation using Fenton's reagent

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ABSTRACT

This work used Fenton's reagent as a coagulating agent in the treatment of water samples with high true colour caused by humic substances (HS) extracted from peat. In addition, the effects of the apparent molecular size of HS on coagulation, flocculation and flotation were studied. To that end, four distinct water samples having the same true colour were prepared using HS with different molecular sizes, which were obtained by ultrafiltration fractioning. Through optimisation of coagulant dosage and coagulation pH, as well as posterior construction of coagulation diagrams for each water sample, it was verified that the sample prepared with the smallest apparent molecular size of HS was the most difficult to treat, requiring higher coagulant (Fenton's reagent) dosages than samples prepared with larger HS molecular sizes. Furthermore, filtration experiments after dissolved air flotation (DAF) were carried out in an attempt to simulate conventional treatment. The most representative results in filtered water were: apparent colour ≤ 3 HU; turbidity < 0.5 NTU; and residual iron concentration < 0.005 mg/L. The absorbance and total organic carbon values of filtered water samples were also very low, suggesting that the formation of disinfection by-products with chlorine would likely be insignificant.

Key words: coagulation, DAF, drinking water, Fenton's reagent, humic substances, molecular size.

INTRODUCTION

Humic substances (HS) are heterogeneous mixture of dark-coloured organic macromolecules of complex composition; they are present in soil and aquatic ecosystems and function as effective carbon reservoirs that prevent carbon dioxide emission. Humic substances comprise 60-70% total soil carbon and 60-90% total carbon dissolved in natural waters (Richard et al. 2008). HS are not well-defined substances but can generally be subdivided in three fractions, namely: humins, representing the insoluble humic components of aqueous solutions at all pH values; humic acids (HA), which are soluble in alkaline and weakly acidic solutions but precipitate at or below pH 2.0; and fulvic acids (FA), which are soluble in aqueous solutions at all pH values (Stevenson 1994). Humic materials may be specifically targeted for removal

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from potable water supplies because they can adversely affect appearance and taste and they can react with chlorine to form potentially carcinogenic chlorinated organic compounds (Lin and Wang 2011, Selcuk et al. 2011). Furthermore, the presence of macromolecular dissolved organic matter may reduce the effectiveness of water treatment processes that employ membranes or microporous adsorbents (Zularisam et al. 2006, Zheng et al. 2011). Even when not specifically targeted for removal, macromolecular dissolved organic matter has been shown to compete with low molecular weight synthetic organic chemicals, reducing their adsorption rates and equilibrium capacities (O'Melia et al. 1999, Katsumata et al. 2008, Vreysen and Maes 2008). The removal of (or the reduction in concentration of) such organic matter is therefore an important factor in water treatment.

The flocs formed by HS coagulation are relatively small and have low specific masses (Fusheng et al. 2008), mainly with low turbidity and high true colour. As a result, their removal by sedimentation is limited. Thus, the use of dissolved air flotation (DAF) is an interesting clarification technology for water with these characteristics.

The use of Fenton's reagent, which entails adding Fe^{+2} ions and hydrogen peroxide (H_2O_2) under acid conditions, is advantageous for drinking water treatment because it provides both pre-oxidation and coagulation in a single process. As shown in Equation (1), Fenton's reaction forms the hydroxyl free radical ($OH^\bullet$), which is a highly reactive and non-selective intermediate oxidant capable of effectively oxidising numerous organic substances (Peyton 1988, Nogueira and Guimarães 2000). Because both Fe^{+2} and Fe^{+3} ions form hydrolysed species that act as coagulants, Fenton's reagent can have the double function of oxidation and coagulation during treatment processes.

$$Fe^{+2} + H_2O_2 \rightarrow Fe^{+3} + OH^\bullet + OH^- \qquad (1)$$
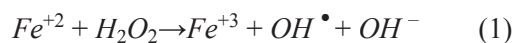
The strong oxidative power of Fenton's reagent that results from the hydroxyl radical ($OH^\bullet$) is also advantageous as the pre-oxidation step becomes increasingly necessary to address poor raw water quality. With Fenton's reagent, undesirable halogenated by-products are not formed (since the raw water does not have the precursor's agents, such as bromide and iodine). Fenton's reagent is further advantageous for natural organic matter (NOM) removal because the coagulants traditionally used in water treatment (alum or iron salts) are frequently incapable of removing recalcitrant NOM (Fabris et al. 2004), making alternative treatment processes necessary. Advanced oxidative processes (AOP), including the application of Fenton's reagent, have thus been introduced as alternatives.

To our knowledge, there is a dearth of reports on the degradation of HS using Fenton's reagent (Fukushima et al. 2001, Murray and Parsons 2004a b, Katsumata et al. 2008). Some studies have been carried out showing the influence of apparent HS molecular sizes on coagulation with traditional coagulants, flocculation and sedimentation (Ratnaweera et al. 1999, Campos et al. 2005, 2007), but data on the use of DAF and Fenton's reagent are limited.

Thus, the main objective of this study was to evaluate the effects of apparent HS molecular size on the efficiency of the coagulation, flocculation and flotation of water samples with the same true colour using Fenton's reagent as coagulant. In addition to that, the aim of this study was to investigate the resulting filtered water quality by means of sand filtration experiments following DAF, using each water sample prepared with HS of different apparent molecular sizes.

MATERIALS AND METHODS

COLLECTION AND EXTRACTION OF HS

The HS were extracted from peat soil collected from the banks of the Mogi Guaçu River in Brazil

(latitude 21.5° S and longitude 47.9° W). Peat samples were dried and then coarsely ground in an agate mortar. The HS extraction method was as follows: the peat was added to a KOH extraction solution (0.5 mol/L) in a 1:20 (m/v) ratio; this solution was mixed for 4 hours at room temperature (~25°C) and then allowed to sediment for 48 hours, after which the supernatant was stored in semi-permeable paper bags. These bags were placed in a hydrochloric acid solution (HCl 1%) until the HS extracts reached a pH close to 6.0. Finally, residual Cl^- was removed via dialysis in non-chlorinated water until HS samples tested negative for chloride (using an $AgNO_3$-based test).

Following extraction, the HS solution was frozen and stored in plastic bottles.

ULTRAFILTRATION (UF) FRACTIONATION OF HS

The extracted HS were diluted to a concentration of 1.0 mg/mL using ground water. The solution was vacuum filtered using a 0.45 mm (Millipore) membrane for subsequent UF fractionation (*polyethersulfone* membranes, Vivaflow 50, Satorius group, tangential flow, Vivascience). During HS fractionation, a sample concentration method using recirculation was adopted (Duarte et al. 2001). The maximum applied flow rate was 300 mL/min with 1.5 bar pressure. The following apparent molecular sizes fractions were obtained: between 100 kDa and 0.45 mm; between 30 and 100 kDa; and < 30 kDa. A composite sample containing all size fractions was also obtained, filtered only through the 0.45 mm membrane.

WATER SAMPLES

Four distinct water samples were prepared for each of the three HS size fractions (100 kDa-0.45 mm, 30-100 kDa and < 30 kDa) and the composite fraction (0.45mm filtered). Each HS fraction was independently added to ground water. The four water samples exhibited true colour values of 100

± 5 HU (Hazen units), and the pH of each sample was adjusted to 5.0 ± 0.1.

COAGULATION, FLOCCULATION AND FLOTATION TESTS

Coagulation diagrams were built for the four water samples by varying the coagulant dosage (Fenton's reagent) and the coagulation pH; 0.1 M sodium hydroxide (NaOH; A.R., Mallinckrodt) and hydrochloric acid (HCl; 36.5-38%, P.A., Synth) solutions were used to vary the coagulation pH. The temperature of the water samples was maintained at 20 ± 1°C.

Ferrous sulphate (P.A. – A.C.S., J.T. Baker) and a 0.1 M solution of hydrogen peroxide (29%, P.A. – A.C.S., Synthy) were applied as Fenton's reagent. A stock solution of ferrous sulphate was prepared at a concentration of 10 g/L.

Fenton's reagent was applied as a coagulant as follows. First, $FeSO_4$ x $7H_2O$ was dosed, followed by H_2O_2. Immediately after the addition of these chemical products, a sample was collected for oxidation pH measurement: 1.5 min of oxidation time (the average velocity gradient of this step was the same as for the rapid-mix step). After this time, the alkalinising agent was dosed (when started to count rapid-mix time) and another sample was collected for coagulation pH measurement. The hydrogen peroxide dosage was equal to three times (3x) the stoichiometric dosage required for Fenton's reagent (Equation 1), being this ratio employed for all tested ferrous sulphate dosages. For example, the mass of 1 mol of $FeSO_4$ x $7H_2O$ is 278.02 g, which corresponds to a Fe^{+2} mass of 55.85 g. According to Equation (1), 1 mol of Fe^{+2} reacts with 1 mol of H_2O_2 (with a weight ratio of 34.01/55.85). Thus, a $FeSO_4$ x $7H_2O$ dosage of 15 mg/L corresponds to 3.01 mg/L of Fe^{+2} (15 x 55.85/278.02); 1:1 stoichiometry therefore establishes a H_2O_2 dosage of 1.83 mg/L (3.01 x 34.01/55.85). For a 3x dosage, 5.5 mg/L of H_2O_2 (3 x 1.83) is required.

All experiments were performed in flotest equipment (Nova Ética, Brazil) using three square 2 L flasks under the following conditions: rapid-mix

(time, T_{rm} = 10 s; velocity gradient, G_{rm} = 1,000 s^{-1}); flocculation (T_{fl} = 15 min; G_{fl} = 25 s^{-1}); and DAF (Saturation chamber pressure = 400 kPa; Saturation time = 8 min; Recirculation rate = 15%; Flotation velocities [V_f] of 15, 10 and 5 cm/min). The control parameters during these experiments were as follows: oxidation pH; coagulation pH; flotation water pH (to choose which curve would be utilised to make the colour measurement) (Digimed); remaining apparent colour (subnatant); and remaining UV_{254} absorbance (DR/4,000 U, Hach, spectrophotometer). During all pH measurements, samples were stirred using a magnetic stirrer (Quimis). In all colour and absorbance measurements, the dilution caused by the introduction of saturated water was taken into account. For colour measurements, (DR/4,000 U, Hach) spectrophotometer calibration curves were constructed with the extracted HS using the successive dilution method, as described in Standard Methods (1998).

For each water sample, a pair of values 'coagulant dosage versus coagulation pH' was selected in the respective diagrams based on remaining apparent colour and UV_{254} absorbance, and taking into account the three flotation velocities studied. However, although 24 coagulation diagrams were

generated, only the diagrams for apparent colour and V_{fl} = 5 cm/min are presented.

In the coagulation diagrams, the abbreviation CI indicates that coagulation was inefficient. Floc formation was not observed for these points, and consequently, no colour or absorbance measurements were done.

COAGULATION, FLOCCULATION, FLOTATION AND FILTRATION TESTS

With the selected pair of values 'coagulant dosage versus coagulation pH' for each water sample two coagulation, flocculation, flotation and filtration tests were carried out in order to simulate a complete treatment process. In addition to the control parameters already mentioned it was also measured on filtered water: pH; apparent colour; UV_{254} absorbance; turbidity (2100P, Hach, Turbidimeter); total organic carbon (TOC analyser 5000A, Shimadzu); and total iron concentration (Atomic absorption spectrophotometer, model AA-1275, Varian).

The filtration step employed a filter column coupled immediately downstream from the flotest flask. The filter column was a 19-mm internal diameter acrylic tube containing sand as the filter media (10 cm deep). It was used three types of
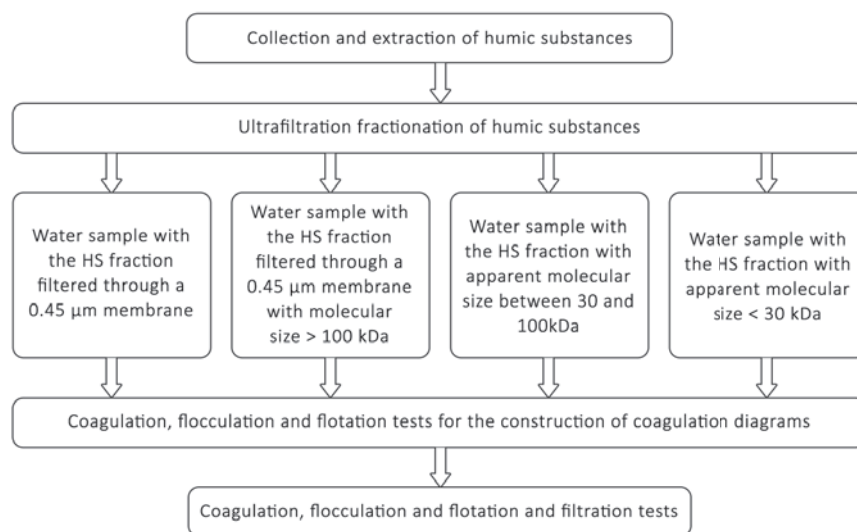

Figure 1 - Schematic flowchart of experiments.

sand (Types 1, 2 and 3) with granulometric ranges between 0.27 and 0.59 mm, 0.42 and 0.84 mm, and 0.59 and 1.41 mm, respectively. The average filtration flow rate was 16 mL/min (corresponding to a filtration rate of 80 m^3/m^2.d), and samples of the filtered water were collected 30 min after the flotation time (flotation velocity of 5 cm/min). Because the filters were backwashed with tap water, it was necessary to filter for 30 min to flush this water out of the filters before collecting samples.

Figure 1 shows schematic flowchart of experiments.

RESULTS AND DISCUSSION

COAGULATION DIAGRAMS

Figures 2-5 show the coagulation diagrams for the four water samples, which were built after coagulation, flocculation and DAF experiments. Hydrogen peroxide and ferrous sulphate dosages are shown on the left-hand y axes, while the correspondent iron-II dosages are shown on the right. The coagulation pH is plotted as the abscissa. The main characteristics of each water sample are also shown.
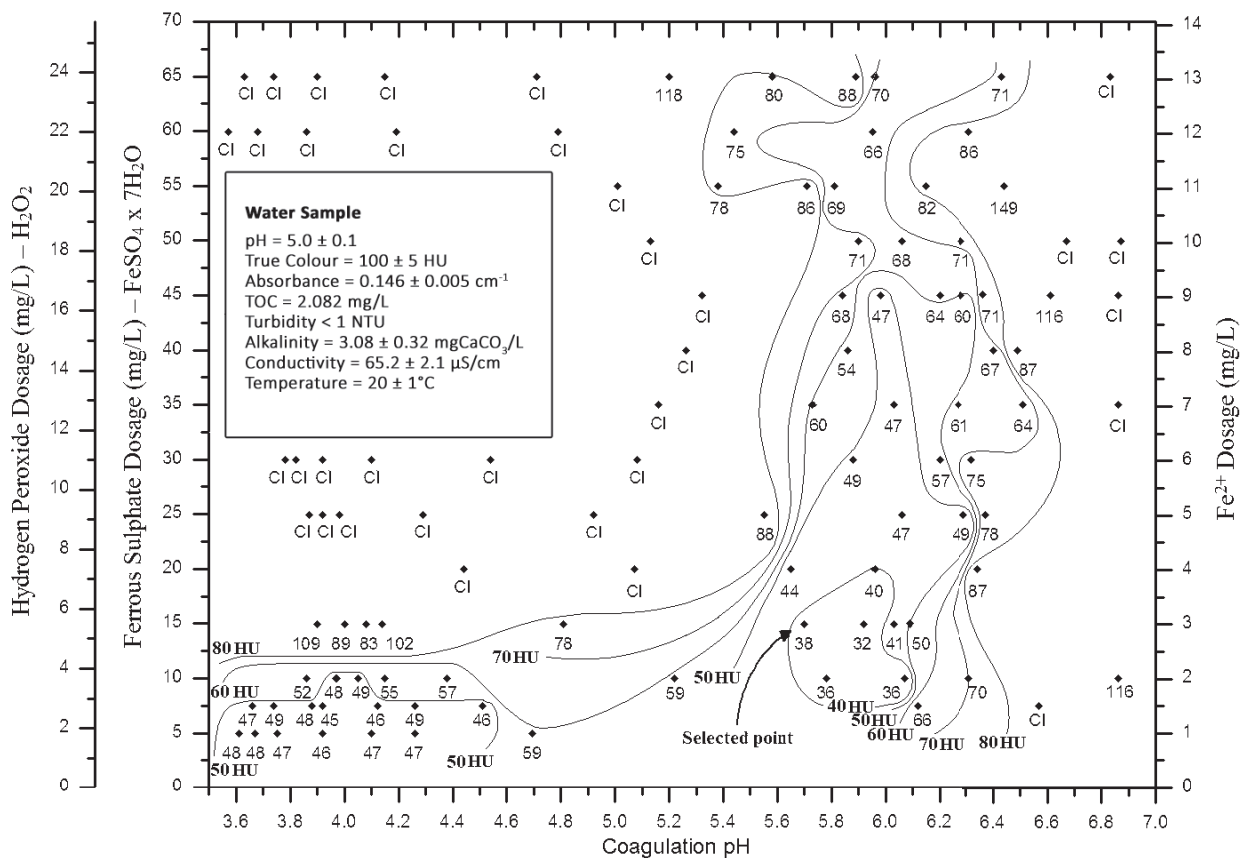

Figure 2 - Fenton dose versus pH coagulation diagram – remaining apparent colour (HU) for the water sample with the HS fraction filtered through a 0.45 μm membrane (V_{fl} = 5 cm/min).
Note: CI indicates that the coagulation was inefficient.

According to classical theories, there are two predominant mechanisms of metal ion coagulation, 'charge neutralisation' and 'sweep coagulation'; the former occurs at lower pH conditions with the coagulant in its cationic form (e.g., Fe[OH]$^{2+}$, Fe[OH]$_2$$^+$), and the latter at higher pH and higher doses where the coagulant precipitates as a metal hydroxide (Duan and Gregory 2003).
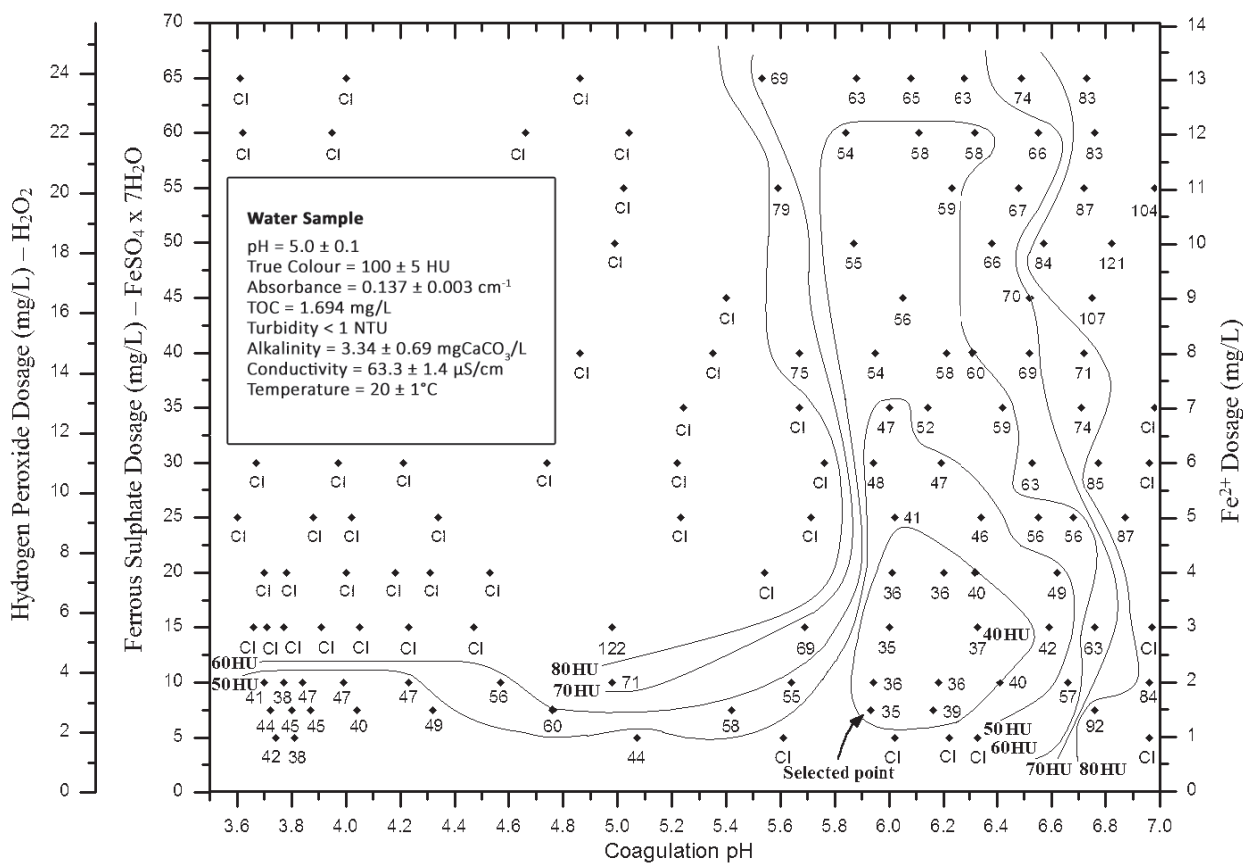
Figure 3 - Fenton dose versus pH coagulation diagram – remaining apparent colour (HU) for the water sample with the HS fraction filtered through a 0.45 μm membrane with apparent molecular size > 100 kDa (V_{fl}= 5 cm/min).

An analysis of Figures 2-5 reveals two regions in which coagulation with Fenton's reagent and subsequent flocculation and flotation produce removal efficiencies greater than or equal to 50% and 60% for the first (lower pH) and second (higher pH) region, respectively. Similar behaviour was observed by Edwards and Amirtharajah (1985), who also worked with water sample with true colour of 100 HU (caused by the addition of humic acid) and turbidity equal to zero, using aluminium sulphate (alum) as a coagulant. These researchers concluded that in the first region, corresponding to approximate coagulation pH values of 3.6 to 4.6 in the current study (Figures 2-5), the hydrolysing species adsorption mechanism was probably dominant, causing charge neutralisation of HS molecules. In the second region, which is approximately between pH

5.6 and 6.6 in the current study, Fe(OH)$_3$ precipitate formation was observed, and removal possibly occurred via the adsorption of HS molecules and their incorporation into the precipitate. Furthermore, coagulant dosages (Fenton) were lower in the first region than for the second region. As observed by Edwards and Amirtharajah (1985), it seems to have a restabilisation region between the two regions in which the coagulation resulted efficient.

Even knowing that Fenton reaction is a combination of oxidation and coagulation, these results suggest that coagulation using Fenton's reagent produces behaviour similar to that observed in studies using other coagulants, such as ferric chloride and alum. Moreover, oxidation and coagulation probably are removing HS – the former changes the chemical structures of HS molecules,
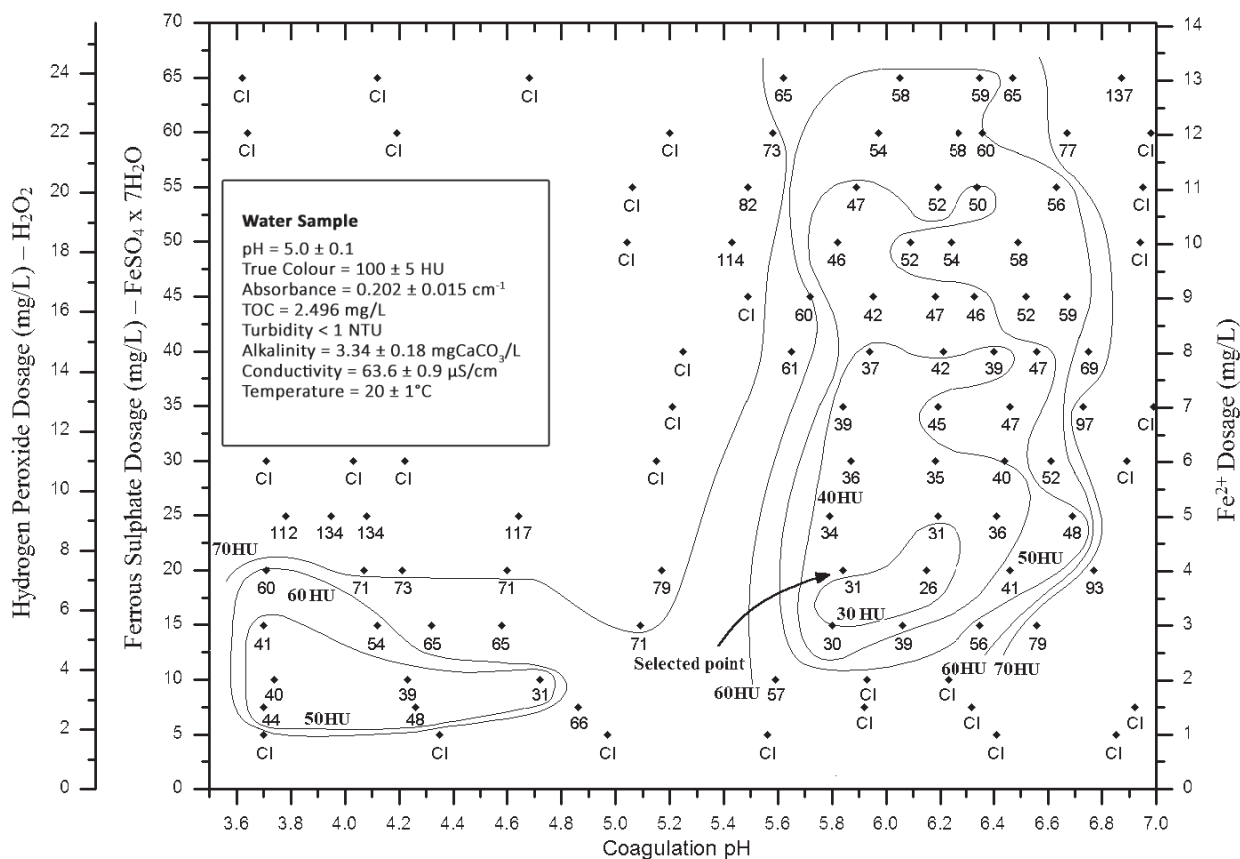
Figure 4 - Fenton dose versus pH coagulation diagram – remaining apparent colour (HU) for the water sample with the HS fraction with apparent molecular size between 30 and 100 kDa (V_{fl} = 5 cm/min).

and the latter transfers HS from one phase to another. Typically, at a low pH, the removal of hydroxyl radical-induced oxidation is maximized, so that the overall removal (due to oxidation and coagulation) may peak in the first region (low pH side). In contrast, at neutral pH, coagulation efficiency may be maximized, so that the overall removal again peaks in the second region.

According to Katsumata et al. (2008) the possible reactions between HA and OH• radicals proposed by Fukushima et al. (2001) involve the addition of OH• radicals to aromatic sites and the abstraction of hydrogen from hydrocarbons. The addition of OH• radicals to aromatic sites in HA yields hydroxycyclohexadienyl radicals (HCHD•) and further oxidation of HCHD• radicals could result in the formation of ring opening products.

As shown by Katsumata et al. (2008), in the photo-Fenton system, the molecular size of HA was decreased as a result of irradiation. In a series of photo-Fenton processes, therefore, the generation of CO_2 and the formation of ring opening products may contribute to a decrease in molecular size. However, the degradation mechanism of HA during the photo-Fenton process is not presently clear.

For the water sample with the HS fraction filtered through a 0.45 μm membrane and with an apparent HS molecular size > 100 kDa, it is evident that the regions formed in the coagulation diagram are wider, and it is observed that the isoefficient curves containing the best results (lower remaining apparent colour) comprise a larger area in Figure 3 than in Figure 2. Furthermore, the highest colour removal efficiency was observed for a ferrous sulphate dosage
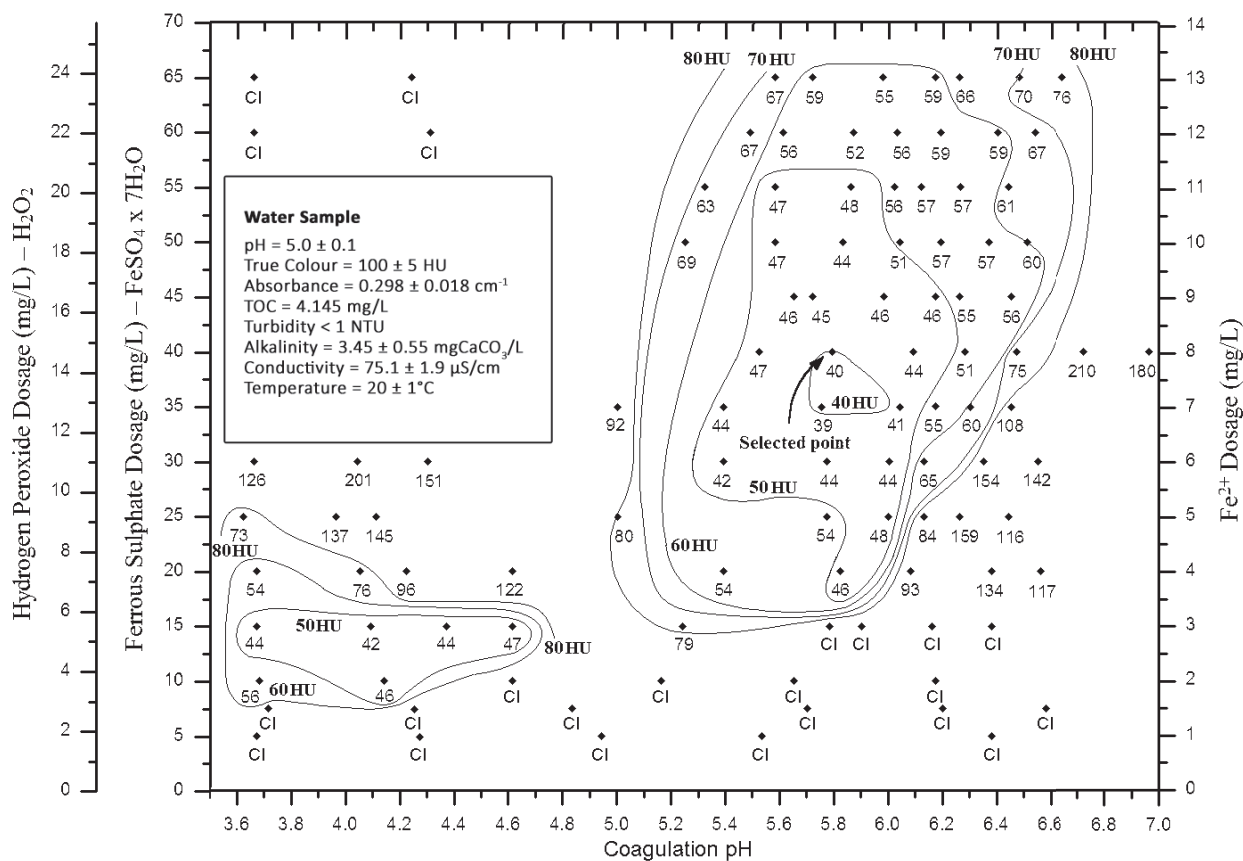
Figure 5 - Fenton dose versus pH coagulation diagram – remaining apparent colour (HU) for the water sample with the HS fraction with apparent molecular size < 30 kDa (V_{fl} = 5 cm/min).

of 7.5 mg/L for the water sample with an apparent HS molecular size fraction between 100 kDa and 0.45 μm, whereas this dosage was between 10 and 15 mg/L for the water sample with the HS fraction only filtered through a 0.45 μm membrane (with similar coagulation pH values). These results can be explained by the hypothesis that for this water sample (between 100 kDa and 0.45 μm), the smallest HS molecules (< 100 kDa) were removed. According to Campos et al. (2005, 2007), these molecules have higher fulvic acid concentrations than humic acid and have higher proportions of bound oxygen groups. These authors concluded that these groups therefore have greater amounts of negative charge due to the non-bonded electrons, which favour repulsion between these electrons and colloidal particles, thereby negatively influencing the coagulation process.

Campos et al. (2005, 2007) worked with the same HS used in the present research (same research group) and characterised the different fractions using nuclear magnetic resonance (NMR) and infrared spectroscopy (IR), in addition to determining the percentage of humic and fulvic acids.

For the water sample with the HS apparent molecular size fraction between 30 and 100 kDa (Figure 4), it can be observed that the isoefficiency curves leading to the most effective coagulation were shifted to a slightly lower coagulation pH range (for the second region on the diagrams). For the size fraction < 30 kDa (Figure 5), these curves showed a more accentuated shift, indicating that the smallest HS molecules – which present higher fulvic acid concentrations in relation to humic acid and higher proportions of bound oxygen groups

(Campos et al. 2005, 2007) – required a somewhat lower coagulation pH in comparison to the larger apparent HS molecular sizes.

For the fraction < 30 kDa, ferrous sulphate dosages up to 15 mg/L (for the second region on the coagulation diagrams) were required for floc formation, indicating that lower dosages were insufficient to destabilise the HS. However, for the larger apparent HS molecular sizes (Figure 3), higher removal efficiencies were reached at dosages lower than or equal to this value.

It was also observed that, for the water sample with an HS size fraction < 30 kDa, the flotation velocity of 15 cm/min was not efficient for removing apparent colour (data not presented), indicating that the smaller HS molecular sizes require lower flotation velocities and, consequently, lower superficial application rates must be used in continuous flow treatment plants.

As previously mentioned, the coagulation diagrams were constructed for flotation velocities of 15, 10 and 5 cm/min and for remaining apparent colour and UV_{254} absorbance. All of these factors were taken into account when the selected point was chosen (which corresponds to a pair of values coagulation dosage versus coagulation pH), and because of this, the lowest remaining apparent colour found in the diagrams for V_{fl}= 5 cm/min was not always selected.

A general analysis of all the coagulation diagrams (Figures 2-5) reveals that the selected point for the HS fraction with apparent molecular size between 30 and 100 kDa required a coagulant dosage (Fenton) close to 166% higher than that for the selected point for the HS fraction between 100 kDa and 0.45 µm, and 33% higher than that required for the water sample having the HS fraction only filtered through a 0.45 µm membrane. The selected point for the HS fraction < 30 kDa required twice the dosage needed for the fraction between 30 and 100 kDa and approximately 432% higher than that for the fraction between 100 kDa and 0.45 µm.

Ratnaweera et al. (1999) also fractionated HS (composed of NOM extracted from natural water by reverse osmosis) using UF (employing *polyethersulfone* membranes with tangential flow) in different apparent molecular sizes (< 10 kDa, between 10 and 50 kDa, between 50 and 100 kDa, and > 100 kDa) and observed that the HS of larger apparent molecular size required lower coagulant dosages in comparison with those of smaller apparent molecular size. These experiments were performed in a jartest apparatus and included coagulation, flocculation and sedimentation. Campos et al. (2005, 2007) also performed jartest experiments using coagulation, flocculation and sedimentation with alum as a coagulant and found similar results. Thus, it is possible to conclude that, regardless of the coagulant used (even Fenton's reagent, which is both an oxidant and a coagulant) and the clarification technology (sedimentation or flotation) employed, waters predominantly containing HS molecules of smaller apparent size are more difficult to treat.

As verified by Campos et al. (2005, 2007) the smallest HS fraction presented a higher percentage of fulvic acids in relation to humic acids. The fulvic acids have smaller chains, with structures dominated by aliphatics, a higher number of functional carboxylic groups, and phenolic and alcoholic hydroxyls. These characteristics make the HS more hydrophilic and acidic (Stevenson 1994). These findings suggest that not only the apparent molecular size but also the structural characteristics of HS fractions play a significant role in the coagulation process.

FILTRATION EXPERIMENTS AFTER DAF

Tables I and II show the results of filtration experiments following DAF (two replicate experiments for each water sample). The chemical product dosages applied correspond to the dosages of the selected points on the coagulation diagrams (Figures 2-5) for each water sample, and its characterization is also shown in Figures 2-5.

TABLE I

Results for sand filtration tests after DAF for the water sample with the HS fraction filtered through a 0.45 μm membrane and for the water sample with the HS fraction between 100 kDa and 0.45 μm.

Sand Type	pH_{oxid}	pH_{coag}	pH_{flot}	pH_{filtr}	*Rem. ap. col. after flotation (HU) 15 cm/min	*Rem. ap. col. after flotation (HU) 5 cm/min	253.7 nm rem. Abs after flotation (cm⁻¹) 15 cm/min	253.7 nm rem. Abs after flotation (cm⁻¹) 5 cm/min	**% rem. Abs after flotation (A/A₀)*100 15 cm/min	**% rem. Abs after flotation (A/A₀)*100 5 cm/min	Rem. ap. col. after filtration (HU)	253.7 nm rem. Abs after filtration (cm⁻¹)	% rem. Abs after filtration (A/A₀)*100	Turbidity after filtration (NTU)	***TOC after filtration (mg/L)	residual total Fe after filtration (mg/L)
Test 1 – Water sample with the HS fraction filtered through a 0.45 μm membrane with 15 mg/L of $FeSO_4 \times 7H_2O$; 5.5 mg/L of H_2O_2; and 4.5 mg/L of NaOH																
1	4.29	5.88	6.39	6.50	69	36	0.106	0.064	70	42	<1	0.007	5	0.28	0.770	< 0.005
2	4.32	5.86	6.40	6.54	51	28	0.083	0.053	55	35	<1	0.009	6	0.28	0.667	< 0.005
3	4.34	5.81	6.35	6.52	61	37	0.098	0.065	64	43	1	0.011	7	0.29	0.398	< 0.005
Test 2 – Water sample with the HS fraction filtered through a 0.45 μm membrane with 15 mg/L of $FeSO_4 \times 7H_2O$; 5.5 mg/L of H_2O_2; and 4.5 mg/L of NaOH																
1	4.28	5.89	6.40	6.48	56	32	0.085	0.058	56	38	<1	0.006	4	0.36	0.689	< 0.005
2	4.30	5.90	6.41	6.50	63	32	0.089	0.057	59	38	<1	0.006	4	0.38	0.592	< 0.005
3	4.31	5.87	6.41	6.50	51	34	0.084	0.060	55	39	1	0.007	5	0.40	0.376	< 0.005
Test 3 – Water sample with the HS fraction filtered through a 0.45 μm membrane and > 100 kDa with 7.5 mg/L of $FeSO_4 \times 7H_2O$; 2.75 mg/L of H_2O_2; and 3.0 mg/L of NaOH																
1	4.75	5.87	6.28	6.51	67	37	0.077	0.042	56	31	<1	0.003	2	0.38	0.517	<0.005
2	4.68	6.06	6.30	6.57	64	34	0.065	0.046	47	33	<1	0.006	4	0.32	0.362	<0.005
3	4.67	5.98	6.27	6.55	74	41	0.089	0.049	65	36	<1	0.008	6	0.33	0.393	<0.005
Test 4 – Water sample with the HS fraction filtered through a 0.45 μm membrane and > 100 kDa with 7.5 mg/L of $FeSO_4 \times 7H2O$; 2.75 mg/L of H_2O_2; and 3.0 mg/L of NaOH																
1	4.75	5.88	6.22	6.51	47	32	0.059	0.048	43	35	<1	0.004	3	0.28	0.696	<0.005
2	4.71	5.97	6.34	6.50	54	35	0.065	0.049	47	36	<1	0.007	5	0.31	0.403	<0.005
3	4.72	6.02	6.34	6.55	73	37	0.082	0.046	60	33	<1	0.007	5	0.30	0.329	<0.005

* Rem. ap. col. - Remaining apparent colour;

** % rem. Abs - Percentage remaining of Absorbance at 253.7 nm (cm⁻¹); (A/A₀)*100 - A is the remaining absorbance (cm⁻¹) and A₀ is the absorbance (cm⁻¹) of the water sample;

*** TOC – Total Organic Carbon.

TABLE II

Results for sand filtration tests following DAF for the water samples with HS fractions with apparent molecular sizes between 30 and 100 kDa and < 30 kDa.

Sand Type	pH_{oxid}	pH_{coag}	pH_{flot}	pH_{filtr}	*Rem. ap. col. after flotation (HU)		253.7 nm rem. Abs after flotation (cm⁻¹)		**% rem. Abs after flotation - (A/A₀)*100		Rem. ap. col. after filtration (HU)	253.7 nm rem. Abs after filtration (cm⁻¹)	% rem. Abs after filtration - (A/A₀)*100	Turbidity after filtration (NTU)	***TOC after filtration (mg/L)	residual total Fe after filtration (mg/L)
					15 cm/min	5 cm/min	15 cm/min	5 cm/min	15 cm/min	5 cm/min						
Test 5 – Water sample with the HS fraction with apparent molecular size between 30 and 100 kDa with 20 mg/L of $FeSO_4 \times 7H_2O$; 7.3 mg/L of H_2O_2; and 6.0 mg/L of NaOH																
1	3.85	5.81	5.99	6.16	64	34	0.079	0.051	50	32	2	0.006	3	0.36	0.824	<0.005
2	3.77	5.81	5.85	6.24	64	32	0.078	0.048	49	30	2	0.004	3	0.41	0.589	<0.005
3	3.80	5.66	5.93	6.16	71	36	0.085	0.054	53	34	3	0.006	3	0.41	0.533	<0.005
Test 6 – Water sample with the HS fraction with apparent molecular size between 30 and 100 kDa with 20 mg/L of $FeSO_4 \times 7H_2O$; 7.3 mg/L of H_2O_2; and 6.0 mg/L of NaOH																
1	3.75	5.75	6.05	6.10	60	32	0.070	0.049	44	31	2	0.002	1	0.49	0.600	<0.005
2	3.81	5.75	6.12	6.18	64	31	0.086	0.048	54	30	2	0.002	1	0.45	0.599	<0.005
3	3.80	5.60	5.85	5.94	60	32	0.078	0.046	49	29	3	0.004	3	0.44	0.586	<0.005
Test 7 – Water sample with the HS fraction with apparent molecular size < 30 kDa with 40 mg/L of $FeSO_4 \times 7H_2O$; 14.7 mg/L of H_2O_2; and 12.0 mg/L of NaOH																
1	3.64	5.70	5.87	5.87	124	48	0.160	0.079	59	29	2	0.011	4	0.52	0.897	<0.005
2	3.65	5.76	5.92	6.02	130	41	0.092	0.068	34	25	2	0.012	5	0.60	0.895	<0.005
3	3.65	5.70	5.86	5.91	114	49	0.160	0.082	59	30	3	0.016	6	0.55	0.850	<0.005
Test 8 – Water sample with the HS fraction with apparent molecular size < 30 kDa with 40 mg/L of $FeSO_4 \times 7H_2O$; 14.7 mg/L of H_2O_2; and 12.0 mg/L of NaOH																
1	3.74	5.83	5.90	6.03	140	46	0.132	0.083	49	31	2	0.010	4	0.44	0.895	<0.005
2	3.67	5.89	6.00	6.02	142	41	0.202	0.067	75	41	2	0.015	5	0.42	0.967	<0.005
3	3.70	5.89	6.08	6.08	135	49	0.187	0.078	69	49	3	0.016	6	0.48	0.915	<0.005

* Rem. ap. col. - Remaining apparent colour;

** % rem. Abs - Percentage remaining of Absorbance at 253.7 nm (cm⁻¹); (A/A₀)*100 – A is the remaining absorbance (cm⁻¹) and A₀ is the absorbance (cm⁻¹) of the water sample;

*** TOC – Total Organic Carbon.

An analysis of Tables I and II shows that, for the eight experiments and the three sand granulometry types, the remaining apparent colour, turbidity and total iron concentrations after filtration were always less than or equal to 3 HU, 0.50 NTU (except for experiment 7, in which this value was ≤ 0.60) and 0.005 mg/L (below the detection limit for all samples), respectively. Brazilian drinking water standard (Brazil 2004) set a maximum value for apparent colour after filtration of 15 HU (the same value recommended by WHO 2006) and a maximum turbidity value of 1 NTU after rapid filtration (the same value require by the Council Directive 1998, for the treatment of superficial waters) and recommend a goal of achieving a maximum turbidity of 0.5 NTU after rapid filtration. The maximum total iron concentration for Brazilian (Brazil 2004) and European (Council Directive 1998) drinking water standards are 0.3 and 0.2 mg/L, respectively. Thus, the coagulation, flocculation, DAF and filtration treatment employing Fenton's reagent as coagulant meet Brazilian and European drinking water standards (in relation to the measured parameters) for the four water samples studied.

The remaining apparent colour, UV_{254} absorbance and turbidity values were very close each other for the three sand types. Curiously, the highest TOC values were obtained for sand of Type 1 (except for experiment 8), which had the smallest granulometry.

Thus, Type 3 sand seems to be the most appropriate for the treatment of water containing a range of apparent HS molecular size fractions because, in addition to producing the best results, this sand has the largest granulometry among the tested sands. This factor would result in a lower head loss in an actual treatment installation and would therefore result in longer filtration run times.

Water samples prepared with the smallest apparent HS molecular sizes also had higher TOC concentrations in the filtered water (sand Type 3) compared to water prepared with larger apparent HS molecular sizes, indicating that the smallest HS size fractions were more difficult to remove. This fact supports the results found in the coagulation diagrams.

According to AWWA (1999a), disinfection by-product (DBP) concentrations depend on several factors, chief among which are TOC level or UV_{254} and disinfectant type and concentration. One way to minimise by-product formation is to limit the TOC concentration of filtered water. To adequately reduce the risk of DBP formation, according to the AWWA (1999b), TOC concentrations (in filtered water) must be less than 2.0 mg/L. Thus, in this work, the TOC concentrations were well below safe levels (always < 1.0 mg/L), particularly for experiments using Type 3 sand, with an average removal efficiency for all HS fractions of 80%, indicating that disinfection by-product formation would likely be insignificant (Brazilian standards also require that water be disinfected with chlorine and an adequate residual be maintained).

The results of this study suggest that the application of Fenton's reagent in water treatment plants (WTP) may be beneficial as this product does not contribute to the formation of halogenated pre-oxidation by-products. In addition, Fenton's reagent accomplishes both pre-oxidation and coagulation, and as observed, conventional treatment (coagulation, flocculation, DAF and filtration) using Fenton's reagent as a coagulant results in lower TOC and UV_{254} absorbance values for the filtered water produced. Therefore, Fenton's reagent seems to be a promising alternative for the treatment of waters containing high concentrations of organic compounds.

With its high oxidative potential (2.33 V; Huang et al. 1993), the free hydroxyl radical ($OH^{\bullet}$) generated during Fenton's reaction may have other benefits, such as the mineralization of hazardous compounds in the water, which can minimize the amount and toxicity of the sludge to be treated and disposed. The first author have already applied

Fenton's reagent in a real scale WTP in Brazil, which treated raw water that received big contribution of wastewater, and obtained good performance concerning the removal of surfactant agents, but the modification in the plant was not adopted because of the high costs of chemical products.

CONCLUSIONS

i) Water samples prepared with the same true colour but with different apparent HS molecular sizes and different humic and fulvic acids percentages showed different coagulation conditions. For water samples with the smallest apparent molecular size fractions, higher dosages of coagulant were needed (up to 432% higher), mainly because these water samples contained higher concentrations of fulvic acids, which have a larger number of negatively-charged groups.

ii) It is recommended that the coagulation conditions of waters from different sources never be extrapolated, even when such waters have similar true colour values. It is necessary to conduct treatability studies to determine appropriate coagulation conditions and design parameters for each water type.

iii) Coagulant dosage versus coagulation pH values were optimised, and posterior coagulation diagrams were constructed. Two distinct regions were observed in these diagrams in which coagulation, flocculation and DAF using Fenton's reagent as a coagulant produced HS removal efficiencies greater than or equal to 50-60%. The first region occurred at a lower pH range (approximately 3.6 to 4.6) and required lower coagulant dosages (Fenton). The second region occurred at a higher pH range (approximately 5.6 to 6.6) and required higher coagulant dosages. In the first region, coagulation was dominated by the hydrolysing species adsorption mechanism, resulting in charge neutralisation of HS molecules. In the second region, $Fe(OH)_3$ precipitate formation was the likely removal mechanism, resulting

in the adsorption of HS molecules and their incorporation into this precipitate. A restabilisation region also appears to exist between the two regions of efficient coagulation.

iv) With filtration experiments following DAF, the filtered water had remaining apparent colour, turbidity and total iron values of less than or equal to 3 HU, 0.50 NTU (except for experiment 7, in which the value was ≤ 0.60) and 0.005 mg/L, respectively. These results comply with Brazilian and European drinking water standards (with respect to these parameters), and suggest that Fenton's reagent can be effectively used as a coagulant and not only as oxidant (as vastly applied in the literature). Furthermore, the replacement of alum (one of the most widely used coagulants) by an iron salt (such as Fenton's reagent) may yield additional benefits because researchers have questioned the use of alum on the grounds that this product may cause health problems. It is therefore recommended that Fenton's reagent be added to the list of chemical products to be tested in treatability studies.

v) The application of Fenton's reagent in WTP may be beneficial because this product is unlikely to contribute to the formation of halogenated pre-oxidation by-products (since the raw water does not contain the precursors agents). Furthermore, Fenton's reagent accomplishes both pre-oxidation and coagulation, and conventional treatment using Fenton's reagent was found to effectively lower TOC (always < 1.0 mg/L and nearly 80% removal efficiency) and UV_{254} absorbance values in filtered water. Therefore, Fenton's reagent seems to be a promising alternative for the treatment of waters with high concentrations of organic compounds.

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RESUMO

Este trabalho empregou o reagente de Fenton como agente coagulante no tratamento de águas contendo cor elevada causada pela introdução de substâncias húmicas extraídas de turfa. Além disto, foi estudado o efeito do tamanho molecular aparente das substâncias húmicas na eficiência da coagulação, floculação e flotação de águas; para isto foram preparadas quatro águas distintas apresentado a mesma cor verdadeira, mas com substâncias húmicas de diferentes tamanhos moleculares, obtidas por fracionamento por ultrafiltração. Por meio da otimização da dosagem de coagulante e respectivo pH de coagulação e posterior construção dos diagramas de coagulação para cada água de estudo, verificou-se que a água preparada com as substâncias húmicas de menor tamanho molecular aparente apresentou maior grau de dificuldade para tratamento, requerendo dosagens de coagulante (reagente de Fenton) bem mais elevadas em relação às águas preparadas com substâncias húmicas de maior tamanho molecular. Adicionalmente, foram realizados ensaios de filtração em areia após a flotação, procurando-se simular tratamento em ciclo completo. Os resultados mais representativos para a água filtrada foram: cor aparente ≤ 3 uH; turbidez $< 0,5$ NTU; e ferro total residual $< 0,005$ mg/L. Os valores de absorbância e carbono orgânico total da água filtrada também foram muito pequenos, indicando que a formação dos subprodutos da desinfecção com cloro seriam insignificantes.

Palavras-chave: coagulação, FAD, água potável, reagente de Fenton, substância húmicas, tamanho molecular.

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