



REMOVAL OF NATURAL ORGANIC MATTER IN WATER FOR HUMAN CONSUMPTION BY HOMOGENEOUS FENTON PROCESS

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ABSTRACT

The presence of natural organic matter (NOM) in natural waters impairs the performance of water treatment plants, the effectiveness of the disinfection process and biological stability. Consequently, loss of drinking water quality may occur due to the formation of disinfection by-products; increased color, odor and taste; and biological growth in the reservation and distribution systems. Thus, there is a need to study technological alternatives to obtain potable water for public supply, meeting drinking standards. Among the promising technological alternatives are the advanced oxidative processes, which involve the formation of highly reactive hydroxyl radicals ($\bullet\text{OH}$), which degrade the organic molecules present in contaminated waters. The aim of this research was to study the application of the homogeneous Fenton process in the removal of humic acid. Several assays were performed by adding pre-determined amounts of ferrous sulfate and hydrogen peroxide in a solution of 30 mg/L of humic acid. The concentrations of humic acid obtained after the experiments were determined by measuring the absorbance at 254 nm. In the experiments carried out, using half of the stoichiometric concentrations of Fe^{2+} and H_2O_2 , there was a significant removal of the organic matter in the initial four minutes, around 88%.

Keywords: Natural Organic Matter; Advanced Oxidative Processes; Homogeneous Fenton process; Potable Water Treatment; Humic Acid.



1. INTRODUCTION

During the last decades, the amount of natural organic matter (NOM) has been monitored in the water bodies that are used as sources for public supply in different parts of the world. The term NOM is used to describe a complex matrix of organic matter present in natural waters. The quantity and characteristics of NOM in surface waters depend on climate, geology and topography, as well as on various other environmental factors. Changes in the quantity and quality of NOM have a significant influence on the selection, design and operation of water treatment processes (Fabris *et al.*, 2008; Wei *et al.*, 2008; Matilainen *et al.*, 2010).

NOM consists of both hydrophilic and hydrophobic substances, which constitute the largest fraction, accounting for more than half of dissolved organic carbon (DOC) content in water. The hydrophobic NOM can be described as humic substances, consisting mainly of humic acids (HA), fulvic acids (FA) and humin. HAs are composed of organic substances of high molecular mass, which are soluble in alkaline media and insoluble in acid media ($\text{pH} < 2$); the FAs comprise organic substances of non-specific composition and of moderate molecular weight that are soluble at all pH values, while humin usually refers to the organic fraction, insoluble in both alkali and acid, remaining after the extraction of humic and fulvic acids. NOM hydrophobic fractions are rich in aromatic carbons, phenolic structures and conjugated double bonds, while NOM hydrophilic fractions contain mainly aliphatic carbons and nitrogen compounds, such as carboxylic acids, carbohydrates, proteins, sugars, and amino acids (Thurman, 1985; Świetlik *et al.*, 2004; Uyguner *et al.*, 2005; Matilainen *et al.*, 2011).

The NOM present in the water sources causes serious problems in the processes of treatment of drinking water, including the negative effects on the quality of the water due to the color, odor and flavor; need for greater dosages of coagulant and disinfectant, resulting in larger generations of sludge and potential formation of disinfection by-products harmful to human health; it works as a substrate for biological growth in the distribution system; and increased levels of complexed heavy metals and adsorbed organic pollutants (Jacangelo *et al.*, 1995). Therefore, in order to achieve quality drinking water, there is a need to remove organic matter.

Generally, among the various technologies available, the most common and economically feasible processes and operations for the removal of NOM are coagulation and flocculation, followed by sedimentation/flotation and sand filtration. The coagulation/flocculation stages remove the NOM by flocculation adsorption and can generally achieve 50% to 80% DOC removal. Increasing the dose of coagulant will increase the removal, but the process is limited when attempting to achieve total organic carbon (TOC) levels below

1 $\text{mg}\cdot\text{L}^{-1}$. Coagulation removes, especially, the hydrophobic fraction from NOM. The residual organic matter, which remains after coagulation, is largely the hydrophilic fraction of NOM. Thus, further treatment will be focused on the removal of this part of NOM (Jacangelo *et al.*, 1995; Murray *et al.*, 2004; Matilainen *et al.*, 2010).

Since the beginning of the 20th century, chlorine has been used worldwide in the disinfection of water, due to the low cost and its efficiency, besides maintaining a residual disinfectant in the treated water. In addition, chlorine was also used in the stage known as pre-chlorination prior to addition of the coagulant in order to facilitate removal of suspended and dissolved impurities and decrease the chlorine load applied in the treatment. The chlorine dosage, even in a smaller quantity in the pre-chlorination stage, reacts with NOM, causing the formation of disinfection by-products (DBP). Among the more than 600 DBPs already identified are trihalomethanes (THMs) and haloacetic acids (HAAs), which are the two groups found in higher concentrations and commonly in drinking water worldwide. Several studies have reported that these compounds have been linked to adverse health effects such as cancer occurrence, growth retardation, miscarriage, and congenital heart defects (Rosin, 1987; Krasner *et al.*, 2006; Singer, 2006; Badawy *et al.*, 2012).

According to De Julio *et al.* (2006), the advantage of using the Fenton process is related to the possibility of pre-oxidation of the humic substances as well as their coagulation. Pre-oxidation is the result of the generation of highly reactive hydroxyl radicals ($\cdot\text{OH}$), while the coagulation occurs as a function of the Fe^{2+} and Fe^{3+} . It is also seen that, with the use of the Fenton process there is no possibility of formation of undesirable halogen compounds during the pre-oxidation process, which are generally present when chlorine is used as the oxidizing agent.

Increasingly stringent water quality regulations have been imposed in different countries to ensure the safety of drinking water by eliminating or reducing to a minimum concentration of contaminants in water. The United States Environmental Protection Agency (US EPA, 2006) limits the concentration of four THM species (chloroform, bromodichloromethane, dibromochloromethane and bromoform) to 0.080 $\text{mg}\cdot\text{L}^{-1}$ and 0.060 $\text{mg}\cdot\text{L}^{-1}$ the concentration of five HAA species (monochloroacetic, dichloroacetic, trichloroacetic, monobromoacetic, and dibromoacetic acids) in treated water.

The drinking water standard for human consumption in Brazil, Ordinance No. 2914 (Brazil, 2011) limits the total THM concentration (trichloromethane or chloroform, bromodichloromethane, dibromochloromethane, and tribromomethane or bromoform) to 0.1 mg/L and the total HAA



concentration (monochloroacetic acid, monobromoacetic acid, dichloroacetic acid, 2,2-dichloropropionic acid, trichloroacetic acid, bromochloroacetic acid, 1,2,3-trichloropropane, dibromoacetic acid, and bromodichloroacetic acid) to 0.080 mg/L.

Noteworthy is the wide variation of the maximum allowed or recommended THM in different countries, such as, 0,35 mg.L⁻¹ in Canada; 0,2 mg.L⁻¹ in Mexico; 0,08 mg.L⁻¹ in the United States; 0,025 mg.L⁻¹ in Germany; 0,1 mg.L⁻¹ in Brazil; 0,075 mg.L⁻¹ in Netherlands; and 0,010 mg.L⁻¹ in France. These differences, to a certain extent, indicate a lack of knowledge of the actual toxic potential of these compounds, reinforcing the need for research, both to safely establish the maximum permissible values of these by-products, and to develop or improve techniques for mitigating their training during water treatment or even for their degradation. (Brasil, 2007).

According to Latifoglu (2003), there are three methods for the control of DBP in water: 1) control of humic substances, which are precursors; 2) removal of by-products generated in the water; 3) use of chlorine alternative disinfectants to reduce or prevent the formation of by-products. The first and third methods may be used to control the formation of by-products, while the second includes methods of treatment which remove these substances after generation. Thus, from a practical point of view, the best alternative to control the formation of by-products would be the removal of precursor organic compounds prior to oxidation/disinfection of water.

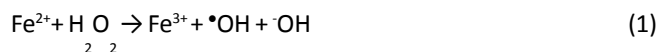
According to Heller *et Padua* (2010), great prominence has been given to the removal of NOM by chemical coagulation, since it can function as a precursor to the formation of undesirable by-products of disinfection. In this way, the traditional coagulation objectives carried out in the water treatment plants (WTP), which are the removal of color and turbidity, are extended, conciliating them with the removal of NOM, which generally requires the use of higher dosages of coagulant and low values of coagulation pH, characterizing what is called enhanced coagulation.

Advanced oxidative processes (AOPs) are defined as hydroxyl radical generating processes (•OH), a highly oxidizing and non-selective agent that can act on the chemical oxidation of a wide range of organic substances. AOPs are considered the most promising alternatives to the limitations of conventional chemical oxidation processes due to their high efficiency and versatility, since in the treatment of non-biodegradable compounds in contaminated waters, atmospheres and soils, they are able to oxidize organic matter in dioxide of carbon and water or, in the case of pre-treatments, making them of smaller molar masses and more biodegradable than their precursors. Hydroxyl radicals are for-

med from oxidants such as hydrogen peroxide (H₂O₂) and/or ozone (O₃), and their efficiency can be increased by combining with ultraviolet (UV) or visible (Vis) irradiation and/or catalysts (metal ions, semiconductors) (Aguiar *et al.*, 2007).

The application of AOP for the removal of organic compounds from water has gained importance in the treatment of water. Among the promising AOPs, which have been much researched in recent years, the Fenton process is highlighted, where the hydroxyl radicals are generated by the decomposition of H₂O₂ in the presence of ferrous ions (Fe²⁺) in acid media. However, the need to operate at low pH values and an additional process for separating colloidal precipitates from ferric hydroxide greatly limits their applicability (Freire *et al.*, 2000).

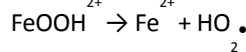
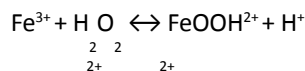
According to Nogueira *et al.* (2007), the Fenton reaction mechanism can be described according to the equations below, in which the ferrous ion (Fe²⁺) starts and catalyzes the decomposition of H₂O₂ in acidic medium, resulting in hydroxyl radical generation (Equation 1). In solution, •OH rapidly attacks organic contaminants, causing chemical decomposition by hydrogen atom abstraction and electrophilic addition to substances containing unsaturations and aromatic rings. In the absence of substrate, the formed hydroxyl radical can oxidize another Fe²⁺ ion (Equation 2), while the ferric ions (Fe³⁺) formed can decompose hydrogen peroxide, catalytically, into water and oxygen (Equations 3-6), also forming Fe²⁺ and radicals.



$$K_1 = 76 \text{ M}^{-1}\text{s}^{-1}, T = 25 \text{ }^\circ\text{C}$$



$$K_2 = 3,2 \times 10^8 \text{ M}^{-1}\text{s}^{-1}$$



$$K_3 = 0,001-0,01 \text{ M}^{-1}\text{s}^{-1}, T = 25 \text{ }^\circ\text{C}$$

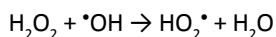




$$K_4 = 1,3 \times 10^6 \text{ M}^{-1}\text{s}^{-1}$$



$$K_5 = 1,2 \times 10^6 \text{ M}^{-1}\text{s}^{-1}$$



$$K_6 = 2,7 \times 10^7 \text{ M}^{-1}\text{s}^{-1} \quad (6)$$

In equation (6), H_2O_2 can act as a hydroxyl radical capture agent and form the hydroperoxyl radical (HO_2^\bullet), which has a lower reduction potential ($E^\circ = 1.42\text{V}$) than $\bullet\text{OH}$ ($E^\circ = 2.8\text{V}$), harming efficiency of the degradation process of organic compounds. This occurs when the H_2O_2 is in excess, because in this situation the concentration of Fe^{2+} in the medium is lower in relation to the concentration of Fe^{3+} , observing that the reaction between Fe^{3+} and H_2O_2 (Equation 3) is slower than the reaction between Fe^{2+} and H_2O_2 (equation 1) (Nogueira *et al.*, 2007).

In many countries, research shows that the removal of NOM by advanced oxidative processes presents promising results. In Brazil, however, it is still a research area to be further explored. Due to the increasing compromise of the quality of the natural waters used for the supply and of the increasingly restrictive requirements of the Ordinance 2914/2011, referring to the potability, in relation to the persistent organic compounds, conducting research in this sector becomes important.

The objective of this research was to evaluate the optimal conditions of the experimental parameters (initial concentrations of H_2O_2 and Fe^{2+} , reaction pH), aiming to determine the efficiency of the homogeneous Fenton process in the removal of HA.

2. METHODOLOGY

All experiments of the homogeneous Fenton process were performed in 250 mL glass beaker at room temperature and with magnetic stirring. Each assay was performed by adding predetermined quantities of commercial humic acid solution ($30 \text{ mg}\cdot\text{L}^{-1}$) (Aldrich), followed by addition of 99% heptahydrate ferrous sulfate (Vetec), supplemented with deionized water to 100 mL. Then pH adjustment was performed with the addition of 0.1M solutions of 95-99% sulfuric acid (Vetec) and 99% sodium hydroxide (Vetec) to the established operating conditions (pH = 3.0) using a pH meter (Tecnopon-mPA-210). The reaction was started with

the addition of pre-established volumes of 50% hydrogen peroxide (Peroxides from Brazil) to the beaker.

The hydrogen peroxide concentration was established based on the initial chemical oxygen demand (COD) of the samples (1 of H_2O_2 to 1 of COD) and the peroxide decomposition reaction, considering that the oxygen produced corresponds to the oxygen demand of the sample. The ferrous sulfate concentration was determined according to the hydrogen peroxide dosage in order to meet the $\text{Fe}^{2+}:\text{H}_2\text{O}_2$ mass ratios of 1:5 and 1:10. Periodically, aliquots were withdrawn with the aid of a pipette, filtered on Quanty-branded filter paper (pores: $28\mu\text{m}$), and with the performance of the UV absorbance analysis. Each experiment was performed in duplicate for a maximum time of 60 minutes. The absorbances of the samples were analyzed in Shimadzu spectrophotometer (UV mini 1240 model).

For the stoichiometric calculations of the concentrations of Fe^{2+} and H_2O_2 used in the research, a COD of $31.5 \text{ mg}\cdot\text{L}^{-1}$ was considered for the solution of $30 \text{ mg}\cdot\text{L}^{-1}$ of humic acid. The efficiency achieved in the removal of HA was calculated taking into account the reduction in HA concentrations during the treatment.

COD analyzes were determined by the colorimetric method of closed reflux, according to the recommendations of the Standard Methods for Examination of Water and Wastewater (Rice *et al.*, 2012). A Hach reactor, model DRB 200, was used for the digestion of the samples and a Hach spectrophotometer, model DR 2800, for the reading of the COD.

2.1 Concentration of organic matter

According to Sargentini Junior *et al.*, (2001), the humic substances can present a concentration of up to 30 mg/L in surface waters. Thus, the assays to evaluate the performance of the homogeneous Fenton process ($\text{H}_2\text{O}_2 + \text{Fe}^{2+}$) in the HA removal were performed based on a solution of $30 \text{ mg}\cdot\text{L}^{-1}$ concentration of humic acid PA, simulating the NOM composition of surface water, which are the main sources of drinking water in many regions worldwide.

2.2 Calibration curve

Initially, a calibration curve of the HA, shown in Figure 1, was made from a stock solution of HA of $1000 \text{ mg}\cdot\text{L}^{-1}$, measuring the UV absorbance at 254 nm (UV254) of filtered samples of dilute solutions of HA. This curve was used to calculate the concentrations of the samples that were submitted to homogeneous Fenton treatment.

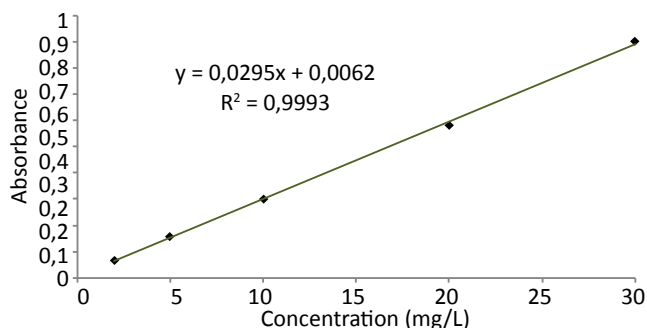


Figure 1. Calibration curve for humic acid (254 nm)

Source: Prepared by the authors, 2017

3. RESULTS AND DISCUSSION

In Figure 2, the effect of the reaction time on the Fenton process for the removal of humic acid was evaluated using a mass ratio of $\text{Fe}^{2+}/\text{H}_2\text{O}_2 = 1/10$, according to the conditions specified below of said figure. A rapid degradation is observed in the first 5 minutes, corresponding to a removal of about 90%. In the following time intervals, there was a slight increase in concentration, which is probably explained by the formation of intermediates absorbing UV radiation. The maximum removal of HA was about 90% in the period of 1 hour, corresponding to the same removal obtained in 5 minutes. Several factors may influence the degradation rate of the organic compound, such as the chemical structure of the substance, iron and hydrogen peroxide concentration, the organic load present, as well as the narrow pH range (2.5-3.0) where the degradation efficiency is maximal. Values above 3.0 causes Fe^{3+} to precipitate as insoluble hydroxide, considering that below 2.5 high H^+ concentrations can sequester hydroxyl radicals (Nogueira *et al.*, 2007). According to Burbano *et al.* (2005), the Fenton reaction is more intense at the beginning of the treatment when only the hydrogen peroxide, the ferrous ions and the contaminant are present.

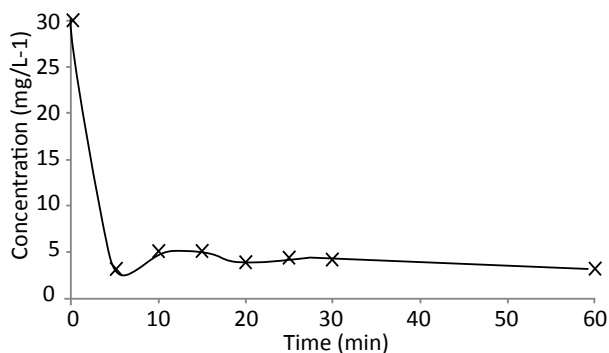


Figure 2. Effect of the reaction time in the Fenton process for the degradation of humic acid ($\text{Fe}^{2+}/\text{H}_2\text{O}_2 = 1/10$). Initial conditions: $[\text{AH}]_0 = 30 \text{ mg/L}$; $[\text{Fe}^{2+}]_0 = 6,7 \text{ mg/L}$; $[\text{H}_2\text{O}_2]_0 = 67 \text{ mg/L}$; $\text{pH} = 3,0$; reaction time = 1 h.

Source: Prepared by the authors, 2017

In the experiments of Figure 3 the results of the increase of the Fe^{2+} concentration are presented, using a mass ratio of $\text{Fe}^{2+}/\text{H}_2\text{O}_2 = 1/5$, in the removal of HA. A rapid degradation of humic acid was observed in the first 5 minutes, corresponding to a removal of approximately 83%. In the next 20 minutes there was an increase in removal, reaching about 91%, very close to the removal obtained at the end of the treatment. Despite the use of twice the concentration of Fe^{2+} ion in relation to the experiments of Figure 2, there was no significant increase in the level of removal. Increasing the iron concentration above the optimum concentration does not mean increasing the COD removal, since the use of a higher Fe^{2+} concentration could lead to the reaction between Fe^{2+} and $\bullet\text{OH}$ radicals (Equation 2), reducing the pollutants degradation rate (Kang *et Hwang*, 2000).

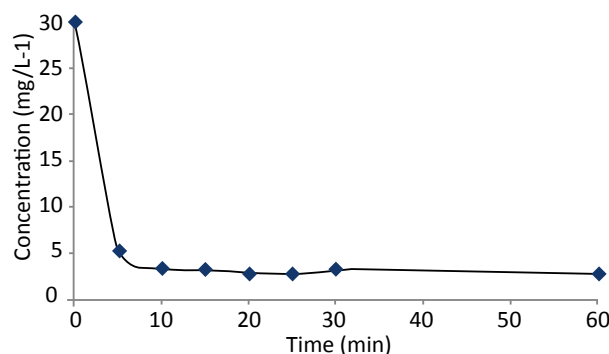


Figure 3. Effect of the reaction time in the Fenton process for the degradation of humic acid ($\text{Fe}^{2+}/\text{H}_2\text{O}_2 = 1/5$). Initial conditions: $[\text{AH}]_0 = 30 \text{ mg/L}$; $[\text{Fe}^{2+}]_0 = 13,4 \text{ mg/L}$; $[\text{H}_2\text{O}_2]_0 = 67 \text{ mg/L}$; $\text{pH} = 3,0$; reaction time = 1 h.

Source: Prepared by the authors, 2017

Figure 4 shows the effect of the Fenton process on the degradation of HA, using the mass ratio of $\text{Fe}^{2+}/\text{H}_2\text{O}_2 = 1/5$ and half of the H_2O_2 concentration. In the initial 10 minutes of treatment, there was an increase in concentration, possibly due to the formation of intermediates, and a reduction of about 97% over the final 50 min of treatment. According to Dezotti *et al.* (2008), the Fenton process may not achieve full mineralization of organic pollutants since organic substances are initially converted into intermediates that are resistant to subsequent oxidation reactions. The reason is due to the complexation of the intermediates (carboxylic acids) with the Fe^{3+} ions and the various competitive reactions that can occur with radicals $\bullet\text{OH}$.

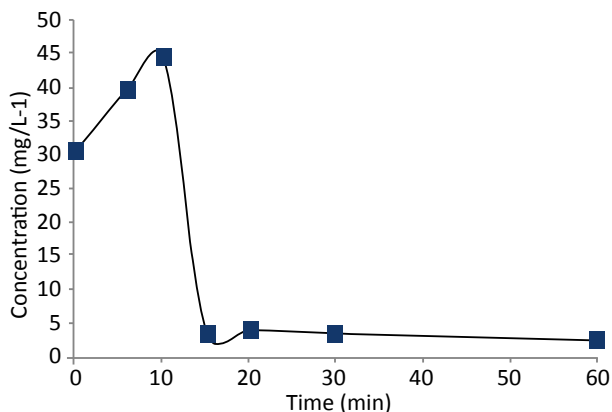


Figure 4. Effect of the reaction time in the Fenton process for the degradation of humic acid ($\text{Fe}^{2+}/\text{H}_2\text{O}_2 = 1/5$; $[\text{H}_2\text{O}_2] = 1/2$). Initial conditions: $[\text{AH}]_0 = 30 \text{ mg/L}$; $[\text{Fe}^{2+}]_0 = 6,7 \text{ mg/L}$; $[\text{H}_2\text{O}_2]_0 = 33,5 \text{ mg/L}$; $\text{pH} = 3,0$; reaction time = 1h.

Source: Prepared by the authors, 2017

Figure 5 shows the results of the experiments performed with the mass ratio of $\text{Fe}^{2+}/\text{H}_2\text{O}_2 = 1/10$, using half of H_2O_2 and Fe^{2+} concentrations, in the degradation of HA with the homogeneous Fenton process. In the initial 4 minutes of treatment, there was a removal of about 88%, little varying at the end of the 24 minutes of treatment. Thus, a significant reduction of HA is observed when using relatively low concentrations of Fe^{2+} and H_2O_2 .

It can be seen from Figure 5 that a crude water with a color equivalent to 30 mg/L humic acid color could be treated by the Fenton process with reaction time of 10 minutes with $[\text{Fe}^{2+}] = 3.35 \text{ mg/L}$ and $[\text{H}_2\text{O}_2] = 33.5 \text{ mg/L}$, yielding an efficiency of about 90% in the removal of HA. The Fenton process could replace the pre-chlorination step in WTP, with the advantage of not causing formation of toxic chlorinated compounds. A pre-chlorination process usually has reaction times of at least 20 minutes; therefore, it requires a tank with twice the volume required for the Fenton process.

A disadvantage of the Fenton process is the formation of sludge when pH is increased for iron removal (Freire *et al.*, 2000), which does not occur in pre-chlorination. However, as in the coagulation, flocculation and decantation stages of the water treatment process, sludge with high concentrations of aluminum sulfate is formed. If a stage occurs with Fenton process before the coagulation, the sludge formed will present high concentrations of aluminum sulfate and iron oxides (which are formed when the pH is high in coagulation). The aluminum and iron compounds can be reused in a pre-treatment step to remove color and turbidity.

According to Heller *et Padua* (2010), much research has shown that the reaction of chlorine with some substances, mainly humic substances, leads to the formation of THM, organochlorine compounds that can cause problems to human health. In addition to THM, other chlorination products, such as haloacetonitriles, haloketones, haloacetic acids and chlorophenols, which are potentially harmful to public health, can be formed. It should be emphasized that the health risks, possibly associated with chlorination by-products, may be much lower than those that result from waterborne diseases that the population may be subject to if the water is not subjected to a disinfection process. Therefore, if the by-products of chlorination are in a concentration higher than the maximum permitted value, other disinfection methods should be chosen, such as the Fenton process, in which there is no formation of chlorination by-products.

In Brazil, there is a belief that safe disinfection of water can only be achieved through the use of chlorine gas or in inorganic compounds, since other disinfectants are unreliable. The use of gaseous chlorine implies high risk of leakage and requires careful transportation, storage and use to reduce the likelihood of occupational accidents. For this reason, small WTPs typically use calcium hypochlorite and sodium hypochlorite, which do not present the risks of chlorine gas, although they are much more expensive. The great advantage of chlorine and its derivatives is its residual, which is necessary in Brazil due to the poor state of conservation of the water distribution systems. Chlorine substitutes and their derivatives may only be used when the water distribution systems are free of leaks. On the other hand, in the pre-chlorination stage of WTP, chlorinated products can be replaced by any other oxidant, provided that it is technically efficient and financially and/or economically viable.

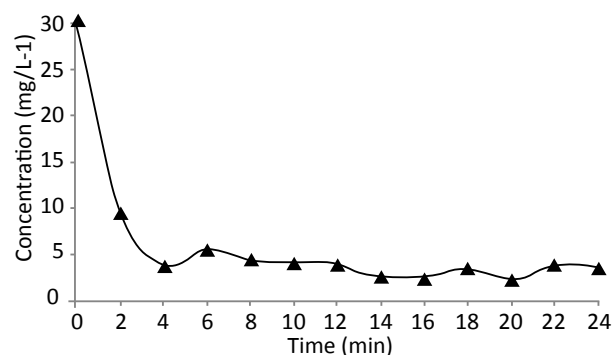


Figure 5. Effect of the reaction time in the Fenton process for the degradation of humic acid ($\text{Fe}^{2+}/\text{H}_2\text{O}_2 = 1/10$; $[\text{Fe}^{2+}]$ e $[\text{H}_2\text{O}_2] = \frac{1}{2}$ of the stoichiometric amount). Initial conditions: $[\text{AH}]_0 = 30 \text{ mg/L}$; $[\text{Fe}^{2+}]_0 = 3,35 \text{ mg/L}$; $[\text{H}_2\text{O}_2]_0 = 33,5 \text{ mg/L}$; $\text{pH} = 3,0$; reaction time = 24 min, at intervals every 2 min.

Source: Prepared by the authors, 2017



4. CONSIDERATIONS ON FINANCIAL AND ECONOMIC VIABILITY

The most expensive reagent in the Fenton process is hydrogen peroxide. In Brazil, before 2004, the cost of hydrogen peroxide was around R\$ 800/t, about 3 to 4 times the cost found in other South American countries and more than four times the cost in the United States. Thus, the use of hydrogen peroxide was restricted to applications where there was no adequate substitute. However, hydrogen peroxide prices fell by 20% in 2004 due to the end of the operation of a cartel formed by the company Peróxidos do Brasil, with 60% of the market, and by Bragussa, with 40% of the market (Lucinda *et Seixas*, 2016). As of 2009, new price reductions were perceived in the Brazilian market due to the increase in production scale and due to technological improvements. Thus, hydrogen peroxide has become a competitor of chlorine in various applications in both economic and technical terms. In bleaching sugar and algae control in dams, its use has become increasingly common. In the environmental area, its consumption has increased greatly due to the price reduction and its technical advantages over competing reagents (Fairbanks, 2017).

In order to evaluate the economic viability of the Fenton process in the removal of HA, which can be used to replace pre-chlorination or improved coagulation, an evaluation of the cost associated with the use of chemicals in pre-chlorination and in the Fenton process was performed.

In this evaluation, the assumptions were:

- The Fenton process can replace the pre-chlorination stage;
- The Fenton process must use the operating conditions associated with the graph of Figure 5: $[Fe^{2+}]_0 = 3,35$ mg/L, $[H_2O_2]_0 = 33,5$ mg/L and hydraulic holding time of 10 minutes. Although the experiment took 24 minutes, the graph shows that in less than 10 minutes a removal of about 90% was achieved. For this reason, we chose the reaction time of 10 minutes as appropriate;
- In the pre-chlorination process a hydraulic holding time of 20 minutes is used, where it is usual to use a total chlorine dosage of about 3 mg/L to 4 mg/L. In this evaluation, a total chlorine dosage of 4 mg/L was adopted;
- The calculation of the cost of the chemicals used in the evaluated processes was carried out considering three WTPs: a small one with a flow rate of 100 L/s (43,200 inhabitants), an average flow rate of 300 L/s (129,600 inhabitants) and a large one with flow of

5,500 L/s (2,376,000 inhabitants). The equivalent population was calculated taking into account a consumption of 200 L/inhabitant;

- The costs of substances used as alkalisers or acids were not included in the assessment. In general, the alkalizing agent is virgin or hydrated lime and the acidulant is sulfuric acid. The costs of such substances were considered to be much lower than the costs of the chemical substances used in the assessment;
- Chemicals' Prices were obtained from state water treatment companies, except for the price of ferrous sulfate heptahydrate, which was reported by a manufacturer. Values considered in the assessment include freight, as in the supply contracts consulted. The prices obtained are shown in Table 1. For preserving these companies, their real names will not be provided and they will be called numbers 1, 2, 3 and 4.

Table 1. Prices of chemical substances used in the processes.

Company	chlorine gas (R\$/Kg)	Ca (OCI)2 (R\$/Kg)	H2O2 (R\$/Kg)	FeSO4.7H2O (R\$/Kg)
1	6,083 in cylinders	10,25 with 65%a	-	-
	2,398 by truck	-	-	-
2	4,800 in cylinders	-	-	-
3	-	-	2,00 with 50%	-
4	-	-	-	2,70 with 99%b

Source: Prepared by the authors, 2017

The percentages refer to the purity of the chemicals: a – 33,0 % de Cl_2 ; b - 20,09 % de Fe

- The hydraulic holding time (t_h) is given by:

$$t_h = \frac{VV}{QQ} \quad \text{and} \quad V = t_h \times Q$$

where:

t_h = hydraulic detention time in days;

V = volume on m^3 ;

Q = flow in m^3 /day.



- According to Richter (2009), the consumption of chemicals in a treatment process is given by:

$$C = Q \times D / 1.000$$

where:

C = consumption of chemicals in kg/day;

Q = flow in m³/day;

D = dosage of the substance used in the process in mg/L.

- The prices of chemical substances were calculated using equation:

$$P = Vq \times (100/p) \times (100/pu)$$

where:

P = price of the chemical in R\$/Kg;

Vq = price of the chemical (R\$/Kg) of which the substance used in the process is part;

p = percentage of the substance used in the chemical;

pu = purity of the chemical in %.

- The prices of the chemicals (Vq) used are shown in Table 1.

Table 2 presents the results obtained in the evaluation of the costs of the products used in pre-chlorination and in the Fenton process. It is observed that the pre-chlorination process is the lowest cost process. The Fenton process, when used in medium and large WTP, has a cost about 19 times higher than that of chlorine, used in pre-chlorination, with hydrogen peroxide costing approximately 14 times that of chlorine. Thus, it is verified that H₂O₂ is mainly responsible for the financial impracticability of the use of the Fenton process in medium and large WTPs.

On the other hand, in small WTPs that use Ca(OCl)₂, the cost of the chemicals used in the Fenton process is slightly higher than that of chlorine (1.44 times). In this case, ferrous sulfate costs less than chlorine and peroxide costs almost the same as chlorine. In this way, the Fenton process becomes financially and economically viable for small WTPs. For medium and large WTPs, the use of the Fenton process requires some form of support, since the extra cost could not be passed on to consumers. The price of peroxide could be reduced in Brazil, as long as the tax burden on it diminished, since, in other countries of South America, its price is much lower. However, even if the price of peroxide were halved, as

in other countries, its use in medium and large WTPs would depend on support.

In medium and large WTPs that require pre-chlorination to remove odor, taste, color and turbidity other processes are used, such as improved coagulation or activated charcoal, avoiding pre-chlorination. However, in small WTPs that capture waters where pre-chlorination is required, pre-chlorination is a usual step. In these cases, the Fenton process could be employed with several advantages: it would avoid the formation of halogenated compounds, increase the removal of persistent organic compounds, which are little removed by the conventional process, and would avoid the manipulation of chlorinated compounds by the operators. And although hydrogen peroxide is less efficient than chlorinated compounds in inactivating microorganisms, that is, it has less efficiency as a bactericide, its use in an earlier stage of chlorination reduces the consumption of chlorine in the chlorination process.

It can be observed in Table 2 that the construction costs (fixed cost) of the tanks used in the Fenton process should be much lower than the construction costs of the tanks used in the pre-chlorination process, since they are associated with the volume necessary to each process. In addition, the calculation of such costs must take into account the agitators, other mechanical devices, the coating and the foundation. A more complete assessment should consider these data.

There are several alternatives to reduce the operational cost of the Fenton process. Among them, to verify if in situ peroxide generation could reduce the cost of peroxide in medium and large WTP; to study the reuse of ferrous sulfate through a stage of increasing pH, precipitating ferrous sulfate and reducing turbidity and, at a later stage, dissolving the precipitated ferric sulfate, which would be used in a pre-treatment stage (similar to that performed with the reused aluminum sulfate); to investigate the use of an immobilized insoluble iron oxide as a catalyst.

5. CONCLUSION

The results obtained in this study showed that the water treatment process by homogeneous Fenton process was efficient for HA removal in a short period. Thus, the Fenton process could replace the pre-chlorination stage in water treatment plants, provided that this process is financially and/or economically viable.

The main attractions of the process are derived from the cheap and non-toxic Fe⁺² and H₂O₂ reagents, together with the simplicity of the process application, since the reaction occurs at ambient temperature and pressure and its high degradation efficiency.



Table 2. Costs of products used in pre-chlorination and in the Fenton process

WTP	Flow rate (L/s)	(mg/L)#	Kg/30 d	(R\$/Kg)	R\$/30 d	V (m3)			
				6,083	6.307				
1	100	4a	1.037	4,800	4.977	120			
				2,398	2.486				
				31,061	32.204				
2	300			3.110	7.459		360		
3	5.500		57.024		136.744	6.600			
1	100	33,5b	8.683	4,000	34.733	60			
2	300						26.050	104.198	180
3	5.500						477.576	1.910.304	3.300
1	100	3,35c	868	13,575	11.788	60			
2	300						2605	35.363	180
3	5.500						47.758	648.323	3.300

Source: Prepared by the authors, 2017

- dosage of the substance responsible for the treatment; a – Cl_2 , b – H_2O_2 , c – $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$

By evaluating the costs of reagents used in pre-chlorination and in the Fenton process, it was found that the latter is financially feasible for small WTPs. However, for the medium and large, it is necessary to subsidize the Fenton process, since the cost of hydrogen peroxide makes this process financially impracticable.

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