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**AOX degradation of the pulp and paper industry bleaching wastewater using
nZVI in two different agitation processes**

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Abstract

The pulp and paper industry has been researching different treatments for the degradation of adsorbable organohalogens (AOX). In this work, two agitation processes (mechanical and ultrasound) were analyzed in the AOX degradation of the bleaching wastewater using nano zero valent iron (nZVI). The work used different variables for the AOX removal process, such as pH, time, nZVI, and hydrogen peroxide (H₂O₂) concentration. Results show an increase in AOX degradation when a higher nZVI concentration is used. The optimal combination of variables for the treatment with mechanical agitation was found in the ratio 2:5 (nZVI : H₂O₂), degrading 85% of AOX in 60 minutes, with acid pH. **Ultrasound treatment consisted of half process time and less degradation than mechanical agitation treatment. The 2:5 ratio in ultrasound agitation degraded 55% of AOX within 30 minutes at the end of the process.** Both methods of the homogenization process of zero valent iron nanoparticles in the bleaching wastewater of the paper and cellulose industry are efficient. However, the mechanical stirring process has a more significant potential for AOX degradation. The variables (pH, concentration of nZVI and H₂O₂ and duration of the process) used in the bleaching wastewater treatment process must be considered for future implementation in the pulp and paper industry.

Key words: nano zero valent iron; bleaching wastewater; degradation; adsorbable organohalogens;

1. Introduction

The pulp and paper industry uses a large amount of water in its manufacturing process (Mandeep et al., 2020; Thompson et al., 2001). Wastewater of the bleaching process is one of the major problems of this industry. In the bleaching process, chlorine dioxide is used to remove the characteristic real color of lignin and leave the paste white because it is cheap and efficient (Dorathi and Kandasamy, 2012). Effluents from this industry may contain dissolved lignin, color, chemical oxygen demand (COD), carbohydrates, inorganic chlorine, adsorbable organo halogens (AOX), extractable organic halogens (EOX), volatile organic compounds (VOCs), chlorophenols and halogenated hydrocarbons (Sridhar et al., 2011). AOX is produced by the pulp bleaching process owing to chlorine dioxide reaction with lignin (Sharma et al., 2020). The adsorbable organochlorides, called AOX, are chloroform, chlorate, resin acids, chlorinated hydrocarbons, phenols, catechols, guaiacols, furans, dioxins, syringols, vanillins (Farooqi and Basheer, 2017). For the degradation of AOX, there are several physicals (Seiss et al., 2001), chemical (Höfl et al., 1997), electrochemical (Rajkumar and Palanivelu, 2004) and biological methods (Deshmukh et al., 2009).

Advanced oxidative processes (AOPs) are techniques for treating contaminated effluents by a generation of hydroxyl radicals (Babuponnusami and Muthukumar, 2014; Cheng et al., 2016; Ye et al., 2020). Hydroxyl generation can be accelerated using other oxidizing agents such as hydrogen peroxide, ozone and UV radiation (Guo et al., 2020). As in Fenton reactions, these agents may be combined, which uses iron catalysts (Rahim Pouran et al., 2014). AOPs have been considered a technology with effective agents in the mineralization of organics.

The inclusion of nanomaterials in wastewater treatment processes is a greater generation of hydroxyl radicals and consequently degrading contaminants. **Nanomaterials can remediate organic pollutants by oxidation, adsorption and degradation** (Lu and Astruc, 2020). Nanomaterials are widely used as catalysts in the contaminant degradation process (Zhao et al., 2018). However, one of the significant concerns about nanomaterials is their destination and transportation (Zhu et al., 2019). Nanomaterials' toxicity is linked to several factors but one of the main factors is their high reactivity (Semerád et al., 2018). **Nevertheless, zero valent iron is possible recovery due to its magnetic properties, so it does not affect the environment so much and can be reused** (Ambika et al., 2016).

The zero valent iron is widely used to treat and remediate of contamination in soil, water and wastewater due to its high reactivity (Stefaniuk et al., 2016). The zero valent iron is a potent reducing agent with potential redox of 0.44V and has low toxicity (Cuervo Lumbaue et al., 2019). nZVI being a strong reducing agent for hydrogen ions, carbonates, sulfates, nitrates and mainly organic behaviors such as adsorbable organo halogens. nZVI can be synthesized by synthesis methods such as precision milling method (Kesavan and Azad, 2008), carbothermal reduction (Nisticò and Carlos, 2019), electrochemical method (Ma et al., 2017), green synthesis (Fazlzadeh et al., 2017) and ultrasound assisted method (Gao et al., 2018). The zero valent iron nanoscale has far greater potential reactive due to its larger surface area (Xue et al., 2018).

This paper aims to analyze the variables in the AOX degradation process of the wastewater from the paper and cellulose bleaching process. Through the synthesis of nZVI and its application in two different agitation processes, it was possible to analyze that there are ideal proportions for each need. It was also possible to note the remarkable capacity to recover and reuse nZVI for the AOX degradation process. This work indicates the best possibility of using nZVI for the industrial environment, considering its variables.

2. Materials and Methods

2.1 Synthesis and characterization of nano zero valent iron (nZVI)

The nano zero valent iron (nZVI) was synthesized by the reduction of ferric chloride hexahydrate ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$, Synth, 98%) with sodium borohydride (NaBH_4 , Dinâmica, 98%), according to Equation 1. This synthesis methodology was chosen due to the ease of maintaining nZVI without oxidizing and with high quality. For this purpose, two solutions (A and B) were prepared with Milli-Q type-1 water. Solution A was titrated with solution B at a flow rate of approximately one drop per 2 seconds, under low agitation. After complete titration, the mixture was vacuum filtered to separate the precipitate formed. The precipitate was washed and stored with acetone to prevent the oxidation of the material. To characterize the synthesized material, the precipitate was dried under a nitrogen atmosphere at 100 °C for 30 min.

The crystalline phases and crystallite sizes were determined using X-ray powder diffraction (Phillips diffractometer, X'Pert MPD model). The diffractometer has a graphite monochromator, Cu-K α radiation ($\lambda = 1.54$) and a fixed anode operated at 40 kV and 40 mA. The crystallite size was calculated with the WinFit software (version 1.2). The experimental peaks were fitted using asymmetric Pearson VII functions.

2.2 AOX degradation experiments

The experiments gave priority to simplicity of the system to eventually be possible to replicate the industrial way. For these experiments, a 0.25 L glass was used, with a heating plate maintaining the temperature at 60 °C, reproducing the industry temperature. In the treatment process, a comparison analysis between a mechanical and ultrasonic agitation was performed. The process was started with the addition of nZVI and hydrogen peroxide.

This study analyzed the initial pH of the natural effluent (pH = 2.7) and modified with 0.1 M NaOH (pH = 4.5). It also analyzed different ratios of nZVI (g.L^{-1}) by H_2O_2 (mL.L^{-1}). At certain times samples were taken for AOX degradation analysis. The mechanical agitation analysis lasted 1 hour, while the ultrasound analysis lasted 30 minutes. This difference is associated with literature, where ultrasound tests reached their potential within 30 minutes (Barzegar et al., 2018; Gao et al., 2018).

After the process, the zero valent iron nanoparticles were recovered by a magnetic magnet. In the ultrasound process, a second process cycle was performed with the recovered material.

The AOX parameter, which aims to quantify the adsorbable organohalogen compounds (chlorine, bromide and iodide), was quantified at the end of the treatment processes. The titration microcoulometry method was used according to ISO 9562: 2004. Thermo TOC 1200 AOX / Total Carbon Analyzer was used for this analysis. Results are given by mass concentration of adsorbed halogens. This work through the average of sample triplicates the results was given concerning the initial and final concentration (C/C_0).

3. Results and discussion

3.1 Characterization of the nZVI

The crystalline structure of the zero valent iron was analyzed by X-ray diffraction. The result is shown in Figure 1. The patterns indicate that the produced particles are composed only by zero valent iron (JCPDS 03-065-4899, Im-3m, n° 229). The diffractogram presents the characteristic peaks of Fe⁰ at $2\theta = 44.8^\circ$, 65.3° and 83° . There is no indication of a second phase presence. In this way, it was possible to synthesize zero valent iron. The Scherrer equation was applied to the diffractogram. The calculated crystallite size was 6.9 nm, corroborating the synthesis of nanoparticles.

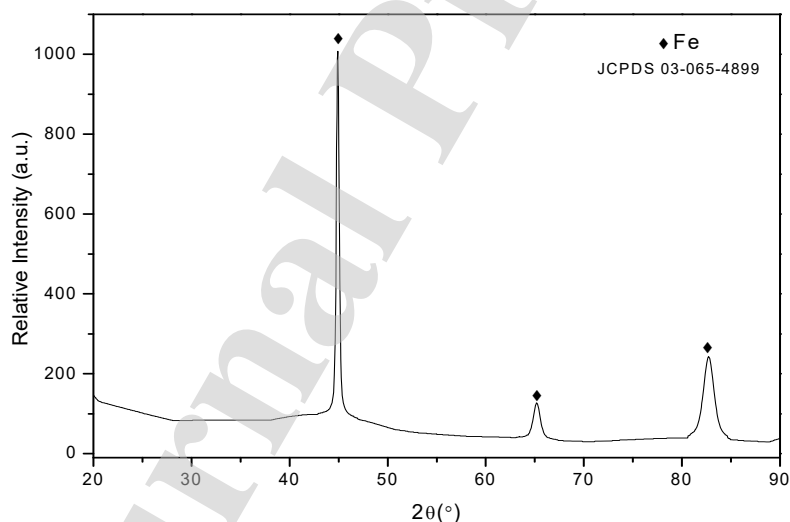


Figura 1 - X-ray diffractogram of then ZVI synthesized.

3.2 Analysis of bleaching wastewater treatment with a mechanical stirrer

The experiments using mechanical agitation were performed first. The use of mechanical agitation has brought some benefits to the process. The use of mechanical agitation with iron has already been studied (He et al., 2020). According to (Dong et al., 2016), the

sedimentation of the nZVI occurs in 10 minutes, where the larger nanoparticles settle and the smaller nanoparticles aggregate and settle. In this way, agitation plays an essential role in the treatment process. Mechanical stirring allows less aggregation of magnetic nanoparticles, which does not occur when using a magnetic stirrer. Magnetic stirring is widely used in wastewater treatment processes (Sridhar et al., 2011), however it is not as efficient in homogenizing magnetic nanoparticles. So there is a greater surface area available for the reaction since there is no aggregation of nanoparticles. As far as feasibility and application in the industry, mechanical agitation could easily be carried out by agitation. At the end of the process, the nZVI could be recovered by a magnet (Gu et al., 2018), in the same way used in the laboratory process.

3.2.1 Analysis of bleaching wastewater pH in AOX degradation

Figure 2 presents the results of the AOX degradation process with bleaching wastewater. The bleaching wastewater characterized with acid pH (≈ 2.7) generated in the bleaching process of the pulp of *Eucalyptus globulus* with the use of chlorine dioxide. The pH is an important factor to be considered as it affects nZVI reduction reactions (Zhu et al., 2017). Comparisons of ratio nZVI concentration and hydrogen peroxide concentration were performed. The 2:5 ratio assay had the highest AOX degradation of 0.15 (C/Co). The test 0:5 not used nZVI, had the lowest degradation, leaving 0.69 (C/Co). All three proportions were stabilized for degradation after 30 minutes. Only the 1:2.5 ratio has seen a significant increase over the last 30 minutes. Most AOX degradation occurs within the first 30 minutes. It should be noted that the 1:2.5, 2:2.5 and 2:5 ratios obtained similar final concentration ratios, between 0.36 - 0.26 (C/Co). After 30 minutes of process there is no major degradation of AOX. Only the 1: 2.5 ratio increased after the first 30 minutes. The degradation in 1: 2.5 went from 41% to 74% of AOX degradation, as seen in Table 1. It

is also observed that the ratio 2:2.5 did not occur degradation after 30 minutes of processing. The degradation in this proportion remained at 64% of AOX degradation until the end of the process.

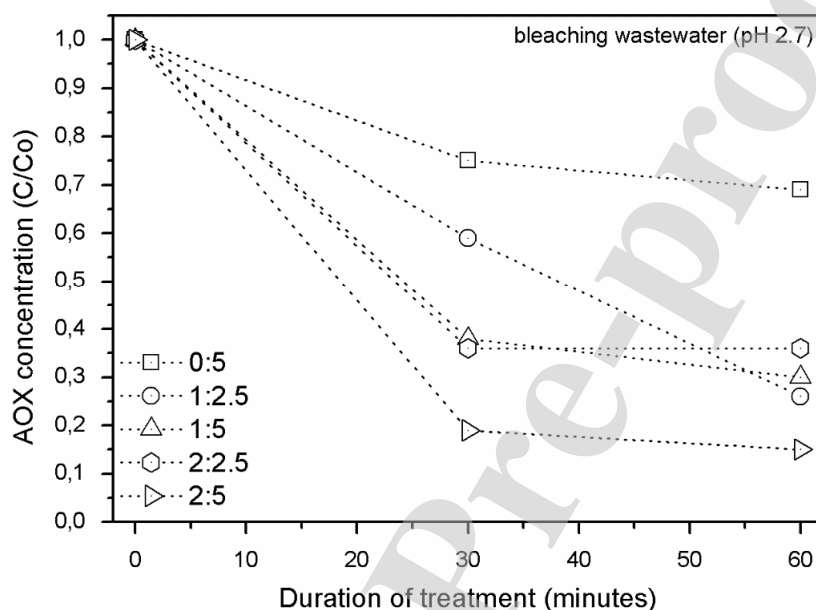


Figure 2 - Graph of AOX concentration (C/Co) in bleaching wastewater (pH 2,7) as a function of treatment duration (minutes) at different ratios between nZVI (g.L⁻¹): H₂O₂ (mL.L⁻¹).

Figure 3 shows the tests performed with effluent at pH 4.5. The 0:5 ratio achieved the lowest AOX degradation, ending with 0.78 (C/Co). Thus, the 2:5 ratio obtained the highest degradation of AOX, with 0.48 (C/Co). The results between bleaching wastewater and bleaching wastewater with pH 4.5 had very similar tendencies, however with pH 4.5 there was less degradation of AOX. The pH 4.5 assays were between 0.78 - 0.48 (C/Co), while the natural pH assays were between 0.69 - 0.15 (C/Co). The 1: 2.5 ratio in the pH 4.5 assay also obtained the same increase in degradation as the natural pH effluent assay.

The pH is directly linked to the efficiency of nZVI for the degradation of contaminants. In this work's case, the more acidic pH was more efficient in using nZVI for AOX degradation. As seen in (Nandi et al., 2020), the iron oxide that may exist in the outer layer of Fe^0 dissolves more easily at an acid pH. At a higher pH, ionization of the nanoparticles and the contaminant occurs due to the surfaces' repulsion. The nZVI in acid effluent is easily formed into complexes. The nZVI contact area increases and accelerates the reaction. The pH controls nZVI solubilization and the availability of Fe^{2+} required to activate H_2O_2 (Lin and Hsu, 2018). A lower pH favors the degradation of contaminants. The oxidative potential of hydroxyl radicals is greatly influenced by pH, so degrading AOX in acid effluent is more timely. In reactions with pH higher than 3, as in the case of work that used pH 4.5, there is a precipitation of iron hydroxide oxides, which reduces Fe^{2+} ion concentration and hydroxyl radical generation (Segura et al., 2012).

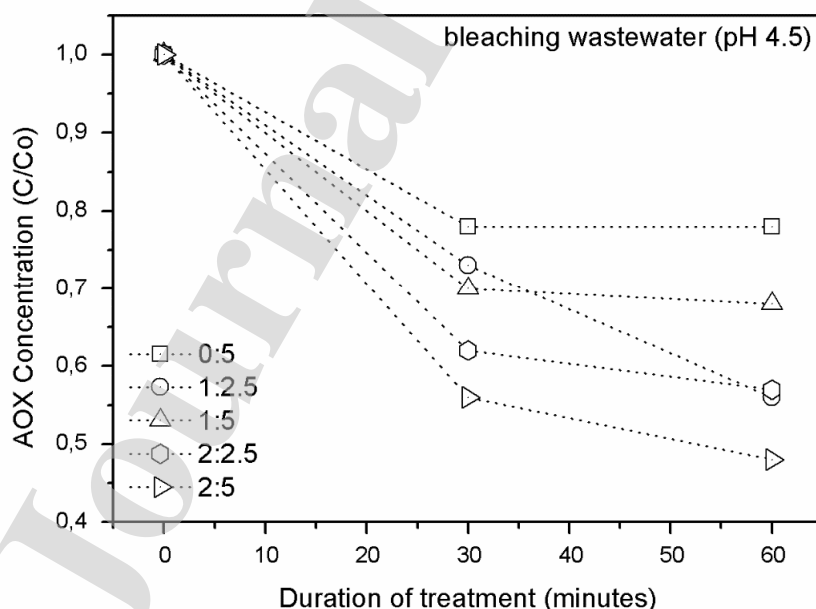


Figure 3 - Graph of AOX concentration (C/C_0) in bleaching wastewater (pH 4.5) as a function of treatment duration (minutes) at different ratios between nZVI (g.L^{-1}): H_2O_2 (mL.L^{-1}).

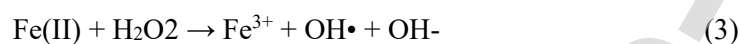
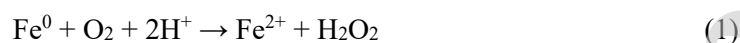
Table 1 – AOX degradation (%) in bleaching wastewater with different pH, treatment duration (minutes) at different ratios between nZVI (g.L^{-1}): H_2O_2 (mL.L^{-1}).

nZVI (g.L^{-1}) : H_2O_2 (mL.L^{-1})	% AOX degradation			
	30 minutes		60 minutes	
	2.7 pH	4.5 pH	2.7 pH	4.5 pH
0:5	25%	22%	31%	22%
1:2.5	41%	27%	74%	44%
1:5	62%	30%	70%	32%
2:2.5	64%	38%	64%	43%
2:5	81%	44%	85%	52%

3.2.2 Analysis of nZVI concentration in AOX degradation

To analyze the impact of nZVI concentration on the process, tests were performed with 1 and 2 g.L^{-1} nZVI and without the use of nZVI. The assays were performed at natural bleaching wastewater pH and pH 4.5, as shown in Figure 3. It is apparent that with increasing nZVI concentration an increase in AOX degradation occurs. In both situations with different pH this increase occurred. The highest degradation of AOX occurred with the use of 2 g.L^{-1} 85% nZVI in the natural effluent. The bleaching wastewater with pH 4.5 also with nZVI 2g/L concentration obtained 52% AOX degradation. A high concentration of nanomaterial and a low pH is favorable to the degradation of AOX

(Zhang and Shen, 2020). The degradation of organic contaminants by nZVI/H₂O₂ reaction happens by hydrogen addition or abstraction and electron transfer, as seen in Equations (1-3) (Sung et al., 2005). By oxygenation occurs the reduction of the nano zero valent iron Fe⁰ by the oxygen that is present in the effluent, as well as by the agitation that forms bubbles by cavitation. So there is the H₂O₂ produced from the reduction and added in the treatment.



Increasing nZVI concentration increases H₂O₂ decomposition and hydroxyl radicals production thus increases the efficiency of AOX degradation. However, the excessive increase in the concentration of nZVI leads to aggregation and results in the formation of a large nanoparticle aggregated which settles rapidly. This also decreases the degradation of AOX by decreasing the contact area, and the nanoparticle becoming part of the oxidation reaction as a reducing agent, consuming hydroxyl radicals.

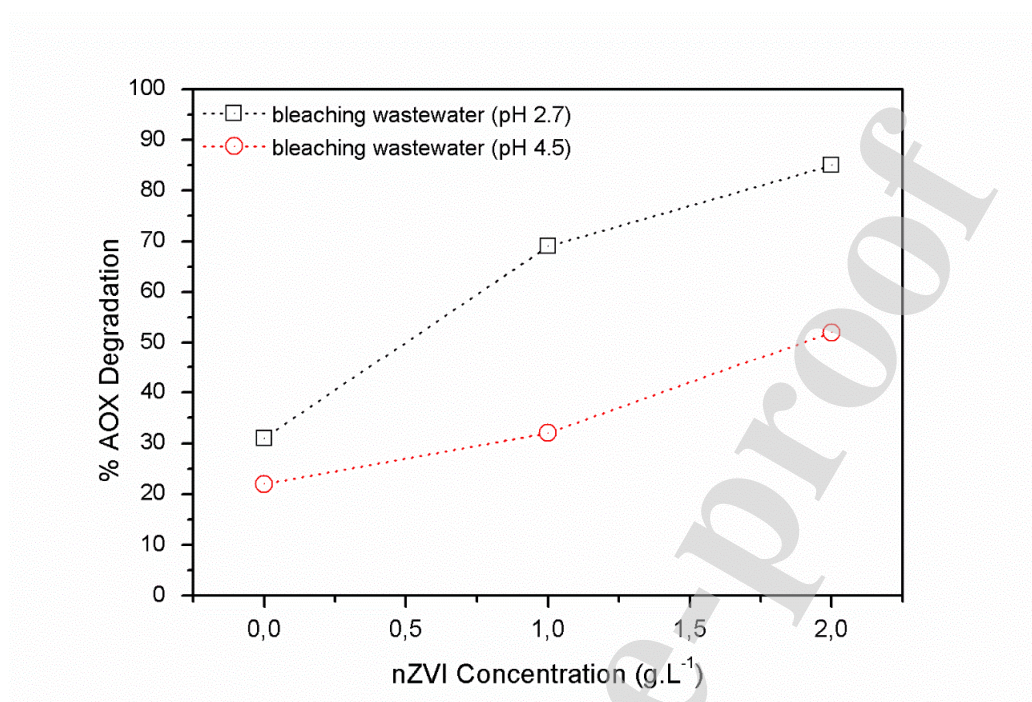


Figure 4 - Graph of the percentage of AOX degradation by nZVI concentration used in the treatment process.

3.2.3 Analysis of hydrogen peroxide concentration in the degradation of AOX

Figure 5 shows the results of the impact of hydrogen peroxide on the treatment process. Tests were performed with natural pH and pH 4.5, analyzing the concentrations of 38mM and 76 mM peroxide and without the use of peroxide. The concentration of 76 mM was the one with the highest degradation of AOX with 85% with natural effluent. Analysis of bleaching wastewater with pH 4.5 had the lowest result at 76 mM concentration, however at 38 mM concentration, it had greater degradation. A higher concentration of H₂O₂ should occur a higher binding with nZVI and produce more hydroxyl radicals (Zhang et al., 2017), increasing the degradation of AOX. However the excessive concentration of

H_2O_2 can react with hydroxyl radicals and form water and perhydroxyl radicals, as shown in Equation 4, which causes them to turn into H_2O , this happens in reaction with organics (Bergendahl and Thies, 2004).

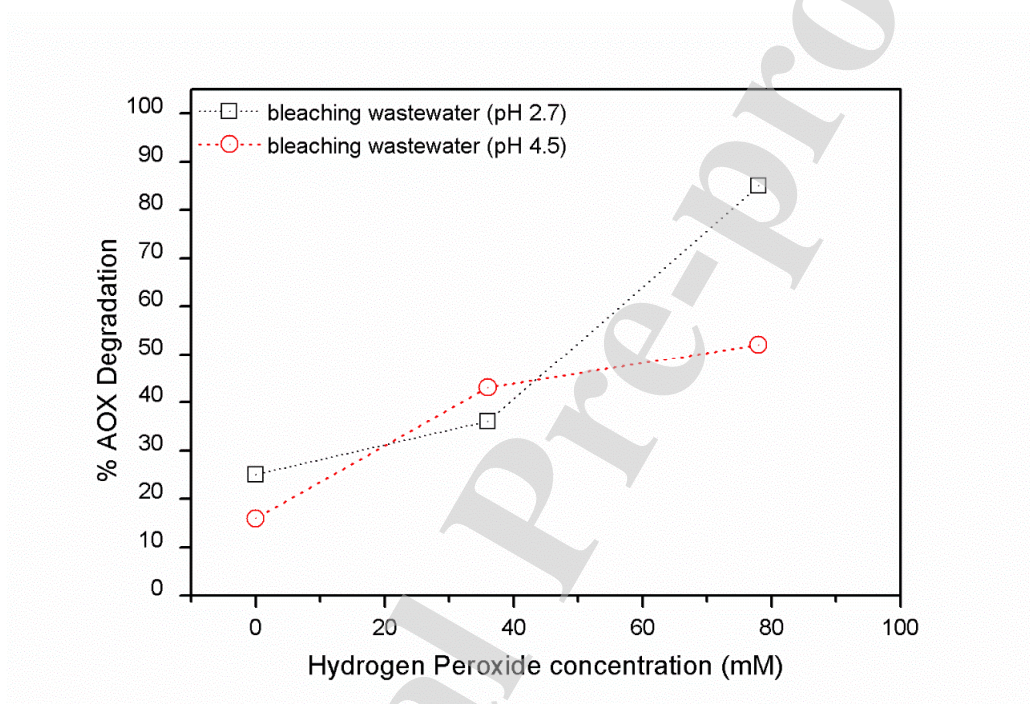
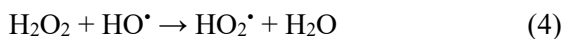


Figure 5 - Graph of the percentage of AOX degradation by hydrogen peroxide concentration used in the treatment process.

3.3 Analysis of AOX degradation results using ultrasound

Tests were performed in the same parameters as the agitation process, but with ultrasound. More measurements were performed in the ultrasound process, samples were taken in 5, 15 and 30 minutes. In these processes there was an emphasis on recovery and reuse of nZVI. Due to the results found in the mechanical agitation tests, no pH 4.5 treatment processes were performed. Figure 6 is the first cycle of the use of nZVI.

At first, it was seen that even the process without nZVI with only 5ml.L⁻¹ of H₂O₂ obtained a minimal reduction in AOX. At the end of the 30 minutes, a degradation of 17% of AOX was obtained. Another important event is the stabilization of degradation after 15 minutes. In all processes there is still degradation but they are small compared to the first 5 minutes. The efficiency in the dispersion of nanoparticles increases with the increase in the ultrasound process time (Sato et al., 2008). In the same way as the mechanical agitation tests the greatest degradation happened with the ratio 2:5 - 0.45 C/Co - the lowest degradation occurred at the ratio 0:5, where there is no use of nZVI. Processes after 15 minutes stabilize for AOX degradation with no major change in C/Co ratio. In ultrasound particles increase the mass transfer rate and disperse aggregation accelerating nZVI corrosion and producing more Fe²⁺, rapidly decomposing H₂O₂ and producing more hydroxyl radicals (ElShafei et al., 2017). The faster oxidation can also occur due to the cavitation effect present in ultrasound functions (Wang et al., 2014), in which there is the formation of air bubbles that speed up the process.

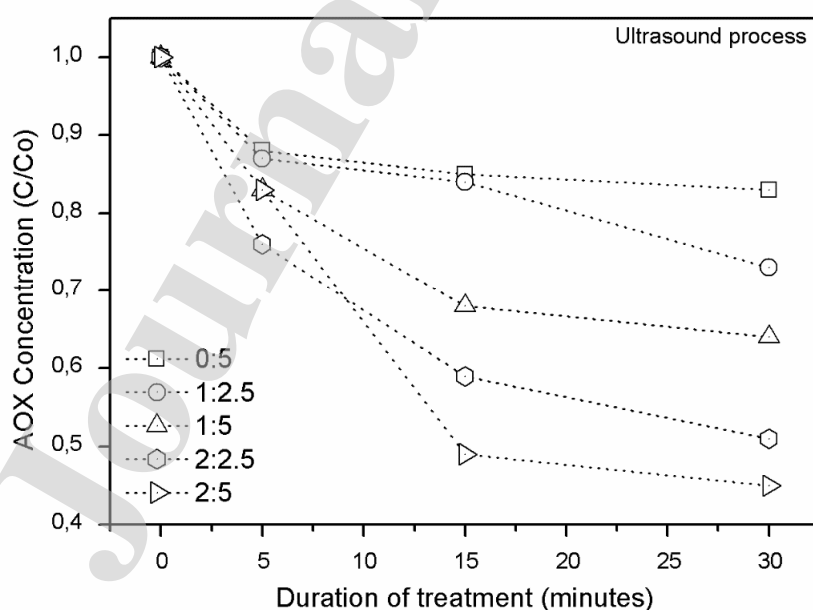


Figure 6 - Graph of the relationship of the final concentration by the initial AOX as a function of time with the natural effluent.

3.3.1 nZVI Recovery and Reuse – Second Cycle

Figure 7 shows the results of the second cycle of the use of nZVI. As seen in other research (Abd El-Lateef et al., 2018; Li et al., 2017), nZVI remains reactive, being very quick to recover. The 2:5 ratio assay degraded the highest AOX to 0.33 concentration. It is also notable that the ratio 2:5 there was a higher AOX degradation in the first five minutes, this fact is related to alleged adsorption that occurred in the first cycle, and after exceeding this there is no more capacity for adsorption. In general, it is possible to notice a greater degradation of AOX in the reuse of these nanoparticles than in the first cycle of the material. This event may be related to the homogenization of this solution.

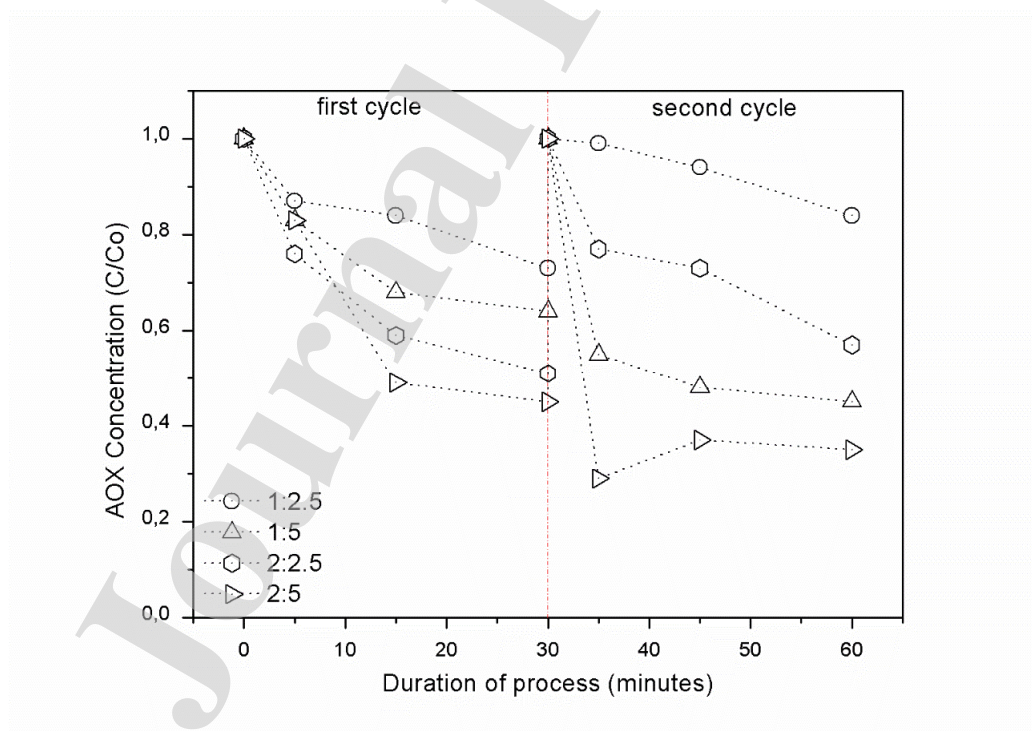


Figure 7 - Graph of the relation of the final concentration by the initial AOX as a function of time, with the natural effluent, with the reuse of recovered nZVI.

3.4 Comparison of stirring methods

To compare the two processing methods used, the same test was performed varying the concentration of nZVI for each process. Each process was carried out in 30 minutes using 5 mL.L⁻¹ of hydrogen peroxide. Figure 8 compares the two stirring methods, with the same proportions of nZVI/ H₂O₂. It is visible that even if the use of nZVI does not occur, the two agitation methods degrade AOX. This may be due to hydrogen peroxide. However, the percentage of AOX degradation in these processes without using nZVI is still not very efficient. With the increase in the concentration of nZVI to 1g.L⁻¹, there is an increase in the AOX degeneration in both processes. However, there is a greater increase in degradation in the process with mechanical agitation than in agitation by ultrasound. With a concentration of 2 g.L⁻¹ of nZVI, both processes degraded AOX in a higher percentage than the lowest concentrations. It is thus stated that the use of mechanical agitation is more efficient than ultrasound agitation in terms of AOX degradation. However, regarding the homogeneity and dispersion of the particles, the ultrasound process is more efficient (Sumitomo et al., 2018). Even with the concentration of 2 g.L⁻¹ of nZVI, the ultrasound agitation did not obtain the percentage of degradation that the process with mechanical agitation using a lower concentration of nZVI.

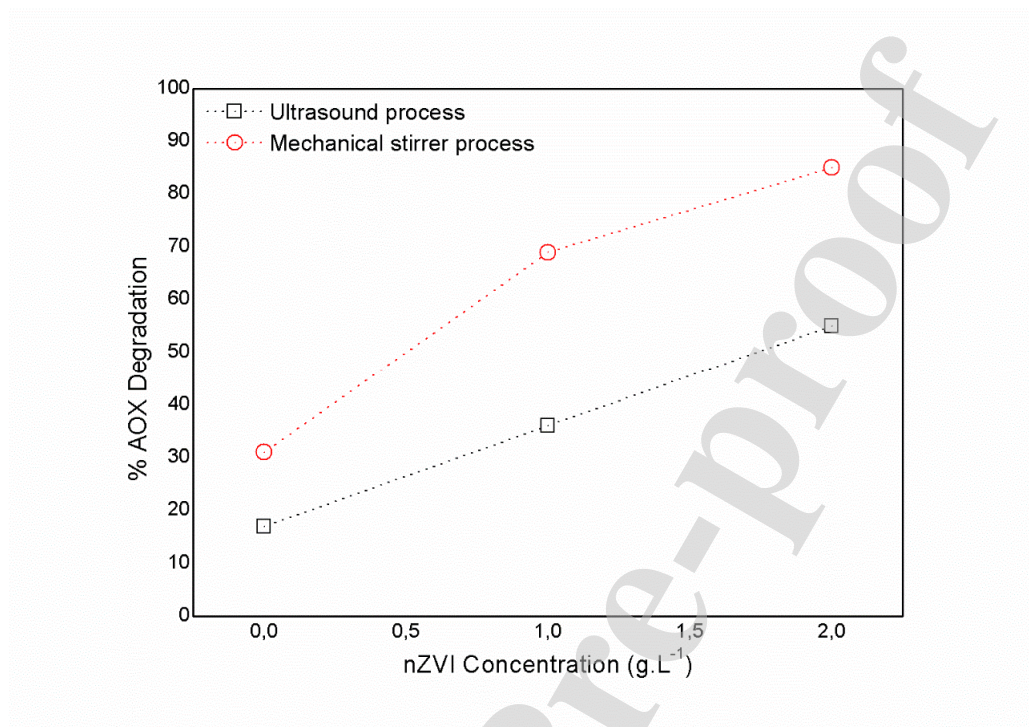


Figure 8 - Comparison between agitation processes by nZVI concentration in 30 minutes.

Both methods degraded AOX efficiently. It is comparing the agitation processes with the same proportions it can be seen that with the same test time, the mechanical agitation process is still the most degrading AOX. Thus, if the main objective of the process is pH, the use of the natural pH of the effluent with a 2:5 ratio would be the most suitable. This process degrades 85% of AOX whereas the processes in general with the modification of the effluent pH obtained less degradation. Since the process was proportioned 0:5 and the effluent was modified to 4.5 with NaOH, it obtained only 22% of AOX degeneneration using the mechanical stirring method. If the objective is the NZVI concentration, the processes using the concentration of 2g.L⁻¹ of nZVI are considered to have the greatest potential for AOX degradation. Since the processes that do not use nZVI obtained very low percentages of AOX degradation. The same is true for the H₂O₂ concentration. As

the concentration of H_2O_2 increases, there is a tendency to increase the percentage of AOX degradation. Also, the use of H_2O_2 alone should not be considered. Hydrogen peroxide must be used as an oxidative agent in the process. In the ultrasound processes it can be seen the same as in the mechanical stirring process. However, in the process with reuse of nZVI, the degradation of AOX is less in the second cycle of use. Therefore, H_2O_2 with nZVI is necessary for the greatest potential for AOX degradation to occur. Since the 2:5 ratio with natural pH obtained the most significant potential, both with mechanical agitation and ultrasound.

Conclusions

The nanoparticles of zero valent iron were produced efficiently by synthesis, proving a single phase. The nZVI demonstrated outstanding potential for AOX degradation in the bleaching wastewater of the pulp and paper industry. It was possible to analyze the variables regarding pH, nZVI concentration, H₂O₂ concentration and the comparison between the two stirring processes. From these assays it was possible to notice the increase of AOX degradation with the increase of nZVI concentration, this being the main variable. As for the effluent pH, being naturally using acid is better than with modification. From the comparison of the agitation process of the nanoparticles, it is visible that the mechanical agitation process obtained better results than the ultrasound process. This study provided information on the important variables in the process of degradation of AOX using nZVI. This work can serve as a basis for parameters to be used in the industry regarding its need and process situation.

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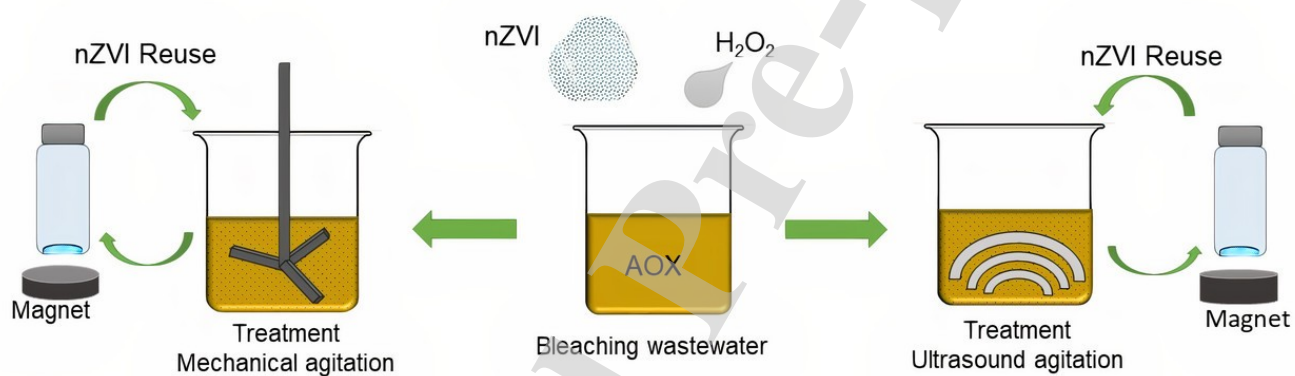
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Highlights

- nZVI has potential for AOX degradation in the bleaching wastewater of the pulp and paper industry;
- Increased nZVI concentration increases AOX degradation;
- The optimal combination of variables for the treatment is the ratio 2:5 (nZVI: H₂O₂)
- Both agitation processes in the effluent treatment are efficient;
- The possibility of reusing nZVI in the treatment of effluent;



Author Statement

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Declaration of interests

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests:

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