

Treatment of Municipal Activated Sludge by Ultrasound-Fenton Process [†]

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Abstract: In this work, the efficiency of ultrasound, Fenton, and ultrasound-Fenton (US-Fenton) processes were evaluated separately for the treatment of municipal activated sludge (MAS). Additionally, the effects of operational parameters such as pH, hydrogen peroxide and ferrous iron concentrations, and cavitation time were studied. During the experiments, the chemical oxygen demand (COD) reduction and the volatile solids (VS)/total solids (TS) ratio were evaluated. Under the best operational conditions, ultrasound and Fenton processes achieved 17.3 and 25.9% COD removal, respectively, while the combined US-Fenton process was more efficient with a 94.8% COD reduction. Regarding the VS/TS ratio, the process that showed better results was US-Fenton, reducing the original value of 0.59 to 0.16. The ultrasound and Fenton processes showed a lower VS/TS ratio reduction to 0.26 and 0.22, respectively. In conclusion, the combination of US-Fenton achieves high COD removal and a significant VS/TS ratio reduction of the municipal activated sludge, showing better efficiencies than both processes separately.

Keywords: advanced oxidation processes; municipal sludge treatment; COD removal; VS/TS ratio; ultrasound-Fenton



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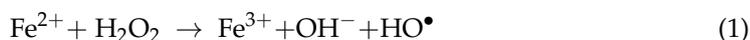


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1. Introduction

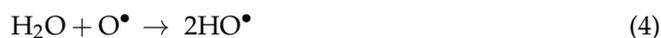
Municipal wastewater treatment produces significant volumes of sludge that requires appropriate treatment so it can be used for another purpose without constituting a threat to the environment, contributing to a sustainable circular economy [1].

Advanced oxidation processes (AOPs) are methods that generate radicals, such as hydroxyl radicals (HO[•]), with high oxidizing power ($E_{HO^{\bullet}} = 2.80$ V) that reduces contaminated organic composites and can be used for water and soil treatment. The Fenton reaction is one of the methods that, through the interaction between ferrous ions (Fe²⁺) and hydrogen peroxide (H₂O₂), generates Fe³⁺ and HO[•] (Equation (1)). However, it is a complex mechanism because the reaction depends on several factors, such as the pH, H₂O₂ concentration, and Fe²⁺ concentration [2,3]. Several studies have been developed in order to optimize the Fenton reaction through association with light, ultrasound, use of nanoparticles, and electrical energy [4,5].

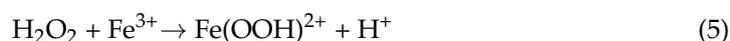


Ultrasound-Fenton (US-Fenton) is the combination of ultrasounds with the Fenton reaction. The ultrasounds can generate short-lived radical species through the cavitation bubble collapses, allowing the radical concentration to be maintained [6]. Under ultrasound

radiation, the waves interact with dissolved gases in the water body, which leads to acoustic cavitation. These phenomena include the following steps: the formation, growth, and implosive collapse of bubbles. The US leads to chemical reactions (bond cleavage), which include splitting the water molecules into a hydrogen atom and hydroxyl radical, as observed in Equations (2)–(4), as follows [7].



In addition to HO^\bullet radical production, the application of US allows the regeneration of the ferric iron to ferrous iron, increasing the kinetic rate of the Fenton process, as observed in Equations (5) and (6) [8], as follows:



The aim of this work was (1) the characterization of the municipal activated sludge, (2) optimization of the US-Fenton process, and (3) the study of efficiency between ultrasound, Fenton, and US-Fenton treatment processes applied to the sludge.

2. Material and Methods

2.1. Reagents and Sludge Sampling

For pH adjustment, sodium hydroxide (NaOH) from Labkem, Barcelona, Spain, and sulphuric acid (H_2SO_4 , 95%) from Scharlau, Barcelona, Spain, were used. For chemical processes, hydrogen peroxide (H_2O_2 30%), supplied by Sigma-Aldrich, St. Louis, MO, USA, and ferrous sulfate heptahydrate ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$), supplied by Panreac, Barcelona, Spain, were used.

2.2. Analytical Methods

Before the experiment, different physical–chemical parameters were determined to characterize the municipal activated sludge. Parameters such as pH, COD, total solids, volatile solids, volatile solids and total solids ratio, electrical conductivity, and iron concentration were used (Table 1).

Table 1. Municipal activated sludge characterization.

| Parameters | Values |
|---|-------------|
| pH | 6.48 ± 0.02 |
| Chemical oxygen demand (mg O_2 /L) | 8512 ± 394 |
| Total solids (mg/L) | 3250 ± 1040 |
| Volatile solids (mg/L) | 1920 ± 75 |
| Volatile solid/Total solids (mg/L) | 0.59 |
| Electrical conductivity ($\mu\text{S}/\text{cm}$) | 1249 ± 10 |

For COD determination, a closed reflux method was used; for total solids (TS) and volatile solids (VS), gravimetric methods were applied, in accordance with standard methods of water and wastewater experiments [9], and reactions were quenched by application of sodium sulfite anhydrous.

2.3. Experimental Set-Up

To study the efficiency of ultrasound and US-Fenton processes in the treatment of municipal activated sludge, an ultrasonic processor (Vibracell Ultrasonic processor VCX 500, Sonics & Materials Inc., Danbury, CT, USA) and a magnetic stirrer (Nahita blue,

Navarra, Spain) for Fenton process were used, as shown in Figure 1. During the US-Fenton and Fenton process, the reagents were well mixed to start reacting. The experiments were processed in a 100 mL beaker, the temperature was maintained at 298 K for 60 min, and every 15 min, a sample was taken for analysis.

The optimization of US-Fenton was performed in the following order: (1) variation of pH (3.0–7.0), (2) variation of H_2O_2 concentration (30–200 mM), (3) variation of Fe^{2+} concentration, and (4) cavitation time ON (1–5 s), OFF (5 s). After obtaining the optimal conditions, the ultrasound and Fenton processes were performed.

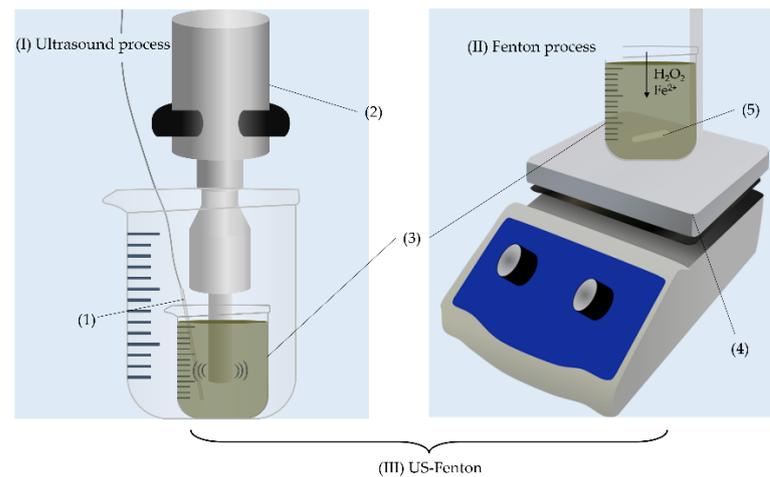


Figure 1. Schematic representation of (I) US and US-Fenton and (II) Fenton processes on the treatment of MAS. (1) equipment for temperature control, (2) ultrasonic processor, (3) 100 mL beaker containing sludge, (4) magnetic stirrer device, and (5) stir bar.

2.4. Statistical Analysis

All the results were analyzed with OriginLab 2019 software (Northampton, MA, USA) to determine the difference between means through analysis of variance (ANOVA), and Tukey's test was used for the comparison of means, which were considerably different when $p < 0.05$. The data are presented as mean and standard deviation (mean \pm SD).

3. Results and Discussion

3.1. Ultrasound vs. Fenton vs. US-Fenton Treatment Process

In this section, the US was compared with the Fenton and US-Fenton process, to understand which treatment process is more efficient for MAS treatment. By analysis of the results in Figure 2, it is possible to see that the process that showed the best results was, without a doubt, US-Fenton, reaching 94.8% COD removal, while ultrasound and Fenton reached 17.3 and 25.9%, respectively. The VS/TS ratio was observed to be in the following order: US-Fenton (0.16) < Fenton (0.22) < US (0.26). Clearly, with the combination of US with Fenton, a higher HO^\bullet radical production occurred, increasing the kinetic rate of COD removal. These results were in agreement with Saleh and Taufic [8], who observed that application of US-Fenton reached higher Methylene Blue and Congo-Red dye removal in comparison to US and Fenton processes.

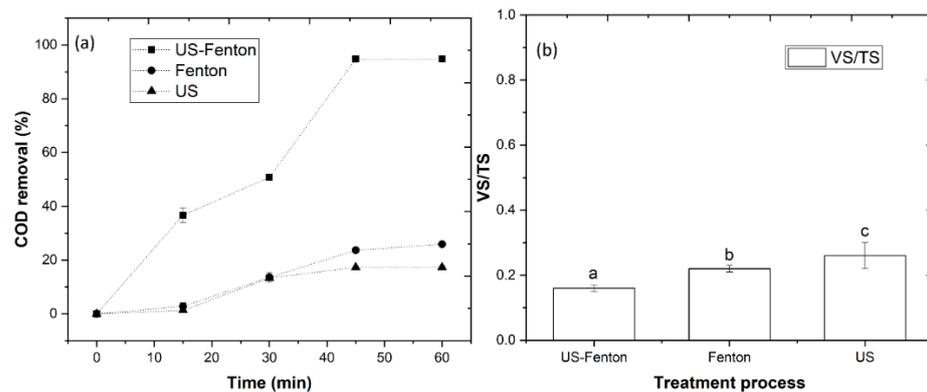


Figure 2. Evaluation of (a) COD removal and (b) VS/TS removal with different treatment processes. Experimental conditions: pH = 4, $[H_2O_2] = 30$ mM, $[Fe^{2+}] = 2.0$ mM, cavitation time 3 s ON: 5 s OFF, A = 40%, T = 298 K, time = 60 min. Means in bars with different letters represent significant differences ($p < 0.05$) within VS/TS by comparing wastewaters.

3.2. Effect of pH

In this section, the US-Fenton process was optimized by variation of the pH (3.0–7.0). As can be observed in Figure 3, pH = 4.0 showed the highest efficiency, with a COD removal of 86.1%. Increasing the pH to 6.0 and 7.0, the COD removal suffers a reduction to 75.1% and 66.4%, respectively. The efficiency reduction at alkaline pH resulted from the iron hydroxides precipitation, which led to lower production of HO^\bullet radicals and inhibited Fe^{2+} regeneration [10,11].

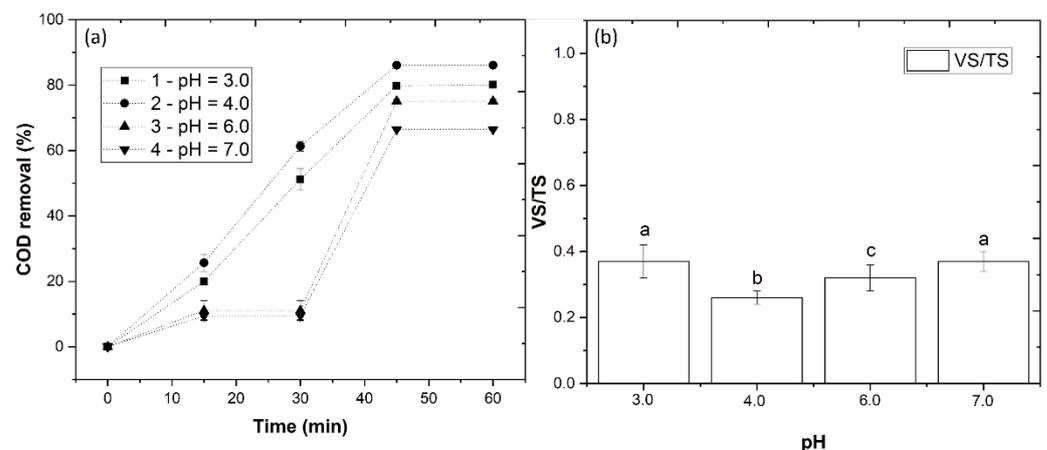


Figure 3. Evaluation of (a) COD removal and (b) VS/TS ratio at different pH (3.0–7.0). Experimental conditions: $[H_2O_2] = 100$ mM, $[Fe^{2+}] = 2.0$ mM, cavitation time 3 s ON: 5 s OFF, A = 40%, T = 298 K, time = 60 min. Means in bars with different letters represent significant differences ($p < 0.05$) within VS/TS by comparing wastewaters.

3.3. Effect of H_2O_2 Concentration

To evaluate the effect of H_2O_2 concentration, different concentrations were tested (30–200 mM). The highest efficiency was achieved with application of $[H_2O_2] = 30$ mM, with a COD removal of 94.8% (Figure 4). In addition, the VS/TS ratio was reduced to 0.16, which showed a reduction in the microbial concentration that existed in the MAS. Increasing the H_2O_2 concentration, a COD reduction of 87.2, 86.1, 78.3, and 69.3%, respectively, was observed for 50, 100, 150, and 200 mM. By increasing the H_2O_2 concentration to values > 30 mM, the excess of H_2O_2 induces the consume of HO^\bullet radicals and produces HO_2^\bullet (Equation (7)), which has a low reduction potential, so, less degradation occurs [12,13].



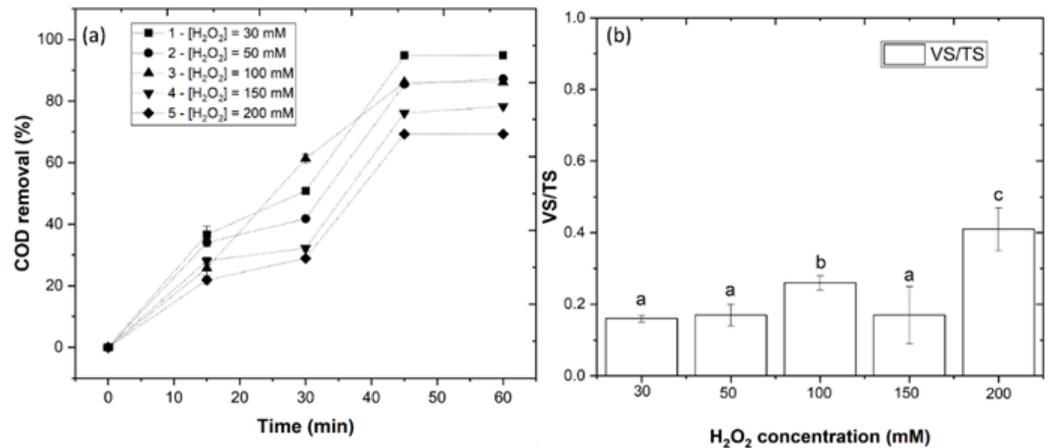


Figure 4. Evaluation of (a) COD removal and (b) VS/TS ratio with different [H₂O₂] (30 mM– 200 mM). Experimental conditions: pH = 4, [Fe²⁺] = 2.0 mM, cavitation time 3 s ON: 5 s OFF, A = 40%, T = 298 K, time = 60 min. Means in bars with different letters represent significant differences (*p* < 0.05) within VS/TS by comparing wastewaters.

3.4. Effect of Iron Concentration

The Fe²⁺ acts as a catalyst in the process of generating HO[•] radicals, an optimum concentration that potentiates greater production of radicals must be achieved [14]. In this section, the Fe²⁺ concentration was varied from 0.5 to 10.0 mM, and in accordance with the results (Figure 5), with application of 2.0 mM Fe²⁺, a COD removal of 94.8% was achieved. Above 2.0 mM, a decrease in COD removal and higher values of VS/TS ratio were observed. The excess of ferrous ions can lead to a consumption of HO[•] radicals producing Fe³⁺ and HO⁻ (Equation (8)), resulting in less degradation [15].

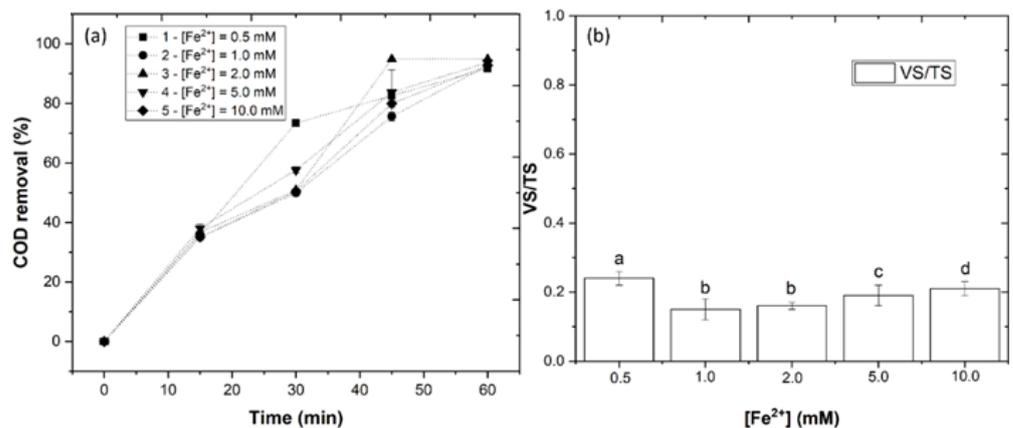


Figure 5. Evaluation of (a) COD removal and (b) VS/TS removal with different [Fe²⁺] (0.5 mM– 10.0 mM). Experimental conditions: pH = 4, [H₂O₂] = 30 mM, cavitation time 3 s ON: 5 s OFF, A = 40%, T = 298 K, time = 60 min. Means in bars with different letters represent significant differences (*p* < 0.05) within VS/TS by comparing wastewaters.

3.5. Effect of Cavitation Time ON

The cavitation time plays an important role in the degradation of organic carbon. Therefore, the US-Fenton process was optimized by variation of the cavitation time ON:OFF (1:5, 2:5, 3:5, and 5:5 s:s). The most efficient cavitation time, with a COD removal of 94.8% and a VS/TS ratio of 0.16, was 3 s ON and 5 s OFF (Figure 6). By increasing the contact time (5:5 s:s), the COD removal was observed to decrease to 90.2% with a VS/TS ratio of 0.26.

These results were in agreement with Sivagami et al. [16], who observed that increasing the contact time leads to a decrease in PHC degradation in the US-Fenton process.

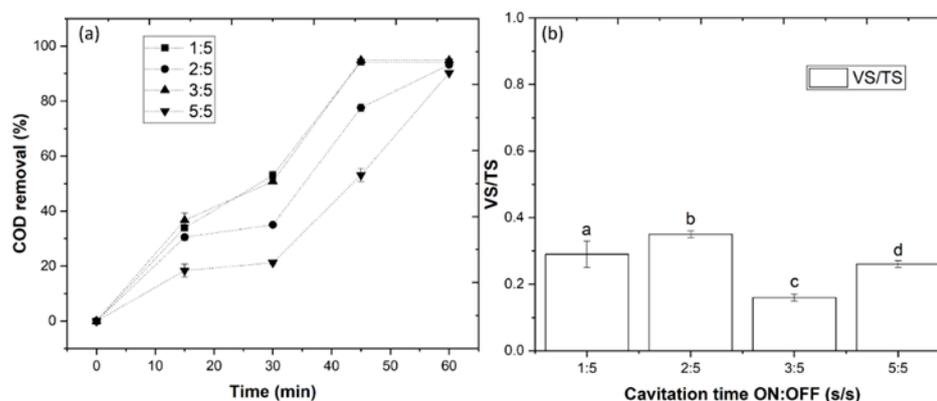


Figure 6. Evaluation of (a) COD removal and (b) VS/TS removal with different cavitation time ON:OFF (1:5, 2:5, 3:5 and 5:5). Experimental conditions: pH = 4, $[H_2O_2] = 30$ mM, $[Fe^{2+}] = 2.0$ mM, A = 40%, T = 298 K, time = 60 min. Means in bars with different letters represent significant differences ($p < 0.05$) within VS/TS by comparing wastewaters.

4. Conclusions

The combination of ultrasound-Fenton (US-Fenton) achieved high COD removal and a significant VS/TS ratio reduction of the municipal activated sludge, showing better efficiencies than both processes separately. The efficiency of the US-Fenton process depends on several variables, mainly pH, concentrations of hydrogen peroxide and ferrous ions, and cavitation time. Under the optimal conditions, 94.8% COD removal and a 0.16 VS/TS ratio is achieved.

Supplementary Materials: The conference presentation file is available at <https://www.mdpi.com/article/10.3390/ECP2022-12666/s1>.

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