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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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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 for a sustainable circular economy [1].

Advanced oxidation processes (AOPs) are methods that generate radicals, such as hydroxyl radicals ($HO^{\bullet -}$), with high oxidizing power ($E^{\circ}_{HO^{\bullet}}$ = 2.80 V) that reduces contaminated organic composites and can be used to water and soil treatment. The Fenton reaction is one of these methods, that through the interaction between ferrous ion (Fe^{2+}) and hydrogen peroxide (H_2O_2) generates Fe^{3+} and $HO^{\bullet}$ (Eq. (1)). However, it is a complex mechanism because the reaction depends on several factors, such as the pH, H_2O_2 concentration, Fe^{2+} concentration [2,3]. Several studies have been developed in order to optimize the Fenton reaction trough association with light, ultrasound, use of nanoparticles and electrical energy [4,5].

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^- + HO^{\bullet} \quad (1)$$

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 includes splitting the water molecules to a hydrogen atom and hydroxyl radical, as observed in Equations 2–4, as follows [7].

$$H_2O + US \rightarrow H^{\bullet} + HO^{\bullet} \quad (2)$$

$$O_2 + US \rightarrow 2O^{\bullet} \quad (3)$$

$$H_2O + O^{\bullet} \rightarrow 2HO^{\bullet} \quad (4)$$

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:

$$H_2O_2 + Fe^{3+} \rightarrow Fe(OOH)^{2+} + H^+ \quad (5)$$

$$Fe(OOH)^{2+} + US \rightarrow Fe^{2+} + HO^{\bullet} \quad (6)$$

The aim of this work was (1) the characterization of the municipal activated sludge, (2) optimization of 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 was used sodium hydroxide (NaOH) from Labkem, Barcelona, Spain and sulphuric acid (H_2SO_4, 95%) from Scharlau, Barcelona, Spain. For chemical processes it was used hydrogen peroxide (H_2O_2 30%), supplied by Sigma-Aldrich, Missouri, USA and ferrous sulfate heptahydrate ($FeSO_4 \bullet 7H_2O$) was supplied by Panreac, Barcelona, Spain.

2.2. Analytical Methods

Before the experiment, different physical- chemical parameters were determined to characterize the municipal activated sludge. Such parameters as pH, COD, total solids, volatile solids, volatile solids and total solids ratio, electrical conductivity, and iron concentration (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 (μS/cm)	1249 ± 10

For COD determination, it was used a closed reflux method, for total solids (TS) and volatile solids (VS) it were applied gravimetric methods, 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, it was used an ultrasonic processor (Vibracell Ultrasonic processor VCX 500, Sonics & Materials Inc., Danbury, CT) and a magnetic stirrer (Nahita blue, Navarra, Spain) for Fenton process, as shown in Figure 1. During the US-Fenton and Fenton process, the reagents were well mixed to start reacting. The experiments were processed on a 100 mL beaker, and 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.

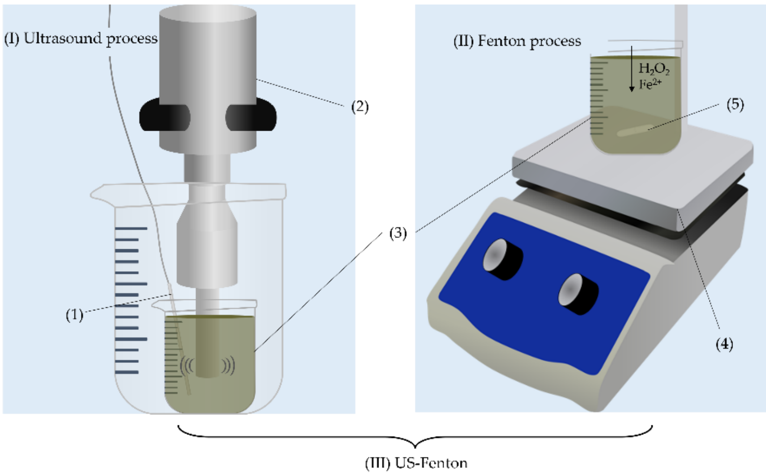

Figure 1. Schematic representation of (I) US and US-Fenton and (II) Fenton processes on the treatment of MAS. (1) equipment for temperatures control, (2) ultrasonic processor, (3) 100 mL beaker containing sludge, (4) magnetic stirrer device and (5) stir bar.

2.4. Statistical Analysis

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

3. Results and Discussion

3.1. Ultrasound vs Fenton vs US-Fenton Treatment Process

In this section, the US was compared with 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's possible to see that the process that showed the best results was, without a doubt, US-Fenton, reaching 94.8% of 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 to Saleh and Taufic [8] who observed that application of US-Fenton reached a higher methylene blue and congo-red dyes removal in comparison to US and Fenton processes.

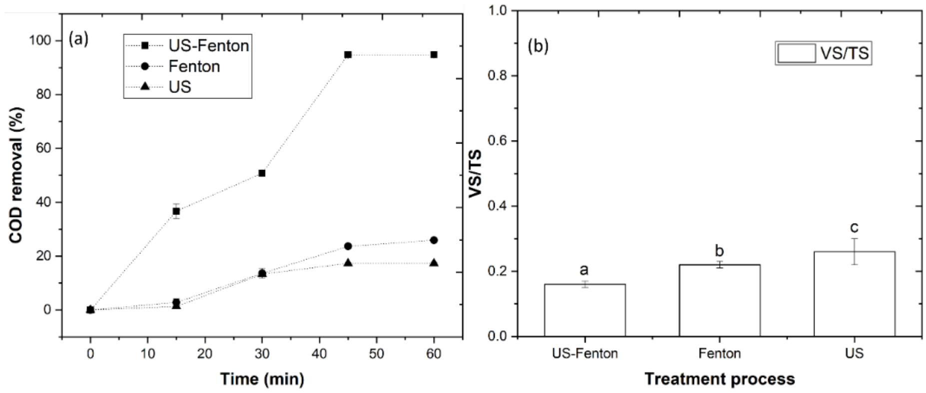

Figure 2. Evaluation of (a) COD removal and (b) VS/TS removal with different treatment processes. Experimental conditions: pH = 4, $[H_2O_2]$ = 30 mM, $[Fe^{2+}]$ = 2.0 mM, cavitation time 3s ON: 5 s OFF, A = 40%, T = 298 K, time = 60 min. Means in bars with different letters represent significant differences ($p < 0.05$) 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 2, 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 lead to a lower production of $HO^{\bullet}$ radicals and inhibits Fe^{2+} regeneration [10,11].

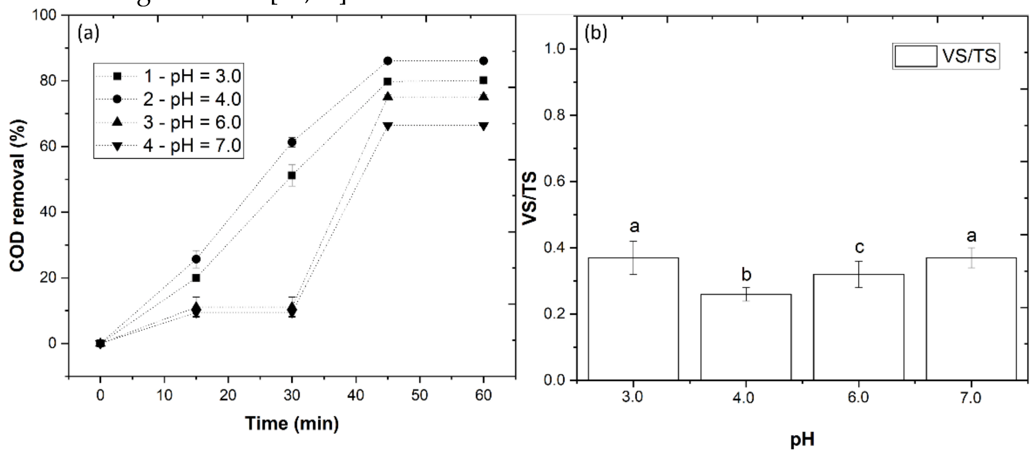

Figure 3. Evaluation of (a) COD removal and (b) VS/TS ratio at different pH (3.0-7.0). Experimental conditions: $[H_2O_2]$ = 100 mM, $[Fe^{2+}]$ = 2.0 mM, cavitation time 3 s ON: 5 s OFF, A = 40%, T = 298 K, time = 60 min. Means in bars with different letters represent significant differences ($p < 0.05$)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

3.3. *Effect of H_2O_2 Concentration*

To evaluate the effect of H_2O_2 concentration, it were tested different concentrations (30–200 mM). The highest efficiency was achieved with application of $[H_2O_2]$ = 30 mM, with a COD removal of 94.8% respectively (Figure 4). In addition, the VS/TS ratio was reduced to 0.16, which showed a reduction of the microbial concentration that existed in the MAS. Increasing the H_2O_2 concentration, it was observed a COD reduction of 87.2, 86.1, 78.3 and 69.3%, respectively, 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 [2,3].

$$H_2O_2 + HO^{\bullet} \rightarrow HO_2^{\bullet} + H_2O \quad (7)$$

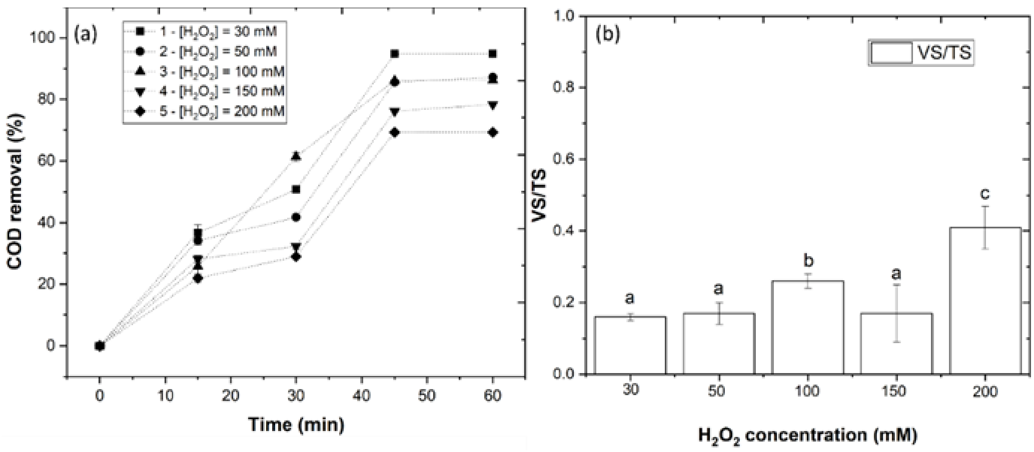

Figure 4. Evaluation of (a) COD removal and (b) VS/TS ratio with different $[H_2O_2]$ (30 mM - 200 mM). Experimental conditions: pH = 4, $[Fe^{2+}]$ = 2.0 mM, cavitation time 3 s ON: 5 s OFF, A = 40%, T = 298 K, time = 60 min. Means in bars with different letters represent significant differences ($p < 0.05$) within VS/TS by comparing wastewaters.

3.4. Effect of Iron Concentration

The Fe^{2+} acts as catalyst in the process of generating $HO^{\bullet}$ radicals, so it must be achieved an optimum concentration that potentiates greater production of radicals [14]. In this section, the Fe^{2+} concentration was varied from 0.5 to 10.0 mM, and in accordance with the results (Figure 5), with application of 2.0 mM Fe^{2+} it was achieved a COD removal of 94.8%. Above 2.0 mM, it was observed a decrease of COD removal and higher values of VS/TS ratio. The excess of ferrous ions can lead to a consume of $HO^{\bullet}$ radicals producing Fe^{3+} and HO^{-} (Eq. 8), resulting less degradation [15].

$$Fe^{3+} + HO^{\bullet} \rightarrow Fe^{3+} + HO^{-} \quad (8)$$

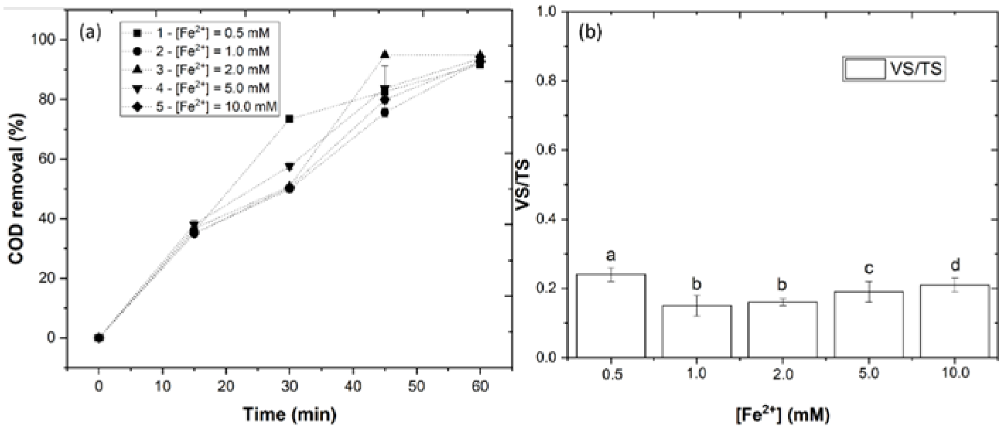

Figure 5. Evaluation of (a) COD removal and (b) VS/TS removal with different $[Fe^{2+}]$ (0.5 mM-10.0 mM). Experimental conditions: pH = 4, $[H_2O_2]$ = 30 mM, cavitation time 3 s ON: 5 s OFF, A = 40%, T = 298 K, time = 60 min. Means in bars with different letters represent significant differences ($p < 0.05$) 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 to Sivagami et al. [16], who observed that increasing the contact time lead to a decrease of the PHC degradation in US-Fenton process.

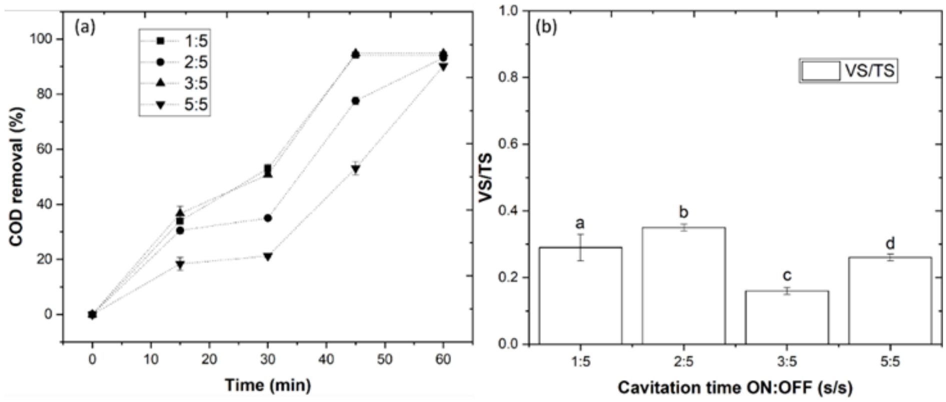

Figure 6. Evaluation of (a) COD removal and (b) VS/TS removal with different cavitation time ON:OFF (1:5, 2:5, 3:5 and 5:5). Experimental conditions: pH = 4, [H_2O_2] = 30 mM, [Fe^{2+}] = 2.0mM, A = 40%, T = 298 K, time = 60 min. Means in bars with different letters represent significant differences ($p < 0.05$) 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 US-Fenton process depends on several variables, mainly pH, concentrations of hydrogen peroxide and ferrous ion, and cavitation time. Under the optimal conditions it is achieved 94.8% of COD removal and 0.16 VS/TS ratio.

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