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CENTRO DE QUÍMICA VILA REAL

Treatment of municipal activated sludge by ultrasound-Fenton process

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Session 2. Environmental and Green Processes

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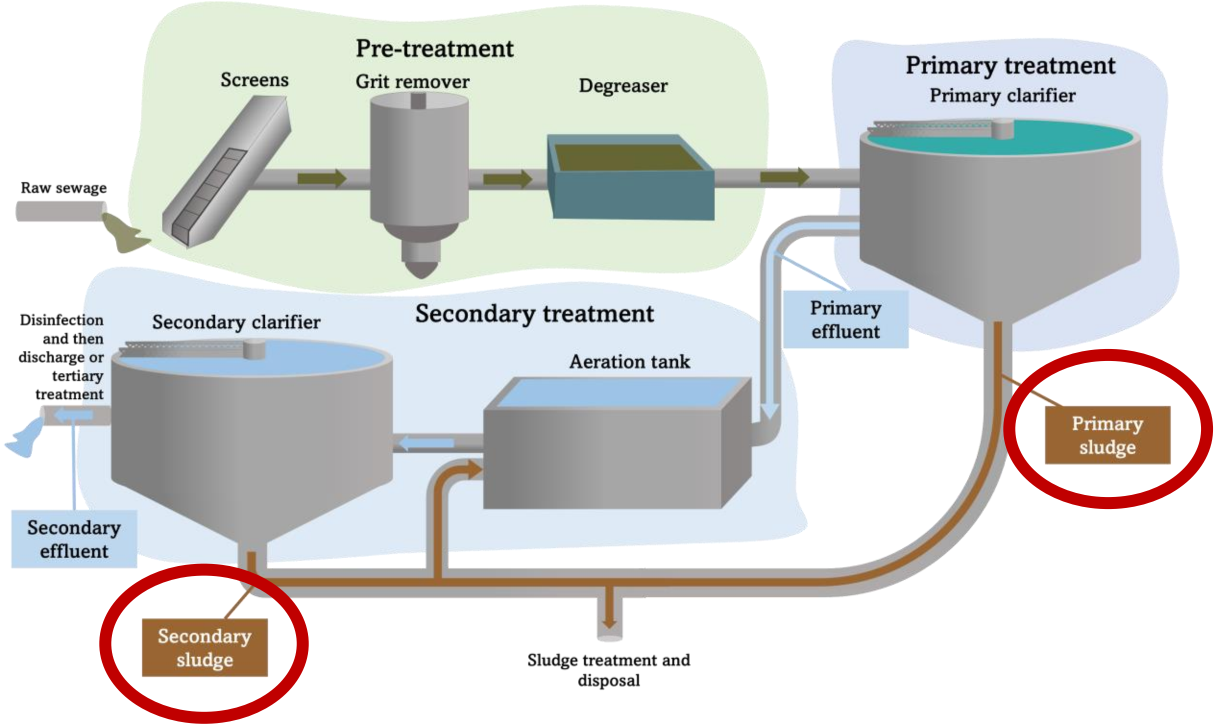
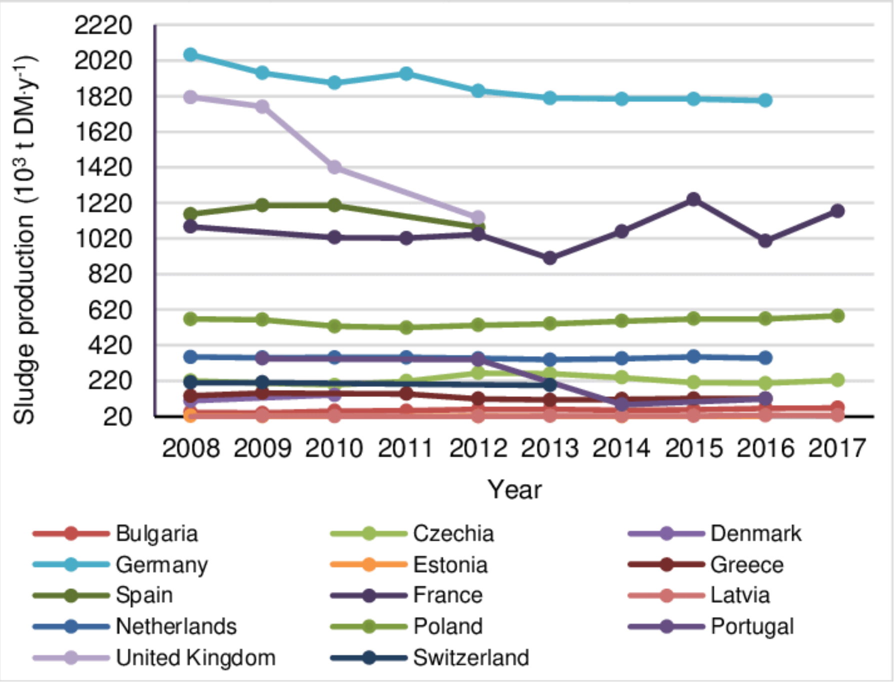
Introduction

Municipal wastewater treatment produces significant volumes of sludge

Municipal wastewater treatment



The production of sewage sludge in selected countries of EU
Source: [1]



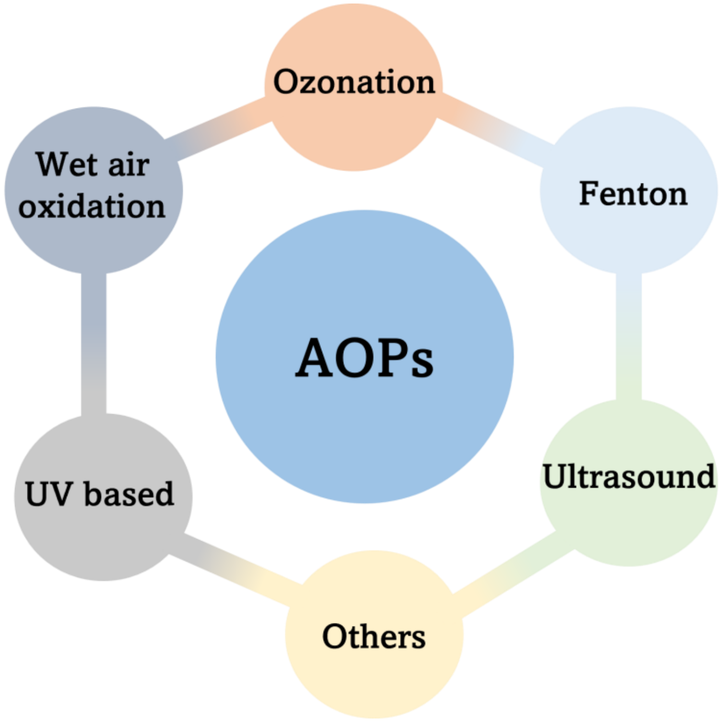
These sludges contains, normally, high values of organic matter, macronutrients and micronutrients and can also contain high content in metals and pathogenic microorganisms.
Therefore, they need the right treatment so they can be reused and don't constitute a threat to the environment.

1 Ghacha A, Ammari M, Ben Allal L. (2020) Sustainable sewage sludge management in Morocco: Constraints and solutions. *J. Water L. Dev.*, 46(October), 71–83.

Introduction

Advanced oxidation processes (AOPs)

AOPs are methods that generate radicals, such as hydroxyl radicals ($HO^{\bullet}$), with high oxidizing power ($E^{o}_{HO^{\bullet}}$ = 2.80 V) that reduces contaminated organic composites and can be used to water and soil treatment.



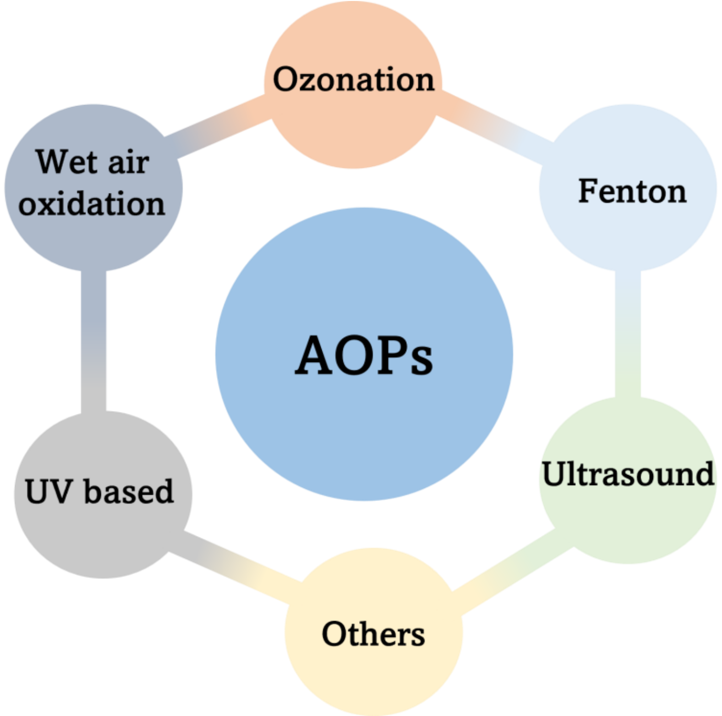
The Fenton reaction produces $HO^{\bullet}$ radicals through the interaction between ferrous ion (Fe^{2+}) and hydrogen peroxide (H_2O_2).

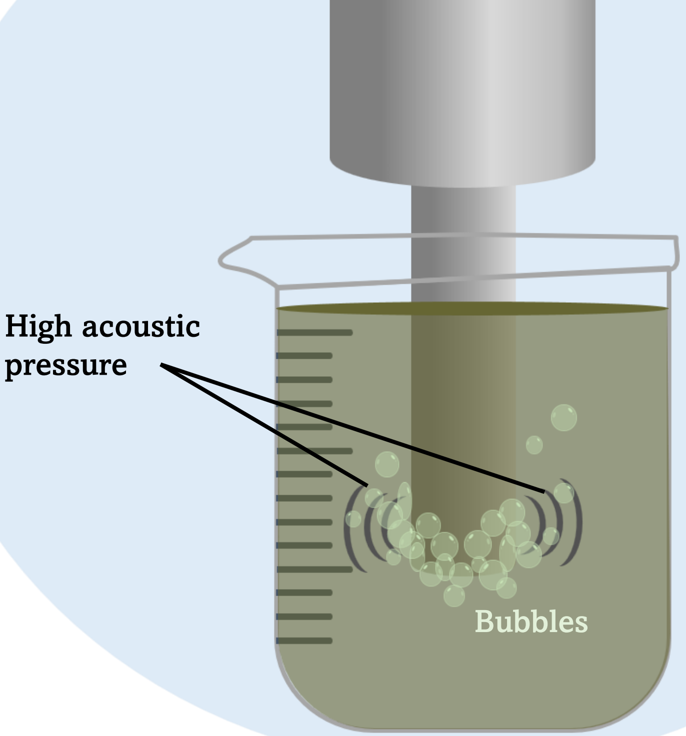
$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^{-} + HO^{\bullet}$$

- Fe^{2+}: Catalyst
- H_2O_2: Oxidant
- $HO^{\bullet}$: High oxidizing power

It is a complex mechanism because the reaction depends on several factors, such as the pH, H_2O_2 concentration, Fe^{2+} concentration, etc.

Introduction





$$H_2O + US \rightarrow H^{\bullet} + HO^{\bullet}$$
$$O_2 + US \rightarrow 2O^{\bullet}$$
$$H_2O + O^{\bullet} \rightarrow 2HO^{\bullet}$$

Under ultrasound radiation, the waves interact with dissolved gases in the water body which leads to acoustic cavitation that can generate short-lived radicals. These phenomena, include the following steps: the formation, growth, and implosive collapse of bubbles.

Ultrasound-Fenton (US-Fenton) is the combination of these two methods. In addition to $HO^{\bullet}$ radical production, the application of ultrasounds allows the regeneration of the ferric iron to ferrous iron, increasing the kinetic rate of the Fenton process.

$$FeHOO^{2+} + US \rightarrow Fe^{2+} + HO^{\bullet}$$

Aim of this work

(1) the characterization of the municipal activated sludge

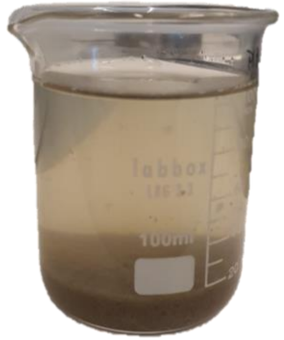
(2) optimization of US-Fenton process

(3) the study of efficiency between ultrasound, Fenton and US-Fenton treatment processes applied to the sludge

Material and methods

Municipal activated sludge characterization

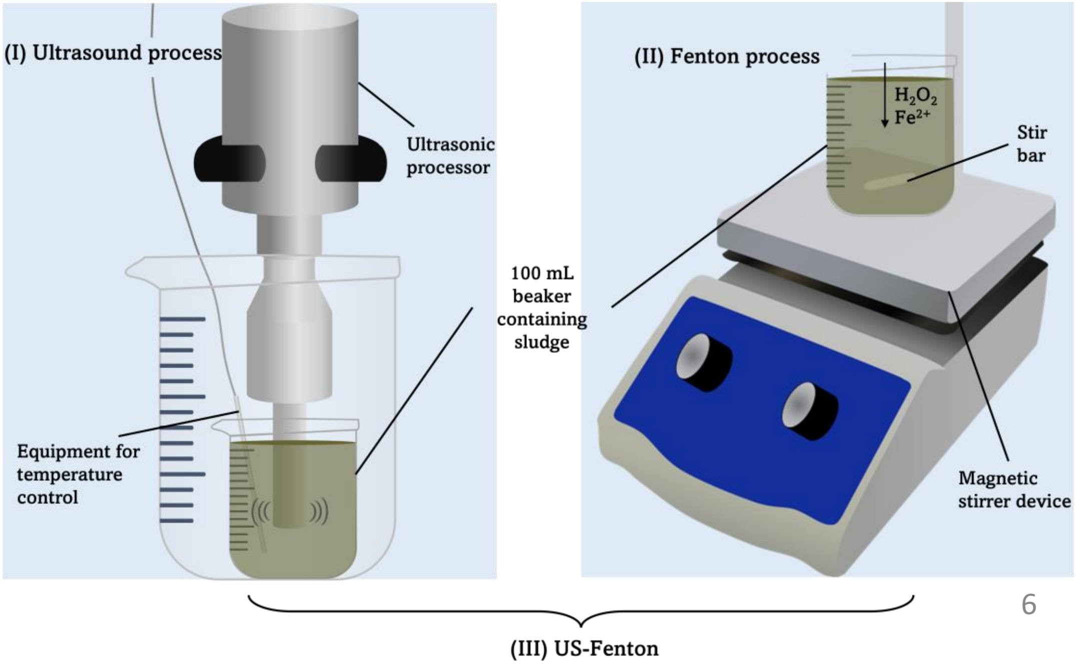
Parameters	Values
pH	6.48
Chemical oxygen demand (mg O_2/L)	8512
Total solids (mg/L)	3250
Volatile solids (mg/L)	1920
Volatile solid/Total solids (mg/L)	0.59
Electrical conductivity (μS/cm)	1249



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.

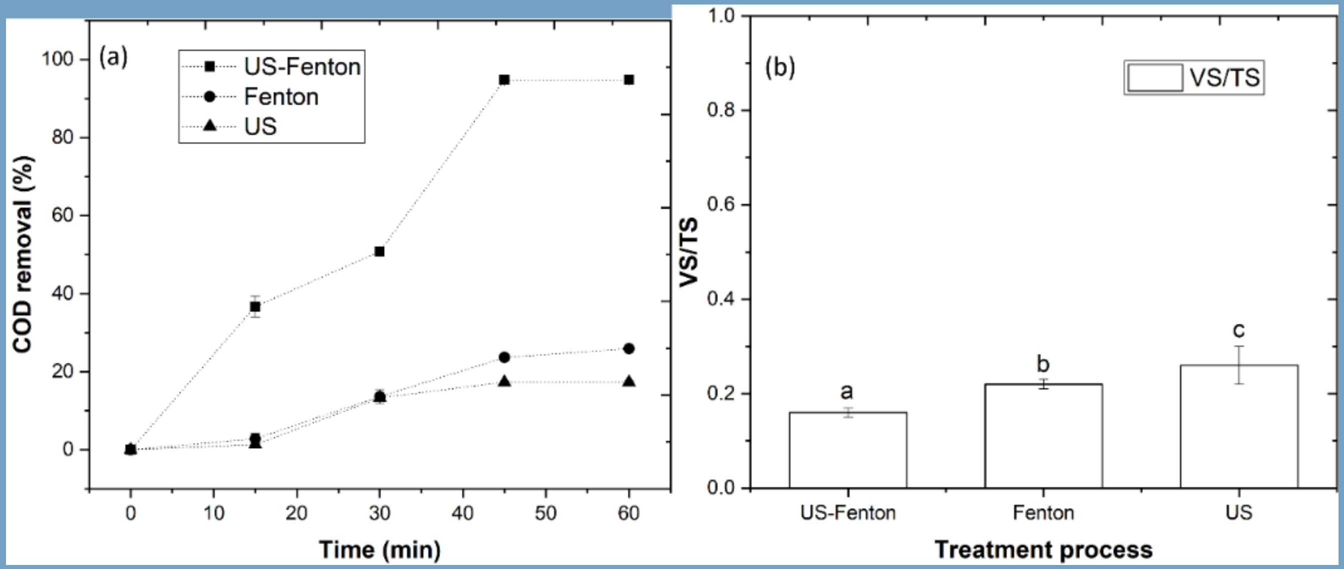
The optimization of US-Fenton was performed in the following order: (1) variation of pH (3.0 - 7.0), (2) variation of H_2O_2 concentration (30 - 200 mM), (3) variation of Fe^{2+} concentration and (4) cavitation time ON (1 – 5 s), OFF (5 s).

Experimental Set-up



Results and discussion

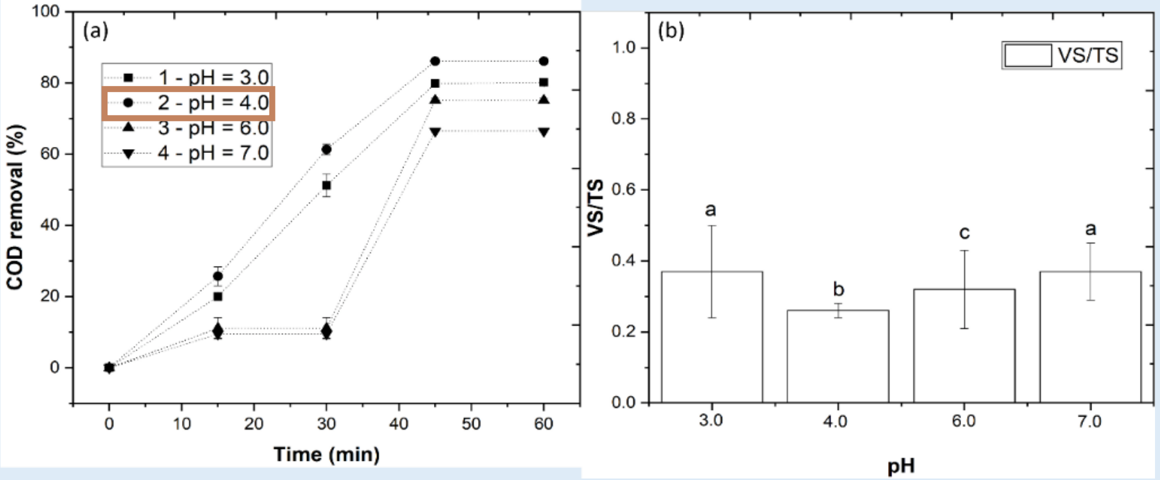
Ultrasound vs Fenton vs US-Fenton treatment process



It's possible to see that the process that showed 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.

Results and discussion

Effect of pH

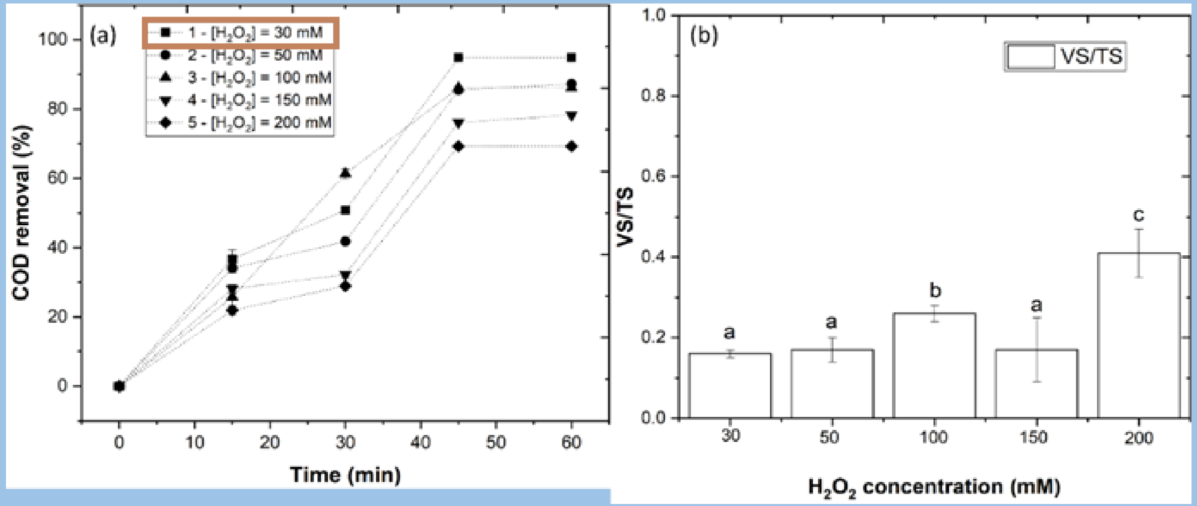


As can be observed, pH = 4.0 showed the highest efficiency, with a COD removal of 86.1%. Increasing the pH to 6.0 and 7.0, the COD removal suffers a reduction to 75.1% and 66.4%, respectively. The efficiency reduction at alkaline pH, resulted from the iron hydroxides precipitation, which lead to a lower production of $HO^{\bullet}$ radicals and inhibits Fe^{2+} regeneration.

Effect of H_2O_2 concentration

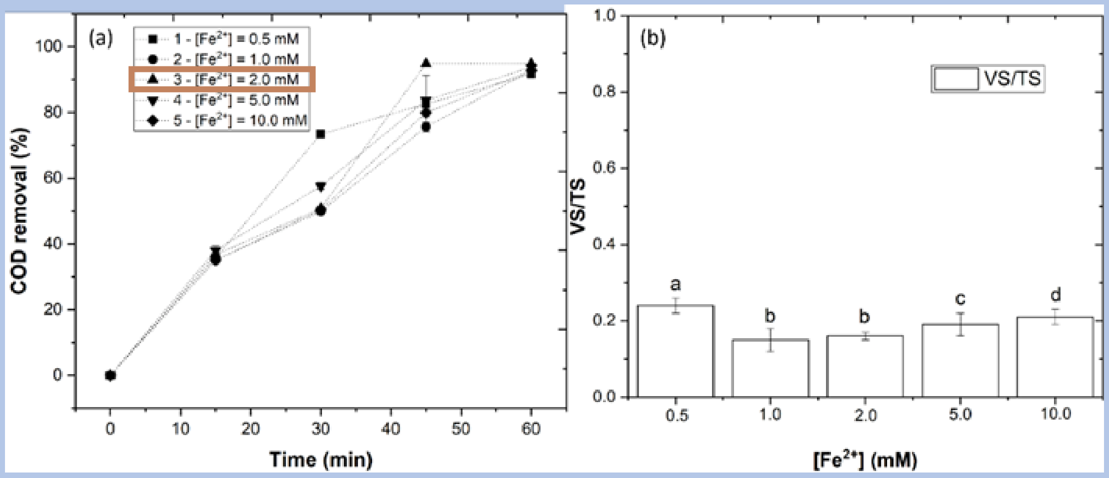
The highest efficiency was achieved with application of $[H_2O_2]$ = 30 mM, with a COD removal of 94.8%. In addition, the VS/TS ratio was reduced to 0.16. It was observed a COD reduction of 87.2, 86.1, 78.3 and 69.3%, respectively, for 50, 100, 150 and 200 mM. By increasing the H_2O_2 concentration to values > 30 mM, the excess of H_2O_2 induces the consume of $HO^{\bullet}$ radicals and produces $HO_2^{\bullet}$ which has a low reduction potential, so, less degradation occurs.

$$H_2O_2 + HO^{\bullet} \rightarrow HO_2^{\bullet} + H_2O$$



Results and discussion

Effect of iron concentration

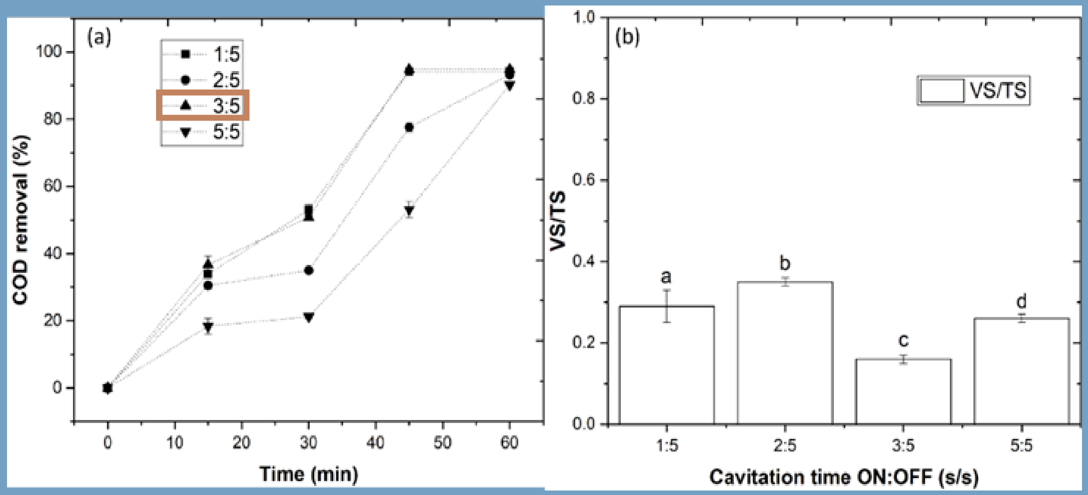


In this section, the Fe^{2+} concentration was varied from 0.5 to 10.0 mM, and in accordance with the results, with application of 2.0 mM Fe^{2+} it was achieved a COD removal of 94.8%. Above 2.0 mM, it was observed a decrease of COD removal and higher values of VS/TS ratio. The excess of ferrous ions can lead to a consume of $HO^{\bullet}$ radicals producing Fe^{3+} and OH^{-}, resulting less degradation.

$$Fe^{3+} + HO^{\cdot} \rightarrow Fe^{3+} + HO^{-}$$

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.



Conclusions

Through the results obtained we can conclude that :

(1) the US-Fenton has a higher efficiency for COD removal and VS/TS ratio decrease

(2) the efficiency of US-Fenton process depends on several variables, mainly pH, concentrations of hydrogen peroxide, ferrous ion and cavitation time

(3) under the optimal conditions it is achieved 94.8% of COD removal and 0.16 VS/TS ratio

Acknowledgements

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Thank you for your attention