

Ultrasound-assisted persulfate degradation of haloperidol in wastewater

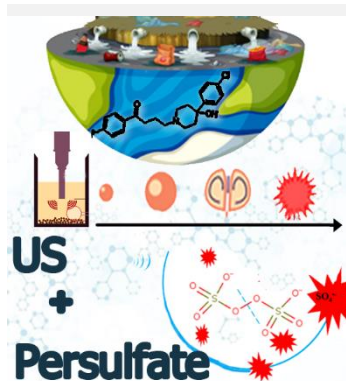
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This study investigated the degradation of haloperidol using activated persulfate (PS), when subjected to ultrasonic (US) irradiation and mechanical mixing (under silent condition). The degradation of recalcitrant organic pollutants by sulfate radical ($\text{SO}_4^{\cdot-}$) represents one of the most recent developments in oxidation-based water treatment. In most cases, PS acts as a precursor of sulfate radicals. This study employed ultrasound-activated PS to generate reactive species, facilitating the degradation of haloperidol. An ultrasound with a frequency of 20 kHz and 750 W power was utilized for the degradation studies. The applied oxidation system successfully resulted in the 37% degradation of haloperidol. The results presented in this study underscore the US/PS system's applicability in removing haloperidol. Optimization studies are under development to achieve maximum process efficiency.

Introduction

Antipsychotic drugs, including haloperidol, are among the pharmaceuticals that are increasingly detected in wastewater. In Brazil, this drug was determined in hospital effluent at concentrations ranging from 1.43 to 2.73 $\mu\text{g L}^{-1}$ [1]. Haloperidol is one of the antipsychotics whose impact on non-target organisms has been understudied. It showed a high risk of inducing toxic effects on wild European fish. Therefore, haloperidol from wastewater and other aqueous matrices must be removed urgently. The degradation of recalcitrant organic pollutants by sulfate radical ($\text{SO}_4^{\cdot-}$) represents one of the most recent developments in oxidation-based water treatment. In recent years, Persulfate (PS) has attracted increasing attention as an alternative to H_2O_2 for advanced oxidation processes due to its high redox potential ($\text{SO}_4^{\cdot-}$, 2.5 V–3.1 V) and longer lifetime than $\cdot\text{OH}$. Based on the above advantages, activated PS oxidation has become a hot spot for the degradation of refractory organics. $\text{SO}_4^{\cdot-}$ is generated with the breakage of O-O bond of PS using various activation methods. Increasing activation methods have been explored in the past decades, including energy (e.g., Heat, ultraviolet and microwave, alkalis, carbon materials, transition metals, and nanometer materials [2]). Among them, using ultrasonic activation of persulfate as an emerging method has gained increasing attention due to its unique cavitation characteristics and the high temperatures and pressures under which persulfate can be activated. Due to this phenomenon, the formation, growth, and collapse of tiny bubbles occur in the water. Local pressure and temperature can increase significantly when the bubbles collapse, producing free radicals [3]. The oxidizing species in the ultrasonic process include $\text{O}_2^{\cdot-}$, $\cdot\text{OH}$, and $\cdot\text{H}$. The ultrasonic waves combined

with PS can accelerate the production of sulfate radicals and increase the process efficiency in removing pollutants [4]. In the present study, the degradation of the haloperidol in aqueous matrices using ultrasound-activated persulfate was investigated.

Material and Methods

Experiments were carried out in a glass-jacketed reactor with a useful volume of 250 mL. A US sonotrode (VCX750, Sonics, USA) operating at a nominal power of 750 W (amplitude of 30%) and a frequency of 20 kHz was used with a Ti-alloy probe (Q630-0217, Sonics, USA) with 13 mm diameter and 254 mm long. The delivered acoustic power P_w was 35 W L^{-1} . Degradation experiments at silent conditions (i.e., PS in the absence of US) were carried out with a stand homogenizer (PT 3100 D, Kinematica, Switzerland) coupled with a stainless-steel homogenizer tip (PT-DA 12/2EC-F154, Kinematica, Switzerland) operating at 1000 rpm. For initial tests, samples were fortified with haloperidol at a concentration of 100 $\mu\text{g L}^{-1}$ with the pH of the solution adjusted to 7. Persulfate was added to obtain the concentration of 5 mmol L^{-1} . To determine the concentration of haloperidol, we used liquid chromatography equipment coupled to a mass spectrometer (LCMS-2020, Shimadzu, Japan). The system consisted of an autosampler, degasser, binary pump, column oven, electrospray ionization source (ESI), and a single quadrupole mass spectrometer.

Results and Discussion

To evaluate the effect of the degradation process on the degradation of haloperidol, initially, a comprehensive investigation of the degradation of haloperidol in PS alone, US alone, and US/PS was

conducted. The results obtained from the US alone and PS alone, as well as their outcomes, are shown in Figure 1.

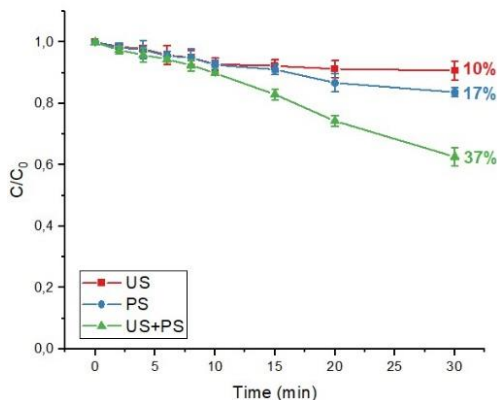


Figure 1. Degradation of haloperidol in different reaction systems. Experimental conditions: $C_0 = 1000 \mu\text{g L}^{-1}$, initial pH = 7.0, $C_{\text{PS}} = 5.0 \text{ mmol L}^{-1}$, $P_w = 35 \text{ W L}^{-1}$, $T = 25 \pm 0.3^\circ\text{C}$.

As is clear from Figure 1, haloperidol undergoes degradation in both the US and PS alone systems at a similar reaction rate. In this process, a very low

content (10% - 17%) of haloperidol was degraded under the effect of ultrasonic radiation or PS because radicals like $\cdot\text{OH}$, $\cdot\text{O}$, and $\text{H}\cdot$ may not form significantly. The slight acceleration in the PS/US system is ascribed to generating sulfate radicals from PS anions. It was removed at a rate of 37 %, which is much higher than the use of US or PS alone, indicating that a positive synergistic activity existed in the PS/US system. A significant difference in degradation efficiencies was observed in the initial stages after 10 minutes of reaction, but complete degradation was not observed after 30 minutes. The components of the water matrix influence the removal of organic pollutants in water treatment processes. A detailed discussion on the importance of these parameters in AOPs and their effects will be explored in the subsequent stages of the study. Therefore, the following steps to complete this research encompass assessing the sample's pH, investigating the influence of the initial concentration of PS, analyzing the impact of the starting concentration of haloperidol, examining the influence of coexisting inorganic anions, exploring various aqueous matrices, such as urban effluent, hospital effluent, surface water, etc., and finally, investigating the oxidation products and degradation pathways of haloperidol.

Conclusions

Using the US combined with ultrasound increases the efficiency of haloperidol degradation. Optimization studies are under development to achieve maximum process efficiency.

Acknowledgments

CNPq, Capes and Fapergs.

References

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