



Ultrasonic power improvement of flumequine degradation effectiveness in aqueous solution via direct and indirect action of mechanical acoustic wave

Malek Harrabi^a, Hafedh Belhadj Ammar^{b,*}, Khadija Mbarki^a, Ikram Naifar^a, Chiraz Yaiche^a, Fatma Aloulou^a, Boubaker Elleuch^a

^a National School of Engineering Sfax, GEET, Tunisia

^b Department of Chemistry, Faculty of Sciences of Sfax, University of Sfax, Tunisia

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ABSTRACT

The current research work aimed to describe the roles of ultrasonic power under sono-Fenton process in the degradation of flumequine (FLU) in water. For this purpose, the effects of some parameters including temperature, ferrous ion concentration, chemical oxidant concentration ($S_2O_8^{2-}$ and Cl^-) and the initial pH value of the reaction kinetics were investigated. Results showed that the degradation of FLU antibiotic was accelerated by ultrasonic irradiation and the presence of an inorganic oxidant. The sono-generation of active species such as hydroxyl radicals (HO^\cdot and HOO^\cdot) and sulfate radicals ($SO_4^{\cdot-}$) as strong oxidizing agents improved the FLU degradation. In fact, the peroxydisulfate anion ($S_2O_8^{2-}$) has been identified as among parameters that enhanced the degradation process. Under optimal conditions, 98% of the flumequine removal was carried out within 80 min at 60 °C.

1. Introduction

The environmental persistence of antibiotics in water has become a global interest due to their different way of diffusion in nature. The elimination of the antibiotic residue in various wastes is critical to minimize potential environmental contamination and the ecological health risk caused by antibiotic pollution [1,2]. Due of their slow biodegradability and persistence in almost all types of matrices, antibiotics generally cannot be permanently eliminated by the typical methods applied in wastewater treatment plants, including coagulation, flocculation, sedimentation and filtration. Moreover, wastewater containing antibiotics is characterized by high chemical oxygen demand (COD) and low biochemical oxygen demand (BOD), as a result, biological processes are found to be ineffective for the treatment of these types of waste waters [3,4].

On the other hand, innovation and development of new physico-chemical techniques, including advanced oxidation processes, such as chlorination, adsorption, photocatalysis, Fenton and photo-Fenton reactions, and the electrochemical process can clearly overcome the disadvantages of biological methods [5–9].

The search of environmentally friendly and efficient wastewater treatment approaches represents a new trend for pollution control and environmental protection during the last years [10]. Ultrasound is

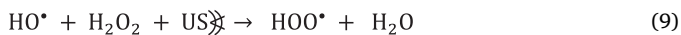
increasingly paying attention to enabling technologies aiming at achieving high efficiency and meeting the green criteria of energy savings and the absence of critical or harsh reagents [11–13]. The advantages of this technology are numerous, starting with a high chemical-free potential and simultaneous oxidation, thermolysis, shear degradation in addition to an improved mass transfer process [14,15]. Thus, the ultrasound technology has a promising ability to the degradation of non-biodegradable and toxic compounds in H_2O and CO_2 [16–19]. For the decontamination of wastewater, ultrasound can act in two modes, either by natural action (direct) or by chemical action (indirect). The direct action induced by the ultrasound is also attractive for the treatment of industrial effluents. In fact, the ultrasound generates cavitation bubbles, creating micro-jets of liquid and potent shear forces during their implosion, which gives a better homogenization of the reaction medium [19,20]. In these extreme conditions, radicals from the water sonolysis are then ejected in the middle where they will react with the compounds in solution. Then, cavitation bubbles act as microreactors. Indeed, during cavitation, destruction/oxidation of pollutants can be done in two different ways, either by a free radical attack, or either by pyrolysis [21].

Generally, the indirect action gives good effects when it is tested at high frequency. Therefore, it leads to the generation of free radicals (HO^\cdot , O^\cdot and HOO^\cdot) from water molecules or oxygen. (Eqs. (1)–(9))

* Corresponding author.

E-mail address: hbelhadammar@yahoo.fr (H. Belhadj Ammar).

[22,23].



Moreover, indirect sonochemical oxidation for treating organic polluted water may occur via reaction with reactive species such as sulfate radicals ($\text{SO}_4^{\bullet -}$) as a stronger oxidizing agent with a redox potential of 2.6 V [24,25]. This result can be explained by the following mechanisms.

Firstly, ultrasonic irradiation can activate the $\text{S}_2\text{O}_8^{2-}$ ions as illustrated in Eq. (10) [25]:



Regarding the next step, the hydroxyl radicals can be formed through the radicals as can be seen in Eq. (11) [26]:



The objective that specifies this current work was to determine the characteristics of sonocatalytic degradation processes for the effective degradation of FLU. To this end, a series of experiments were conducted to determine the most important process variables such as pH, temperature, time of treatment and the effect of the inorganic oxidant.

2. Experimental

2.1. Chemical and apparatus

In this work, all solutions were prepared in GEET laboratory. All chemical reagents used were of the highest purity grade. Flumequine antibiotic (99%) was purchased from Sigma-Aldrich (Barcelona, Spain). All solutions used throughout the experiment were freshly prepared in bidistilled water in a cylindrical container containing 200 mL solution of FLU (1 mM). For pH adjustment, Sulfuric acid (0.1 mol L^{-1}) had been employed. Ferrous sulfate heptahydrate ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$) which used as the Fe (II) catalyst, potassium peroxydisulfate ($\text{K}_2\text{S}_2\text{O}_8$) and sodium chloride (NaCl) were obtained from Riedel-de Haën (Seelze-Hannover, Germany). Hydrogen peroxide (35% v/v) was provided from Honeywell Fluka™ (France) and sulfuric acid from Merck (Darmstadt, Germany).

Sonocatalytic degradation of FLU was carried out in an ultrasonic bath (ELISONIC-CUS 103) which was operated at a frequency of 40 kHz and with an effective power output of 120 W.

2.2. Analysis of liquid samples

Samples (1 mL) were withdrawn from the reactor over a fixed interval of 20 min for FLU analysis by spectrophotometer. Before Analysis, 1 mL NaOH (0.1 mol L^{-1}) had been added to each sample and mixed for at least 10 min to eliminate the residual of H_2O_2 . Then the samples were filtered through a $0.3 \mu\text{m}$ membrane.

Flumequine concentration was monitored by reading the absorbance of samples at 244.5 nm (Maximum wavelength of FLU), in a spectrophotometer (Agilent Technologies – Cary 60 – UV-Vis).

At first, the spectra of the standards were obtained with a scanning in a range of 200–600 nm (a step of 1 nm), after, following the results obtained, the range of spectra for the samples was reduced in range

240–250 nm (a step of 0.5 nm). A 10 mm quartz cell was used for all samples. Its walls were cleaned before each measurement. Two light sources are used: a halogen tungsten visible lamp and a deuterium UV lamp. The scanning speed was set at 1000 nm/min. The blank was made with demineralized water and with the same measuring cell. All spectra were obtained without dilution.

The quantification of FLU was performed by calibration using standards with a known concentration (10 mg L^{-1} ; 50 mg L^{-1} ; 100 mg L^{-1} ; 150 mg L^{-1} ; 200 mg L^{-1} ; 250 mg L^{-1} ; 300 mg L^{-1}).

All samples were analyzed in triplicate.

3. Results and discussion

3.1. Effect of pH on US/ H_2O_2 process

It is often reported that pH is one of the most important parameters that has a direct impact on Fenton reactions. It was approved that the Fenton process has critical limits in terms of pH solution. For $\text{pH} > 4$, the total concentration of Fe(II) and Fe(III) decreases considerably in the solution. It is deduced that Fe(II) and Fe(III) complexes or hydroxides are formed, reducing the availability of iron for the Fenton reactions [27]. For $\text{pH} < 2$, Fe(II) and Fe(III) ions exist as $[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$ and $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$ respectively. In this pH range, the regeneration of Fe (II) in the form of $[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$ from $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$ is slow.

Moreover, at a low pH (< 2), hydrogen peroxide forms oxonium ions (H_3O_2^+). These latter are more stable than H_2O_2 and their reactivity with ferrous ions decreases. In addition, at this pH range, the scavenging effect of the $\cdot\text{OH}$ by H^+ is enhanced [28,29].

In order to investigate the effect of the initial pH on the degradation process of FLU, experiments were performed at different initial pH (2, 3 and 4).

Fig. 1 shows the effect of the initial pH on FLU removal rate. As can be seen from this figure, the high efficiency of the process is obtained at $\text{pH} = 4$. After 120 min of treatment, FLU removal reaches 59%.

Differential rate laws are generally used to describe what is occurring on a FLU degradation rate during a reaction, whereas integrated rate laws are used for determining the reaction order and the value of the rate constant from experimental measurements. The kinetics fundamentally relates the rate of FLU degradation (r) and [FLU] in aqueous solutions at reaction time t is expressed by the following equation:

$$r = -\frac{d[\text{FLU}]}{dt} = k_{\text{obs}}[\text{FLU}]^\alpha \quad (12)$$

where k_{obs} : the observed degradation rate constant.

The integrated rate equation describing the first-order kinetics ($\alpha = 1$) is given below:

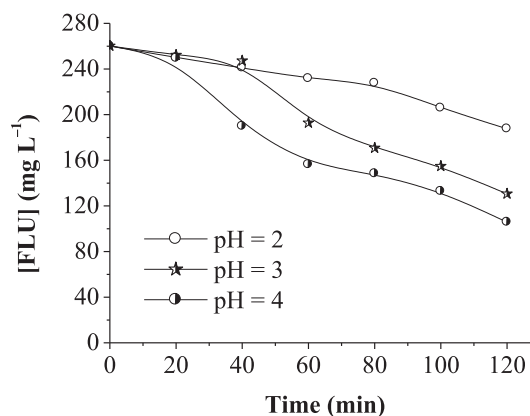


Fig. 1. Effect of pH on the trend of flumequine removal during US/ H_2O_2 process. $[\text{H}_2\text{O}_2] = 20 \text{ mmol L}^{-1}$ and $T = 20^\circ\text{C}$.

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