



Degradation of Brevetoxin-3 by the combined process Fenton and Ultrasound

*Nadia Ben Abderrazik¹, Urooj Khan², Kevin F. O'Shea²

¹Marine Ecotoxicology Laboratory, Abdelmalek Essâadi University, Tétouan, Morocco,

²Department of Chemistry and Biochemistry, Florida International University, Miami, FL 33199, USA,

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* Email: nabderrazik@yahoo.com

Abstract

Brevetoxins induce toxicity at very low concentration, and their elimination is critical to protect the environment and human health. The degradation of Brevetoxin-3 (PbTx-3) in aqueous solution by advanced oxidation processes (AOPs): Fenton and ultrasound was studied. This study investigates the sonolytic degradation of 4.5 ppm of PbTx-3 at 665 KHz under operational power of 500W and at neutral pH which decreases during the ultrasonic irradiation. In all the reactions, Brevetoxin solutions prepared, were taken from a stock solution and were gently purged with oxygen or argon for 5 min prior to irradiation.

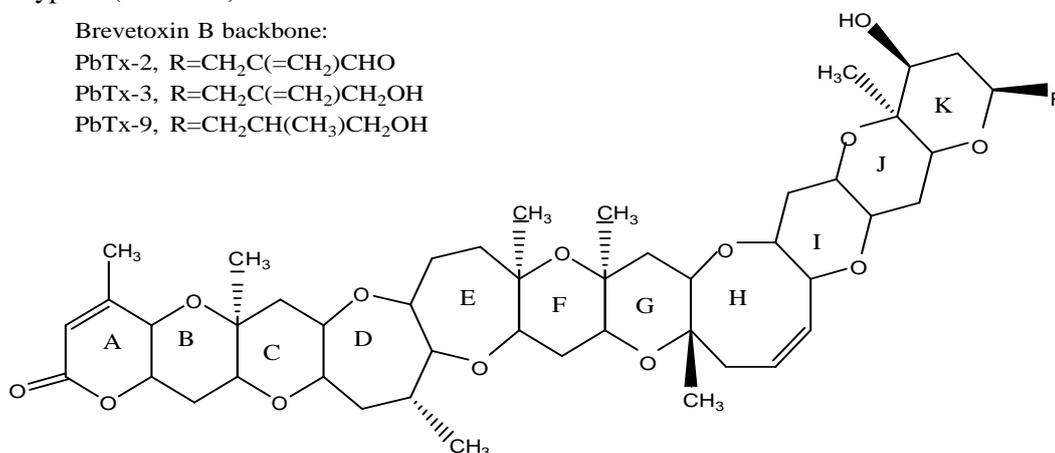
A kinetic study of PbTx-3 degradation under argon, oxygen and air atmospheres showed a pseudo-first-order reaction kinetics. The effect of Fe (II) on H₂O₂ accumulation during ultrasound reaction was investigated and showed a decrease of H₂O₂ concentration which explains the formation of hydroxyl radicals that enhance the degradation of the pollutant.

Also, the degradation of the toxin was studied by different systems: PbTx-3/US; PbTx-3/H₂O₂/US; PbTx-3/Fe/US; PbTx-3/Fe/H₂O₂/US. The last system combining Fenton and ultrasound enhanced remarkably the rate of degradation of PbTx-3, and yields to its complete removal in less than 15 min.

Key words: Brevetoxin-3, Fenton and ultrasound, kinetic study

1. Introduction

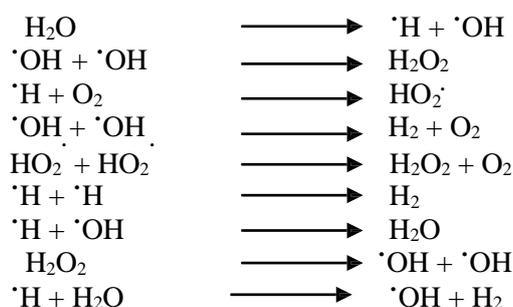
Red tides are the result of blooms of the dinoflagellate *Karenia brevis* algae. They have been known in many coastal areas of United States and all around the world by the false odor, discoloration of water to red or brown, and production of family of toxic compounds called brevetoxins (PbTx) (1). Blooms of *K. brevis* pose serious health risks to mammals and humans upon inhalation and ingestion via fish. Even small concentrations have been fatal to massive amounts of fish, birds, and mammals (2-5). Brevetoxins are neurotoxins that bind with high affinity to an active site 5 of voltage sensitive sodium channels on neuronal membrane (6, 7). They are of two types: Type A and B. The most abundant ones in the environment are PbTx-2, PbTx-3, and PbTx-9, all belonging to type B (Scheme1).



Scheme1: Structures of the three most abundant brevetoxins previously isolated from *K. brevis* (= Gymnodinium breve).

In order to achieve the degradation of Brevetoxin, a lot of work has been performed. Earlier in our lab, we have used an advance oxidation process (AOP) of TiO₂ Photocatalysis for degradation of PbTx-3 (8, 9). In the present study, we used another oxidation technique, which is the irradiation by ultrasound. Power ultrasound is able to produce chemical effects through the phenomenon of cavitation, by production of micro bubbles in a liquid when a large negative pressure is applied. Ultrasonic irradiation involves the generation of a number of radicals such as $\cdot\text{OH}$, $\text{H}\cdot$, $\text{HO}_2\cdot$, H_2O_2 (Equation 1), and can lead to complete mineralization of pollutant (10,11).

Equation1: Ultrasonic radical production in aerated aquatic environment.



In the present study, we investigated the ultrasonically induced degradation of PbTx-3 in aqueous solution under a variety of conditions. Our results showed that the Fe (II) can act as a catalyst and the combined process Fenton with ultrasound enhance remarkably the degradation of brevetoxin.

2. Materials and methods

Materials

Brevetoxin-3 was provided by Center for Marine Science, University of North Carolina, Fe (II) sulfate heptahydrate, hydrogen peroxide 30 % and HPLC grade solvents were purchased from Fisher Scientific. For all the experiments, water was purified by Millipore Milli-Q system (resistivity 18 M Ω cm). All gases were supplied by air products and were of at least 99.9 % purity. Due to the low solubility of PbTx-3 in water (5 %), a saturated stock solution of PbTx-3 was prepared in Milli-Q water then centrifuged. The liquid was withdrawn carefully and analyzed by HPLC. In all the experiments, the solutions were prepared from the stock solution. The solutions of brevetoxin prepared were gently purged with oxygen or argon for 5 min prior to irradiation.

Apparatus

The experimental apparatus for the ultrasonic irradiation consisted of a multi wave ultrasonic generator (Ultrasonic Energy systems, model 1.5-660) equipped with a 500 mL glass reactor, operating at 665 KHz under operational power of 500 W. The reactor vessel was submerged in an ice bath. The temperature was kept at 12 ± 3 °C by circulation of ice water throughout the reaction process. The pH of the solutions was not adjusted (neutral), but gradually becomes acidic with ultrasonic irradiation.

Analytical methods

Samples were taken prior to irradiation and at various reaction times. A 3 mL aliquot of the reaction mixture was removed for analysis. The analyses were conducted using Beckman high-performance liquid chromatography (HPLC) equipped with a UV-vis detector (at 215 nm) and an ODS2 C-18 reverse-phase column (250 mm x 4.6 mm). The eluent was a mixture of water and methanol (15 % water / 85 % methanol) at a flow rate of 1 mL/min. Concentrations of PbTx-3 were determined by HPLC using a calibration curve. The production of hydrogen peroxide during the ultrasound reactions was measured using the iodine method (12) and the samples were analyzed at $\lambda = 351$ nm using a Varian UV-visible spectrophotometer (Cary 100 Bio).

3. Results and discussion

Sonolysis of brevetoxin-3

A kinetic study of 4.5 ppm of PbTx-3 under argon, oxygen and air atmospheres was performed. The results showed that PbTx-3 exhibits a pseudo-first-order reaction kinetics as illustrated in Fig.1.

In the presence of oxygen, the reactive radicals such as $\cdot\text{O}$, $\cdot\text{OH}$, $\cdot\text{OOH}$ will be produced by a series of reactions and may participate in the decomposition of the solutes (13,14).

Equations 2: Sonolysis of water and formation of reactive radicals in presence of oxygen

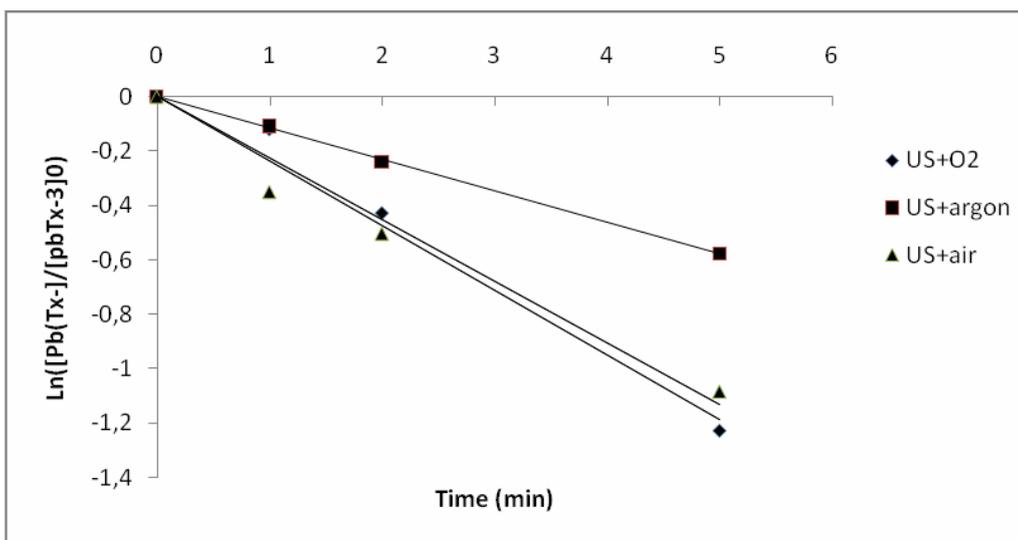
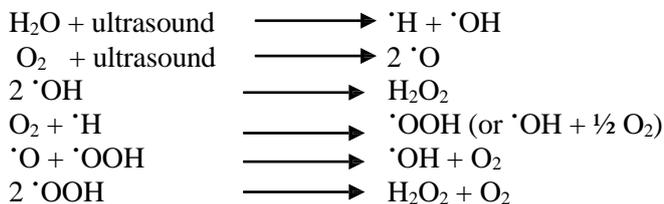


Figure 1: Ultrasonically induced degradation of PbTx-3 (4.5 ppm) under oxygen, argon and air saturated conditions in the absence of Fe (II).

Under oxygen, the degradation of the pollutant was faster compared with air and argon; the rate constant decreased respectively. This suggests that oxygen plays an important role in the rate of ultrasonically induced degradation (15). The kinetic parameters are summarized in Table 1.

Table 1: Rate constants and correlation coefficients of ultrasonically induced degradation of PbTx-3 (4.5 ppm) under oxygen, argon and air saturated conditions in the absence of Fe (II).

	Rate constants (min ⁻¹)	R ²
PbTx-3/US/O ₂	0,237	0,980
PbTx-3/US/air	0,226	0,967
PbTx-3/US/argon	0,115	0,999

1.1. Effect of Fe(II)

Fenton-type chemistry involves the reduction of hydrogen peroxide by Fe (II) to produce one equivalent of hydroxyl radical that enhance the rate of the reaction. Ultrasonic irradiation under oxygen, increases the formation of reactive radicals and H₂O₂, and leads to greater formation of hydroxyl radicals if an appreciate amount of Fe (II) is present in the solution.

Therefore, a set of experiments were performed at different concentrations of iron (II) and at fixed concentration of PbTx-3 (4.5 ppm). The results illustrated in Fig.2 suggest that in the presence of high concentration of Fe (II), the sonolytic degradation of PbTx-3 was enhanced by the increase in hydroxyl radicals induced from the decomposition of the recombined H₂O₂.

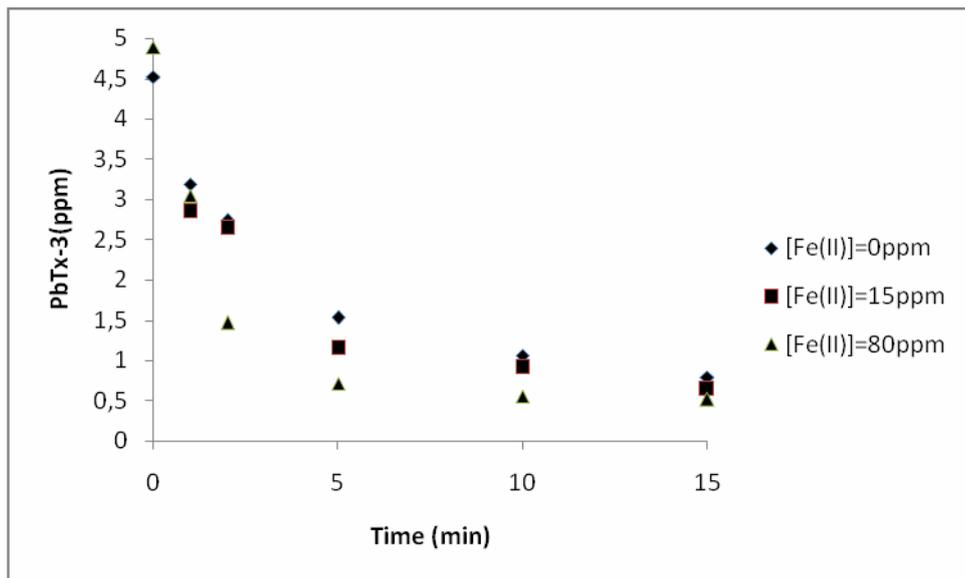


Figure 2: Sonolysis of PbTx-3 under different concentrations of iron (II), $[PbTx-3]_0=4,5ppm$

Effect of hydrogen peroxide

The effect of hydrogen peroxide was also studied and results showed faster degradation at increased concentration of H_2O_2 . The results are illustrated in figure 3.

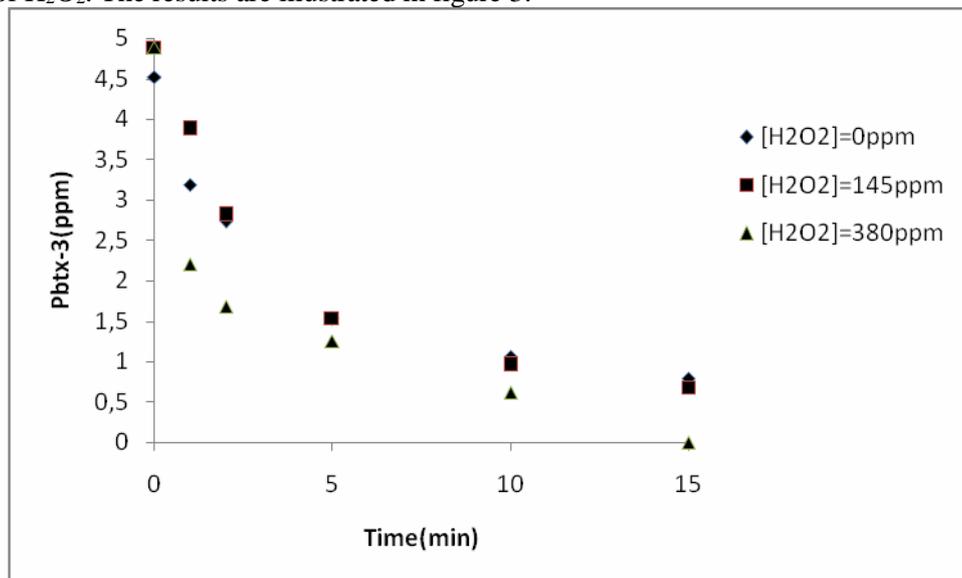


Figure 3: Sonolysis of PbTx-3 under different concentrations of hydrogen peroxide $[PbTx-3]_0 = 4.5 ppm$

Hydrogen peroxide accumulation during ultrasonic irradiation

During the ultrasonic reaction, H_2O_2 is continuously produced, and it is effectively used for the degradation of the organic compounds. To measure the extent of H_2O_2 accumulation during the reaction, its concentration was monitored at different irradiation times using the colorimetric method described by Fang (12). The ultrasonic irradiation of pure water showed a higher concentration of hydrogen peroxide compared with the irradiation of brevetoxin solutions. The effect of Fe (II) addition was studied as well and showed substantial decrease in the concentration of H_2O_2 with increasing Fe (II) concentration. This is explained by the production of hydroxyl radicals at the expense of hydrogen peroxide via photo-Fenton reaction (16). The results are illustrated in figure4.

Equation 3: Production of hydroxyl radicals via photo-Fenton reaction

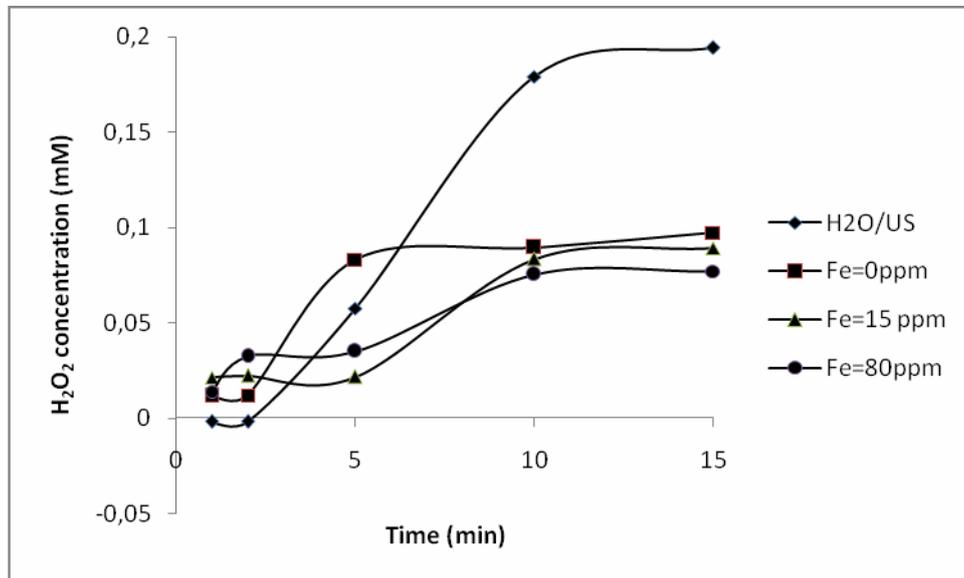
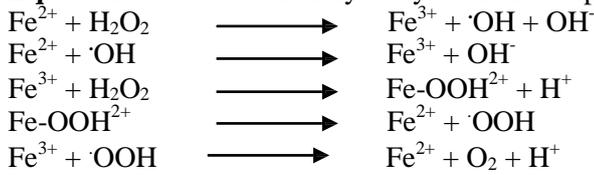


Figure 4: Effect of Fe (II) addition on the accumulation of H₂O₂ for PbTx-3/ Fe (II)/ultrasound system, [Pbtx-3]₀ = 4.5 ppm.

Also, the degradation of PbTx-3 was studied by different systems: PbTx-3/H₂O₂/US; PbTx-3/US; PbTx3/Fe/US; PbTx-3/Fe/H₂O₂/US. The results presented in Figure 5 showed that the system involving the combination of ultrasound, Fe (II) and H₂O₂ leads to faster degradation of PbTx-3 and to its complete removal in 15 min irradiation time.

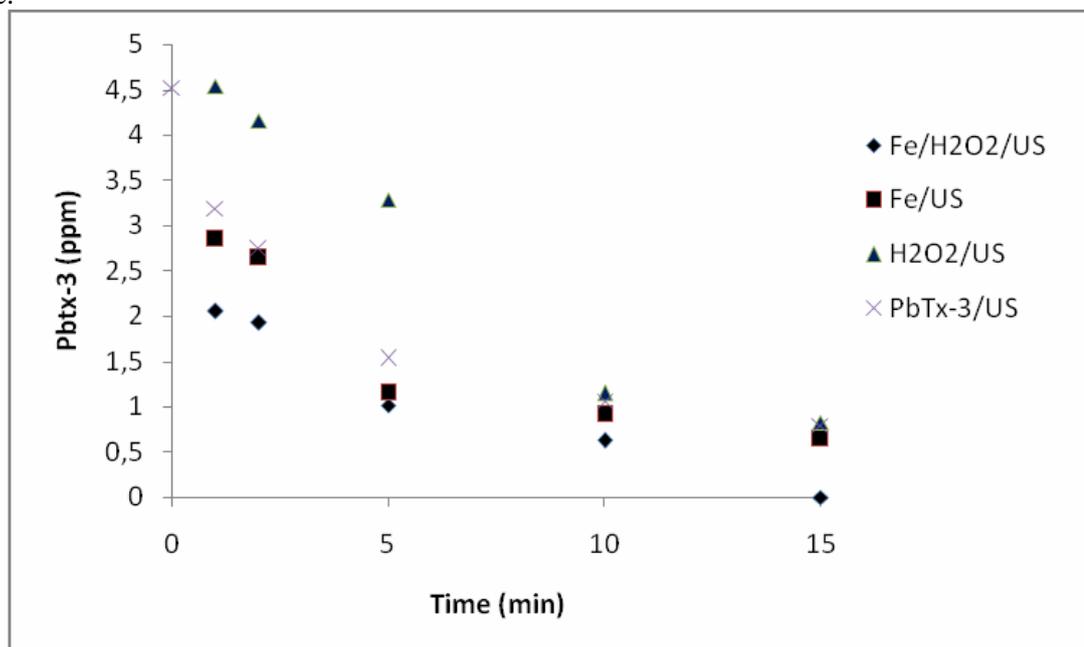


Figure 5: Kinetic study of PbTx-3 by different systems: PbTx-3/H₂O₂/US ; PbTx-3/US; PbTx-3/Fe/US; PbTx3/Fe/H₂O₂/US; [Pbtx-3]₀ = 4.5 ppm; [Fe (II)]₀ = 15 ppm; [H₂O₂]₀ = 70 ppm.

The kinetic study of these systems; PbTx-3/H₂O₂/US, PbTx-3/US, PbTx-3/Fe/US and PbTx-3/Fe/H₂O₂/US showed that the rate constant increased respectively and the combined process of ultrasound and Fenton reagents: Fe (II) and H₂O₂ improved the degradation rates of PbTx-3 compared with other systems and followed a pseudo-first-order kinetics reaction. The kinetic parameters are summarized in table 2.

Table 2: Kinetic study of PbTx-3 by different systems, [Pbtx-3]₀ = 4.5 ppm; [Fe (II)]₀ = 15 ppm; [H₂O₂]₀ = 70ppm

System types	Rate constants (min ⁻¹)
Fe/H ₂ O ₂ /US	0,243
Fe/US	0,159
PbTx-3/US	0,132
H ₂ O ₂ /US	0,128

Conclusion

1. The degradation of PbTx-3 in water by ultrasonic irradiation follows a pseudo-first-order process.
2. The process required oxygen to produce hydroxyl radicals during the ultrasonic reaction.
3. The Fenton reagents play an important role in the degradation of PbTx-3 by ultrasound and they enhance the rate of the reaction.
4. The combined process Fenton and ultrasound showed an improvement in the degradation of brevetoxin and appears to be an effective method for its elimination.

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