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Iron(II)-catalyzed enhancement of ultrasonic-induced degradation of diethylstilbestrol (DES)

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Abstract

The oxidation of the endocrine disruptor, diethylstilbestrol (DES) in aqueous media by ultrasound is significantly enhanced by Fe(II) catalyst. The observed enhancement is likely the result of increased levels of hydroxyl radicals from the iron-promoted reduction of the hydrogen peroxide produced during ultrasonic irradiation. The degradation is effective over a range of concentrations and is consistent with pseudo first-order kinetics. Relatively high concentrations of hydrogen peroxide, ~450 mM, are present in solution under our experimental conditions after 1 h of ultrasonic irradiation (665 kHz). The concentration of H_2O_2 in solution decreased with the addition of Fe(II) along with an increase in the degradation of DES. Hydrogen peroxide alone does not appreciably degrade DES. Our results demonstrate ultrasonic-induced degradation of DES can be accelerated with the addition of Fe(II). The combination of ultrasonic irradiation and Fe(II)-promoted conversion of H_2O_2 to hydroxyl radical may provide a valuable strategy for the treatment of organic pollutants.

Keywords: Diethylstilbestrol; Ultrasound; Advanced oxidation; Catalysis; Hydroxyl radicals

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1. Introduction

The increased occurrence of endocrine disruptors (EDs) in ground and surface waters during the past decade has created a serious environmental problem. These exogenous substances, introduced into water supplies from chemical discharges, sewage treatment plants and landfills, can interfere with the hormonal system, thus causing adverse effects on the physiology of organisms, without inducing immediate toxicological risks [1,2]. Endocrine disrupters can induce a variety of biological effects. Synthetic estrogen diethylstilbestrol (DES) was prescribed to millions of pregnant women to prevent miscarriages and other pregnancy complications from 1940 to 1970. The use of DES by mothers during the first trimester of pregnancy was linked to several cases of vaginal clear-cell carcinoma in their female offspring. Juvenile alligators in a Florida lake contaminated with EDs, organo-chlorine pesticides, were found to possess disorganized reproductive tissues and showed abnormal ratios of estrogen and testosterone [3]. Alkylphenol polyethoxylates (APEOs) were detected in the fish downstream of sewage treatment plants and fish treated with environmentally relevant concentrations of APEOs exhibited increased levels of vitellogenin or modified gonadosomatic indices [4–8]. Given the variety of hormonal disruption/abnormalities linked to EDs it is critical to identify an appropriate water treatment technology to remove/destroy these compounds.

The application of advanced oxidation technologies (AOTs) has been effective for the degradation of a tremendous variety of hazardous organic compounds. Advanced oxidation technologies, involve the generation of hydroxyl radicals as the predominant oxidant and can lead to complete mineralization. Ultrasound has been employed for the degradation of the hazardous or toxic environmental contaminants in aqueous solutions [9–13] (Fig. 1). Ultrasonic irradiation leads to the growth, oscillation and violent collapse of gas bubbles in solution leading to hot spots [14]. The extreme temperatures and pressures during this process lead to the homolytic cleavage of the hydrogen–oxygen bond of the water molecules in the vapor phase of the

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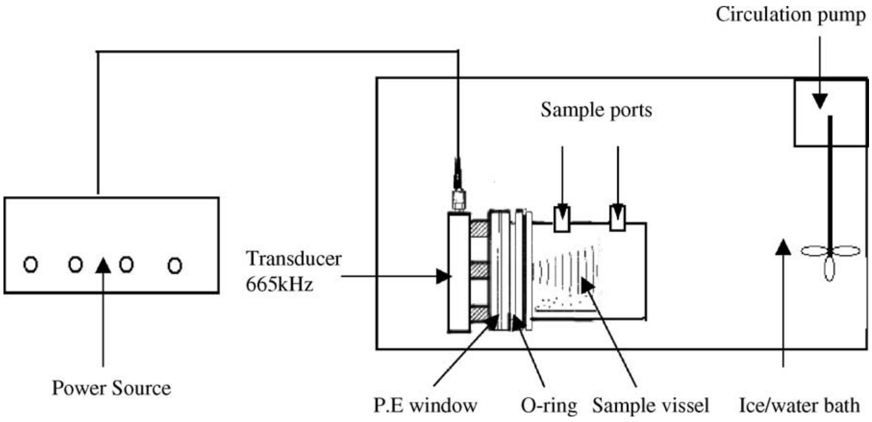

Fig. 1. Ultrasound sample cell. The transducer is separated from the sample solution by a polyethylene film. The sample vessel and the transducer are submerged in ice water during sonolysis experiments.

collapsing bubble, yielding, hydrogen atom and hydroxyl radical, Eq. (1). In the presence of oxygen the hydrogen atom will react to produce hydroperoxyl radical, which can disproportionate to give hydrogen peroxide, Eq. (2). Hydroxyl radical–hydroxyl radical combination reactions also produce significant quantities of H_2O_2, Eq. (3).

$$\mathrm{H{-}O{-}H} \rightarrow \mathrm{H}^\bullet + \mathrm{HO}^\bullet \quad (1)$$

$$\mathrm{O_2} + \mathrm{H}^\bullet \rightarrow \mathrm{HO_2}^\bullet \rightarrow \mathrm{H_2O_2} \quad (2)$$

$$\mathrm{HO}^\bullet + \mathrm{HO}^\bullet \rightarrow \mathrm{H_2O_2} \quad (3)$$

Although ultrasonically induced oxidation is a complex processes, it is generally accepted to involve hydroxyl radicals and the formation of hydrogen peroxide. Hydrogen peroxide, a relatively mild oxidant, can be converted to hydroxyl radicals by reduction. Fenton-type AOTs require the addition of hydrogen peroxide and Fe(II) which reduces the hydrogen peroxide to hydroxyl radical (and hydroxide), as shown in Eq. (4).

$$\mathrm{Fe(II)} + \mathrm{H_2O_2} \rightarrow \mathrm{Fe(III)} + \mathrm{HO}^\bullet + \mathrm{HO}^- \quad (4)$$

Since hydrogen peroxide is generated during ultrasonic irradiation it may be advantageous to simply add Fe(II) to increase the yield of hydroxyl radical, through reduction of the hydrogen peroxide generated during ultrasonic irradiation [15,16]. Fe(II) is oxidized to Fe(III) upon reduction of hydrogen peroxide. Fe(II) can be regenerated by reactions involving peroxyl radicals generated during sonolysis [15], shown in Eq. (5), hence providing a process for regeneration of the Fe(II) catalyst.

$$\mathrm{Fe(III)} + \mathrm{HO_2}^\bullet \rightarrow \mathrm{Fe(II)} + \mathrm{O_2} + \mathrm{H}^+ \quad (5)$$

In this study, we investigated the ultrasonically induced degradation of DES in aqueous solution under a variety of conditions. Our results demonstrate that the Fe(II) can act as a catalyst in significantly enhancing the degradation of DES during ultrasonic irradiation while dramatically reducing the level of hydrogen peroxide in solution.

2. Experimental equipment and method

2.1. Materials

Diethylstilbestrol (DES) (>99% pure), Fe(II) sulfate heptahydrate, hydrogen peroxide 30% and acetonitrile (HPLC grade) were purchased from Fisher Scientific and used without further purification. For all the experiments, water was purified by Millipore Milli-Q system (resistivity 18 MΩ cm). All gases were supplied by air products and were of at least 99.9% purity. Due to the low solubility of DES in water (0.26 mg/L at 25 °C), a saturated concentration of DES was prepared in 500 mL of Milli-Q water. The saturated solution was filtered to eliminate any residual particle matter. Four hundred milliliters of the resulting solution was transferred to the sonolytic reactor. The solutions were gently purged with oxygen or argon for 5 min prior to irradiation.

2.2. Ultrasonic irradiation

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. Due to the transfer of power the steady state reaction temperature was kept at 12 ± 3 °C by circulation of ice water throughout the reaction process. The initial pH of the solutions was not adjusted (neutral), but gradually becomes acidic with ultrasonic irradiation (pH = 4.1 after 60 min). No precipitates were formed during the irradiation or analysis stages.

2.3. Analytical methods

Samples were taken prior to irradiation and at various reaction times. A 10 mL aliquot of the reaction mixture was removed for analysis using a glass syringe. The analyses were conduced using Beckman high-performance liquid chromatography (HPLC) equipped with a UV–vis detector (at 280 nm) and an ODS2 C-18 reverse-phase column (250 mm × 4.6 mm). The eluant was a mixture of acetonitrile and water (60% acetonitrile/40% water) at a flow rate of 1 mL/min. Concentrations of DES were determined by HPLC using a calibration curve. The production of hydrogen peroxide during the ultrasound reactions was measured using the iodine method [18] and the samples were analyzed at $\lambda = 351$ nm using a UV-visible spectrophotometer Shimadzu (UV-2101PC).

3. Results and discussion

3.1. Sonolysis of diethylstilbestrol

To establish the kinetic parameters of the sonolytically induced degradation of diethylstilbestrol, experiments were preformed in the absence of Fe(II) under argon and oxygen saturated conditions. Control experiments without ultrasonic confirmed that there was no loss of DES due to air stripping, adsorption, or volatilization. The degradation of 30 μM DES exhibits pseudo first-order reaction kinetics under argon and oxygen saturation, as illustrated in Fig. 2.

The degradation of DES under argon saturation may be slightly faster than with oxygen. A faster degradation of DES under argon saturation may be the result of the more extreme conditions (higher temperatures and pressures) produced under argon saturation relative to oxygen saturation. At higher temperatures more radicals are produced and/or a higher level of pyrolysis takes place in the vapor phase during cavitation. Because of the low volatility of DES, direct pyrolysis is unlikely since it requires partitioning of DES to the gas phase. The results indicate that oxygen does not play a significant role in the rate of ultrasonically induced degradation of DES.

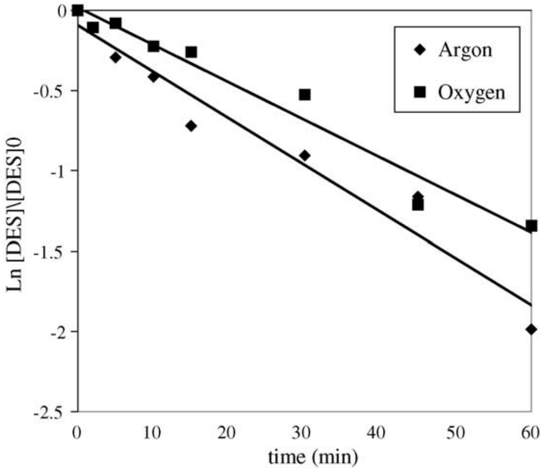

Fig. 2. Ultrasonically induced degradation of DES under argon and oxygen saturated conditions in the absence of Fe(II). Argon $y = -0.029x$, $R^2 = 0.96$; Oxygen $y = -0.023x$, $R^2 = 0.96$.

3.2. Kinetic evaluation

We studied the degradation of DES by ultrasound, varying the initial concentration of the DES ($[\mathrm{DES}]_0 = 7$–30 μM). Under our experimental conditions the rates of disappearance are parallel to the initial DES concentrations, the fastest degradation occurred at the lowest concentration and the slowest removal rate of DES occurred at the highest DES concentration, as summarized in Table 1. The results suggest that the degradation of DES is limited by the effective concentration of hydroxyl radicals and/or other reactive species produced during cavitation. During cavitation there may be high local concentrations near the hydrophobic interface such that we have a heterogeneous distribution of DES. Hence the overall concentration is expected to affect the local/interface concentrations to a different extent (lower concentrations minimal effect–high concentrations higher effect). The rate constants, do not exhibit a true first-order behavior, decreases with DES concentration, this may be due to mass transfer limitations at the interface and/or limited availability of $\mathrm{HO}^\bullet$ in the reaction zone. A significant number of hydroxyl radicals react with each other to form hydrogen peroxide at or near the dynamic formation and collapses of cavitation sites, hence the concentration of hydroxyl radicals available for reaction with DES will be dependent on the concentration of DES and as a function of distance and the relative concentration of hydroxyl radicals. In any case the concentration of DES appears to be a rate-limiting factor under our experimental conditions.

3.3. Effect of Fe(II) during ultrasonic irradiation

Ultrasonic irradiation of aqueous solutions can produce significant quantities of hydrogen peroxide. While hydrogen peroxide has a low reactivity toward most organic pollutants it can be converted to the strong oxidant, hydroxyl radical using chemical or photochemical techniques. Fenton-type chemistry involves the reduction of hydrogen peroxide by Fe(II) to produce one equivalent of hydroxyl radical. The hydrogen peroxide generated during ultrasonic irradiation, can be effectively utilized when Fe(II) is added to the

Table 1
Effect of the initial concentration of DES on the pseudo first-order rate constant of ultrasonically induced degradation of DES under oxygen saturation

[DES] (μM)	Rate constants (min^{-1})[a]	R^2
7	0.029 (0.002)	0.96
26	0.026 (0.001)	0.97
30	0.023 (0.001)	0.96

[a] The reproducibility of the individual data points is within 5% based on triplicate runs. The reported uncertainty is based on the standard deviation.

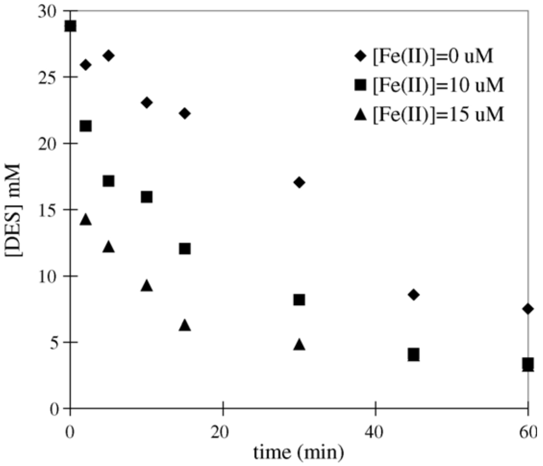

Fig. 3. Effect of Fe(II) on the ultrasonically induced degradation of 30 μM DES.

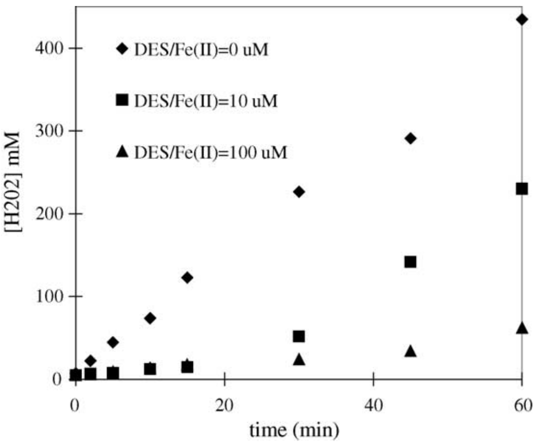

Fig. 4. Effect of Fe(II) addition on the rate of H_2O_2 formation for the DES/Fe(II)/ultrasound system, $[DES]_0 = 30$ μM.

system, leading to an enhanced $^{\bullet}OH$ generation via Fenton's reaction [12]. The initial rate of ultrasonically induced degradation of the DES increases significantly with Fe(II) concentration, as illustrated in Fig. 3. The concentration of initial Fe(II) was kept low relative to the concentration of hydroxyl radicals since Fe(II) can react directly with $HO^{\bullet}$ inhibiting the degradation pathways. Without Fe(II) less than 10% of the initial concentration of DES is degraded in the first 2 min of irradiation, while in the presence of 10 and 15 μM Fe(II) the extent of degradation increases to ~25 and 50%, respectively, in the same period of time.

The rate of degradation decreases upon continued irradiation. This could be the result of reaction by-products competing with DES for the radicals responsible for the degradation. Fe(III) can be converted to Fe(II) by the hydroperoxyl radicals produced under the experimental conditions [15], such regeneration of Fe(II) is needed for subsequent reduction of hydrogen peroxide and production of hydroxyl radicals. The by-products may also form iron complexes which interfere with the Fe(II) ↔ Fe(III) catalytic cycle.

3.4. Role and Fe(II)-catalyzed degradation of hydrogen peroxide

Hydroxyl radicals produced during the sonolysis of water can react to form H_2O_2 in significant amounts especially when volatile radical scavengers (i.e., organic compounds) are not present in the water. Hydrogen peroxide can also react with hydroxyl radical behaving as an $^{\bullet}OH$ sink. Hydrogen peroxide can undergo ultrasonically induced degradation to yield hydroxyl radicals, but this is a relatively slow process. To determine the effect of H_2O_2 and its ultrasonic degradation products on the degradation DES, the concentration of hydrogen peroxide was monitored during ultrasonic irradiation. A colorimetric method [17] was used to measure the concentration of H_2O_2. The concentrations of Fe(II) and H_2O_2 were varied at a constant concentration of DES (30 μM). The effect of Fe(II) concentration on amount of H_2O_2 in solution as a function of irradiation time is illustrated in Fig. 4. The concentration of H_2O_2 in solution decreases substantially with increased Fe(II) concentration, as expected. The amounts of H_2O_2 produced directly by ultrasonic irradiation should be the same regardless of the Fe(II) and DES concentrations, but as the concentration of Fe(II) increases the conversion of H_2O_2 to hydroxyl radicals increases accordingly. The concentration of H_2O_2 is significantly reduced in the presence of relatively low concentrations of Fe(II) indicating a catalytic or chain process is involved in the conversion of H_2O_2. At 100 μM Fe(II) ~90% of the H_2O_2 is degraded. The addition of Fe(II) not only increases the degradation of DES, it also catalyzes the elimination of peroxides which is critical for treatment of drinking water by oxidation processes.

Hydrogen peroxide was added prior to irradiation with constant 10 μM Fe(II) and 30 μM DES concentrations to assess the change in H_2O_2 concentrations. A slight decrease in the initial concentration of H_2O_2 was observed during the initial reaction period, but the level of H_2O_2 gradually increased upon continued irradiation. This observation is consistent with the conversion of the Fe(II) to Fe(III), which does not promote the subsequent conversion of H_2O_2. The regeneration of the Fe(II) catalyst likely occurs, but on longer time scales than the reactions times of our experiments. Given the concentration of H_2O_2 was 10–100 times higher than the concentration of Fe(II), this result is not surprising. The rates of ultrasonic-induced degradation of DES in the presence of Fe(II) and in the presence of Fe(II) and added H_2O_2 were compared with the degradation of DES by ultrasonic irradiation alone. The results are illustrated in Fig. 5.

The use of ultrasound alone leads to the slowest degradation of DES, addition of Fe(II) to the reaction solution enhanced the rate of degradation of DES presumably via formation of hydroxyl radicals from hydrogen peroxide produced during sonolysis. The fastest

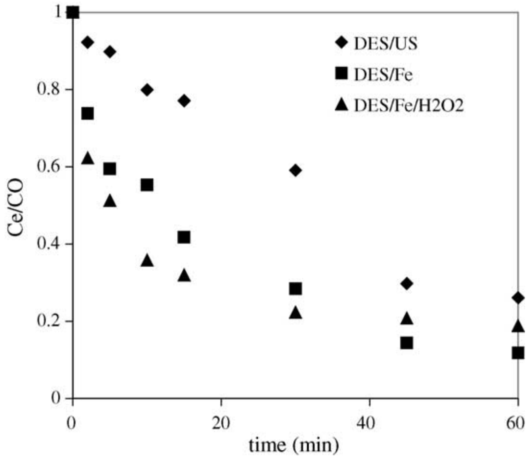

Fig. 5. Degradation of diethylstilbestrol by different systems: DES/US; DES/US/Fe; DES/US/Fe/H_2O_2; $[DES]_0 = 30\ \mu M$; $[Fe]_0 = 10\ \mu M$; $[H_2O_2]_0 = 25.5\ \mu M$.

degradation was observed when Fe(II) and hydrogen peroxide were added to the solution. A system involving the combination of ultrasound, Fe(II) and H_2O_2 leads to faster degradation rates of the target compound while eliminating the residual hydrogen peroxide.

4. Conclusions

The degradation of DES in water by ultrasonic irradiation, follows a pseudo first-order process. The process does not require oxygen, indicating that the radicals produced during cavitation play the key role in the degradation process. The initial rates of ultrasonic-induced degradation is enhanced by 2–3-fold with the addition of Fe(II) catalyst, likely the result of hydroxyl radicals produced from reduction of sonolytically produced H_2O_2. The rate of degradation of DES is further increased with the addition of H_2O_2 in the presence of Fe(II). The Fe(II) catalyst also eliminates hydrogen peroxide. The elimination of hydrogen peroxide is required for the treatment of drinking water by oxidation processes. In addition eliminating hydrogen peroxide during the treatment process, minimizes the level of hydroxyl radicals lost by reaction with hydrogen peroxide. The addition of Fe(II) catalyst during ultrasonically induced oxidation has considerable potential for the decomposition of persistent and toxic compounds such as the endocrine disruptor, diethylstilbestrol.

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