Ultrasound-assisted oxidation processes for the removal of aromatic contaminants from aqueous effluents

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Abstract

The effect of low frequency (20 kHz) ultrasonic irradiation on the removal of sodium dodecylbenzene sulfonate (SDBS), phenol, 2-chlorophenol and 2,3-dichlorophenol from synthetic aqueous effluents has been investigated. Sonolytic degradation of SDBS (at an initial concentration of 1 g/L) results in the formation of lower molecular weight compounds and is accompanied by low total oxidation rates. In parallel, water sonolysis results in the formation of hydrogen peroxide. Several heterogeneous catalysts (three noble metals and a metal oxide) were tested with respect to their effect on SDBS sonolysis. Of these, a CuO.ZnO supported on alumina catalyst appears to enhance both SDBS fragmentation and total oxidation rates as well as hydrogen peroxide formation. Phenolic compounds (at an initial concentration of 0.1 g/L) are only partially removed by ultrasound irradiation with 2-chlorophenol being more susceptible to degradation than phenol and 2,3-dichlorophenol. However, the presence of Fe²⁺ ions at concentrations as low as about 0.2 10⁻³ g/L generally substantially increases the rate of the uncatalysed sonolytic degradation. This is attributed to iron being capable of readily decomposing hydrogen peroxide (generated by water sonolysis) in a Fenton-like process to form reactive hydroxyl radicals as well as being an effective oxidation catalyst. All phenols are readily removed by the Fenton reagent without ultrasonic irradiation. However, at the conditions employed in this study, a combination of ultrasound and Fenton reagent has a detrimental effect on the efficiency of Fenton oxidation.
Introduction

The second half of the last century has witnessed a rapidly deteriorating water environment as the outcome of enormous use of complex organic compounds, the spent parts of which were discharged into conventionally designed and operated wastewater treatment systems. Given that biological processes have little effect in successfully treating biorefractory wastewaters, several chemical treatment technologies have been developed for either the partial or complete destruction of hazardous and toxic organic pollutants. Such treatments, mainly oxidative in nature, can broadly be classified as (a) thermochemical processes including, amongst others, sub-critical and super-critical wet air oxidation, catalytic wet air oxidation and incineration, and (b) advanced oxidation processes (AOPs) such as ultraviolet irradiation, ozonation, Fenton and photo-Fenton oxidation, electrochemical oxidation as well as various combinations of the above.

Only very recently, has considerable interest been shown in the application of an innovative treatment for hazardous chemical destruction based on the use of ultrasound. Although ultrasound has a broad range of industrial applications, its potential as a water and wastewater treatment technology has not been explored extensively. The chemical effects of ultrasound derive from acoustic cavitation i.e. the formation, growth and implosive collapse of cavitation bubbles in a liquid. Extreme temperatures of several thousand degrees and pressures of several hundred atmospheres are developed locally within the bubbles during their collapse with these bubbles serving as hot spot microreactors in an otherwise cold liquid. It is believed that there are three potential sites for chemical reactions in ultrasonically irradiated aqueous solutions, namely: (a) the bubble itself where pyrolysis of volatile species takes place in the gas phase, while water decomposes thermally to form H and OH radicals, (b) the interface between the bubble and the surrounding liquid where the temperature is lower than that in the bubble but is still high enough to cause thermal decomposition, and (c) the solution bulk. Organic pollutants may be destroyed either at the first two sites due to the synergistic effects of pyrolytic decomposition and hydroxylation or/and in the solution bulk through oxidative degradation by OH radicals [1].

In previous studies, the beneficial effect of ultrasonic irradiation on the complete removal of several target compounds from model aqueous solutions has been demonstrated. Such compounds include, amongst others, phenol, chlorophenols, nitrophenols, polychlorinated biphenyls, pesticides and polycyclic aromatic hydrocarbons [2-6]. Typical treatment conditions include dilute aqueous solutions of initial concentrations less than about $10^{-3}$ M (such concentrations are typical of refractory compounds found in natural waters or in already treated effluents), low to medium ultrasound frequencies from 20 to 500 kHz and irradiation times from several minutes to several hours.

The scope of this work is to study the effect of low frequency ultrasound on the removal of various organic pollutants, such as surfactants and chlorinated phenols, typically found in wastewaters produced by chemical processing. In
particular, the synergy between ultrasonic irradiation and several heterogeneous and homogeneous catalysts has been investigated.

**Experimental & analytical**

Sodium dodecylbenzene sulfonate (SDBS), phenol, 2-chlorophenol (CP) and 2,3-dichlorophenol (DCP) were supplied by Fluka and used without further purification. Aqueous solutions containing either 1 g/L of SDBS or 0.1 g/L of the phenolic compound were prepared and loaded into a glass vessel. A horn-type sonifier (Ultrason 250 manufactured by Labplant, UK) operating at a fixed frequency of 20 kHz was used for sonication experiments.

Sonication of 1 L SDBS solutions was carried out with or without catalysts. Several heterogeneous catalysts were used in catalytic experiments as follows: (a) noble metals: platinum (Pt), palladium (Pd) and ruthenium (Ru) at a noble metal concentration of 5% w/w supported on alumina, and (b) a CuO.ZnO supported on alumina. In all cases, 0.05 g/L of catalyst was used in the form of slurry. All experiments with SDBS were performed at ambient conditions without temperature control.

0.05 L solutions containing phenolic compounds were subject to various sonication treatments as follows: (a) sonication alone (US), (b) sonication in the presence of Fe$^{2+}$ ions (US+Fe$^{2+}$) and (c) a combination of US and the Fenton reagent (US+Fenton). Furthermore, 0.2 L solutions were oxidised by the Fenton reagent (Fe$^{2+}$+H$_2$O$_2$). In all cases where iron ions were used as a homogeneous catalyst, the appropriate amount of FeSO$_4$.7H$_2$O was added to the solution to give a metal concentration of 0.81 $10^{-3}$ g/L (unless otherwise stated); in those experiments where hydrogen peroxide was added to the solution, its initial concentration was 0.35 g/L. All experiments with phenolic compounds were carried out at a constant liquid phase temperature of 35°C. Samples periodically drawn from the vessel were analysed as follows:

High Performance Liquid Chromatography (HPLC) was used to follow concentration profiles of the original organic substrates. Different analytical methods were developed to analyse SDBS and phenols as follows: (a) SDBS was analysed on a C18 column using a gradient mobile phase comprising a 70% acetonitrile solution (buffered with 0.15 M sodium perchlorate) and pure water (also buffered with 0.15 M sodium perchlorate) at a flowrate of 1 ml/min. Detection was through a UV detector set at 210 nm, (b) phenols were analysed on a C18 column using 40:60 acetonitrile:water as an isocratic mobile phase at 1 ml/min. Detection was through a UV detector set at 276 nm.

The liquid phase total organic carbon content (TOC) was measured by combustion/non-dispersive infra red (NDIR) gas analysis with a Shimadzu 5050 TOC analyser. Total carbon was measured first followed by inorganic carbon and TOC was determined by subtracting inorganic carbon from total carbon. The relative standard deviation of three separate measurements was always less than 2%. TOC proved to be useful in assessing the extent of total oxidation of organics to carbon dioxide that had occurred.
The concentration of hydrogen peroxide generated during SDBS sonication experiments was determined using the titanium spectrophotometric method according to the procedures described elsewhere [7]. In some cases, samples were also analysed with respect to their chemical oxygen demand (COD) content and active detergency (AD) using the dichromate [8] and crystal violet [9] methods respectively.

Results & discussion

Sonolysis of SDBS

Figure 1 shows the TOC-time profiles during the sonication of SDBS with and without various catalysts. Of the various catalysts tested, CuO.ZnO/Al₂O₃ appears to be the most effective in terms of TOC removal. In all cases though, the final (i.e. after 120 min) TOC removal was never greater than about 20%. Figure 2 shows the change of pH during the sonication of SDBS. It can be seen that the initial pH of 8 drops to 6.5-7 within 10-20 min of sonication and then remains almost constant throughout the course of reaction up to 120 min. These results imply that SDBS sonolysis is accompanied by the formation of acidic compounds, and that their concentration remains quite stable. At the conditions under consideration, these acidic compounds appear to be refractory to total oxidation; however, interestingly, AD analysis showed that sonified solutions had decreased levels of detergency. For instance, a 30% AD decrease was recorded after 180 min of uncatalysed sonication. Figure 3 shows the molecular weight (MW) distribution of original SDBS as well as of solutions obtained after 120 min of sonication with and without CuO.ZnO/Al₂O₃, where the UV detector response is plotted against the elution time from the chromatographic column. All peaks of both sonication runs have been magnified by a factor of 2.4 for clarity. As can be seen, peaks originally present at elution times greater than about 8.6 min which correspond to higher mass fractions of SDBS, do not appear in the treated solutions, thus implying that partial fragmentation of SDBS has occurred. (Similar results were also obtained for those experiments performed with noble metal catalysts.) It has to be pointed out that separation of peak clusters to narrower MW ranges was not possible with the present equipment and techniques; consequently, quantification based on peak areas was found to be inaccurate. However, for the CuO.ZnO/Al₂O₃-catalysed run most of the remaining peaks are clearly smaller than those of the original solution as well as of the corresponding uncatalysed run, and this is also consistent with the TOC profiles shown in Figure 1.

Aqueous phase sonolysis is likely to result in the formation of hydrogen peroxide, which may be formed through the recombination of OH radicals at the gas-liquid interface, and/or in the solution bulk. Moreover, if the solution is saturated with oxygen, peroxyl (O₂H) and more OH radicals are formed in the bubble and the recombination of the former at the interface and/or in the solution bulk results in the formation of additional hydrogen peroxide [1,10]. Hydrogen peroxide formation was confirmed analytically and its concentration-time
profiles during sonolysis of SDBS with and without catalysts are shown in Figure 4. As can be seen, the concentration of hydrogen peroxide reaches a maximum within the first 30 min of sonication with CuO,ZnO/Al₂O₃, Pt/Al₂O₃ and Ru/Al₂O₃ after which it decreases presumably due to its decomposition.
Conversely, hydrogen peroxide concentration remains relatively low throughout the experiments with Pt/Al₂O₃ and without catalyst, which implies that it is not formed at appreciable concentrations or, if it is formed, it readily
decomposes. Given the non-volatile and hydrophilic character of SDBS, sonolytic degradation is likely to proceed through the reactions with OH radicals in solution bulk rather than through thermal reactions in the cavitation bubble or the bubble-liquid interface.

![Figure 4: H$_2$O$_2$ concentration-time profiles during SDBS sonication](image)

From the results presented so far, it could be hypothesised that interactions between ultrasound and the metal catalyst (i.e. CuO.ZnO/Al$_2$O$_3$) result in increased rates of formation of OH radicals that partly recombine to hydrogen peroxide. Moreover, radicals are capable of oxidising the organic substrate to lower organics and eventually to carbon dioxide and water, a process promoted by the catalytic activity of copper, which is known to be an effective oxidation catalyst. It could be argued that the beneficial effects arising from increased OH radical formation are compromised by the fact that radicals are wasted through recombination reactions. This is so since hydrogen peroxide in its molecular form is a rather ineffective oxidant for the aqueous phase oxidation of organics. However, copper is known [11] to be an effective catalyst for hydrogen peroxide decomposition to several reactive species (OH radicals mainly) and this is consistent with the concentration profiles shown in Figure 4.

**Sonolysis of phenolic compounds**

Figures 5, 6 and 7 show the concentration-time profiles of phenol, CP and DCP respectively during various treatments. As can be seen, all phenols are only partially removed by US treatment alone with about 10%, 15% and 25% removals being recorded after 180 min for phenol, DCP and CP respectively. Given that water sonolysis generates OH radicals partial recombination of which
would result in the formation of hydrogen peroxide, it was decided to investigate
the effect of Fe$^{2+}$ ions on the sonolysis of phenols. The rational behind this is
associated with the fact that iron (a) is an effective oxidation catalyst for several
classes of organics capable of degrading the organic radicals formed via
reactions of free radicals with the organic substrate and (b) readily decomposes
hydrogen peroxide to regenerate more OH radicals (classic Fenton chemistry),
thus promoting the oxidation of phenols in the solution bulk. As can be seen,
with the exception of DCP, iron (at a concentration as low as 0.81 $10^{-3}$ g/L)
substantially increases the rate of substrate removal. This was more pronounced
in the case of CP, where a 55% removal was recorded after 180 min of
sonication. The experiment with CP was also performed at a reduced Fe$^{2+}$
concentration of 0.18 $10^{-3}$ g/L (data points - ■ - in Figure 6); a nearly fivefold
(from 0.81 $10^{-3}$ to 0.18 $10^{-3}$ g/L) decrease in catalyst concentration only slightly
decreased removal rates. These results are in line with those reported by Nagata
et al [4] who studied the sonolysis of 3-chlorophenol (initial concentration of 0.1
mM) at 200 kHz and found that degradation rates increased by as much as 2.4
times in the presence of 56 $10^{-3}$ g/L of Fe$^{2+}$.

It has to be pointed out that, in this series of experiments, hydrogen peroxide
concentration was not determined analytically. However, an indication of its
presence in the reaction mixture came through measuring the COD content of
various samples. In several cases, COD values exceeded that of the original
solution even by as much as 2-3 times, implying the presence in the reaction
mixture of compounds interfering with the COD test. It is well documented in
the literature [12] that H$_2$O$_2$ has a positive effect on the COD content of organic-
containing samples due to its reaction with potassium dichromate. (Increased
COD values are not likely to be due to chloride interference as this was
prevented by the addition of mercuric sulfate in the digestion solution.)

Figure 5: Concentration-time profiles of phenol during various treatments
Phenols were also treated by the Fenton reagent with and without ultrasonic irradiation. As can be seen, all phenols are readily oxidised by the Fenton process with about 85% substrate removal being recorded after 130, 40 and 30 min for phenol, DCP and CP respectively. However, coupling the Fenton reagent
with ultrasonic irradiation had a considerable detrimental effect on the efficiency of the Fenton process. It can be hypothesised that iron ions and the ultrasound compete for hydrogen peroxide decomposition through different routes which could possibly involve (a) catalytic decomposition to OH radicals and (b) thermal decomposition (which may occur inside or near the cavitation bubble where extreme local conditions exist) to water and oxygen rather than to reactive radical species. If this is the case, hydrogen peroxide is partly consumed through wasteful reactions and this would explain the decreased efficiency of the combined Fenton and ultrasound treatment. However, further investigations are needed to understand the mechanisms involved in the process.

Conclusions

The sonolytic degradation of an anionic surfactant and three phenolic compounds with and without several catalysts has been investigated. Sonolysis of non-volatile, hydrophilic organics occurs in the solution bulk through free radical oxidation reactions involving the participation of hydroxyl radicals and hydrogen peroxide both of which are formed during water sonolysis. A stable and inexpensive material capable of promoting the oxidation of organic substrate and effectively utilising hydrogen peroxide would make a promising catalyst for the sonocatalytic degradation of organic pollutants. In this respect, a copper-containing heterogeneous catalyst and homogeneous iron were capable of promoting the sonolytic degradation of SDBS and phenols respectively.

Although complete mineralisation was not possible at the conditions employed in this study, sonolysis intermediates may be more biodegradable than the original compound. On this assumption, sonication could be used as a pre-treatment step to convert initially bioresistant molecules to more readily biodegradable compounds followed by a biological treatment step.

Current research focuses on the effect of various treatment conditions such as ultrasound frequency, volume and concentration of the liquid phase and type of catalyst on the chemical and biological properties of the waste stream. Such information may prove useful in designing an effective integrated treatment process.

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References


