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Chapter 10

Ultrasound in Electrochemical Degradation of Pollutants

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Additional information is available at the end of the chapter

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1. Introduction

The increase of industrial activities and intensive use of chemical substances such as petroleum oil, polycyclic aromatic hydrocarbons, BTEX (benzene, toluene, ethylbenzene and xylenes), chlorinated hydrocarbons as polychlorinated biphenyls, trichloroethylene and perchloroethylene, pesticides, dyes, dioxines and heavy metals have been contributing to environmental pollution with dramatic consequences in atmosphere, waters and soils (Martínez-Huitle & Ferro, 2006; Megharaj et al., 2011). Electrochemical technologies have been extensively used for degradation of toxic compounds since these technologies present some advantages, among them: versatility, environmental compatibility and potential cost effectiveness (Martínez-Huitle & Ferro, 2006; Chen, 2004; Ghernaout et al., 2011; Panizza & Cerisola, 2009). However, a loss in the efficiency of such degradation processes is observed due to the adsorption and/or insolubilization of the oxidation and/or reduction products on the electrodes surfaces (Garbellini et al., 2010; Lima Leite et al., 2002).

In this sense, power ultrasound has been employed to overcome such electrode fouling problem (passivation) due to the ultrasound ability for cleaning the electrode surface, called sonoelectrochemistry (Compton et al., 1997). The production of ultrasound is a physical phenomenon based on the process of creating, growing and imploding cavities of steam and gases, known as cavitation. During the compression step, the pressure is positive, while the expansion results in vacuum called negative pressure formed in a compression-expansion cycle that generates cavities (Mason, 1990; Martines et al., 2000). In chemistry, ultrasound has been used in organic synthesis, polymerization, sonolysis, preparation of catalysts and sonoelectrosynthesis (Mason, 1990; Martines et al., 2000).

The introduction of ultrasound into electrochemical cells/reactors has a marked effect upon the mass transport and surface activation characteristics of an electrochemical system (Compton et al., 1996a). Mass transport is greatly increased via acoustic streaming and

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micro jetting (Banks & Compton, 2003a), resulting from cavitational collapse close to the electrode surface (Compton et al., 1997; Compton et al., 1996a). Ultrasound can be combined with electroanalytical determination, for example, of the pesticides and metabolites (Garbellini et al., 2009; Garbellini et al., 2007), metals (Banks & Compton, 2004; Hardcastle & Compton, 2001), nitrite (Oliveira et al., 2007), etc., in complex samples exploring the great effect in mass transport and the cleaning of the electrode surface.

The combination of an ultrasonic field with an electrochemical oxidation and/or reduction can result in a powerful method for pollutant degradation. Power ultrasound can improve the electrochemical degradation of pollutants by physical and chemical mechanisms. The propagation of acoustic waves in a liquid medium induces cavitation and even their violent collapse at high acoustic pressure (Mason & Lorimer, 2002). Among the physical effects of these collapses are the high rates of micromixing, the cleaning of the electrodes surfaces by dissolving or pitting the inhibiting layers. These effects result mainly in an enhancement of the solid-liquid mass transfer between the electrodes and the solution (Compton et al., 1997). The chemical effects are also a consequence of the violent collapses. The "hot spot" theory predicts temperatures of many thousands of Kelvin and pressures of hundreds of atmospheres inside the bubble during the final compression. Under such drastic conditions, oxidizing species are generated by the homolytic cleavage of molecules (gases and solvent). In aqueous media and in the presence of oxygen, radicals such as $HO^{\bullet}$, $HO_2^{\bullet}$ and $O^{\bullet}$ are produced (Dai et al., 2006). Therefore the generation of •OH radicals is the key to the efficient decomposition of organic materials (Martínez-Huitle & Ferro, 2006).

In view of these interesting aspects, the use of ultrasound is a technologically advanced application of oxidation in the treatment of effluents, for accelerating the destruction of contaminants in the liquid phase (Adewuyi & Appaw, 2002; Appaw & Adewuyi, 2002; Lu & Weavers, 2002; Hua & Hoffmann, 1997). There are three major regions which should be considered in relation to the sonochemical processes in aqueous media. The first region is the inside of cavitation bubbles collapse in the extreme thermodynamic conditions which are due to the high temperatures and pressures (Mason & Lorimer, 2002; Flint & Suslick, 1991). In this region, fast pyrolysis of volatile solutes occurs. Water molecules undergo thermal decomposition to produce H atoms and •OH radicals, which are strong and non-selective oxidants of the organic pollutants present in effluents (Makino et al., 1983, Hart & Henglein, 1985). The second region is the interfacial boundary between the liquid and gas phases in which the temperature is lower than inside the bubbles, but still high, to cause thermal decomposition of organic solutes. Possibly, the reactive radicals are mainly located in this region. The third region is the bulk of the solution (usually at room temperature) in which several reactions between radicals and organic solutes can occur (Henglein, 1987). In the liquid phase, a constant concentration of reactive radical species is maintained by continuous irradiation of the ultrasound. Despite the generation of •OH radicals being the key of the efficient decomposition of organic materials, the recombination of •OH to produce H_2O_2 both in the gas phase of the bubbles or in the liquid phase of the solution, is the main process that limits the amount of reactive radicals accessible to organic molecules. This limitation results in a loss of the overall efficiency, since the H_2O_2 sonochemically

generated cannot react with the desired organic molecule and thereby decompose it (Abdelsalam & Birkin, 2002).

In this chapter, theoretical aspects of power ultrasound including the effects on mass transport and on the cleaning of the electrodes surfaces, experimental considerations about the ultrasound application to electrochemical experiments and the use of power ultrasound in electrochemical degradation of pollutants including direct sonoelectrochemistry, sonoelectrochemistry with Fenton reactions or ozonation and ultrasound in association with photoelectrocatalysis using different electrode materials, such as boron doped diamond (BDD), lead, platinum and glassy carbon will be presented and discussed.

2. Experimental considerations

Parameters as the frequency (Hz), the intensity (W) and the ultrasonic power (W cm^{-2}), determined by calorimetry (Mason et al., 1992), and the sources of ultrasound should be considered when the power ultrasound is applied to an electrochemical system. Ultrasonic power is the most important parameter since there is a direct relation with the current value of the redox process. On the other hand, the frequency, generally from 20 to 800 kHz, does not strongly affect the current intensity of a redox process. Ultrasonic sources of high frequency produce a great quantity of hydroxyl radicals in aqueous media in relation to those with low frequency using the same ultrasonic power. High frequency generally favours the chemical mechanisms involving radicals (cleavage of substrate ligations or by water sonolysis). On the other hand, low frequencies are more efficient for mechanical effects, as gases elimination and the cleaning of the electrodes surfaces.

Concerning the published papers in the literature which explore the introducing of power ultrasound into an electrochemical cell, the two major sources are ultrasonic baths and ultrasonic immersion horn probes. The ultrasonic bath (Figure 1A) consists of a number of fixed frequency (20-100 kHz) transducers below the physical exterior of the bath unit and it has the capacity to clean surfaces and to help the dissolution of substances (Compton et al., 1997). The bath is filled with distilled water and the conventional electrochemical cell is placed into a fixed position (Walton et al., 1995). In this arrangement, the cell is electrically separated and the sound waves penetrate a glass wall before entering the electrochemical reactor. This type of source has been used in polymerization reactions (Yildiz, 2002), metal electrodepositions (Kobayashi et al., 2000; Agullo et al., 1999) and in studies showing the effect of ultrasound in the sonoelectrochemical response of some compounds (Lorimer et al., 1996; Walton et al., 2000).

On the other hand, studies with the ultrasonic horn transducer as a tip shape (Figure 1B) are very frequent. This titanium alloy tip (Ti-6Al-4V) is properly insert in the electrochemical cell. The instrument which produce ultrasound converts 50/60 Hz at a high frequency of electric energy, which is transmitted to a piezoelectric transducer, transforming in mechanical vibrations. These vibrations are intensified by the probes, creating pressure waves on liquids. This action produces millions of microscopic waves (cavities) that expand during the negative pressure and implode violentally during the positive pressure. As the

bubbles implode, millions of shock waves are produced, generating extreme pressures and temperatures in the implosion sites, with a huge energy liberation. In this way, in front of the horn tip, the formation of a cavitation bubbles cloud can be observed at at sufficiently high intensities (Compton et al., 1997) (Figure 2). Alkire and Perusich (1983) and Compton' works (West, 2002; Saterlay et al., 1999; Saterlay et al., 2001; Villagrán, 2005) present diverse configurations for the determination of different analytes, as example, when the working electrode and the tip are placed in the same or in different compartments in the same electrochemical cell. Concerning the degradation of pollutants by association of power ultrasound to electrochemical tecnhiques, many configurations of sonoelectrochemical cells and/or reactors are available and presented in the published papers, being difficult in this book chapter to describe all systems.

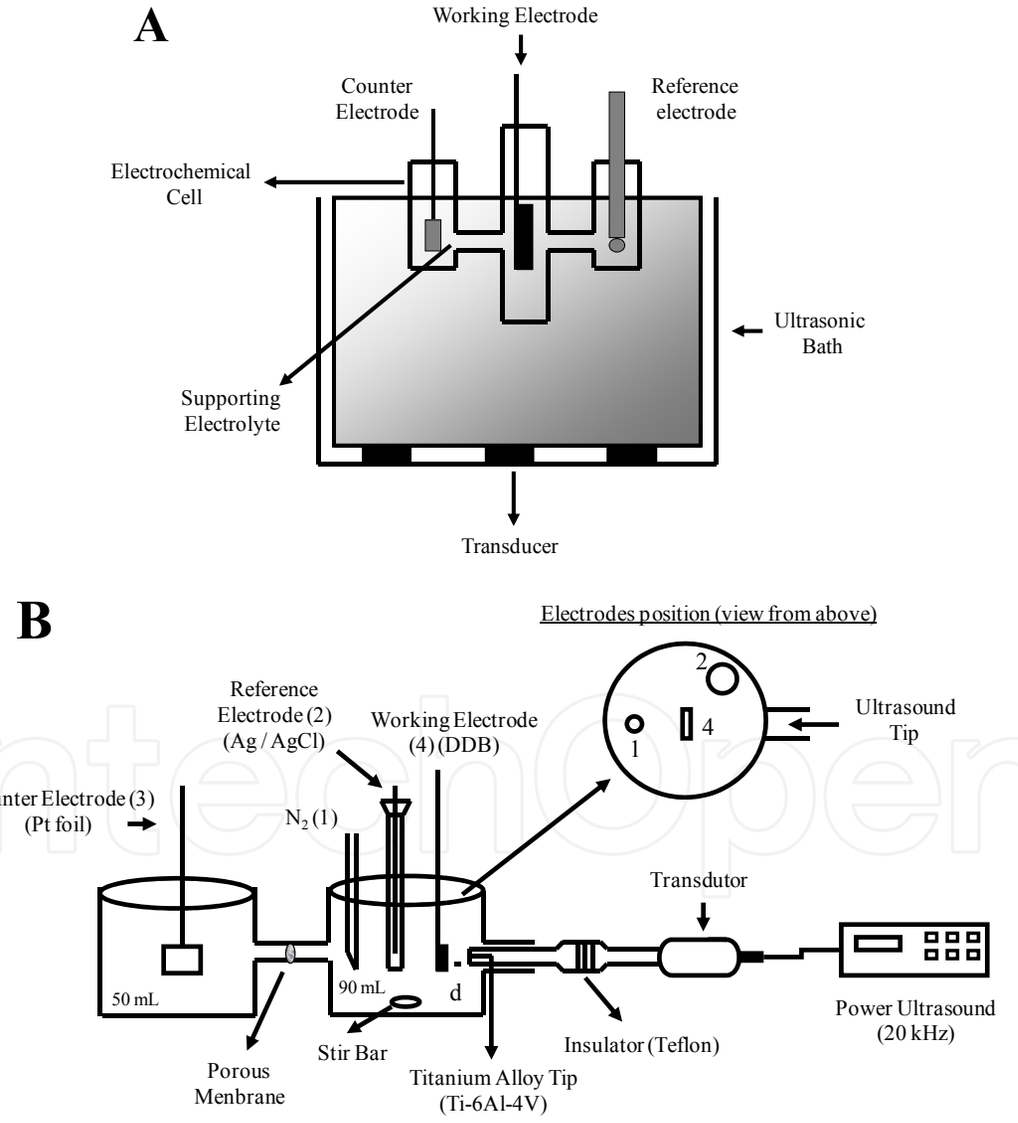


Figure 1. (A) Ultrasonic bath containing an electrochemical cell and (B) Sonoelectrochemical cell whose ultrasound tip is placed in a distance *d* from the electrode surface (BDD electrode in this case) (Garbellini et al., 2010).

The ultrasonic horn has a number of advantages (Compton et al., 1997) over an ultrasonic bath: (i) the horn can supply higher ultrasound intensities (10-1000 W cm^{-2}). This radiation directly applied to the electrochemical system can be controled by the amplitude of the tip vibration; (ii) the distance from the tip to the electrode can be used as a parameter for controlling the ultrasound radiation in the electrochemical system; (iii) the tip of the horn can be used as an electrode and (iv) the geometry and the dimensions of the electrochemical cell has a little effect on the electrode process. However, this transducer has limitations (Compton et al., 1997) as (i) the erosion of the titanium alloy tip that liberates titanium particles in the chemical system of interest causing contamination; (ii) difficulty to maintain the temperature constant during the electrochemical experiment due to the heating effect resulting from the solution agitation and (iii) the need for bipotentiostatic control of the titanium horn tip (Marken & Compton, 1996) due to the direct contact of the tip with the electrochemical system, i.e, the titanium alloy tip present a potential in relation to the reference electrode. This potentiostatic control can be eliminated by insulating the transducer from the probe with a Teflon® disk, as demonstrated in Figure 1B.

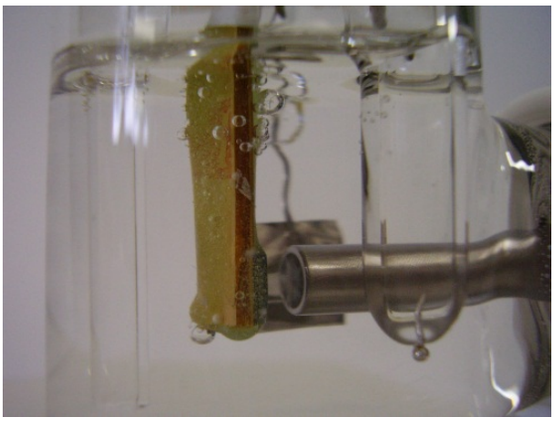


Figure 2. Ultrasound tip in front of BDD electrode (distance = 5 mm).

Additionally, the experiments with the system of Figure 1B, and also with other configurantions, can be conduced using alternative geometric arrangements of the tip in relation to the working electrode, (a) face on geometry (Compton et al., 1994; Compton et al., 1995a; Compton et al. 1995b; Lee et al., 1995): the ultrasound tip is placed in front of the working electrode; (b) side on geometry (Eklund et al., 1996): the working electrode is placed perpendicularly to the ultrasond tip and (c) the ultrasound tip can be used with working electrode (sonotrode) (Compton et al., 1996b).

3. Effect of ultrasound on mass transport

The transport of fluids in an ultrasonic field occurs by acoustic flows, movement induced by field and cavitation (Cooper & Coury Jr, 1998). For acoustic flows, the power ultrasound or certain energy intensity generates a significant flow when the ultrasonic energy is absorbed by the media. This effect is the result of the acoustic energy conversion into kinetic energy in the bulk solution. The movement induced by the field occurs when the ultrasound pass

through a fluid creating a periodic displacement of fluid particles. If an electrode surface is placed sufficiently close to the ultrasonic transducer, the periodic movement contributes to the signal current through alternate increase or decrease of the transport of species to the electrode surface. This process is analogous to what happens in the rotating disk electrode. As commented, the acoustic cavitation involves the nucleation, growth and collapse of vapor cavities in a liquid subjected to ultrasound. The violent collapse of these bubbles in the electrolyte can produce shock waves that contribute to the mass transport (Cooper & Coury Jr, 1998). If the bubble collapses near the electrode surface, it generates a jet which improves the fluid transport (Figure 3).

In summary, the improvement of mass transport provided by ultrasound is due to two transient processes. The bubble collapses at or near the electrode-solution interface with the formation of high speed flows directed to the electrode surface, besides the movement of the bubble in or near the electrode diffusion layer. It is interesting to note that the acoustic flows are largely responsible for the convective flow to the solid-liquid interface. As example, cyclic voltammograms of the electrochemical process of $K_4[Fe(CN)_6].3H_2O$ were obtained on BDD electrode in 0.1 mol L^{-1} KCl in the absence and presence of ultrasound (Figure 4).

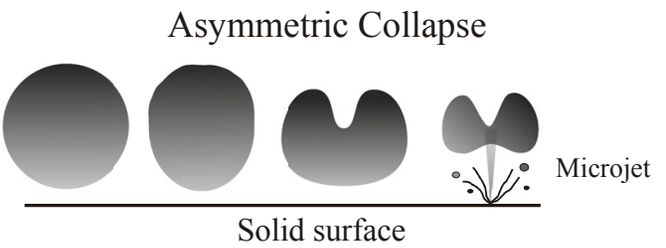


Figure 3. Occurrence of micro-jets when the bubble collapses near the surface (adapted from Banks & Compton, 2003a).

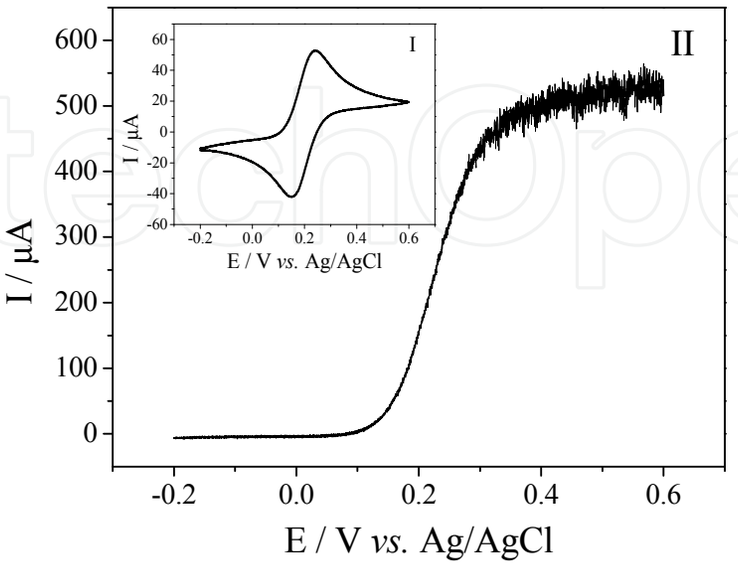


Figure 4. Cyclic voltammograms (50 mV s^{-1}) for 1.0×10^{-3} mol L^{-1} $K_4[Fe(CN)_6]$ obtained in 0.1 mol L^{-1} KCl in the absence (I) and presence of ultrasound, direct and reverse scans (II).

The voltammogram of Figure 4 (I) is characteristic of a reversible system (par redox). Figure 4 (II) shows a measure under the same conditions in the presence of ultrasound directed to the electrode surface of BDD electrode with a distance from the ultrasound probe relative to the electrode of 10 mm. The current intensity of the sonovoltammogram, in which diffusion and convection participate of the mass transport, is significantly greater when compared to the current in voltammogram obtained without the use of ultrasound, in which only the diffusion contributes to the transport of the material. In addition, the profile of response in the absence of ultrasound is modified from a typical cyclic voltammogram to a voltammogram with a sigmoidal shape corresponding to the steady state, and the magnitude of this current is controlled by convective transport of the electroactive species to the electrode surface. It is also important to note that sonovoltammogram from 0.3 V is obtained originally with "noise", which represents cavitation processes occurring in electrode-solution interface and turbulent microflows provided by ultrasound.

Thus, the increase in mass transport to the electrode surface provided by the ultrasound can be measured by assuming a reduction of the diffusion layer thickness (δ). The diffusion layer model enables a description of the mass transport to the interface of the electrode considering a laminar sublayer near the surface and a concentration gradient approximately linear through a thin layer adjacent the electrode. The Equation 1 (where n is the number of electrons transferred, F the Faraday constant, D the diffusion coefficient, A the electrode area and C is concentration in the bulk solution) describes the transport in an electrode subjected to ultrasound based on the model of electrode "accessibly" uniform (δ constant value over the electrode surface), being the electrode larger than the size of δ (Compton et al., 1997; Banks et al., 2003b).

$$I_{lim} = \frac{nFDAC_{bulk}}{\delta} \quad (1)$$

In sonoelectrochemistry, the analysis of the currents based on the Nernst diffusion layer model gives additional criteria regarding the mass transport if electroactive species with different D are compared. The δ value is a function of D, δ(D) = Dx, which exponent can be considered an indicator of the mass transport process nature (Holt et al., 2001). In addition, δ depends on the applied power ultrasound and electrode radius (Compton et al., 1996a). The δ value is considerably smaller for microelectrodes in relation to the electrodes with conventional dimensions, although, in both cases, δ in the presence of ultrasound is significantly lower than in the absence of ultrasound (Compton et al., 1995a). It is noteworthy that electrodes with dimensions on the order of micrometres (between 0.8 and 50.0 μm), known as ultramicroelectrodes, have advantageous properties compared to conventional electrodes (greater than 50.0 μm). Its dimensions are similar to those of the diffusion layer, resulting in a high-speed mass transport, due to the spherical shape of the diffusion layer, which facilitates the study of fast electrochemical reactions under steady state conditions achieved in a shorter time than with conventional electrodes (Correia et al., 1995).

Sonoelectrochemical experiments in which the ultrasound probe is placed in front of the electrode have show that this one behaves as an hydrodinamic electrode. In such cases, the processes of diffusion and convection occur simultaneously, contributing to the transport of electroactive material to the electrode surface (Compton et al., 1997; Banks et al., 2003b). An example of the mass transport increase can be illustrated in the electrolyses of an organochlorine pesticide, pentachlorophenol (PCP) on BDD electrode (Figure 5).

A comparison between electrolyses of the PCP at 3.0 V in the absence and presence of ultrasound on the BDD electrode showed an increase in mass transport promoted by ultrasound, since sonoelectrolyses (curve 2) showed current intensities 1.5 times higher than that obtained by silent electrolyses (in the absence of ultrasound) (curve 1), as shown in Figure 5. In both electrolyses, there was no decay of current due to the occurrence of water oxidation in this high value of applied potential.

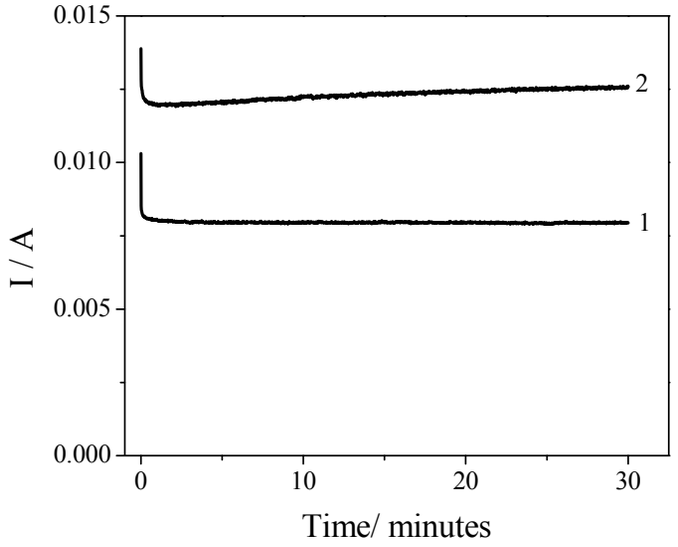


Figure 5. Electrolyses of the PCP at 3.0 V vs. Ag/AgCl in the absence (1) and presence (2) of ultrasound for 30 minutes. Conditions: [PCP] = 5.0×10^{-5} mol L^{-1} in BR buffer 0.1 mol L^{-1} at pH 5.5 and ultrasound tip-BDD electrode distance (d) = 7 mm, (Garbellini et al., 2010).

4. Cavitation effects on electrodes surfaces

Acoustic cavitation is the centre for many cleaning operations in laboratories and for in situ electrode depassivation. The ultrasound, when applied directly to an electrode surface, can provide a severe degradation of the surface by erosion of the electrode material (Compton et al., 1994), as well as it induces the activation and enhancement in the performance due to the electrode cleaning (Compton et al., 1994; Zhang & Coury Jr, 1993).

The beneficial effect of electrode cleaning is widely used for analysis of metals or organic compounds in complex matrices. The organic compounds and/or samples constituents have usually strong interactions with the surface of solid electrodes (adsorption process) thus hindering their use in analytical determinations. Moreover, numerous problems associated with the direct determination of these compounds in real and complex samples are

encountered. For example, the presence of fats, proteins and carbohydrates in food matrices, lead to electrode fouling due to adsorption of these species and it can also reduce the sensibility of the detection methods. In this sense, power ultrasound has been employed to overcome such electrode fouling problem (passivation) due to the ultrasound ability for cleaning the surface electrode (Saterlay et al., 2001), allowing sensitive electroanalysis of some analytes to be carried out in a range of hostile media including eggs (Davis & Compton, 2000), blood (Kruusma, et al. 2004a), wine (Akkermans et al., 1998), among others (Hardcastle & Compton, 2001; Kruusma, 2004b). Recently, the direct determination of methylparathion in potato and corn extracts and its degradation product 4-nitrophenol in lemon and orange juices was performed by ultrasound-assisted square wave voltammetry using diamond electrodes (Garbellini et al., 2009). The sonovoltammetric results for both analytes in pure water and in complex food samples showed greater sensitivity and precision and much lower limits of detection and quantification than the silent measurements.

Evaluations of the changes in various types of electrode surfaces after ultrasound application should be performed by ex situ and in situ methods available for the investigation of surface properties, such as, atomic force microscopy (Compton et al. 1997). Studies performed by Compton´s group (Compton et al., 1994), showed that platinum and aluminium electrodes were degraded after some minutes of ultrasound exposure. In materials like glassy carbon (Zhang & Coury Jr, 1993; Marken et al., 1996), no damage was detected after 30 minutes of ultrasound applied. On the other hand, this time of ultrasound application on gold electrodes (Marken et al., 1996) cause a significant rugosity. Nevertheless, these materials can be used for sonoelectrochemical experiments, since the damages depend on, for example, the intensity of the power ultrasound and the distance between the electrode and ultrasound tip. A viable alternative for these materials is the diamond, due to their extreme hardness and corrosion resistance. BDD electrode, since over violent conditions, has not presented indications of erosion or surface damage (Compton et al., 1998; Goeting et al., 1999).

As discussed, the cavitation process produces active radicals, e.g, hydroxyl, strong oxidizing agents which undoubtedly contribute to increase the degradation levels of pollutants. In the next section of the chapter, some works will be presented.

5. Ultrasound in electrochemical degradation of pollutants

Residues of toxic organic compounds in environment certainly cause problems to human health, degradation of natural resources, leading to biological and ecological imbalances, including the contamination of groundwater and aquifers, damage to microorganisms in aquatic and soil and reduce the productivity of marine plants and corals. Therefore, the development of methodologies for the degradation of these compounds and the metabolites is increasingly necessary. Concerning the technologies for this purpose, in this topic, power ultrasound in electrochemical degradation of pollutants will be discussed including direct sonoelectrochemistry, sonoelectrochemistry with Fenton reactions and with ozonation and ultrasound in association with photoelectrocatalysis using different electrode materials.

5.1. Direct sonoelectrochemical degradation

As aforementioned discussed, the association of power ultrasound with electrochemical techniques can be a powerful tool for degradation of pollutants, since the ultrasound is responsible for the increase of mass transport, activation of electrodes surfaces and generation of active hydroxyl radicals due to the water sonolysis. Some works considering the use of sonoelectrochemistry for pollutants degradation are discussed in this section and the type of pollutant and applied techniques are collected in Table 1.

Pollutant	Methodology	Reference
Sandolan Yellow dye	Sonoelectrolyses in galvanostatic mode	Lorimer et al., 2000
2,4-dihydroxybenzoic acid	Sonoelectrolyses in potentiostatic and galvanostatic modes	Lima-Leite et al., 2002
N,N-dimethyl-p-nitrosoaniline	Sonoelectrolyses in galvanostatic mode	Holt et al., 2003
Perchloroethylene	Sonoelectrolyses in galvanostatic mode	Sáez et al., 2010
P-substituted phenols	Sonoelectrolyses in galvanostatic mode	Zhu et al., 2010
Pentachlorophenol	Sonoelectrolyses in potentiostatic mode	Garbellini et al., 2010
Trichloroacetic acid	Sonoelectrolyses in galvanostatic mode	Esclapez et al., 2010
Reactive blue 19 dye	Sonoelectrochemistry	Siddique et al., 2011
Diuron	Sonoelectrolyses in galvanostatic mode	Bringas et al., 2011

Table 1. Some published papers concerning the direct sonoelectrochemical degradation of pollutants.

Lorimer et al. (2000) applied procedures as sonolysis, electrolysis and sonoelectrolysis to degraded solutions of the acidic dye, Sandolan Yellow, using platinum electrodes and sodium chloride as supporting electrolyte. The process involves the liberation of chlorine at the anode and hydroxide ion at the cathode, resulting in the in situ generation of the hypochlorite ion (equations 2-4), which is a powerful oxidant. The electro-oxidation of Sandolan Yellow process is significantly improved by the use of ultrasound in conjunction with electrolysis, and an optimum acoustic ultrasonic power was observed when using a source at a frequency of 20 kHz.

$$\text{Anode: } 2Cl^- \rightarrow Cl_2 + 2e \quad (2)$$

$$\text{Cathode: } 2e + 2H_2O \rightarrow 2OH^- + H_2 \quad (3)$$

$$\text{Overall reaction: } 2OH^- + Cl_2 \rightarrow Cl^- + OCl^- + H_2O \quad (4)$$

Lima Leite et al. (2002) investigated the electroxidation of the 2,4-dihydroxybenzoic acid (2,4-DHBA) by potentiostatic and galvanostatic electrolyses on platinum electrode with the ultrasound at two frequencies (20 e 500 kHz). Potentiostatic sonoelectrooxidation of 2,4-DHBA was carried out at three different potentials (1.2; 1.5 and 2.0 V), according to the rate of dioxygen production. Under 20 kHz ultrasound irradiation alone, 2,4-DHBA is almost unaffected. Degradation rate increases with the applied electrode potential. Improvement in 2,4-DHBA electrodegradation by low-frequency ultrasound proved to be more marked than in the case of high-frequency ultrasound, certainly due to mechanical effects. Variation in the electrolysis current during the process shows that 2,4-DHBA electrooxidation under low-frequency ultrasound irradiation can be carried out at a greater current density than in the case of electrooxidation alone. Current drops are also reduced in the presence of an acoustic field. As previously mentioned, it can be explained by the elimination of the passivating polymer film formed at the electrode surface: the electrode active surface area increases and the intensity, which is directly proportional to it, increases too. The improvement in the mass transfer and the more rapid desorption of the reaction products are also responsible for the lower current drops.

After the study of potentiostatic sonoelectrolysis parameters, the galvanostatic operation was investigated since it is most widely used on an industrial scale. Key parameters such as current density, initial pollutant concentration and ultrasonic power were studied. For a 300 mg l^{-1} initial concentration and a 300 A m^{-2} current density, the TOC decrease was 47% after passing an electricity amount of 1.5 A h at low frequency and only 32% after passing 3.5 A h at high-frequency sonoelectrooxidation or electrooxidation. At low frequency, 2,4-DHBA degradation is accelerated and final TOC is lower: cavitation phenomena ensure the cleaning of the electrode surface thus increasing the active electrode surface. Observed by-products of sonoelectrodegradation are the same as for electrooxidation alone, including the following: 2,3,4- and 2,4,5-trihydroxybenzoic acids (THBA), maleic acid, glyoxylic acid and oxalic acid. Fewer intermediate aromatic compounds are formed at low-frequency irradiation. Moreover, the faradaic yield increases under low-frequency sonication, showing a more efficient use of electrochemical energy. Nevertheless, the overall energy consumption remains high (>200 kW kg^{-1}).

Additionally, power ultrasound in association with electrolyses for degradation of phenols and phthalic acid (Zhao et al., 2008; Zhao et al., 2009), N,N-dimethyl-p-nitrosoaniline (Holt et al., 2003) and reactive dye Procion Blue (Foord et al., 2001) have also been reported. A preliminary study of the 20 kHz sonoelectrochemical degradation of perchloroethylene in 0.05 mol L^{-1} aqueous sodium sulfate has been carried out by Sáez et al. (2010) using controlled current density degradation sonoelectrolyses in batch mode. PCE sonoelectrolysis experiments were performed at different ultrasound intensities of 1.84, 3.39, 5.09, 6.36 and 7.64 W cm^{-2}, with T=20°C, 362 μM, and the value of the working current density fixed at 3.5 mA cm^{-2}. An analysis for all ultrasound intensities, all of these volatile compounds: PCE, trichloroethylene (TCE) and dichloroethylene (DCE), chloride and chlorate anions were totally degraded in the first 2.5 h of the process, in contrast to the electrochemical route, for which, steady state remaining concentrations of TCE and DCE (higher than 10% of the initial

concentration of PCE for each one) were routinely detected even after 5 h of treatment. The main contribution of the ultrasound field presence during the ECT (electrochemical treatment) is not only the total degradation of the main volatile compounds (PCE, TCE and DCE), but also the decrease of the effective reaction time. The energetic consumption with sonoelectrochemical treatment is lower than that presented by sonochemical treatment, due to the fact that the treatment time is significantly reduced.

The effects of low-frequency (40 kHz) ultrasound on the electrochemical oxidation of p-substituted phenols (p-nitrophenol, p-hydroxybenzaldehyde, phenol, p-cresol, and p-methoxyphenol) at BDD and PbO_2 anodes were evaluated by Zhu et al. (2010). The oxidation was performed at constant current density (20mA cm^{-2}) and room temperature (25°C) using sodium sulphate as supporting electrolyte. At the BDD anode, the % increase values were in the range 73–83% for p-substituted phenol disappearance and in the range 60–70% for chemical oxygen demand removal. However, at the PbO_2 anode, the corresponding % increase values were in the range 50–70% for disappearance of p-substituted phenols and only 5–25% for chemical oxygen removal, much lower values than obtained at the BDD anode. The hydroxyl radicals were mainly free at the BDD electrodes with a larger reaction zone, but adsorbed at the PbO_2 electrodes with a smaller reaction zone. Therefore, the enhancement due to ultrasound was greater at the BDD anode than at the PbO_2 anode.

In our work (Garbellini et al., 2010), the beneficial effects of the ultrasound (fixed frequency of 20 kHz in a maximum power of 14 W) were evaluated in association with potentiostatic electrolyses for the degradation of pentachlorophenol at 3.0 V vs. Ag/AgCl, using a BDD electrode during 270 minutes using a Britton-Robinson (BR) 0.1 mol L^{-1} buffer solution as electrolyte. The sonoelectrochemical cell used for this work is presented in Figure 1B. Different decay levels of the PCP spectrum bands in 220, 251 and 321 nm, respectively, were observed after application of ultrasound without electrochemical process (18.1, 17.7 and 19.8 %), silent electrolyses (29.3, 71.6 and 70.8 %), pulsed sonoelectrolysis (31.0, 75.1 and 76.3%) and sonoelectrolyses (39.2, 80.0 and 82.6 %). Specifically, the pulsed sonoelectrolysis involved a combination of electrolysis in the presence (30 min) and absence (5 min) of ultrasound. This process was carried out purposely without cleaning/reactivation of the diamond electrode surface. The effects of the electrode surface activation provided by ultrasound and simultaneous generation of hydroxyl radicals by both radiation and polarized BDD surface contributed to higher levels of degradation of the pesticide in comparison to the values obtained for the silent electrolyses.

The sonoelectrochemical treatment of aqueous solutions of trichloroacetic acid (TCAA) has been scaled up from the voltammetric analysis to pre-pilot stage, as it has been reported by Esclapez et al. (2010). All the bulk electrolyses in batch mode were carried out using a home-made galvanostat (120 mA) using a titanium disk as working electrode. Sonoelectrolyses at batch scale (carried out with a horn-transducer 24 kHz positioned at about 3 cm from the electrode surface) achieved little improvement in the degradation. However, when a specifically designed sonoelectrochemical reactor (not optimized) was used during the scale-up, the presence of ultrasound field provided better results (fractional conversion 97%,

degradation efficiency 26% and current efficiency 8%) at lower ultrasonic intensities and volumetric flow.

Recently, Siddique et al. (2011) reported the decomposition of un-hydrolyzed and hydrolyzed forms of reactive blue (RB) 19 dye by ultrasound assisted electrochemical process using lead oxide as working electrode. The experiments were conducted at various pH values in the range of 3–9 and various ultrasonic frequencies (20–80 kHz) using 50 mg L^{-1} dye concentration for 120 min. The results showed that almost complete 90% color removal and a maximum of 56% TOC removal for 50 mg L^{-1} dye concentration of un-hydrolyzed RB 19 dye was achieved at an ultrasonic frequency of 80 kHz, pH of 8 after 120 min. In case of hydrolyzed dye, the TOC reduction observed was 81%. The sonoelectrolysis for dye decomposition and decolorization proved to be more effective and the energy consumption reduced to half as compared with the electrolysis/sonochemical decomposition.

Macounova et al. (1998) and Bringas et al. (2011) investigated the effects of power ultrasound in the electrochemical oxidation of the herbicide diuron using the glassy carbon and BDD electrodes, respectively. In Macounova's work, the ultrasound was just used to avoid a total blockage of the electrode surface by a passivating film. A mechanism involving dimmers formation was reported; however, no information about degradation rates of herbicide was mentioned. Bringas's work reports the degradation and mineralization of diuron at a BDD anode enhanced by low frequency (20 kHz) ultrasound. Under the operation conditions, 60 mA cm^{-2}, pH = 12, T = 10 °C and 8 h of experimental running, results demonstrated improvements on the mineralization kinetics of diuron closely to 43% when ultrasound was coupled to the electrochemical treatment. In addition, the results showed that alkaline pH favours the mineralization rate obtaining reductions of the total organic carbon higher than the 92% after 6 h of degradation at a constant current density of 60 mA cm^{-2} using sodium sulphate as supporting electrolyte.

5.2. Sonoelectrochemical degradation in association with different methods

The application of the sonoelectrochemical processes associated to other methods for the oxidation of organic compounds has been developed as a powerful tool to treatment of effluents. This way, the Fenton reaction (equation 5) (Brillas et al., 2009) is well known in the degradation of organic material by extra generation of hydroxyl radicals.

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^- + {}^{\bullet}OH \quad (5)$$

Hydrogen peroxide generated through cavitation action (ultrasound) or electrochemical reduction of molecular oxygen is not highly active towards the destruction of an organic species. Fenton's reagent system can be applied to circumvent this problem what enabled the maximum amount of free radicals (specifically hydroxyl radicals) to be generated. This was achieved by the addition of Fe^{2+} to the solution that is known to catalyse the destruction of organic material through the generation of extra hydroxyl radicals, according to a Fenton's type mechanism (Brillas et al., 2009). Some works are discussed here and the kind of pollutant and techniques are collected in Table 2.

Pollutant	Methodology	Reference
Meldola blue dye	Sonoelectro-Fenton	Abdelsalam *et al*., 2002
2,4-dichloro-phenoxyacetic acid and 2,4-dichlorophenol	Sonoelectro-Fenton	Yasman *et al*., 2004
1,3-dinitrobenzene and 2,4-dinitrotoluene	Sonoelectrochemistry with ozonation	Abramov *et al*., 2006
Methyl orange dye	Sonophotoelectrocatalysis	Zhang et al., 2008
2,4-dichloro-phenoxyacetic acid, 4,6-dinitro-o-cresol and azobenzene dye	Sonoelectro-Fenton	Oturan *et al*., 2008
Azure B dye	Sonoelectro-Fenton	Martinez *et al*., 2012

Table 2. Some published papers concerning the sonoelectrochemical degradation in association with different methods of pollutants.

Abdelsalam et al. (2002) reported the degradation of an organic dye molecule (specifically meldola blue, MDB) under the influence of power ultrasound in combination with electrochemically-generated hydrogen peroxide. A novel flow system was employed to measure the degradation as a function of time while minimizing the disturbance to the acoustics of the sonoelectrochemical reactor employed. The sonoelectrochemical reactor contained a 100 cm^3 solution consisting of 0.1 mmol dm^{-3} MDB, 50 mmol dm^{-3} Na_2SO_4, 10 mmol dm^{-3} H_2SO_4 , 0.5 mmol dm^{-3} $FeSO_4$ sonicated at 124 kHz. A constant potential of -0.7 V vs. Ag was applied to the reticulated vitreous carbon electrode (RVC). The degradation of a model dye species has been shown to be significantly enhanced by both the presence of Fe^{2+}, electrochemically generated hydrogen peroxide and the presence of ultrasound. Prolonged exposure of the solution to the degradation conditions resulted in a 60.7% reduction in the chemical oxygen demand after 100 min. The constant rate for the complete destruction of MDB, determined by chemical oxygen demand, was found to be significantly slower at $(10.2\pm2.6) \times 10^{-3}$ min^{-1}.

Yasman et al. (2004) presented a method for detoxification of hydrophilic chloroorganic pollutants, 2,4-dichlorophenoxyacetic acid (2,4-D) and its derivative 2,4-dichlorophenol (2,4-DCP), in effluent water using a combination of ultrasound waves, electrochemistry and Fenton's reagent. Both cathode and anode were made of nickel foil and the support electrolyte was Na_2SO_4 (0.5 g L^{-1}). Sonoelectroxidation was carried out in the galvanostatic mode at current intensities not exceeding 100 mA and the sonication was achieved at low frequencies (20 kHz). The application of the sonoelectrochemical Fenton process (SEF) using a current density of 100 mA resulted in a practically completed degradation of the 1.2 mmol L^{-1} 2,4-D solution in 600 s, also an considerable oxidation of 2,4-DCP. The efficiency of the SEF process was much higher than the other conventional degradation methods and the required times for the complete degradation were considerably shorter.

Oturan et al. (2008) also reported the use of sonoelectro-Fenton process for the degradation of organic pollutants in aqueous medium, such as herbicides 4,6-dinitro-o-cresol (DNOC)

and 2,4-dichlorophenoxyacetic acid (2,4-D) and the azobenzene (AB) dye. A cylindrical Pt mesh used as anode was centered in the electrolytic cell and surrounded by the carbon-felt cathode. Aqueous solutions of 250 ml were prepared for each individual pollutant, containing 1 mM 2,4-D, 0.5 mM DNOC or 0.025 mM AB, with 0.05 M Na_2SO_4 as background electrolyte and 0.1 mM Fe^{3+} as catalyst at pH 3.0 adjusted with H_2SO_4 to be comparatively treated by EF process under galvanostatic conditions at 200 mA. The same experimental conditions mentioned above were used to study sono-EF process, but coupling with ultrasound irradiation at low (28 kHz) or high (460 kHz) frequencies provided by a ceramic piezoelectric transducer. The SEF process allowed the obtainment of a higher degradation rate than that provided by the two techniques separately for 2,4-D and DNOC. Similar results have been obtained at low and high frequency, what suggests that the main contribution to the oxidation process arises from Fenton's reaction, not from the effects of sonication on organics. In contrast, the output power greatly influences the sono-EF process performance, being 20W the optimum power because higher values hamper the dissolved O_2 concentration and, consequently, affects the cathodic H_2O_2 electrogeneration required for Fenton's reaction. On the other hand, readily oxidizable compounds such as AB, which undergoes the easy cleavage of azo bond by ultrasounds, are so quickly destroyed by EF process alone that ultrasound irradiation is unable to improve the treatment.

Martinez et al. (2012) recently presented the degradation of azure B dye ($C_{15}H_{16}ClN_3S$; AB) by Fenton, sonolysis and sono-electroFenton processes employing ultrasound at 23 kHz and the electrogeneration of H_2O_2 at the reticulated vitreous carbon electrode. The best oxidative degradation of AB by Fenton reaction was obtained at pH between 2.6 and 3.0 using 0.8×10^{-3} mol L^{-1} Fe^{2+} and 2.4×10^{-3} mol L^{-1} H_2O_2. The oxidative degradation of AB followed apparent first order kinetics, where the rate constants decreased in the following order: sono-electroFenton > Fenton > sonolysis. The rate constant for AB degradation by sono-electroFenton is 10-fold that of sonolysis and 2-fold the one obtained by Fenton under silent conditions. The chemical oxygen demand was abated 68% and 85% by Fenton and sono-electroFenton, respectively, achieving AB concentration removal over 90% with both processes. This way, the sono-EF process offers optimistic perspectives regarding the development of more efficient sonoelectrochemical treatment processes for organic compounds.

On the other hand, there are other methods associated to sonoelectrochemical processes, such as those in the presence of ozone and in conjuction with photoelectrocatalysis.

The molecular ozone in aqueous solutions is one of the most active oxidizing agents. Interaction of ozone with an electron donor, D, or by reduction at a cathode, leads to the formation of the O^{-3} ion (Abramov et al., 2006):

$$O_3 + e^- (D) \rightarrow O_3^- (+D+) \quad (6)$$

The O_3^- ion is a stronger oxidant than molecular ozone, and in acid media it rapidly undergoes reaction with the formation of the $O^{-\bullet}$ anion–radical and oxygen:

$$O^{-}_{3} \rightarrow O^{-\bullet} + {}^{1}O_{2} \quad (7)$$

Alternatively, it can interact with water, giving oxygen, hydroxyl ion and radical •OH:

$$O_{3}^{-} + H_{2}O \rightarrow HO\bullet + {}^{1}O_{2} + HO^{-} \quad (8)$$

Thus the cathodic reduction of ozone yields highly active oxidizing agents. Abramov et al. (2006) reported a method for the destruction of 1,3-dinitrobenzene and 2,4-dinitrotoluene in aqueous solutions using sonoelectrochemistry treatment with ozone addition. A titanium ultrasonic horn radiator was used as a cathode (sonotrode) and the intensity used in all sonochemical experiments was 5 W cm^{-2}. 100 cm^3 of 1% acetic acid solution containing DNB, and DNT at concentrations of 100 mg dm^{-3} were introduced into the cathode compartment. The compounds have shown to be stable to reaction with ozone, even under ultrasonic activation. The use of ultrasound enhances the rate of electrochemical reduction but the overall rate of reaction is still slow. However, the simultaneous application of ultrasound and ozonation to the electrochemical reaction allows virtually complete destruction of the compounds in short times. The effect is attributed to the ultrasonic enhancement of the electrochemical process giving intermediates that are susceptible to ozone oxidation.

Among methods that can be associated with power ultrasound in order to destruct organic compounds is the photocatalysis using TiO_2 as photocatalyst. However, the low photocatalytic efficiency limited the application of this technology in degradation treatments. Ultrasonic-assisted photocatalysis can enhance the photocatalytic efficiency (Bejarano-Perez et al., 2007). Zhang et al. (2008) used hybrid processes involving both electro-assisted and ultrasonic assisted ways to enhance the photocatalytic efficiency, sonophotoelectrocatalysis (SPEC), to investigate the degradation of azo dye methyl orange (MeO) in aqueous solution using TiO_2 nanotubes. Different power of ultrasound (from 60 to 150 W) and different dye concentrations (from 1 x 10^{-5} to 2 x 10^{-4} mol L^{-1}) for a total period of 60 minutes were applied in the experiments. The results showed that the hybrid processes could efficiently enhance the degradation efficiency of MeO, and followed pseudo-first-order kinetics. Thus the constants rate of decolorization of MeO were 0.0732 min^{-1} for SPEC process; 0.0523 min^{-1} for photoelectrocatalysis process, 0.0073 min^{-1} for sonophotocatalysis process and 0.0035 min^{-1} for photocatalysis process. The constants rate values indicated that there was synergistic effect in the ultrasonic, electro-assisted and photocatalytic processes.

6. Conclusion

Ultrasound combined with electrochemical process and Fenton reactions is a promising method for the degradation of some toxic organic compounds and treatment of wastewater.

The beneficial effects of the power ultrasound use, e.g, cleaning/activation of the electrodes surfaces, enhancement of the mass transport and generation of hydroxyl radicals by water sonolysis contributed to higher levels of pollutants degradation in comparison to the values obtained for the silent electrolyses.

The main drawback of ultrasound is its energetic cost. However, the ultrasonic intensity series has shown that it is not necessary to use very high ultrasound power. Therefore, working at low power ultrasound and with different strategies (pulsed ultrasound) should be planned in order to overcome this drawback and provide economically viable treatments. This way, an optimized sonoelectrochemical reactor design is mandatory. Specifically for the case of pulsed sonoelectrolysis, the absence of reactivation and/or cleaning of the electrode surface could allow future automation of the process for industrial applications for long periods of time.

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