Sonoelectrochemistry: fundamental and applied studies

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1.- Introduction.

The characterization of the behaviour of sonoreactors in order to identify the actives zones is very important, so chemical and physical effects generated by the cavitation can be determined. Spatial distribution of effects generated by the application of an ultrasound field becomes important in the efficient design and scale-up.

Ultrasound field emitted by a sonoreactor supplied by Undatim have been characterized using classical method such as aluminium foil analysis, thermal distribution analysis, Fricke reaction and yodine oxidation. Moreover two electrochemical probe have been used, the redox system based on $Fe(CN)_6^{3-}$ anion reduction and the process of lead dioxide electrodeposition.

2.- Numerical Simulations.

Linear wave propagation and scattering in a quiescent inhomogeneous media can be described with the wave equation

$$\nabla\left(\frac{1}{\rho}\nabla p\right)-\frac{1}{\rho c^2}\frac{\partial^2 p}{\partial t^2}=0$$

where P is the acoustic pressure, ρ is the density and c is the speed of the sound. The transducer system used in ultrasound works at certain frequency so it is natural to consider case when pressure P is time harmonic. In time harmonic case

$$P(r,t)=p(r)e^{i\omega t}$$

where spatial variable r = r(x, y, z) and ω is the angular frequency. The space dependent part of the pressure is the solution of the Helmholtz equation

$$\nabla\left(\frac{1}{\rho}\nabla p\right)+\frac{\kappa^2}{\rho}p=0$$

where κ is the wavenumber (κ = 2πf/c) and f is the frequency of the field. The limitations of the Helmholtz model are it does not take into account nonlinear wave propagation and the generation of transversal elastic waves (shear waves).

With suitable boundary conditions the Helmholtz equation can be solved using a variety of numerical methods. The standard approach is the low-order finite element method.

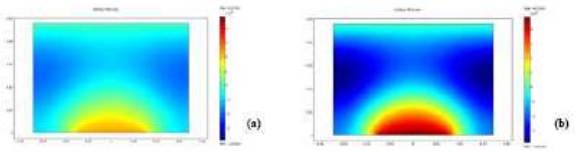

Fig 1.- Spatial variations in pressure amplitude for a circular plane piston transducer with a radius=15mm, working at 20 kHz (a) global ultrasonic intensity 1.84 W cm^{-2} (b) 7.64 W cm^{-2}.

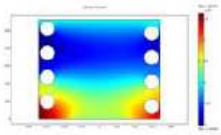

Fig 2.- Influence of the glass cooling coil on ultrasonic field at a global ultrasonic intensity of 5.09 W cm^{-2} in the spatial variations of the pressure amplitude

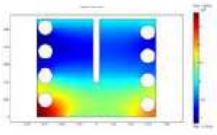

Fig 3.- Influence of a rod on the ultrasonic field at a global ultrasonic intensity of 5.09 W cm^{-2} in the spatial variations of the pressure amplitude

3.- Lead Dioxide Electrocrystallization.

Lead dioxide electrodeposition shows a complex mechanism with several stages. First stage is related to the adsorption of hidroxil radicals under electrode surface. Since the application of ultrasound field generates hidroxil radicals, the process will be strongly influenced by the presence of an ultrasound field.

$$H_2O \longrightarrow OH_{ads} + H^+ + e^-$$
$$Pb^{2+} + OH_{ads} \longrightarrow Pb(OH)^{2+}$$
$$Pb(OH)^{2+} + H_2O \longrightarrow PbO_2 + 3H^+ + e^-$$

It has been studied the effect of the application of an ultrasound field under the process of lead dioxide electrodeposition. Potential step experiments, obtained under crystallization overpotential, show lead dioxide electrodeposition is favoured in the presence of ultrasound moreover can be observed a strong influence of the irradiation power amplitude in the electrocristallization process. This effect is related with the generation of hidroxil radicals developed during the water sonolysis. Experimental curves can be fitted to a simple progressive tridimensional nucleation and crystal growth model. This model provides kinetic parameters characteristic of the electrocrystallization process. Table 1 shows the kinetics constants: t_0, induction time, j_0, current density at induction time, N_0A, nucleation constant and k, growth constant obtained from the mathematical approximations. As you can see in table 1 nucleation constant depend of the ultrasonic amplitude, however growth constant doesn't vary with the ultrasonic ampitude. These experiments have been carried out at 20kHz of frequency. More work is in progress using a sonoreactor of 300kHz.

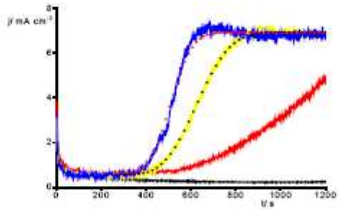

Fig. 4.- Influence of ultrasonic amplitude: - silent, - 1.8Wcm^{-2}, 3.4Wcm^{-2}, - 5.1Wcm^{-2}, • theoretical fit 3.4Wcm^{-2},• theoretical fit 5.1Wcm^{-2}.Chronoamperometric curves for lead dioxide electrodeposition in 0.1M lead(II) nitrate + 1M nitric acid at a glassy carbon electrode. Potential step 1480 mV vs SCE. Temperature 22°C. Ultrasonic frequency 20kHz. Distance electrode-probe 1 cm.

P/ W cm^{-2}	t_0 /s	j_0 /mA cm^{-2}	N_0A /mol cm^{-2} s^{-1}	k /mol cm^{-2} s^{-1}
5.1	311±2	0.65±0.02	(690±3)10^5	(3.580±0.005)10^{-6}
3.4	326±2	0.60±0.01	(598.5±0.5)10^5	(3.580±0.005)10^{-6}

Table 1

4.- Treatment of chlorinated compounds.

Ultrasound are widely used waste treatment due cavitation produces highly reactive oxidizing species in water. These radicals can oxidise organic pollutants such as aromatic compounds in dilute aqueous solutions. Chlorinated organic compounds such as dichloromethane, trichloroethylene and perchloroethylene are used as solvent in large industry. These organic compounds are toxic and harmful to human health and the environment, moreover are persistent in the environment and can be broken down to another compound which are hazard to the ozone layer. Removal of these compounds from water is not easy. In the literature can be found some methods of removal but all have their own limitations. Currently in our laboratory it has studied the percloroethylene remove using sonochemical methods. The variables to study were ultrasonic amplitude and frequency. In these preliminary experiments aqueous solutions of perchloroethylene was irradiated with 20kHz ultrasonic waves in a sonochemical reactor at 20°C, further experiments will be carried out using 300kHz.

Thus, first experiments shows perchloroethylene under ultrasound is completely dehalogenated , almost the chlorine originally present as perc was recovered as chloride ion at the end of the experiment. Percent destruction in this conditions is close to 85% . In view of the first result, the sonochemical treatment appears to be efficient for the destruction of this compound.

In the future it will be studied perchloroethylene decomposition using electrochemical and sonoelectrochemical methods.