

ELECTROCHEMICAL BEHAVIOUR OF HEXACHLOROCYCLOHEXANE

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The chemical industry produces large amounts of wastewater contaminated with compounds that are toxic and/or non-degradable. On the other hand, pesticides are widely used over the world to protect crops against different kinds of pests [1]. Therefore, a marked increase in their presence in air, soil and waters has been detected. Organochloride insecticides, such as hexachlorocyclohexane (commonly known as lindane) are serious environmental pollutants and are normally extremely resistant to biodegradation. Chemical and biological methods have been developed for decontamination of polluted environments but the first methods use dangerous chemicals and the others are only effective with compounds of lower chlorine content.

It has been demonstrated that electrochemical methods are an alternative means for dechlorination [2] and in the present study results obtained with the reduction of lindane at a millimetric vitreous carbon electrode and at a carbon microelectrode are reported.

Lindane has a low solubility in water and therefore, ethanol or ethanol / water solutions are better media for electrochemical studies. The electrochemical behaviour is apparently identical in both solvents and in their mixtures. Figure 1 displays a cyclic voltammogram of a 3 mM solution of lindane in ethanol containing tetrabutylammonium tetrafluoroborate (TBAB) at a vitreous carbon electrode. The voltammetry was carried out in a three electrode, two compartment cell where the reference electrode was an Ag / AgCl electrode and the secondary electrode was a platinum spiral. A well-defined reduction peak appears at a potential close to -2.1 V vs Ag / AgCl at 0.2 V/s, which shifts to more negative values as the sweep rate increases. This is a diffusion controlled process, since a plot of the peak current (I_p) vs the square root of sweep rate (v) is a straight line with an approximately zero intercept. No other reduction processes are observed apart from the medium reduction which occurs at potentials above -2.5 V vs Ag / AgCl.

The number of electrons involved per molecule in the reduction process was determined by two different methods. The first was based in the comparison of the cyclic voltammetry of lindane with that of a well-known reversible system (the oxidation of ferrocene) upon correction for the wave shape, assuming that the diffusion coefficients of both species are equal [3]. The second method combines steady state voltammetry at a microelectrode and chronoamperometry of both lindane and ferrocene and no assumptions are needed for the diffusion coefficients [4]. Both methods seem to indicate that six electrons are involved in the reduction mechanism, probably suggesting that three chlorines are removed from the molecule. This hypothesis will have to be confirmed by carrying

out controlled potential electrolyses followed by product identification but these preliminary results seem to indicate that cathodic reduction may degrade the molecule by dechlorination. Furthermore, they suggest that electroanalytical techniques are appropriate for the detection and quantification of lindane in ethanol solutions.

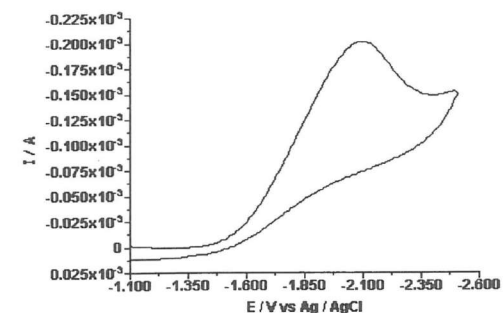


Figure 1. Cyclic voltammogram of a 3 mM solution of lindane in ethanol containing 0.1 M of TBAB at a vitreous carbon electrode (area = 0.072 cm²) and at the scan rate of 0.2 V / s.

Square wave voltammetry is known to provide a high sensitivity and resolution electroanalytical method with low detection limits [5]. On the other hand it has been demonstrated that microelectrodes offer advantages over conventional sized electrodes in analytical applications [6].

Hence, several experiments were carried out by square wave voltammetry employing a carbon microelectrode to investigate the electrochemical response of ethanol solutions of lindane. Figure 2 shows a voltammogram of a solution of lindane in ethanol containing TBAB and a peak is observed at potentials close to -2.0 V vs Ag / AgCl.

The effect of concentration on the peak height was investigated and it was found that down to a value of 10^{-7} M a linear relationship was observed. Equation (1) describes the variation of current, ΔI_p (A) with the concentration, c (M).

$$\Delta I_p = 2 \times 10^{-6} c + 5 \times 10^{-12} \quad (1)$$

The detection limit was calculated from the intercept of the straight line and a value of 5×10^{-8} M was obtained.

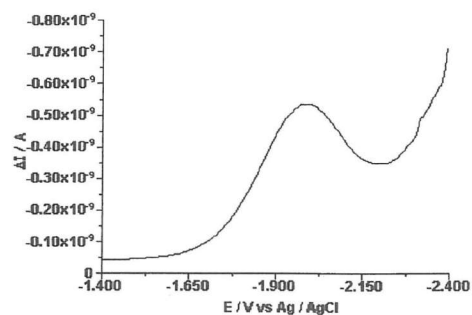


Figure 2. Square wave voltammetry of a 1.98×10^{-4} M solution of lindane in ethanol containing 0.1 M TBAB at a carbon microelectrode (radius = 3.5 μm). Square-wave amplitude = 60 mV; Frequency = 10Hz.

To evaluate the possibility of carrying out this type of analysis in sediments, a sediment from the estuary of the river Tejo was simulated by mixing 45 % SiO_2 , 33 % NaCl , 13 % Al_2O_3 , 7 % Fe_2O_3 , and 2 % CaCO_3 . 10 cm^3 of a 1.98×10^{-4} M solution of lindane in ethanol containing TBAB was added to 3.5 g of the sediment. The mixture was placed in the electrochemical cell and stirred for several minutes. Square wave voltammograms with and without stirring were recorded and a peaked voltammogram was obtained at a potential close to that of lindane reduction as observed in figure 3 a). In both cases the electrochemical response was similar, as expected since diffusion is the dominant mode of mass transport to microelectrodes and therefore it is not dependent on convection. Figure 3 b) shows the voltammogram presented in figure 2, for comparison, and figure 3 c) shows the response obtained under the same conditions of a) but without lindane. A shift towards slightly more positive potentials of the reduction process is observed and the peak is very well defined for analytical purposes.

An attempt to carry out similar experiments without the deliberate addition of the electrolyte was made, and figure 4 a) presents a square wave voltammogram obtained in the same conditions as those in figure 3 a) but without TBAB; figure 4 b) shows, for comparison, the result obtained with TBAB. It is clear that the height of the peak obtained without the addition of electrolyte is smaller. A possible explanation for this observation is that negatively charged species will be formed during the reduction process and they will migrate away from the electrode surface in the absence of a high concentration of supporting electrolyte, thus decreasing the reduction current. Despite the decrease in current, this experiment shows the feasibility in carrying out direct analysis of lindane in

sediments in media of low ionic strength. It should also be noted a small shift of the potential peak to more negative values. This fact may be associated to some ohmic drop.

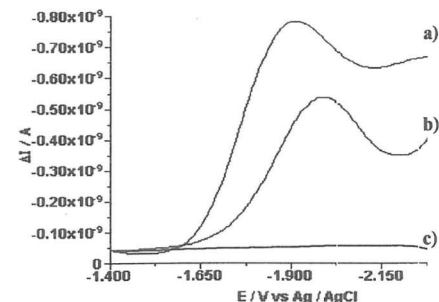


Figure 3 – Square wave voltammograms obtained under the same conditions as in figure 2 of: a) a mixture of 10 cm^3 of a 1.98×10^{-4} M solution of lindane in ethanol containing 0.1 M TBAB and 3.5 g of the sediment; b) same as in a) but without sediment; c) same as a) but without lindane.

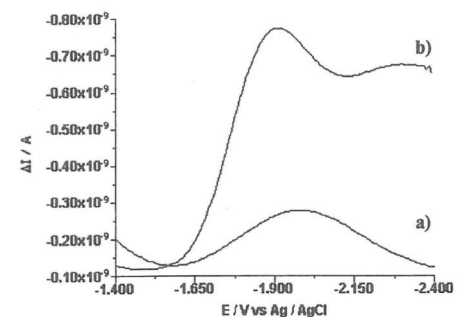


Figure 4 – Square wave voltammograms obtained under the same conditions as in figure 3: a) without TBAB; b) same as figure 3 a).

These preliminary results indicate that by square wave voltammetry employing microelectrodes it is possible to develop a method of analysis of lindane in solutions and sediments. Furthermore, they show that electrochemical reduction may constitute the basis of a method for, at least, partial decontamination of solutions containing lindane.

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