Adsorption of Simazine on a Glassy Carbon Electrode

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Differential capacity–potential curves have been measured for the s-triazine herbicide simazine at different concentrations. The decrease in capacity was independent of the applied potential, so the adsorption is also independent of the potential. The adsorption follows a Langmuir type isotherm. The adsorption constant was obtained.

Triazine herbicides are commonly applied as pre- and post-emergent weed control agents in agricultural fields containing corn, apple, grapes, wheat, etc. The environmental half-lives of these herbicides are in the order of weeks to several months. Large amounts of triazines (100–150 million pounds, approximately) are applied annually and thus pose a major threat to the environment. This wide utilization of triazines for agriculture saves billions of dollars a year but has already contributed to the increasing contamination of the environment, water and sediments, mainly owing to their physicochemical properties such as water solubility, adsorptivity (K_{oc}), and hydrolysis half life (>25 weeks).[1] Simazine (SMZ, 2-chloro-4,6-bis(ethylamino)-1,3,5-triazine) (Figure 1) is a triazine herbicide and algaecide used in agriculture and in the home and garden. Simazine products are used for the control of a large variety of weed species in fruits, vegetables, lentils, vineyards, home garden, and non-agricultural situations. They are also used to control algae in pools, aquariums, and ponds. Triazine herbicides are used in olive groves in Andalusia, but the use of simazine has been banned since 2002 because together *tert*-butylazine has created serious pollution episodes in water reservoirs of Andalusia in recent years.

The removal of such compounds at low levels from water always constitutes a problem. Among the methods employed are destruction oxidation with ozone,[2,3] hydrogen peroxide,[4,5] or adsorption into porous solids such as activated carbon, zeolites, and clays.[6–9] Active granular carbon and active powdered carbon are the most commonly used due to the porous structure and high specific area compared with other adsorbents such as metallic oxides and many clays.[10–16] Other forms of using active carbon involve fiber and cloths, both for sorption and electrosorption experiments,[17–20] which decrease the environmental aggression because they minimize the carbon particles accessing to the environment. A necessary condition is that the application of a potential must increase the adsorption of the pollutant.

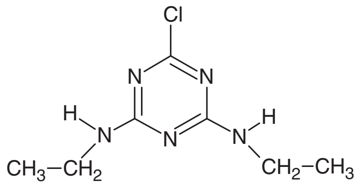

Figure 1. Chemical formula of simazine.

In this work, the electrosorption of simazine onto a glassy carbon electrode is studied to explore the possibility of improving the adsorptive removal of such contaminants from water by applying a potential.

To establish the experimental conditions for the electrosorption experiments, it is necessary to know the electrode processes involved. The electroreduction of simazine[21] takes place below pH 5. The process consists of a two-electron cleavage of a chlorine atom to give 4,6-bis(ethylamino)-1,3,5-triazine, followed by the two-electron reduction of the triazine ring of the above compound. This mechanism is common to all chlorinated s-triazines. In the case of simazine, the molecules are adsorbed on a mercury electrode forming a monolayer and with the triazine ring parallel to the electrode surface, whereas atrazine and propazine do not form a monolayer[21–26] in the same conditions. Nevertheless, measurements of capacity and ac voltammetry have revealed that *tert*-butylazine and atrazine can form monolayers on mercury[27] if both the temperature and the adsorption time are adequate.

Experimental

In all cases, Merck analytical grade reagents were used without further purification, with the exception of simazine that was from polyscience (chromatographic standard quality). The working concentration of simazine was 2×10^{-4} M, with the exception of the experiments in which the influence of this variable was studied. All potentials were measured against a Metrohm 6.0733.100 $Ag|AgCl|KCl_{sat}$ electrode.

Measurements were made on a CHI650A electrochemical workstation from IJCambria coupled to an EF-1400 stand from BAS instruments. The glassy carbon electrode was IJCambria (area: 38.5 mm^2). Measurement of differential capacity curves were made by recording impedance potential curves and obtaining the capacity from the imaginary component of the impedance. The recordings were made at very low rates, to reach the equilibrium.

0.1 M $NaClO_4$ solutions in ultra pure water obtained with a MILLIPORE-MILLI Q were used as supporting electrolytes. All the measurements were made at 25 °C. High purity nitrogen was bubbled for at least 10 min to avoid the presence of oxygen that could originate undesired redox reactions on the electrode.

Results and Discussion

Differential capacity measurements have been made as a function of the potential for the supporting electrolyte and at different simazine concentrations. As it can be seen in Figure 2, in all cases, the differential capacity decreased with respect to that obtained for the supporting electrolyte, this indicating that the double layer was altered by the presence of the herbicide, that is, that simazine is adsorbed on the glassy carbon surface.

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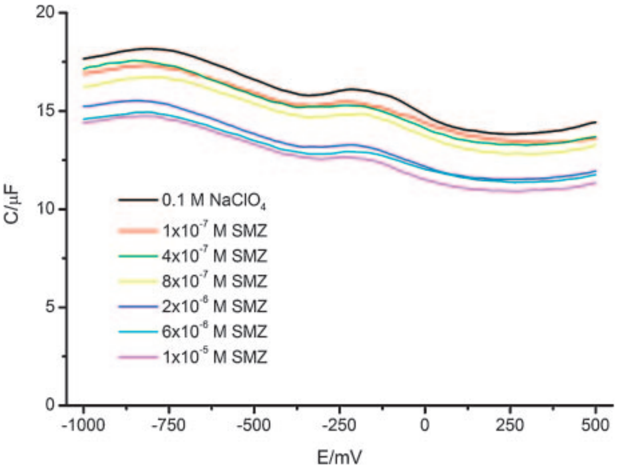

Figure 2. Differential capacity curves at 25 °C. Simazine (SMZ) concentrations are given in the legend.

The decrease in capacity was independent of the applied potential, in a very wide range of potentials, and thus the adsorption of simazine must also be potential-independent. This must be related to the fact that at the pH of the supporting electrolyte (not less than 6) the molecule of simazine is not charged.

The differential capacity curves exhibits two maximums observed at ca. −200 and −800 mV that could be attributed to the adsorption–desorption processes of the cations and anions of the supporting electrolyte replacing water molecules on the electrode surface.

At any potential, the capacity varied with the simazine concentration from a maximum value corresponding to the supporting electrolyte (absence of simazine) to a minimum value above a given simazine concentration. In this last case the maximum amount of adsorption is reached and the electrode is saturated.

The decrease in capacity can be visualized as two contributions. First, it can be assumed that the accumulation of simazine molecules on the electrode surface gradually decreases the effective area of the capacitor formed by the double layer, A, by replacing water molecules (and ions) by simazine molecules. On the other hand, the dielectric constant of the double layer formed by the electrode covered by the herbicide molecules, ε, must be different to that corresponding to the electrode in the absence of adsorbate. Both parameters, A and ε, are proportional to the differential capacity, C. Thus, by assuming that the decrease in capacity is proportional to the number of adsorbed molecules, that is, to the superficial concentration, and that the thickness of the double layer remains constant, it is easily shown that the coverage, θ, of the electrode can be expressed as:

$$\theta = \frac{C_{\max} - C}{C_{\max} - C_{\min}} \tag{1}$$

The adsorption equilibrium can be represented as:

$$\text{SMZ} + \text{electrode} \rightleftharpoons \text{SMZ–electrode} \tag{2}$$

By assuming that the coverage is related to the simazine concentration, [SMZ], through a Langmuir isotherm, after a series of trivial steps, it can be written:

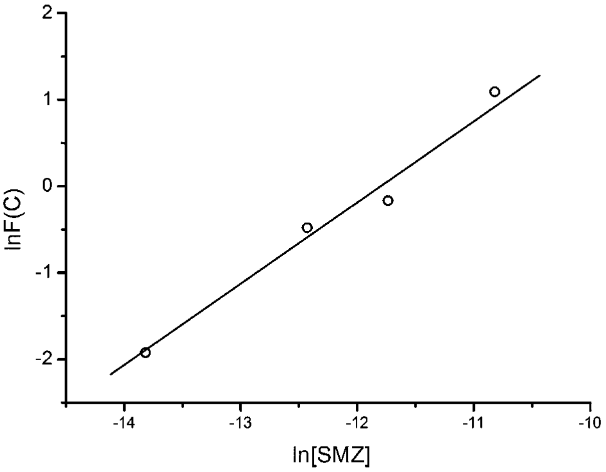

Figure 3. Plot corresponding to eq 3.

$$\ln\left(\frac{C_{\max} - C}{C - C_{\min}}\right) = \ln K_{\text{ads}} + \ln[\text{SMZ}] \tag{3}$$

where K_{ads} is the equilibrium constant of the adsorption reaction (2).

Equation 3 means that the plot of ln F(C) vs. ln[SMZ], being F(C) the argument of the logarithm in the first member of eq 3, must result in a straight line having a slope unity and an intercept ln[SMZ]. This is shown in Figure 3 from which a value of $K_{\text{ads}} = 1.3 \times 10^5$ is obtained.

Both the above value of K_{ads} and the linear plot observed in Figure 3 with slope unity are obtained irrespective of the potential at which the capacity was measured, this indicating that the approximations made above are reasonable and that simazine is adsorbed on the glassy carbon surface through a Langmuir isotherm.

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