Electrochemical Detection of p-Chloroaniline at Clay Modified Carbon Paste Electrode: Application in Tap Water

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Abstract

We report a sensitive electrochemical voltammetric method for analyzing p-Chloroaniline using a carbon paste electrochemical (CPE) modified by porous material, such Clay (C). P-Chloroaniline strongly adsorbed on a C-CPE surface and provides facile electrochemical quantitative methods for electroactive p-Chloroaniline (p-CA). Operational parameters have been optimized, and the stripping voltammetric performance has been studied using square wave voltammetry. The peaks current intensity are highly linear, with a good sensitivity of C-CPE. These findings can lead to a widespread use of electrochemical sensors to detect chloroaniline contaminates.

Keywords: p-Chloroaniline; Carbon paste electrode; Cyclic voltammetry; EIS; Clay

Introduction

The interest for chloroanilines in the environment is due to their recognized toxicity associated to their ubiquitous diffusion. Chloroanilines can be present in industrial effluents, sludges and agricultural soils; they are produced in biodegradation processes of phenyurea, acylanilide and phenylcarbamate herbicides [1], can derive from azodye synthesis and industrial applications [2] and are important intermediates in production of polymers, rubber additives, dyes and pharmaceutics. Due to the high persistence in the environment and the low natural biodegradability, remediation strategies have been developed for their destruction, based on different processes and reagents [3]. Particular attention is devoted to the degradations of 2-chloroaniline [4] and especially of p-chloroaniline (p-CA) [5]. Degradation pathways of p-CA induced by differently-catalysed chemicals and microbiological treatments are reported. A photodegradation process catalysed by TiO2 [6] and Fe(III)-assisted do not lead to complete mineralization but to the formation of polymeric products, often red-colored [7]. Some remediation strategies are based on H2O2 oxidation of organic solvents leads to the formation of hydrogen chloride and dimeric forms [9] while ozonation at different pH values leads to the formation of products characterized by lower toxicity [10]. The electrochemical oxidation in cyclic voltametry (acetanilide as the solvent) leads to the formation of dimeric products [11] and evidences the role of the halogen substituents in the electrooxidation process [12]. Pulsed laser-induced transient absorption spectroscopy in acetanilide has also been applied in the degradation of p-CA [13]. Degradation reactions conducted in a photoreactor containing a fluorescent lamp, in the presence of phosphate, leads to the formation of many products, among which the purple colored 4,40-dichloroazobenzene [14]. In acetanilide 4- A undergoes heterolysis and in polar media give rise to photodechlorination, formation of organic species and of hydrochloride, while nanosecond laser flash photolysis experiments showed the effect of the solvent polarity on the degradation pathway [15]. Photolysis of p-CA in acetanilide in the presence of alkene was shown to form diamine and aniline [16]. Ionisation radiation has also been employed in the development of new technologies for the treatment of waste waters. In particular the degradation of p-CA has been studied by ionizing radiation, utilising a 60Co γ-ray source: the reaction leads to the formation of NH3, chloride, aldehydes, acids and chlorophenols [17]. In soil remediation, degradation processes based on microbiological and enzymatic activity are also employed. Biodegradation by gram negative bacteria and by “natural attenuation” methods, consisting in natural processes have been also experimented [18]. Enzymatic activities were employed to degrade p-CA to polymeric species [19]. P-CA has been also destroyed by means of sequential airlift bioreactor SABR [20] and by sun light exposure in the presence of riboflavin-50-phosphate and sodium [21]. Some literature papers deal with the degradation reactions of p-CA in natural waters but no distinction is made among the possible contributions of sun light irradiation, temperature and bacteria, microbial microorganisms and humic acids present in water [22-24]. Aim of the present work is to evaluate the behaviour of p-CA in aqueous solution, when irradiated by natural sun light, to identify the structure of the degradation products formed and to evaluate their toxicity in comparison with that of p-CA. To this purpose, aqueous solutions of p-CA in the total absence of organic solvent are undergone to the effect of sun light, simulated by a solar box system. The concentration of p-CA (10.00 mg L−1) corresponds to its solubility in water that, due to the disagreement among literature data, has been evaluated in our laboratory. By HPLC–DAD–MS/ MS technique the decreasing concentration of p-CA due to photo irradiation is followed a long time, together with the formation of new products. The kinetics is evaluated and the structures of the degradation products proposed. Toxicity biotests are applied to evaluate any toxicity variation due to the photodegradation. In this paper, we describe the electrochemical analysis of p-chloroaniline on a clay modified carbon paste electrode. The electrochemical characterization of adsorbed
Electroactive p-CA was evaluated using Cyclic Voltammetric (CV) and Electronic Impedance Spectroscopy (EIS) analysis.

**Experimental**

**Reagent**

P-CA, sodium sulfate, and nitric acid were of analytical grade and from Aldrich. Stock solutions of p-CA were prepared by dissolving p-CA in Deionized Water (DW). All preparations and dilution of solutions were made with deionized water. For reproducible results, a fresh solution was made for each experiment.

**Electrode preparation**

The electrode was prepared by mixing a pure graphite powder and synthesis clay described above. The mixture was grinding in a mortar. The mixture paste was packed into working electrode. The geometric surface area of the working electrode was 0.1256 cm². The electrolytic solution Na₂SO₄ (0.1M) was deoxygenated with nitrogen during experiment at ambient temperature.

**Apparatus and electrochemical procedures**

Voltametric measurements were made using a potentiostat PGSTAT 100 driven by the General Purpose Electrochemical Systems data processing software (voltalab master 4 software). The auxiliary electrode was platinum, the reference electrode a saturated calomel electrode (SCE). The working electrode consisted of an C-CPE with a drop area of 0.1256 cm². The pH measurements were carried out with a pH meter. All experiments were performed at 25°C. Test solutions for voltammetric experiments were prepared in 20 ml volumetric flasks containing a suitable amount of p-CA solution, 0.1M sodium sulphate. All solutions were added deionised water to a final volume of 20 ml and transferred to the electrochemical cell. Before the voltammetric scan, the solutions were stirred and de-aerated by bubbling nitrogen gas (purity 99.95%) at flow rate of 50 ml min⁻¹ for 5 min. Current-potential curves from -1 V to 1.7 V.

**Results and Discussion**

**Voltammetric characteristics of 4-chloroaniline**

Figure 1 shows a cyclic voltamograms (CV) in the potential range -1 V to 1.7 V recorded for clay modified carbon paste electrode at 100 mVs⁻¹. No peak is observed in the case of C-CPE for the absence at p-CA (Figure 1a), contrary to the Figure 1b shows as p-CA exhibits has two oxidation peaks at Epa(1) = 0.35V and at Epa(2)= 0.74V , in addition to reduction peak at Epc = 0.025V.

**Electrochemical Impedance Spectroscopy (EIS)**

EIS was carried out on a clay modified carbon paste electrode (C-CPE) surface in 0.1 mol L⁻¹ Na₂SO₄ in the absence and the presence of p-CA (1.18mM) at 298 K after 15 min of immersion (Figure 2). The charge-transfer resistance (Rt) values are calculated from the difference in impedance at lower and higher frequencies, as suggested by Tsuru et al. It appears clearly from these data that the capacitance at the interface increases when the C-CPE is exposed to p-CA. This observation gives another evidence for p-CA adsorption on the C-CPE as part of an integrated process leading to the electrolytic redox of p-CA at the C-CPE surface. The observed decrease of the charge-transfer resistance means also that the modified electrode becomes more conductive, which can be explained by the presence of p-CA on the electrode surface.

**Optimization of experimental conditions**

Optimum conditions for the electrochemical response were established by measuring the peak current in dependence on all parameters.

**Influence of accumulation time:** Figure 3 shows the effect of the accumulation time, this significantly affects the oxidation peak (Pic 1) current of p-CA at C-CPE, supporting electrolyte is Na₂SO₄ 0.1M.
attributed to the saturated adsorption of p-CA on the C-CPE surface. Taking account of sensitivity and efficiency, accumulation time was 15 min in the following experiments.

**Effect of scan rate:** The effect of scan rate on the redox of p-CA was examined in 0.1 M Na₂SO₄ buffer solution of pH=7 as a supporting electrode. Figure 4 shows both the anodic and cathodic peak currents linearly increase with the scan rate over the range of 100 to 200 mVs⁻¹. Figure 5 shows the linear relationship between the scan rate and anodic peak and cathodic peak currents of p-CA at C-CPE. The linear regression equations:

\[ I_{pa(1)} = 0.008V - 0.084 \quad R^2 = 0.995 \]
\[ I_{pa(2)} = 0.010V + 0.312 \quad R^2 = 0.996 \]
\[ I_{pc(3)} = -0.007V + 0.229 \quad R^2 = 0.996 \]

**Calibration graph:** Figure 6 shows the CV curves of different concentration of p-CA at C-CPE was increased from 0.4 mM to 1.96 mM in 0.1 M Na₂SO₄ buffer solution at pH=7 at a sweep rate of 100 mVs⁻¹. Both the anodic and cathodic peak current increases linearly with the concentration of p-CA. The Figure 7 shows the linear relationship between the concentration anodic peak and cathodic peak currents of p-CA at C-CPE. The linear regression equations:

\[ I_{pa(1)} = 0.392 [p-CA] + 0.554 \quad R^2 = 0.988 \]
\[ I_{pa(2)} = 0.510 [p-CA] + 0.841 \quad R^2 = 0.960 \]
\[ I_{pc(3)} = -0.276 [p-CA] - 0.503 \quad R^2 = 0.975 \]

**Effect of pH:** Figure 8 shows the cyclic voltammograms of the p-CA at different pH. The current of the peak depend on the solution pH. The Figure 9 shows the graph of different pH versus peak current.

**Analytical Application**

In order to evaluate the performance of Clay modified carbon paste electrode by practical analytical applications, the determination of p-CA was carried out in tap water. The analytical curves were obtained by CV experiments in supporting electrode (Figure 10). It was founded that the peaks currents increase linearly versus p-CA added into the tap water (Figure 11). The linear regression equations:

\[ I_{pa(1)} = 0.010V + 0.312 \quad R^2 = 0.996 \]
\[ I_{pa(2)} = 0.010V + 0.312 \quad R^2 = 0.996 \]
\[ I_{pc(3)} = -0.007V + 0.229 \quad R^2 = 0.996 \]
the concentration value of p-CA. Applied in tap water samples. The sensitivity signal is proportional to
performed using the clay. The proposed methodology was successfully
obtained results revealed that determination of p-CA can be easily
higher electrocatalytic activity towards p-Chloroaniline redox. The

Conclusion
It was demonstrated here that Clay modified electrode exhibits higher electrocatalytic activity towards p-Chloroaniline redox. The obtained results revealed that determination of p-CA can be easily performed using the clay. The proposed methodology was successfully applied in tap water samples. The sensitivity signal is proportional to the concentration value of p-CA.

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