

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

Tarik El Ouafy, *Abdelilah Chtaini, Hassan Oulfajrite and Rachida Najih

Equipe of Molecular Electrochemistry and Inorganic Materials, Sultan Moulay Slimane University, Faculty of Science and Technology of Beni Mellal, Morocco

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 recognised toxicity associated to their ubiquitous diffusion. Chloroanilines can be present in industrial effluents, sludges and agricultural soils; they are produced in biodegradation processes of phenylurea, 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 pharmaceuticals. 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 catalysed by mixed metal oxides, metals and Fenton-type heterogeneous mixtures. The oxidation with hydroxyl radicals leads to the formation of aminohydroxybenzene and HCl and then to complete mineralization, the kinetics depending on the kind of the catalyst [8]. The photolytic reaction performed at 313 nm and assisted by electron transfer reactions to 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 voltammetry (acetonitrile 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 acetonitrile 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 acetonitrile 4- A undergoes heterolysis and in polar media gives 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]. Photoirradiation of p-CA in acetonitrile 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 ionising radiation, utilising a 60Co g-rays 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

***Corresponding author:** Abdelilah Chtaini, Equipe of Molecular Electrochemistry and Inorganic Materials, Sultan Moulay Slimane University, Faculty of Science and Technology of Beni Mellal, Morocco, Tel: +212523485112; Fax: +212523485201, E-mail: a.chtaini@usms.ma

Received November 15, 2014; Accepted December 12, 2014; Published January 03, 2015

Citation: Ouafy TE, Chtaini A, Oulfajrite H, Najih R (2015) Electrochemical Detection of p-Chloroaniline at Clay Modified Carbon Paste Electrode: Application in Tap Water. J Drug Metab Toxicol 5: 174. doi:10.4172/2157-7609.1000174

Copyright: © 2015 Ouafy TE, et al. This is an open-access article distributed under the terms of the Creative Commons Attribution License, which permits unrestricted use, distribution, and reproduction in any medium, provided the original author and source are credited.

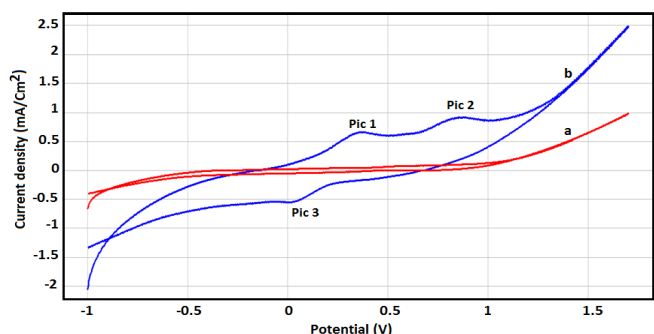


Figure 1: CV recorded for 1.18 mM p-CA at pH=7 at bare C-CPE (a) and C-CPE/p-CA(1.18mM) (b), scan rate 100 mV/s, preconcentration time (tp) = 15min.

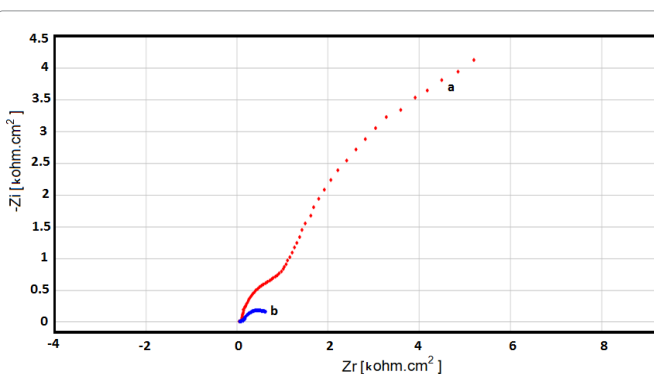


Figure 2: Impedance spectra at 0 V C-CPE (a) and (p-CA)-C-CPE (b).

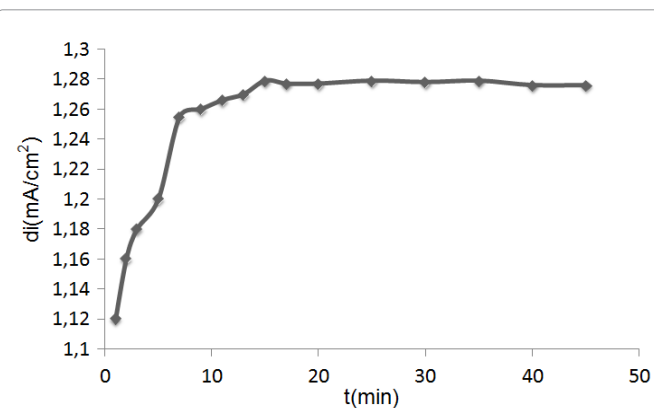


Figure 3: Effects of accumulation time on oxidation peak (1) currents of 0.4 mmol L⁻¹ p-CA (pH=7) at C-CPE, supporting electrolyte is Na₂SO₄ 0.1M.

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

Volta metric measurements were made using a potentiostat PGSTAT 100 driven by the General Purpose Electrochemical Systems data processing software (votalab 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 0.1256cm². 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 voltammograms (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.

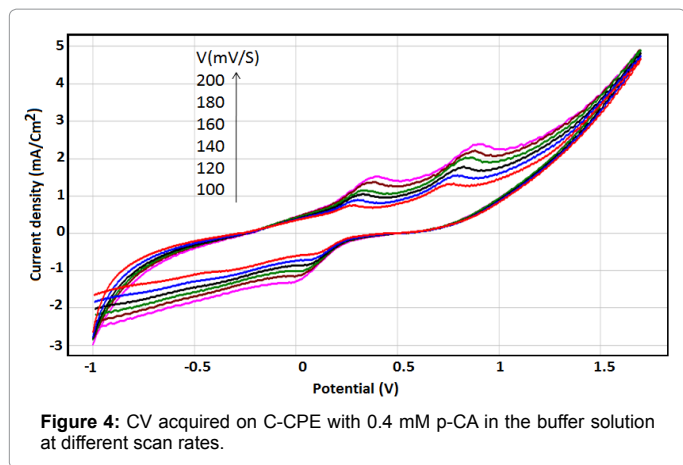
Electrochemical Impedance Spectroscopy (EIS)

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. The peak current of 0.4 mmol L⁻¹ p-CA increases greatly within the first 15min. Further increase in accumulation time does not increase the amount of p-CA at the electrode surface owing to surface saturation, and the peak current remains constant. This phenomenon is due to the cavity structure of C-CPE that improves the ability of the electrode to adsorb electroactive p-CA. Maybe this is



$$I_{pa(1)} = 0.008V - 0.084 \quad R^2 = 0.995$$

$$I_{pa(2)} = 0.010V + 0.312 \quad R^2 = 0.996$$

$$I_{pc(3)} = -0.007V + 0.229 \quad R^2 = 0.996$$

Calibration graph: Figure 6 shows the CV curves of different concentrations of p-CA at C-CPE. The concentration of p-CA 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 mV s⁻¹. Both the anodic and cathodic peak current increase linearly with the concentration of p-CA. Figure 7 shows the linear relationship between the concentration of anodic peak and cathodic peak currents of p-CA at C-CPE. The linear regression equations:

$$I_{pa(1)} = 0.392 [p-CA] + 0.554 \quad R^2 = 0.988$$

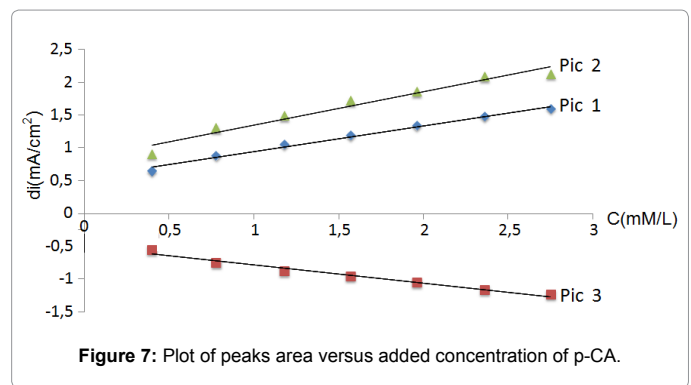
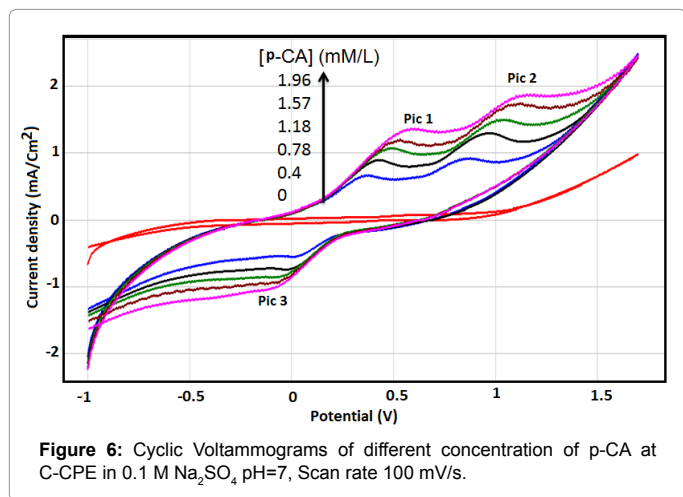
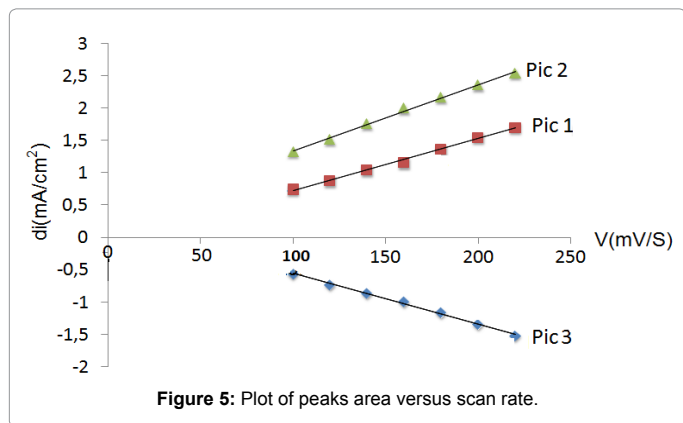
$$I_{pa(2)} = 0.510 [p-CA] + 0.841 \quad R^2 = 0.960$$

$$I_{pc(3)} = -0.276 [p-CA] - 0.503 \quad R^2 = 0.975$$

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

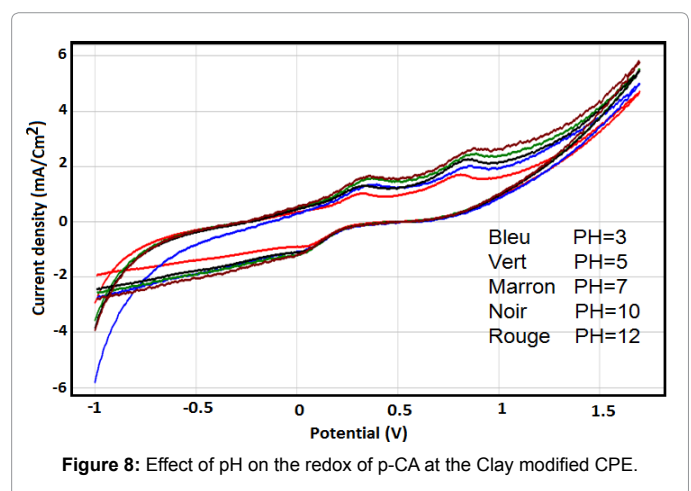
Analytical Application

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 found that the peak currents increase linearly versus p-CA added into the tap water (Figure 11). The linear regression equations:



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 the cathodic peak currents linearly increase with the scan rate over the range of 100 to 200 mV s⁻¹. Figure 5 shows the linear relationship between the scan rate anodic peak and cathodic peak currents of p-CA at C-CPE. The linear regression equations:



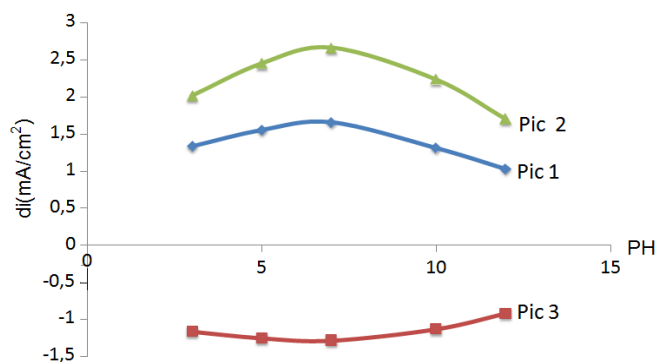


Figure 9: Plot of the relationship between solution pH and the redox peaks Current.

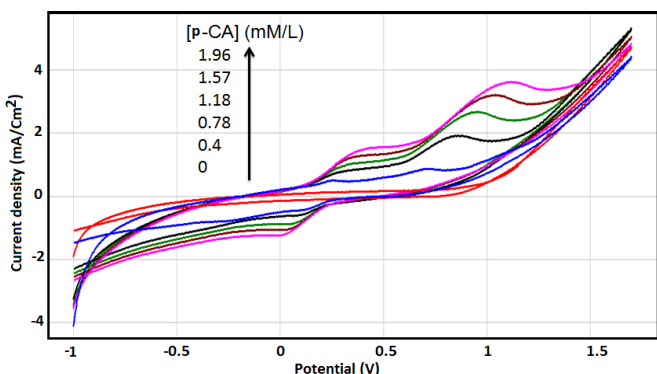


Figure 10: Cyclic Voltammograms of different concentration of p-CA at C-CPE in tap water, Scan rate 100 mV/s.

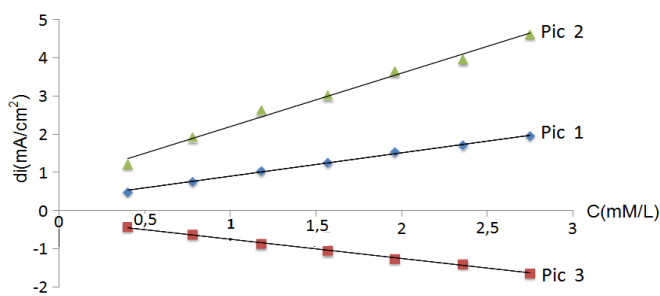


Figure 11: Plot of peaks area versus added concentration of p-CA.

$$I_{pa(1)} = 0.616 [p-CA] + 0.278 \quad R^2 = 0.997$$

$$I_{pa(2)} = 1.394 [p-CA] + 0.841 \quad R^2 = 0.989$$

$$I_{pc(3)} = -0.504 [p-CA] - 0.245 \quad R^2 = 0.995$$

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.

References

- Lacroix J C, Kanazawa K K, Diaz A, (1989) Polyaniline: A Very Fast Electrochromic Material J Electrochem Soc 136 : 1308-1313.
- Brouwer E R, Van-Iperen D J, Liska I, Lingeman H, Brinkman U A T, (1992) Int. J. Environ. Anal. Chem. 47:257– 266.
- Brillas E, Calpe J C, Casado J, (2000) Mineralization of 2,4-D by advanced electrochemical oxidation processes. Water Res. 34: 2253– 2262.
- Brillas E, Casado J, (2002) Aniline degradation by Electro-Fenton® and peroxi-coagulation processes using a flow reactor for wastewater treatment. Chemosphere 47:241–248.
- Brillas E, Mur E, Sauleda R, Sanchez L, et al. (1998) Aniline mineralization by AOP's: anodic oxidation, photocatalysis, electro-Fenton and photoelectro-Fenton processes. Appl Catal. B: Environ.16 : 31–42.
- Chiang L C, Chang J E, Wen T C, (1995) Indirect oxidation effect in electrochemical oxidation treatment of landfill leachate. Water Res. 29:671– 678.
- Cominellis C, (1994) Electrocatalysis in the electrochemical conversion/ combustion of organic pollutants for waste water treatment Electrochim. Acta 39 : 1857–1862.
- Cominellis C, Nerini A, (1995) Anodic oxidation of phenol in the presence of NaCl for wastewater treatment. J. Appl. Electrochem. 25 : 23–28.
- Do J S, Chen P, (1994) In situ oxidative degradation of formaldehyde with hydrogen peroxide electrogenerated on the modified graphites. J. Appl. Electrochem. 24:936–942.
- Grob R L, Cao K B, (1990) High performance liquid chromatographic study of the recovery of aromatic amine and nitro compounds from soil J. Environ. Sci. Health. 25:117–136.
- Panizza M, Bocca C, Cerisola G, (2000) Electrochemical treatment of wastewater containing polyaromatic organic pollutants. Water Res. 34:2601– 2605.
- Qiang Z, Chang J H, Huang C P, (2002) Electrochemical generation of hydrogen peroxide from dissolved oxygen in acidic solutions. Water Res. 36:85–94.
- Kadar M, Nagy Z, Karancsi T, Farsang G, (2001) The electrochemical oxidation of 4-chloroaniline, 2,4-dichloroaniline and 2,4,6-trichloroaniline in acetonitrile solution. Electrochimica Acta 46:1297–1306.
- Loos R, Hanke G, Eisenreich S J, (2003) Multi-component analysis of polar water pollutants using sequential solid-phase extraction followed by LC-ESI-MS. Journal of Environmental Monitoring 5 :384–394.
- David B, Lhote M, Faure V, Boule P, (1998) Ultrasonic and photochemical degradation of chlorpropham and 3-chloroaniline in aqueous solution. Water Research 32:2451–2461.
- Coppo P, Fagnoni M, Albini A, (2001) Photochemical conversion of 4-chloroaniline into 4-alkylanilines. Tetrahedron Letters 42:4271–4273.
- Sayyah S M, Abd El-Rehim S S, El-Deeb M, (2003) Electropolymerization of pyrrole and characterization of the obtained polymer films. J Appl Polym Sci 90:1783-1792.
- Bahgat A A, Sayyah S M, Abd El- Salam H M, (2003) Study of ferroelectricity in polyaniline. Int J Polym Mater 52:499-515.
- Kobayashi N, Yamada K, Hirohashi R, (1992) Effect of anion species on electrochemical behavior of poly(aniline)s electropolymerized in dichloroethane solution. Electrochim Acta 37:2101-2102.
- Brusic V, Angelopoulos M, Grahmi T, (1997) Use of Polyaniline and Its Derivatives in Corrosion Protection of Copper and Silver. J Electrochem Soc 144 :436-442.
- Kobayashi T, Yoneyama H, Tamoura H, (1984) Polyaniline film-coated electrodes as electrochromic display devices. J Electroanal Chem 161:419-423.
- Zeyer J, Kearney PC, (1982) Microbial degradation of para-chloroaniline as sole carbon and nitrogen source. Biochem Physiol. 17 :215-223.
- A Malinauskas, R Garjonyte, R Mazeikiene, I Jureviciute, (2004) Talanta 64 :121.
- Zoteman B C J, Harmsen K, Linders J B H J, Morra C F H, (1980) Persistent organic pollutants in river water and ground water of the Netherlands. Chemosphere 9: 231-249.