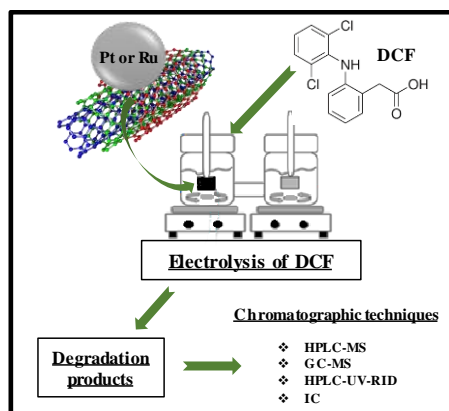


Electrochemical degradation of Diclofenac on catalysts based on CNT and M/CNT modified electrodes

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Diclofenac (DCF) - a nonsteroidal anti-inflammatory drug - is one of the most frequently detected pharmaceutical compounds in the aquatic environment. Because of its negative effects on public health and environment, this emerging pollutant monitoring and removal from wastewater are of high importance. Electrochemical oxidation has attracted growing interest in the last years, due to its versatility, high efficiency and environment compatibility. Electrochemical oxidation of DCF has been studied using multiwalled carbon nanotubes (CNT) and monometallic catalysts based on carbon nanotubes (M/CNT), at different pH media. The electroreactivity of DCF on modified electrodes and the kinetic parameters of the redox reactions were determined using cyclic voltammetry. Electrodegradation of DCF in aqueous medium was carried out using long-term electrolyses. The products of these electrolyses were identified and quantified by HPLC-MS, GC-MS, HPLC-UV-RID and IC.

Introduction

In the recent years, the intensive use of pharmaceutical products resulting from the growing populations and the interest to promote human health and personal care [1-3], have led to the accumulation of these products into the environment as emerging contaminants. These organic pollutants have been found in many types of water bodies such as: wastewater treatment plant influents and effluents, hospital and pharmaceutical manufacturer wastewater and industrial wastewater [4]. Diclofenac (DCF) (Figure 1) is a synthetic non-steroidal anti-inflammatory drug and among all the anti-inflammatories is the most frequently prescribed for the treatment and protection of different diseases like inflammation, arthritis and other rheumatic diseases [5]. It is considered a persistent toxic pollutant and one of the most relevant compounds in terms of ecotoxicity. Among several technologies studied for the removal of pharmaceutical products in water, electrochemical oxidation has attracted growing interest, by providing efficient conversion in mild conditions, replacing harmful redox agent by electricity [6]. The use of multiwalled carbon nanotubes (CNT) as a heterogeneous catalyst or support material, has attracted growing attention for environmental applications thanks to their peculiar characteristics, like high active surface area and electrical conductivity [7-8].

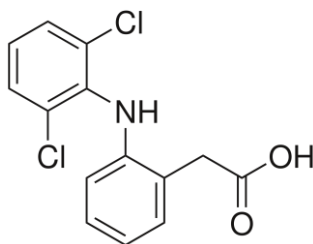


Figure 1. Molecular structure of Diclofenac.

Objectives

Study of electroreactivity and determination of kinetic parameters of DCF using cyclic voltammetry. Electrocatalytic

oxidation of DCF in aqueous medium on CNT and M/CNT modified electrodes. Identification/quantification of the reaction products by chromatographic methods.

Methods

Preparation of CNT and M/CNT modified electrodes. The preparation of the modified electrodes was performed by a previously established procedure described in our published works [7,9] from CNT or M/CNT suspensions in Nafion/water solution. After deposition of the suspension on Carbon Toray (CT, 4 cm²) paper, the electrocatalytic material must dried at room temperature during 24 h. The amounts of Pt or Ru used for the carbon nanotubes supported metal catalysts were always 1 wt%. The cleanness of the surface was tested prior to each experiment by recording voltammograms in the supporting electrolyte medium alone.

Electrochemical Setup. All the supporting electrolytes were prepared using ultrapure water with analytical grade reagents. The electrochemical studies were performed in a thermostated two-compartment glass cell separated by ion exchange membranes (Nafion 117). The reference and counter electrodes were a saturated calomel electrode and platinum foil (99.95%) respectively. The electrochemical instrumentation consisted of a potentiostat/galvanostat from Amel Instruments coupled to a computer by an AD/DA converter. The Labview software (National Instruments) and a PCI-MIO-16E-4 I/O module were used for generating and applying the potential program as well as acquiring data, such as current intensities.

Results

Voltammetric studies of Diclofenac. The stability of electrocatalyst based on multiwalled carbon nanotubes (CNT and M/CNT) was confirmed by cyclic voltammetric studies. The electroreactivity of DCF, in the concentration range of 1.0 and 2.0 mM at CNT and M/CNT modified electrodes, in carbonate buffer 0.10 M and NaOH 0.50 M media were studied by cyclic voltammetry. Cyclic voltammograms of Pt/CNT and Ru/CNT modified electrodes (in NaOH medium) in presence of DCF are

given in Figure 2. In the presence of DCF in carbonate buffer and NaOH media, several oxidation/reduction processes were noticed. These results confirm the interaction between DCF and the CNT or M/CNT surface, necessary for further oxidation. High anodic and cathodic current densities were noticed in presence of DCF in both studied media.

Electrolysis of Diclofenac. The electrolysis of DCF (1.0 and 2.0 mM) in carbonate buffer 0.10 M and NaOH 0.50 M media was carried out using CNT, Pt/CNT and Ru/CNT modified electrodes with an applied potential of 1.5 and 2.0 V vs SCE. After 7 h of electrolysis, the decrease of the initial DCF concentration in NaOH medium reaches more than 50% for all used modified electrodes. In carbonate buffer medium, the conversion rate for 8 h of electrolysis reach approximately 90% for Ru/CNT electrode and almost 50% for CNT and Pt/CNT electrodes. A decrease of the conversion rate was noticed due to the decrease of the reaction rate.

Conclusion

The degradation of DCF in aqueous media was carried out by electrochemical methods using CNT and M/CNT modified electrodes. The results show that the modified electrodes were stable in the experimental conditions and it was efficient for the degradation of DCF. Degradation products of DCF such as low molecular weight carboxylic acids and mineralization products was identify by chromatographic techniques.

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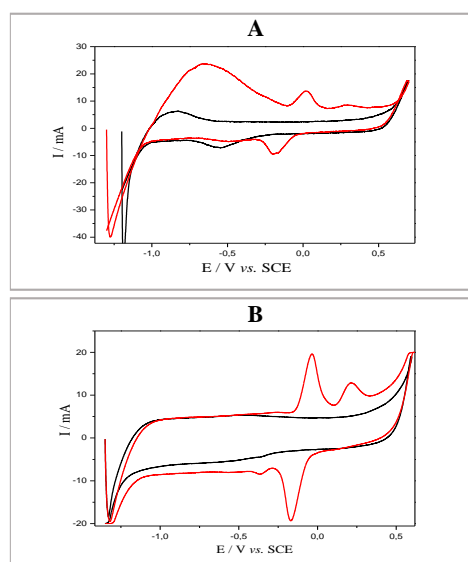


Figure 2. Cyclic voltammograms of A) Pt/CNT and B) Ru/CNT in 0.50 M NaOH medium (black) in absence and (colour) in presence of 1.0 mM DCF. Scan rate of 50 mV/s.