Applied Clay Science 123 (2016) 99–108

Contents lists available at ScienceDirect

Applied Clay Science

journal homepage: www.elsevier.com/locate/clay

Research paper

Electrocatalytical effect of montmorillonite to oxidizing ibuprofen: Analytical application in river water and commercial tablets

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ARTICLE INFO

Article history:
Received 6 June 2015
Received in revised form 12 January 2016
Accepted 15 January 2016
Available online 4 February 2016

Keywords:
Montmorillonite
Differential pulse voltammetry
Ibuprofen
Electrochemical impedance spectroscopy

ABSTRACT

The electrochemical oxidation of ibuprofen was investigated at a montmorillonite-doped carbon paste electrode (Mt–CPE). A well-defined oxidation peak was observed at around 1.02 V/AgCl in phosphate buffer (pH 8). The experimental condition was optimized by varying chemical and electrochemical parameters. The oxidation peak current is linear to the ibuprofen concentration in the ranges 1.0×10^{-3}–1.0×10^{-6} mol L^{-1} and $1.0 \times 10^{-6} - 1.0 \times 10^{-7}$ mol L^{-1} with a detection limit of 6.80×10^{-8} mol L^{-1}. The precision ($n = 8$) assessed as relative standard deviation (R.S.D.) were 1.24% for 1.0×10^{-6} mol L^{-1} and 1.07% for 4.0×10^{-5} mol L^{-1} respectively. Possible interferences were tested and evaluated in 1.0×10^{-5} mol L^{-1} ibuprofen in the presences of common organic and inorganic interfering agents. Based on its high sensitivity and good selectivity, the Mt–CPE was successfully applied to determine ibuprofen in river water and commercial tablets. The satisfactory obtained results confirm the applicability of this sensor in practical analysis.

1. Introduction

Ibuprofen, 2-(4-isobutylphenyl) propionic acid, is a non-steroidal anti-inflammatory drug (NSAID). Its use is often limited by frequent side effects affecting the gastrointestinal tract (Wolfe et al., 1999), the central nervous system (Gennaro, 1990) and ulcerogenic effect (Arida et al., 1999). Ibuprofen (IBu), is one of the most common drugs found in hospital wastewaters (Verlicchi et al., 2010). In fact, it has been detected in the effluents from several sewage-treatment plants at concentrations up to 24.6 μg L^{-1} (Miège et al., 2008) and possibly presenting a potential hazard for human health (Kot-Wasik et al., 2007). For this, its detection in environment becomes necessary.

Several methods have been reported in the literature to determining IBu e.g., spectrophotometry (Hassan, 2008; Khoshayand et al., 2008), HPLC (Whelan et al., 2002), GC–MS (Ternes, 2001), infrared spectrometry (Dreassi et al., 1995), supercritical fluid chromatography (Jagota and Stewart, 1992) and Electrophoresis (Hamoudová and Pospíšilová, 2006). Most of these methods are costly and require expertise. Electrochemical methods are also widely used as analytical technique of ibuprofen. The electroanalytical reported in literature have employed selective membrane electrode or silver functionalized carbon nanofiber composite electrodes and Ag-Doped Zeolite-Expanded Graphite Composite Electrode using cyclic voltammetry and differential pulse voltammetry (Stefan-van Staden et al., 2009; Motoc et al., 2011; Manea et al., 2012). Several processes for the electrooxidation of ibuprofen have already been reported (Lima et al., 2013; Loaiza-Ambuludi et al., 2013; Motoc et al., 2013; Thokchom et al., 2015; Tran et al., 2015).

Montmorillonite has been widely used as an adsorbent for several compounds. Its properties such as high surface area (Hu and Luo, 2010), low cost (Gil et al., 2011), eco-friendly, non-toxicity and high adsorption tendency (Karaoglu et al., 2010) make it a good adsorbent, especially for organic pollutants (Almeida et al., 2009; Ely et al., 2009; Zhou et al., 2010; Su et al., 2011). Montmorillonite has been successfully used in electro-analytical chemistry as a modifier of carbon electrodes for assay of different organic (Manisankar et al., 2005, 2006; Muralidharan et al., 2006; Beltagi, 2009) and inorganic (Navratilova and Kula, 2000; Kula and Navra´tilova´, 2001; Huang et al., 2002; Ji and Hu, 2004; Sun et al., 2007) species.

This work investigates the use of montmorillonite as modifier of carbon electrode for catalyzing the oxidation of ibuprofen in aqueous

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http://dx.doi.org/10.1016/j.clay.2016.01.013
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solution. This clay is one of the very promising modifiers, because of its high chemical stability and their high oxides content which catalyzes the oxidation of ibuprofen.

2. Experimental

2.1. Instrument and reagent

All chemicals used were of analytical grade. Sodium phosphate dibasic, monopotassium phosphate, sodium hydroxide and chloridric acid, chromium(II) acetate, sodium chloride, sodium sulfate, dimer monohydrate, Sodium ascorbate, uric sodium acid salt, dopamine hydrochloride and nitrate of copper(II), nickel (II), lead(II), cobalt(II), calcium(II), magnesium(II), lithium(I), ammonium(I), sodium(I), and potassium(I) were obtained from Fluka, Scharlau, Janssen Chimica, Riedel de Haen, Chemical Companies Merk and Sigma-Aldrich and were used as received. The analyzed pharmaceutical preparations were tablets of Rhumix (Galencia, Morocco), Ibumac (Ipharma, Morocco), No-Del fn (Sanofi-aventis, Morocco) and Nurodol (Synthemedic, Morocco). Ibuprofen ((IBu) drug (was provided by Birds Chemotec Karachi, Pakistan)) was dissolved in phosphate buffer (pH 8) to prepare stock solutions of 1.0×10^{-2} mol L^{-1}. Then the working standard solutions were prepared by successive dilution by phosphate buffer. Carbon paste was supplied from Carbone, Lorraine, ref. 9900, France. The sodium montmorillonite (Cloisite-Na^+) with a cation exchange capacity of 92.6 cmol/kg, was obtained from Southern Clay Products, Inc. The composition of sodium montmorillonite particles as follows (wt.%): Na_2O 7.223, MgO 4.133, Al_2O_3 19.986, SiO_2 56.851, P_2O_5 0.022, K_2O 0.442, CaO 0.698, MnO 0.053, TiO 0.368, and Fe_2O_3 7.936. It has two tetrahedral sheets sandwiching a central octahedral sheet with a basal spacing of 12.1 Å.

Cyclic voltammetry, chronoamperometry and differential pulse voltammetry were carried out with a voltalab (model PST 050, Radiometer Analytical Inc.) driven by the general purpose electrochemical systems data processing software (voltalab master 4 software). The electrochemical cell was configured to work with three electrodes; using Mt–CPE as the working, platinum plate for counter and a system Ag/AgCl (3.00 mol L^{-1} KCl) as reference electrodes. Electrochemical impedance spectroscopy analyses were performed with a PGZ 100 potentiostat (Radiometer Inc.). The pH-meter (Radiometer, SENSIONTM, PH31 and Spain) was used for adjusting pH values.

Scanning electron microscopy (SEM) measurements were performed on an FEI Nova SEM (Philips) instrument with an AMETEK energy dispersive X-ray (EDX) system (Nova 200) operated at an accelerating voltage of 30 kV.

2.2. Preparation of Mt–CPE and measurements procedure

An amount of graphite powder and the montmorillonite-Na clay were mixed uniformly by milling in a small agate mortar. Various modified carbon pastes containing different mass percentages of Na–Mt clay (0.0, 1, 2 and 5% *w*/w) were similarly prepared. Portions of the resulting composite material were then packed into a home built electrode assembly consisting of the cavity (geometric area 0.1256 cm^2) of PTFE cylindrical tube electrode of a plastic pipette tip. Electrical contact was established with a bar of carbon.

Twenty-milliliter test solutions of supporting electrolyte were delivered into the voltammetric cell. No electrochemical activation procedure and no deaeration before voltammetric determination were needed. After recording the differential pulse voltammogram of the blank, aliquots of ibuprofen were added and the corresponding signals were recorded. A cell containing 1.0×10^{-3} mol L^{-1} of ibuprofen was utilized to investigate the influence of all chemical and electrochemical parameters. After 90 s of deposition time, a voltammetric scan was performed without agitation. Initially, the scan parameters were amplitude 80 mV and frequency 20 Hz. The detection limit was estimated as seven repetition of the blank signal. Bulk stripping voltammetric signals (without blank subtraction) were used for peak current measurement.

2.3. HPLC analysis of ibuprofen

HPLC chromatographic separation was investigated using a LaChrom® instrument Merck-Hitachi (Barcelona, Spain) chromatographic system equipped with a quaternary L-7100 pump a L-7455 diode array detection system and a L-7485 programmable fluorescence detector, and a Rheodyne manual injection valve Model 7725i with 20-μL loop volume. A monolithic silica type HPLC column Chromolith® Performance RP-18e (100–4.6 mm i.d.) (VWR, Darmstadt, Germany) preceded by a guard column Chromolith® RP-18e (5–4.6 mm i.d.) (VWR, Darmstadt, Germany) was used for the separation. The collected Chromatograms with an interface module D-7000 and a personal computer were investigated by a HPLC-System-Manager HSM D-7000 (Merck-Hitachi). The HPLC was performed at a flow rate of 2.5 mL min^{-1}. 5 min was waited between injections, using a mobile that is phase constituted of 0.1% formic acid and methanol, the programmed linear elution gradient was from 40% to 70% methanol in 10 min and identification of IBu was made at 225.0 nm.

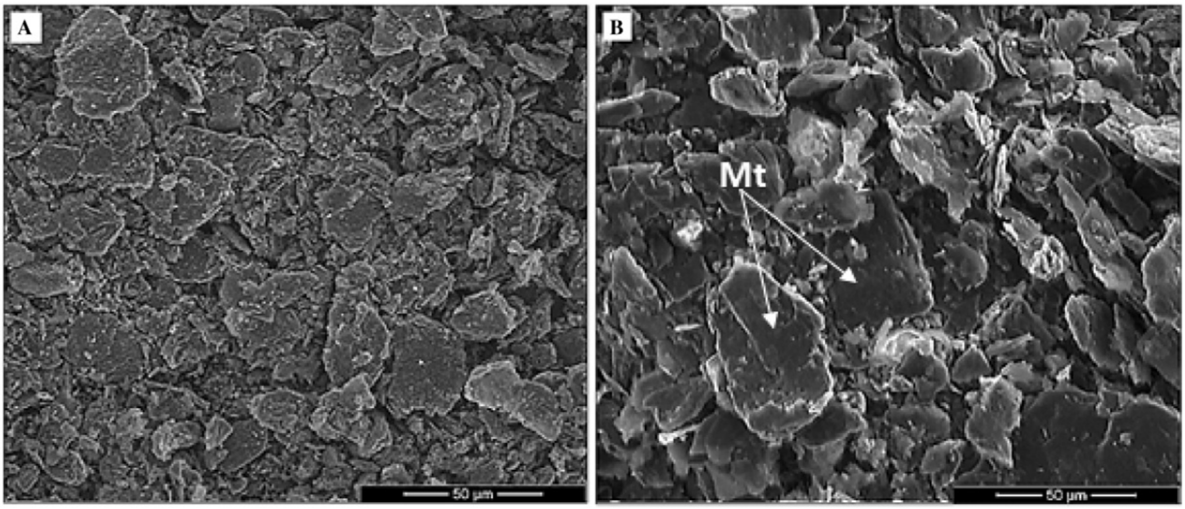

Fig. 1. SEM images of CP and sodium montmorillonite-modified carbon paste: (a) CP, (b) Mt–CP, 5% of Mt.