

Physical-chemical and electrochemical characterization of Fe-exchanged natural zeolite applied for obtaining of hydrogen peroxide amperometric sensors



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ABSTRACT

This work demonstrates that a Fe-exchanged zeolitic volcanic tuff from Cepari (Fe/CV) (Bistrita-Nasaud County, Romania) is suitable for the amperometric detection of H₂O₂, using new modified carbon paste electrodes based on this material (Fe/CV-CPEs). The physical-chemical characterization of natural (CV) and modified (Fe/CV) forms was realized using chemical analysis, optical microscopy, scanning electron microscopy (SEM), X-ray diffraction spectroscopy (XRD), energy dispersive X-ray spectroscopy (EDX) and Fourier transformed infrared (FTIR) spectroscopy. The resulting electrodes (Fe/CV-CPEs) were investigated using cyclic voltammetry and chronoamperometry measurements. The new electrodes showed good electrocatalytic activity toward H₂O₂ reduction. The calibration curve for H₂O₂ determination was linear up to 0.1 mM, with a detection limit (signal to noise ratio of 3) of 20 μM.

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1. Introduction

In the last decades, volcanic tuffs were the subject of some research, due to their zeolite content and properties exhibited by these minerals (cation exchange and adsorption-desorption) (Misaelides, 2011; Calvo et al., 2009; Han et al., 2010; Malekian et al., 2011; Motsi et al., 2009). Zeolitic volcanic tuffs of Badenian-Sarmatian age are present in large amounts in Romania, especially in Transylvanian Depression, partly exploited for several purposes, mainly as construction materials. Given the large reserves of zeolite volcanic tuffs deposits, their high zeolite content (over 50%) and relatively low price we consider that these raw materials can be widely used in various fields.

Due to their specific three-dimensional crystalline framework, which contains different size channels filled with water and exchangeable cations, zeolites possess some specific properties: adsorption-desorption capacity, ion exchange capacity, and catalytic properties (Maicananu et al., 2008a). One of these specific properties, ionic exchange capacity, allows the modification of zeolites (natural or synthetic) by introducing in their structure of metal

ions such as iron. Zeolite modification with iron broadens the range of their applications. For example, iron exchanged clinoptilolite was used for removal of Cu²⁺ (Doula and Dimirkou, 2008), Zn²⁺ and Mn²⁺ (Dimirkou and Doula, 2008) from drinking water or arsenic from aqueous solutions (Davila-Jimenez et al., 2008). Other applications of iron modified zeolites include removal of organics (e.g. dyes, phenol) from wastewaters using catalytic wet air oxidation or advanced oxidation (heterogeneous Fenton) (Maicananu et al., 2008a; Neamtu et al., 2004; Calleja et al., 2005; Kasiri et al., 2008; Parkhomchuk (Kuznetsova) et al., 2008; Maicananu et al., 2008b; Gonzalez-Olmos et al., 2009). Fe-zeolite catalyst was used in the selective oxidation of benzene to phenol in liquid-phase in a flow-through ultrafiltration membrane reactor (Molinari et al., 2010). Iron exchanged zeolites proved also to have high activity in selective catalytic reduction (SCR) of NO and N₂O with hydrocarbons or ammonia, and direct catalytic N₂O decomposition (Ates, 2007).

Determination of H₂O₂ is of great importance for modern medicine, environmental pollution control and various branches of industry. The Fenton-like processes have been used as a powerful source of hydroxyl radicals from H₂O₂ in the presence of transitional metal cations, in mild reaction conditions. Fenton's reagent (Fe²⁺/Fe³⁺/H₂O₂) has been one of the most common homogeneous systems proposed for the treatment of wastewaters (Neamtu et al., 2004; Calleja et al., 2005; Kasiri et al., 2008; Parkhomchuk

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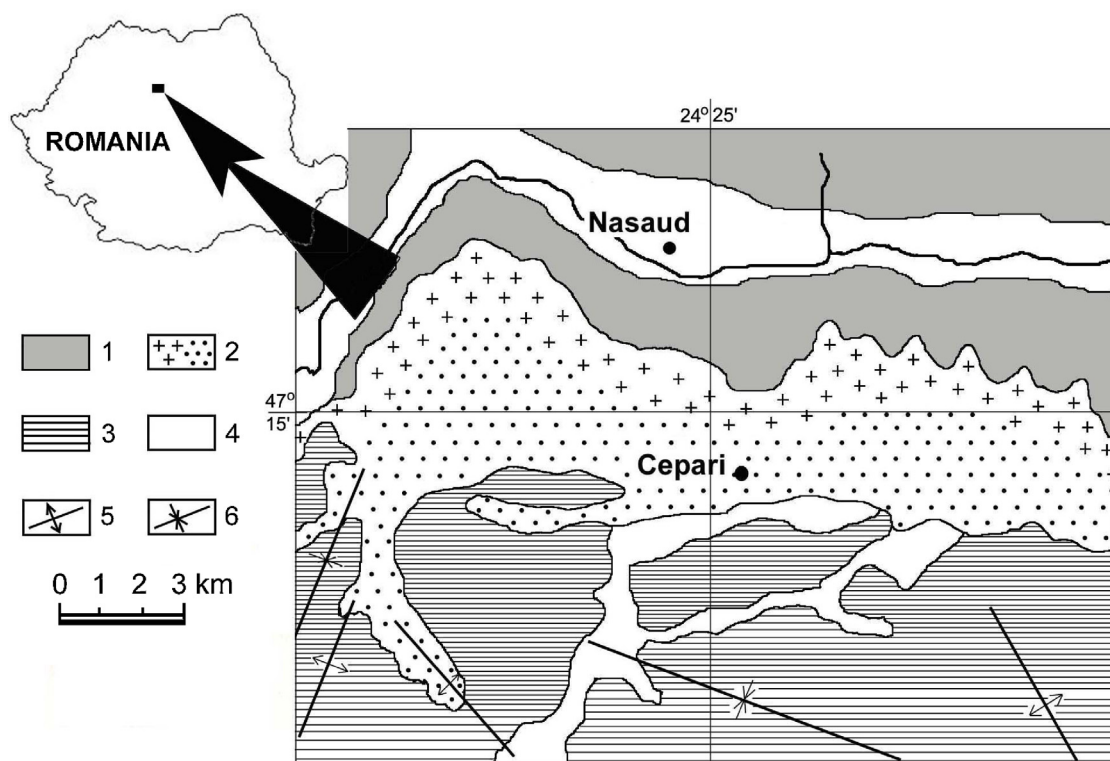
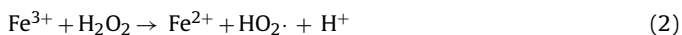


Fig. 1. Geological sketch of Cepari area (modified after [Marinescu and Peltz, 1967](#)). (1) Eggenburgian-Upper Ottnangian (conglomerates, sandstones, sands, marls); (2) Badenian inf. (volcanic tuff); (3) Sarmatian (marls, clay, sands); (4) Quaternary (aluvial deposits); (5) Anticline axis; (6) Syncline axis.

Table 1
Chemical composition of the zeolitic volcanic tuff sample (bulk) in natural form.

Sample	SiO ₂ , %	TiO ₂ , %	Al ₂ O ₃ , %	Fe ₂ O ₃ , %	CaO, %	MgO, %	Na ₂ O, %	K ₂ O, %	L.O.I.1000 °C	Total
CV	62.99	0.35	14.12	1.94	5.93	0.31	1.28	1.16	11.92	100

(Kuznetsova) et al., 2008; Maicaneanu et al., 2008b; Gonzalez-Olmos et al., 2009). Common homogeneous Fenton processes involve the application of ferrous or ferric salts and H₂O₂ in order to produce hydroxyl radical, as shown in the following equations (Centi et al., 2000):



Zeolite modified electrodes (ZMEs) have found numerous applications in various fields, most of those developed in electro-analytical chemistry were based on zeolite modified carbon paste electrodes (ZMCPEs) (Walcarius, 1996, 1999, 2008).

Continuing our previous work in the field of CPEs based on zeolites (Gligor et al., 2007, 2009, 2010a), especially Fe-enriched natural zeolite (Gligor et al., 2010a), in this work we proposed to explore the possibility of using a Fe-exchanged zeolitic volcanic tuff from Cepari (Fe/CV) (Bistrita-Nasaud County, Romania) containing 65–68% clinoptilolite, for the preparation of an amperometric sensor for H₂O₂ detection. Thus, the electrochemical reduction of H₂O₂ was investigated using an electrode based on Fe-exchanged Romanian natural zeolite, incorporated in carbon paste conductive matrix (Fe/CV-CPE). The mineralogy and properties of the zeolitic volcanic tuff, in natural (CV) and modified (Fe/CV) forms, were also determined using chemical analysis, optical microscopy, scanning electron microscopy (SEM), X-ray diffraction spectroscopy (XRD), BET analysis and Fourier transformed infrared spectroscopy (FTIR). The electrochemical behavior of Fe/CV-CPE has been

characterized by using cyclic voltammetry and the electrocatalytic activity toward H₂O₂ reduction with chronoamperometry.

Therefore, the overall goal of this work was to prove that a “simple” local mineral could be valorized in a superior way as an electrode material.

2. Materials and methods

2.1. Materials

The zeolitic tuff sample was collected from a natural outcrop in Cepari area (Bistrita-Nasaud County, Romania). In order to prepare the electrode material, the zeolitic tuff sample was brought to a grain size of 0.2–0.6 mm by grinding and size separation, then washed with distilled water and dried at 105 °C. This physical treatment was followed by an acidic treatment (1 M HCl) and a NaCl treatment (1 M) as described in our previous work (Bedelean et al., 2010). The zeolitic tuff sample was contacted with an iron synthetic aqueous solution in a column, in continuous down flow mode (flooded, $d_i = 15$ mm). The ionic exchange process took place, Eq. (3), when iron solution (10 mg/l) was passed through a fixed bed consisting of 5 g zeolitic volcanic tuff with a flow rate of 3.3 ml/min as described in our previous publication (Maicaneanu et al., 2008a). Determination of iron ions (as total iron) in solution was realized using a Jenway 6305 spectrophotometer (orthophenanthroline, $\lambda = 510$ nm), (according to Romanian and European standards STAS 8634-70, SR ISO 6332-96).



FeSO₄·7H₂O (melanterite in mineral terms) was obtained from Reactivul (Bucharest, Romania), graphite powder and paraffin oil from Fluka (Buchs, Switzerland) and H₂O₂, K₂HPO₄·2H₂O and KH₂PO₄·H₂O from Merck (Darmstadt, Germany). All reagents were of analytical grade and used as received. The supporting electrolyte was 0.1 M phosphate buffer solution, obtained by mixing appropriate solutions of K₂HPO₄·2H₂O and KH₂PO₄·H₂O.

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