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Properties and Utilization of Natural Zeolites

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Edited by Wojciech Franus, Jarosław Madej

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Preface

It is a great honor to welcome you to the 10th International Conference on the Occurrence, Properties and Utilization of Natural zeolites – Zeolite 2018 that was organized under the auspices of the International Natural Zeolite Association – INZA and the following hosting institutions: Lublin University of Technology (Lublin, Poland), AGH University of Science and Technology (Kraków, Poland) and the Mineral and Energy Economy Research Institute, Polish Academy of Science (Kraków, Poland).

The primary focus of the INZA is to promote and encourage interest in natural zeolite materials throughout the scientific and technical community. INZA was officially organized in 2005 as a formal outgrowth from the International Committee on Natural Zeolites (ICNZ). Through the efforts of Dr. Frederick A. Mumpton, the ICNZ began as an *ad hoc* organization during the Zeolite '76 conference, the first International Conference on the Occurrence, Properties and Utilization of Natural Zeolites, held in Tucson, Arizona (USA) in 1976. The organization is open to any person interested in any aspect of natural zeolites.

In keeping with the primary purpose of the ICNZ and INZA, the organization encourages the advancement of natural zeolite science and technology, promotes research and scientific interest in natural zeolites and increases the diffusion of knowledge of natural zeolite science and technology.

Zeolite 2018 is the latest in a series of conferences organized under auspices of the ICNZ and INZA. Following the initial Zeolite '76 conference, subsequent conferences were held in Budapest, Hungary (Zeolite '85); Havana, Cuba (Zeolite '91); Boise, Idaho, USA (Zeolite '93); Ischia (Naples), Italy (Zeolite '97); Thessaloniki, Greece (Zeolite '02); Socorro, New Mexico, USA (Zeolite '06); Sofia, Bulgaria (Zeolite 2010) and Belgrade, Serbia (Zeolite 2014).

Every four years, researchers and students interested in natural zeolites present their results on all aspects of research on natural zeolites. It is a privilege to have participants from 40 countries around the world attending the Zeolite 2018 conference.

We wish you a pleasant stay in Krakow and hope that you will have a very successful and beneficial conference.

Aleksandra Daković, INZA President
Wojciech Franus
Magdalena Wdowin
Tomasz Bajda

Cracow, Poland
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Ibuprofen adsorption on a clinoptilolitic zeolitic tuff modified with cationic surfactant: direct method of composites preparation

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Introduction

Interactions of cationic surfactants with natural zeolites have been extensively studied since they proved to be excellent adsorbents for various drug molecules contributing their functionality as drug carriers. Investigations related to nonsteroidal anti-inflammatory drugs (NSAIDs) are particularly interesting, since they are one of the most frequently used medications (Krajišnik et al., 2017). Sorption and release of ibuprofen (IBU) (a representative of NSAIDs; practically insoluble in water) by modified clinoptilolitic zeolitic tuff, in two step preparation procedure, was previously investigated (Krajišnik et al., 2015). According to this procedure, in the first step surfactant modified zeolites were prepared and then in the second step drug-modified zeolite composites were obtained by adsorption of IBU on modified zeolites.

The aim of this work was to carry out a study of direct method of drug-modified zeolite composites preparation and the influence of cationic surfactant:drug molar ratio on adsorption properties of clinoptilolitic zeolitic tuff.

Experimental Methods

In experiments, the initial clinoptilolitic zeolitic tuff from Zlatokop deposit (Serbia) (Krajišnik et al., 2011) was treated with solutions comprising surfactant–hexadecyltrimethylammonium bromide (HB) in amounts equivalent to 100, 200 and 300% of its external cation exchange capacity (ECEC). In surfactant solutions (prepared at 40 °C) IBU was solubilized at the same drug:surfactant molar ratio. The 10% aqueous suspensions were mixed on a high-speed disperser at 6000 rpm for 10 min. After mixing, the suspensions were filtered and the filtrates were collected for the drug assay by HPLC analysis. The obtained drug/modified zeolites composites, prepared by direct method, were denoted as ZHB-10 IBU/DM, ZHB-20 IBU/DM and ZHB-30 IBU/DM.

The average droplet size (Z-ave) and polydispersity index (PdI) in the starting drug/surfactant solutions were determined by photon correlation spectroscopy (PCS) using a ZetasizerNano ZS90 (Malvern Instruments, Malvern, UK). The zeta potentials of the starting zeolite and the prepared samples (drug/modified zeolites composites) were performed on the same apparatus. FT-IR spectra of the prepared samples and their individual components were recorded using a Nicolet iS50 spectrometer (Thermo Scientific, USA) in the range of 4000–400 cm^{-1} at a resolution of 2 cm^{-1}.

Results and Discussion

In the starting drug/surfactant solutions, both IBU and HB were used at equimolar concentrations of 0.011 M, 0.022 M and 0.033 M for ZHB-10 IBU/DM, ZHB-20 IBU/DM and ZHB-30 IBU/DM, respectively. The HB concentration in all solutions was higher than its critical micelle concentration (cmc 0.92 mM at 20-25 °C). Instead of an intensive peak pattern associated with HB micelles, a group of very low intensity peaks was observed in a wider size range. The observed changes can be interpreted by disturbing the structure of the micelles under the conditions of agitation and temperature during the preparation of the starting solutions, and the formation of IBU complexes with individual HB molecules (Bunton et al., 1981), as well as their associates.

The changes in zeta-potential of clinoptilolitic zeolitic tuff (ZVB) (Fig. 1a) were more pronounced for the samples with higher HB content compared with the sample ZHB-10 IBU/DM. Since the adsorbed amount of IBU on the prepared composites was lower for ZHB-10 IBU/DM (~ 20 mg/g) and approximately the same for ZHB-20 IBU/DM and ZHB-30 IBU/DM (~ 40 mg/g), increasing zeta potentials probably correspond to different surfactant coverage and organization at the mineral surface.

The bands in FT-IR spectrum of ZHB-30 IBU/DM (Fig. 1b) at 3618, 3420 and 1640 cm^{-1} are clinoptilolite characteristic bands related to acidic hydroxyls SiO(H)Al, hydrogen-bonding hydroxyl groups, and bending vibration of absorbed water, respectively (Korkuna et al., 2006). Compared to the FT-IR spectrum of ZVB the following bands were observed: the CH_2 symmetric and asymmetric stretching vibrations of alkyl chain at 2919 and 2850 cm^{-1} and C–H scissoring vibrations of $CH3–N^+$ moiety with peak at 1463 cm^{-1}, which evidence the presence of HB (Sui et al., 2006). A weak band at 1384 cm^{-1} implies the presence of anionic form of adsorbed IBU (Krajišnik et al., 2015).

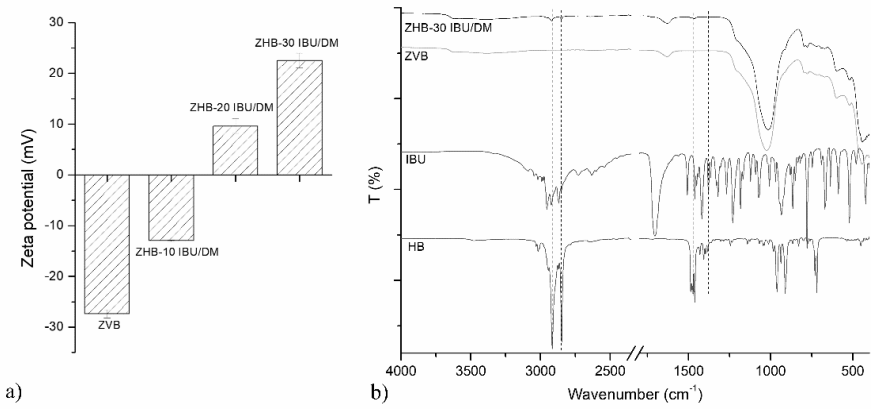

Figure 1. a) Zeta potentials of ZVB and the tested composites; b) FTIR spectra of the starting materials and IBU-loaded modified ZVB (ZHB-30 IBU/DM)

The presented results of drug uptake by surfactant/zeolite composites revealed that drug adsorption from IBU/HB solutions could be successfully performed by the direct method of preparation, while cationic surfactant:drug molar ratio had influence on adsorbed amounts and organization of molecules on the zeolitic surface. Further investigations of pharmaceutical technical characteristics and drug release from the obtained composites would reveal their possible pharmaceutical application.

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