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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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New insights on surface modified natural clinoptilolite-rich carrier for sorption and *in vitro* release of ibuprofen sodium salt

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Introduction

Ion-exchange capacity represents a very important property of natural zeolites and has been widely investigated for environmental remediation and drug delivery (Mercurio et al., 2018 and references therein). Thanks to this property, zeolite can be surface modified via adsorption of long-chain cationic surfactants, providing an organo-mineral composite known as Surface Modified Natural Zeolite (SMNZ) able to sorb specific molecules by anion-exchange and partition mechanisms (Farías et al., 2010; Mercurio et al., 2018).

This study aims to test the technological performance of a surface modified clinoptilolite-rich rock in the loading and *in vitro* release of ibuprofen sodium salt (IBU), in order to evaluate its possible use in high-value technological applications based on the sorption of non-steroidal anti-inflammatory drugs (NSAIDs).

Experimental Methods

A clinoptilolite-rich rock (CLI) from an economic deposit of zeolite located in the East-Slovakia basin (Nižný Hrabovec) has been surface modified using four cationic surfactants, namely cetylpyridinium chloride (CC), benzalkonium chloride (BC), hexadecyltrimethylammonium chloride (HC) and bromide (HB). Briefly, CLI (clinoptilolite content ~55.7 wt%) was added to a surfactant solution with an initial concentration equivalent to 200% of the external cation exchange capacity (ECEC) of starting material (~0.119 mEq/g). The so formed SMNZs (labelled CLI_CC, CLI_BC, CLI_HC and CLI_HB) were used to carry out IBU equilibrium sorption isotherms and loading/release kinetic tests according to Mercurio et al. (2018). Experimental points were fitted using several mathematical models, which non-linear fitting parameters and applicability were evaluated by considering determination coefficient (R^2) and Bayesian Information Criterion (BIC). Further details about mineralogical and technological characterization of starting material, SMNZs preparation and mathematical modeling of sorption/release profiles are reported in Cappelletti et al. (2017), de Gennaro et al. (2016) and Mercurio et al. (2018), respectively.

Results and Discussion

Table 1 reports the preliminary results of equilibrium sorption tests indicating that the best-fit for isotherms was attained implementing Langmuir and Toth mathematical models, as already observed for other zeolite carriers (Mercurio et al., 2018). Goodness-of-fit (GOF) indicates that R^2 values are quite similar for the two mathematical models used for the fitting of experimental data in samples CLI_CC and CLI_BC, although a preference for the Langmuir model can be observed. On the contrary, BIC values of Toth model decrease in both SMNZs, as well as in sample CLI_HC. It means that Toth equation could be considered as the best-fitting model, since BIC provides a better discrimination between a two-parameters model (i.e., Langmuir) and a three-parameters one (i.e., Toth), especially in non-linear regressions. These results can be generally explained taking into account that chlorinated surfactants form onto the surface of the zeolite a patchy bilayer, where sorption of NSAIDs is controlled by a dual mechanism: *a)* external anionic exchange and *b)* partition into the hydrophobic portion of the micelle. In fact, the best-fit in equilibrium sorption isotherms of CLI_HB was provided by Langmuir equation. In this case, as well known in literature (de Gennaro et al., 2014), the presence of bromide counterion tend to form a complete bilayer micelle promoting the adsorption mechanism, properly described by a simple Langmuir equation. It is worth to note that the values of IBU sorbed by CLI_HB represent a prediction of the amounts of ibuprofen that could be sorbed by SMNZ at the equilibrium (asymptotic plateau), and could be not appreciated from a graphical point of view.
Loading kinetic runs (Fig. 1a), modelled with a pseudo-second order equation, highlight a very fast loading process, where most of the IBU is sorbed by SMNZs within half an hour. Furthermore, maximum sorption

capacities found in loading kinetic runs (16.9 mg/g for CLI_CC, 15.0 mg/g for CLI_BC, 22.5 mg/g for CLI_HC and 25.9 mg/g for CLI_HB) generally fit the experimental points of isotherms.
Lastly, drug release occurred quite completely within the first hour and dissolution profiles (Fig. 1b) were fitted by a first-order equation according to literature (Mercurio et al., 2018).

Table 1. Isotherm parameters

		Parameters				GOF	
Samples	Mathematical model	K (L/mg)	n	S_m (mg/g)	S_m (mEq/g)	R^2	BIC
CLI_CC	Langmuir	0.019		18.2	0.080	0.999	12.7
	Toth	0.012	1.67	17.0	0.074	0.996	11.2
CLI_BC	Langmuir	0.017		17.9	0.078	0.999	10.1
	Toth	0.013	1.38	16.9	0.074	0.997	9.5
CLI_HC	Langmuir	0.064		21.0	0.092	0.996	16.8
	Toth	0.038	1.72	20.3	0.089	0.998	11.0
CLI_HB	Langmuir	0.004		33.0	0.145	0.996	16.7
	Toth	0.004	1.19	30.5	0.134	0.996	18.2

Implications

The examined starting material represents an important georesource in the economy of Slovakia, since it was already used in several technological applications as, for example, water cleanup processes. This study sheds new light on NSAIDs sorption mechanisms from clinoptilolite, encouraging further practical uses of this geomaterial both in pharmaceutical sector and environmental remediation (Płuciennik-Koropczuk, 2014).

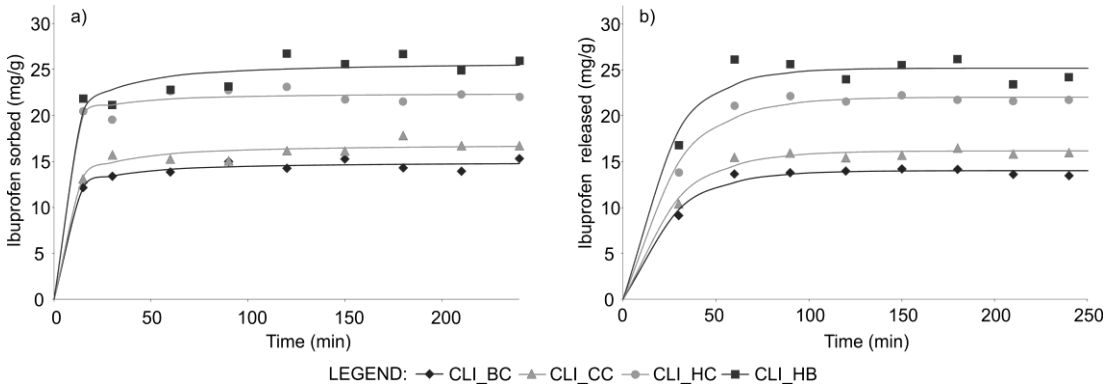

Figure 1. Kinetic loading (a) and release (b) curves.

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