# **ZEOLITE 2018**

10<sup>th</sup> International Conference on the Occurrence, Properties and Utilization of Natural Zeolites

## **Book of Abstracts**

Edited by Wojciech Franus, Jarosław Madej

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#### Preface

It is a great honor to welcome you to the 10<sup>th</sup> 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

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## Emerging contaminants and surface modified natural zeolites as a new promising environmental challenge

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#### Introduction

The emerging contaminants (ECs) are chemicals that can have negative ecological and health effects but they are still unregulated by legal frameworks (E.J.Tiedeken et al., 2017). Monitoring survey of ECs in waters (surface waters, wastewater treatment plants (WWTPs) effluents, underground water) in several European countries evidenced different concentrations (ng/l to  $\mu$ g/l) of pharmaceuticals, personal care products, plasticizers, flame retardants, surfactants, steroid hormones, pesticides, etc (Loos et al., 2013, and references therein). Although these concentrations are not considered high, the possible issue could be the accumulation of ECs (for example, hormones) that can show biological activity even in small doses (Liu et al., 2013). Many studies have been conducted in order to investigate these issues.

#### **Experimental Methods**

The results acquired from WWTPs effluents have shown that the conventional treatment procedures of the wastewater are not always effective in the removal of the ECs (Bolong et al., 2009). At neutral pH, pharmaceuticals (clofibric acid, diclofenac, hormones, ibuprofen, etc.) usually appear as ions in a water phase, and cannot be removed by the activated sludge (Urase and Kikuta, 2005). Non-steroidal anti-inflammatory drug (NSAID) diclofenac was found to be very persistent and hard to remove (Płuciennik, 2014). In order to remove persistent ECs, it is necessary to apply an additional treatment such as ozonation, UV irradiation, adsorption on the activated carbon, etc. or their combination (E.J.Tiedeken et al., 2017). Moreover, these treatments are expensive, most of the WWTPs cannot easily implement them and, last but not least, they are not obligated by law regulation to remove ECs. In order to solve these issues, it is necessary to explore achievable and low-cost methods for water treatment. For this purpose, the adsorption has been considered as the very promising mechanism and different adsorbents can be potentially studied (activated carbon and zeolites) due to their very high specific surface area and their attitude to exchange ions (Li et al., 2011). Moreover, the use of surface modified natural zeolites (SMNZs) instead of other adsorbents could be preferred due to abundance, worldwide availability, low cost of the natural zeolites, and because these adsorbents are considered as eco-friendly materials for water treatment (Delkash et al., 2015).

#### **Results and Discussion**

SMNZs were used for adsorption of inorganic anions (de Gennaro et al. 2014) and organic molecules from BTEX group (Bowman, 2003), humic acid (Li et al. 2011), mycotoxins (Daković et al. 2005), etc. Also, it has been shown that SMNZs have the ability to adsorb pharmaceutical NSAIDs such as ibuprofen (IBU) (Krajišnik et al., 2010) and diclofenac sodium (DS) (de Gennaro et al., 2015). Natural zeolites (clinoptilolite, phillipsite, and chabazite) from different geographical areas were characterized and their ability to be functionalized with different cationic surfactants (hexadecyltrimethylammonium bromide/chloride, benzalkonium chloride, and cetylpyridinium chloride) has been verified (Cappelletti et al., 2017). A new approach for fast functionalization has also been proposed (de Gennaro et al., 2016). The adsorption of anionic DS on a clinoptilolite-rich rock modified with cetylpiridimum chloride has been conducted and kinetic models of adsorption were suggested. It has been shown that 40.3 and 65.0 mg of DS can be adsorbed per g of SMNZ (de Gennaro et al., 2015). Surface modified phillipsite-rich tuff from the Campania region (southern Italy) was examined for adsorption of IBU by loading and release kinetics tests. Depending on the stabilizing anions, Cl<sup>-</sup> and Br<sup>-</sup>, loading amounts were 26.8 and 28.1 mg/g, respectively (Mercurio et al., 2018).

The possible pharmaceutical application of SMNZs for the adsorption of the two NSAIDs (IBU and DS) has been confirmed. Whereas for the application of the SMNZs as adsorbents of ECs it is necessary to define the following:

- 1- To determine affinity for each of the ECs towards SMNZs.
- 2- A detailed characterization and leaching test to prevent potential toxicity of SMNZs.
- 3- To consider a real medium (a wastewater from a WWTP).
- 4- To set up the best experimental conditions for a most effective adsorption of the ECs.
- 5- To select a novel cationic eco-friendly surfactant not harmful to the aquatic organisms.

#### References

- Bolong, N., Ismail, A.F., Salim, M.R. and Matsuura, T. (2009) A review of the effects of emerging contaminants in wastewater and options for their removal. *Desalination*, **239**(1-3), 229-246.
- Bowman, R. S. (2003) Applications of surfactant-modified zeolites to environmental remediation. *Microporous and Mesoporous Materials*, **61**(1-3), 43-56.
- Cappelletti, P., Colella, A., Langella, A., Mercurio, M., Catalanotti, L., Monetti, V. and de Gennaro, B. (2017) Use of surface modified natural zeolite (SMNZ) in pharmaceutical preparations Part 1. Mineralogical and technological characterization of some industrial zeolite-rich rocks. *Microporous and Mesoporous Materials*, 250, 232-244.
- Daković, A., Tomašević-Čanović, M., Dondur, V., Rottinghaus, G.E., Medaković, V. and Zarić, S. (2005) Adsorption of mycotoxins by organozeolites. *Colloids and Surfaces B: biointerfaces*, **46**(1), 20-25.
- de Gennaro, B., Catalanotti, L., Bowman, R.S. and Mercurio, M. (2014) Anion exchange selectivity of surfactant modified clinoptilolite-rich tuff for environmental remediation. *Journal of colloid and interface science*, **430**, 178-183.
- de Gennaro, B., Catalanotti, L., Cappelletti, P., Langella, A., Mercurio, M., Serri, C., ... & Mayol, L. (2015) Surface modified natural zeolite as a carrier for sustained diclofenac release: A preliminary feasibility study. *Colloids and Surfaces B: Biointerfaces*, **130**, 101-109.
- de Gennaro, B., Mercurio, M., Cappelletti, P., Catalanotti, L., Daković, A., De Bonis, A., Grifa, C., Izzo, F., Kraković, M., Monetti, V. and Langella, A. (2016). Use of surface modified natural zeolite (SMNZ) in pharmaceutical preparations. Part 2. A new approach for a fast functionalization of zeolite-rich carriers. *Microporous and Mesoporous Materials*, 235, 42-49.
- Delkash, M., Bakhshayesh, B.E. and Kazemian, H. (2015) Using zeolitic adsorbents to cleanup special wastewater streams: A review. *Microporous and Mesoporous Materials*, **214**, 224-241.
- Krajišnik, D., Milojević, M., Malenović, A., Daković, A., Ibrić, S., Savić, S., Dondur, V., Matijašević, S., Radulović, A., Daniels, R. and Milić, J. (2010) Cationic surfactants-modified natural zeolites: improvement of the excipients functionality. *Drug development and industrial pharmacy*, 36(10), 1215-1224.
- Li, C., Dong, Y., Wu, D., Peng, L. and Kong, H. (2011) Surfactant modified zeolite as adsorbent for removal of humic acid from water. *Applied clay science*, **52**(**4**), 353-357.
- Liu, J.L. and Wong, M.H. (2013) Pharmaceuticals and personal care products (PPCPs): a review on environmental contamination in China. *Environment international*, **59**, 208-224.
- Loos, R., Carvalho, R., António, D.C., Comero, S., Locoro, G., Tavazzi, S., Paracchini, B., Ghiani, M., Lettieri, T., Blaha, L. and Jarosova, B. (2013) EU-wide monitoring survey on emerging polar organic contaminants in wastewater treatment plant effluents. *Water research*, 47(17), 6475-6487.
- Mercurio, M., Izzo, F., Langella, A., Grifa, C., Germinario, C., Dakovic, A., ... & de Gennaro, B. (2018) Surface-modified phillipsite-rich tuff from the Campania region (southern Italy) as a promising drug carrier: An Ibuprofen sodium salt trial. *AMERICAN MINERALOGIST*.
- Płuciennik-Koropczuk, E. (2014) Non-Steroid Anti-Infflamatory Drugs in Municipal Wastewater and Surface Waters/Niesteroidowe Leki Przeciwzaplane W Ściekach Mieskich I Wodach Powierzchniowych. *Civil and Environmental Engineering Reports*, 14(3), 63-74.
- Tiedeken, E. J., Tahar, A., McHugh, B., & Rowan, N. J. (2017) Monitoring, sources, receptors, and control measures for three European Union watch list substances of emerging concern in receiving waters-a 20 year systematic review. *Science of the Total Environment*, **574**, 1140-1163.
- Urase, T. and Kikuta, T. (2005) Separate estimation of adsorption and degradation of pharmaceutical substances and estrogens in the activated sludge process. *Water research*, **39**(7), 1289-1300.