

## 8<sup>th</sup> Serbian-Croatian-Slovenian Symposium on Zeolites



# Proceedings

Editors

Vesna Rakić  
Jasna Hrenović  
Alenka Ristić

Belgrade, 2019

**Proceedings of the 8<sup>th</sup> Serbian-Croatian-Slovenian  
Symposium on Zeolites  
Proceedings of the 8<sup>th</sup> Croatian-Slovenian-Serbian  
Symposium on Zeolites  
Proceedings of the 8<sup>th</sup> Slovenian-Serbian-Croatian  
Symposium on Zeolites**

**ISBN:  
978-86-916637-2-8**

Publisher  
Serbian Zeolite Association (SZA)

Editors  
Vesna Rakić  
Jasna Hrenović  
Alenka Ristić

Print  
Development and Research Centre of Graphical Engineering  
Faculty of Technology and Metallurgy  
Belgrade  
SERBIA

Copies 80

Belgrade, 2019

PROCEEDINGS OF THE  
8<sup>th</sup> SERBIAN-CROATIAN-SLOVENIAN  
SYMPOSIUM ON ZEOLITES

3 - 5 October 2019.

Belgrade, Serbia

Organizers

SERBIAN ZEOLITE ASSOCIATION  
CROATIAN ZEOLITE ASSOCIATION  
SLOVENIAN ZEOLITE ASSOCIATION

Co-organizers

CHAMBER OF COMMERCE AND INDUSTRY OF SERBIA  
FACULTY OF PHYSICAL CHEMISTRY, UNIVERSITY OF BELGRADE

Under the auspices of

Federation of European Zeolite Associations (FEZA)

The Proceedings is printed under auspices of the

Ministry of Education,  
Science and Technological Development, Republic of Serbia

All articles in the Proceedings were reviewed.

#### Organizing committee

Prof. **Vesna Rakić**, University of Belgrade, Faculty of Agriculture, Serbia.

Prof. **Nevenka Rajić**, University of Belgrade, Faculty of Technology and Metallurgy, Serbia.

Prof. **Vladimir Simić**, University of Belgrade, Faculty of Mining and Geology, Serbia.

Dr. **Aleksandra Daković**, Institute for Technology of Nuclear and Other Mineral Raw Materials, Serbia.

Prof. **Ljiljana Damjanović-Vasilić**, University of Belgrade, Faculty of Physical Chemistry, Serbia.

**Dragan Stevanović**, Chamber of Commerce and Industry of Serbia

Prof. **Nataša Zabukovec Logar**, National Institute of Chemistry, Ljubljana, and University of Nova Gorica, Slovenia.

Prof. **Nataša Novak Tušar**, National Institute of Chemistry, Ljubljana, and University of Nova Gorica, Slovenia.

Dr. **Josip Bronić**, Ruđer Bošković Institute, Zagreb, Croatia.

Dr. **Tatjana Antonić-Jelić**, Ruđer Bošković Institute, Zagreb, Croatia.

#### Scientific Committee

Prof. **Đorđe Stojaković**, University of Belgrade, Faculty of Technology and Metallurgy, Serbia.

Prof. **Vera Dondur**, University of Belgrade, Faculty of Physical Chemistry, Serbia.

Prof. **Dragana Životić**, University of Belgrade, Faculty of Mining and Geology, Serbia.

Dr. **Ana Radosavljević-Mihajlović**, Institute for Technology of Nuclear and Other Mineral Raw Materials, Serbia.

Prof. **Aleksandar Simić**, University of Belgrade, Faculty of Agriculture, Serbia.

Dr. **Sanja Jevtić**, University of Belgrade, Faculty of Technology and Metallurgy, Serbia.

Dr. **Vladislav Rac**, University of Belgrade, Faculty of Agriculture, Serbia.

Prof. **Gregor Mali**, National Institute of Chemistry, Ljubljana, Slovenia.

Dr. **Matjaž Mazaj**, National Institute of Chemistry, Ljubljana, Slovenia.

Dr. **Alenka Ristić**, National Institute of Chemistry, Ljubljana, Slovenia.

Dr. **Tomislav Ivanković**, University of Zagreb, Faculty of Science, Croatia.

Prof. **Vesna Tomašić**, University of Zagreb, Faculty of Chemical Engineering and Technology, Croatia.

Dr. **Marin Ugrina**, University of Split, Faculty of Chemistry and Technology, Croatia.

Dr. **Ana Palčić**, Ruđer Bošković Institute, Zagreb, Croatia.

**CIP- Каталогизација у публикацији**

**Народна библиотека Србије**

549.67(082)

**SERBIAN-Croatian-Slovenian Symposium on Zeolites (8 ; 2019 ; Beograd)**

Proceedings of the 8th Serbian-Croatian-Slovenian Symposium on Zeolites, 3 - 5 October 2019, Belgrade, Serbia / organizers Serbian Zeolite Association ... [et al.] ; [editors Vesna Rakić, Jasna Hrenović, Alenka Ristić]. - Belgrade : Serbian Zeolite Association, 2019 (Belgrade : Development and Research Centre of Graphical Engineering, Faculty of Technology and Metallurgy). - VIII, 158 str. : ilustr. ; 30 cm

Tiraž 80. - Bibliografija uz svaki rad. - Registar.

ISBN 978-86-916637-2-8 (SZA)

a) Зеолити -- Зборници

COBISS.SR-ID 279616268

---

## ORGANOPHILLIPSITE AS POTENTIAL LOW COST ADSORBENT FOR REMOVAL OF IBUPROFEN

Milica Spasojević<sup>1</sup>, Aleksandra Daković<sup>1</sup>, George E. Rottinghaus<sup>2</sup>, Milena Obradović<sup>1</sup>,  
Danina Krajišnik<sup>3</sup>, Mariano Mercurio<sup>4</sup>, Danijela Smiljanić<sup>4</sup>

<sup>1</sup>Institute for Technology of Nuclear and Other Mineral Raw Materials, Franše d'Epere 86, 11000 Belgrade, Serbia

<sup>2</sup>Veterinary Medical Diagnostic Laboratory, College of Veterinary Medicine, University of Missouri, Columbia, MO 65211, USA

<sup>3</sup>University of Belgrade, Department of Pharmaceutical Technology and Cosmetology, Faculty of Pharmacy, Vojvode Stepe 450, 11221 Belgrade, Serbia

<sup>4</sup>Department of Science and Technologies, University of Sannio, Via dei Mulini 59/A, 82100 Benevento, Italy  
E-mail: a.dakovic@itnms.ac.rs

### ABSTRACT

Zeolite – phillipsite was modified with long chain organic surfactant – hexadecyltrimethyl-ammonium bromide (HB). Two different amounts of HB were used to modify the zeolitic surface (150 % and 200% of phillipsite external exchange capacity - ECEC). Adsorption of non-steroidal antiinflammatory drug – ibuprofen (IBU) was studied at pH 7, at different initial drug concentrations. Adsorption increased with increasing the initial drug concentrations as well as with increasing amounts of organic phase at the phillipsite surface. From the Langmuir model, the maximum IBU adsorption capacity for phillipsite modified with surfactant at 150 % of ECEC was 12.72 mg/g, while for organophillipsite containing surfactant in amount of 200 % of ECEC, the maximum adsorption capacity was 18.25 mg/g.

Keywords: zeolite, phillipsite, surfactants, ibuprofen, adsorption.

### INTRODUCTION

Pharmaceuticals in the aquatic environment have attracted special attention as one of the most significant groups of pollutants. Commonly found pharmaceuticals are non-steroidal antiinflammatory drugs (NSAIDs), antibiotics,  $\beta$ -blockers, and hormones. Non-steroidal antiinflammatory drugs are usually used to treat human and animal diseases in terms of analgesic, antiinflammatory, and antipyretic actions. It was reported that conventional wastewater treatment methods are not completely effective in eliminating and/or degrading the majority of these pharmaceuticals. Ibuprofen (IBU) (Figure 1) is one of the most common NSAIDs and due to its high consumption can be found in drinking water at concentrations up to 24.6  $\mu\text{g/L}$ , thus represents hazardous pollutant for human health [1–4].

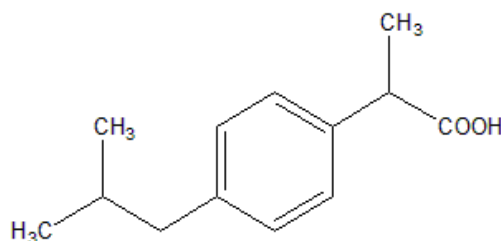


Figure 1. Chemical structure of ibuprofen

Several methods have been applied for treatment of NSAIDs, among these adsorption is one of the most common technique. Commonly used adsorbents are activated carbon, clay, zeolite, mesoporous silica and carbon nanotubes. However, natural clays and zeolites are hydrophilic and possess inorganic cations, thus they are effective in the removal of cationic

pollutants and are less effective in binding anions or relatively non-polar molecules. Incorporation of long chain organic cations, polymers or even magnetic particles have been used to modify the natural minerals in order to increase their affinities for anions and organic pollutants. The aim of this study is to prepare a composite adsorbent by modification of the natural zeolite – phillipsite with cationic surfactant which will be capable of removing ibuprofen from aqueous solutions.

## **EXPERIMENTAL**

The starting raw material was the Neapolitan Yellow Tuff (Campania, Italy) containing mainly phillipsite (69.6 %) with smaller amounts of chabazite, analcime, pyroxene, K-feldspar and an amorphous phase, based on the quantitative X-Ray Powder Diffraction (XRPD) analysis. The cation exchange capacity (CEC) of phillipsite was 247 mmol M<sup>+</sup>/100 g, while its external cation exchange capacity (ECEC) was 13 mmol M<sup>+</sup>/100 g [5]. Two organophillipsites were prepared by treatment of the starting material with two levels of hexadecyltrimethyl ammonium bromide equal to 150 and 200 % of the phillipsite ECEC value. The procedure for preparation of the organophillipsites was described elsewhere [6].

Ibuprofen (IBU) was supplied from Sigma-Aldrich. A primary IBU stock solution (1000 mg/L) was prepared in methanol, while test solutions for adsorption studies were prepared by adding appropriate amounts of methanol stock solution to 10 mL of 0.1 M phosphate buffer adjusted to pH 7. For the determination of adsorption isotherms for the two organophillipsites, 5 mg of each adsorbent was treated with 10 mL of buffer solution containing different IBU initial concentrations (2 - 20 mg/L). All experiments were done in duplicate. Controls were also prepared by addition of 10 mL of buffer solution and 5 mg of each adsorbent. Tubes were shaken for 30 min and after that centrifuged at 13000 rpm for 2 min. Supernatants were kept for HPLC analyses. An aliquot of the original buffered IBU test solution was used as the HPLC standard. HPLC analyses were performed on a Hitachi L-7100 pump with a Hitachi L-7200 autosampler, and UV detection with a Hitachi UV spectrophotometer ( $\lambda = 220$  nm). The mobile phase was acetonitrile:water (65:35) with 2 mL of acetic acid. The mobile phase was pumped at the flow rate of 1 mL/min. Data were recorded and processed by a Hitachi D-7000 data acquisition package with Concert Chrom software on a microcomputer. The amount of IBU adsorbed was calculated from the difference between the initial and final IBU concentration in the supernatant.

## **RESULTS AND DISCUSSION**

It is well known that long chain organic cations such as hexadecyltrimethyl-ammonium (HB) cationic surfactant can only replace inorganic cations at the external surface of zeolite (external cation exchange capacity - ECEC) and form a monolayer of surfactant at the zeolitic surface. The monolayer at the zeolitic surface creates sites where relatively non-polar molecules can be adsorbed. At surfactant concentrations above the ECEC of the zeolite, the adsorbed organic cations usually form a bilayer at the external zeolitic surface. A bilayer of surfactants creates sites suitable for adsorption of both organic molecules and anions [7]. The natural zeolite – phillipsite was modified with surfactant in amounts above the ECEC value (150 and 200 % of ECEC), thus bilayer probably exists at the phillipsite surface. Based on the structure (Figure 1) and physico-chemical characteristics, IBU is relatively non-polar molecule with low solubility in water. Its dissociation constant ( $pK_a = 4.4$ ) suggests that at pH 7, at which adsorption experiments were done, exists in anionic form.

Ibuprofen adsorption isotherms are presented at Figure 2 and model parameters are given in Table 1. It can be observed that adsorption of IBU by the two surfactant modified zeolites increased with increasing of the initial IBU concentration. Adsorption of IBU by both organophillipsites followed non-linear isotherms at pH 7. The experimental data were

fitted to the Langmuir and Freundlich models and a good correlation was obtained for both models. From the Langmuir model, the maximum adsorption capacity for phillipsite modified with surfactant in amount of 150 % of ECEC was 12.72 mg/g, while for organophillipsite containing surfactant in amount of 200 % of ECEC, the maximum adsorption capacity was 18.25 mg/g.

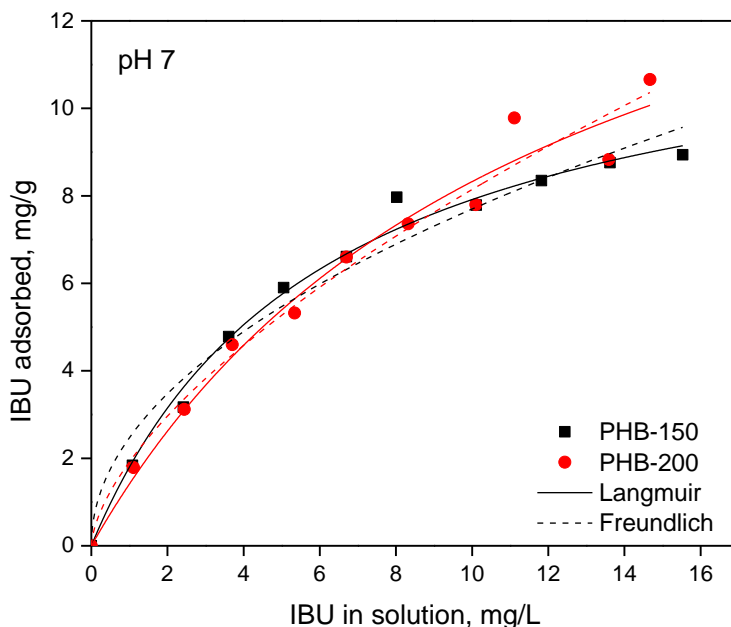


Figure 2. Ibuprofen adsorption by organophillipsites PHB-150 and PHB-200.

Table 1. Characteristic parameters of adsorption isotherms.

	pH 7					
	Langmuir			Freundlich		
	$q_m$ (mg/g)	$K_L$ (L/mg)	$r^2$	$n$	$K_F$ (L/mg)	$r^2$
PHB-150	12.72	0.165	0.990	2.026	2.471	0.966
PHB-200	18.25	0.084	0.974	1.592	1.918	0.973

Adsorption of IBU increased with increasing amounts of HB at the phillipsite surface, suggesting that organic cations are the active sites onto which drug is adsorbed. From the Freundlich model,  $K_F$  values for the two samples were between 1.92 and 2.47 L/mg. The values of  $n$  for the two organophillipsites changed from 1.59 for the sample containing the lower amount of HB to 2.02 for the zeolite with the higher amount of HB. These values are greater than unity, indicating that IBU is preferentially adsorbed by both organophillipsites. Usually, if hydrophobic interactions (partitioning) between relatively non-polar organic contaminants and the non-polar part of a surfactants occurred, linear isotherms are obtained. Since a bilayer of surfactants was probably formed at the phillipsite surface and IBU at pH 7 exists in anionic form, non linear adsorption isotherms suggest that specific adsorption interactions between IBU anion and HB ions together with partitioning take place simultaneously.



## CONCLUSION

Organophilippsites were obtained by treatment of the natural zeolite – phillipsite with two levels of surfactant – hexadecyltrimethyl ammonium bromide (HB). The amounts of surfactant were above the external cation exchange capacity (ECEC) of phillipsite (150 % and 200 % of ECEC). Adsorption of ibuprofen was studied at different initial drug concentrations at pH 7. Adsorption of the drug increased with increasing of the initial concentration and with increasing amounts of surfactant at the zeolitic surface. High adsorption of ibuprofen by obtained organophilippsites suggested that these materials may be effective for removal of this drug from contaminated water.

## ACKNOWLEDGMENT

These experiments were done under the projects 172018 and 34013 funded by the Ministry of Education, Science and Technological Development of Republic of Serbia. Ibuprofen adsorption experiments were done at the Vet. Med. Diag. Lab., University of Missouri, Columbia, MO 65211, USA.

## REFERENCES

- [1] V. Arya, L. Philip, *Microp. Mesop. Mater.*, 2016, **232**, 273–280.
- [2] E.M. Cuerda-Correa, J.R. Domínguez-Vargas, F.J. Olivares-Marín, J.B. de Heredia, *J. Hazard. Mater.*, 2010, **177**, 1046–1053.
- [3] A.A. Basheer, *J. Mol. Liq.*, 2018, **261**, 583–593.
- [4] T.M. Salem Attia, X.L. Hu, D.Q. Yin, *Chemosphere*, 2013, **93**, 2076–2085.
- [5] B. de Gennaro, L. Catalanotti, P. Cappelletti, A. Langella, M. Mercurio, C. Serri, M. Biondi, L. Mayol, *Colloids Surf. B*, 2015, **130**, 101–109.
- [6] M. Marković, A. Daković, D. Krajišnik, M. Kragović, J. Milić, A. Langella, B. de Gennaro, P. Cappelletti, M. Mercurio, *J. Mol. Liq.*, 2016, **222**, 711–716.
- [7] Z. Li, R.S. Bowman, *Environ. Sci. Technol.*, 1997, **31**, 2407–2412.