PHYSICAL CHEMISTRY 2021

15th International Conference
on Fundamental and Applied Aspects of
Physical Chemistry

Proceedings
Volume II

The Conference is dedicated to the

30th Anniversary of the founding of the Society of Physical Chemists of Serbia

and

100th Anniversary of Bray-Liebhafsky reaction

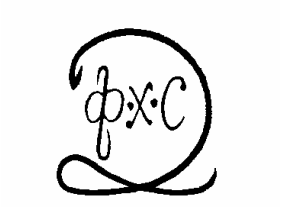
September 20-24, 2021
Belgrade, Serbia

Title: Physical Chemistry 2021 (Proceedings) **ISBN** 978-86-82475-40-8
Volume II: ISBN 978-86-82475-39-2
Editors: Željko Čupić and Slobodan Anić
Published by: Society of Physical Chemists of Serbia, Studentski Trg 12-16, 11158, Belgrade, Serbia
Publisher: Society of Physical Chemists of Serbia
For Publisher: S. Anić, President of Society of Physical Chemists of Serbia
Printed by: ″Jovan″, <Printing and Publishing Company, 200 Copies
Number of pages: 6+388, Format A4, printing finished in December 2021

Text and Layout: ″Jovan″

200 - *Copy printing*

CONTENT



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15th International Conference on Fundamental and Applied Aspects of Physical Chemistry

Organized by

The Society of Physical Chemists of Serbia

in co-operation with

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Boreskov Institute of Catalysis Siberian Branch of Russian Academy of Sciences

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ADSORPTION OF IBUPROFEN BY SURFACTANT MODIFIED KAOLIN

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ABSTRACT
In this paper, results of ibuprofen (IBU) adsorption by organokaolins obtained by modification of the natural kaolin (KR) with surfactant - hexadecyltrimethyl ammonium bromide (H) are presented. Two different amounts of surfactant were used for modification of KR (50 and 90% of kaolin's cation exchange capacity). Samples are denoted as HKR-50 and HKR-90. Adsorption of IBU on organokaolins was investigated with different initial drug concentrations (2 – 20 mg/L) in phosphate buffer at pH 7. Compared with KR which has no affinity to adsorb IBU, modification of KR with H improved adsorption of this drug. Results showed that adsorption of IBU increased with increasing of the amount of surfactant in organokaolins as well as with increasing of the initial concentration of the drug in solution. Adsorption of IBU by both adsorbents followed nonlinear isotherms and from the Langmuir model, the maximum adsorption capacities were 2.05 mg/g for HKR-50 and 3.12 mg/g for HKR-90.

INTRODUCTION
Pharmaceuticals are a large group of emerging contaminants extensively used in human health; therefore, they often occur in the aquatic environment. These substances are becoming a concern due to their high environmental persistence and possible negative effects on human health and aquatic ecosystems. Emerging contaminants could be hazardous even at their low concentrations. Measured concentrations of non-steroidal anti-inflammatory drugs (NSAIDs) can vary from several ng/L to even mg/L in case of the effluents from the pharmaceutical industry [1,2]. Wastewater treatment plants effluents represent major sources of pharmaceuticals in the aquatic environment since many of them are not significantly removed and flow into receiving water sources [3]. Thus, finding a low cost method for eliminating pharmaceuticals from water is required. Several treatment methods like advanced oxidation processes, membrane techniques, adsorption, and constructed wetlands are usually used for removal of pharmaceutical from water systems. Among all of these methods, adsorption is the most promising approach for removal of emerging contaminants because of it low cost, highly efficient and has simple operating design.

IBU is the one of the most common NSAIDs, widely used in treatment of rheumatic disorders, pain and fever. Thus, it is frequently found in water systems [4]. Chemical structure of IBU ((2RS)-2-[4-(2-methylpropyl)phenyl]propanoic acid) is presented in Figure 1.

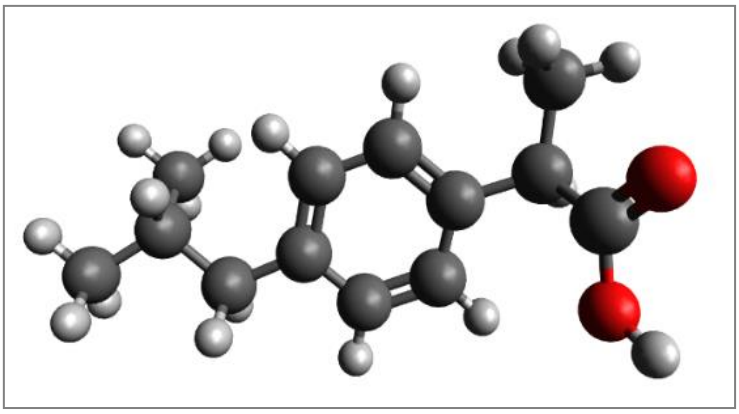

Figure 1. Chemical structure of IBU (Colour code: C: grey, H: light grey, O: red)

Zeolites and clays are usually used as adsorbents for removal of different pollutants. These minerals are aluminosilicates that possess hydrated exchangeable inorganic cations which make their surface hydrophilic. Accordingly, they are less able to bind relatively nonpolar - like most of the pharmaceuticals are. In order to adsorb these relatively nonpolar molecules, modification of minerals is required. It is reported that surfactant modified zeolites are effective adsorbents for removal of drugs – diclofenac sodium, ibuprofen and ketoprofen from water systems [3,5]. It was also shown that organoclays modified with cationic surfactants are efficient in removing organic compounds from aqueous solutions [6]. Surfactant modified montmorillonite and kaolinite have been considered for removal of relatively low polar molecules from water solutions. For example, adsorption of phenol by montmorillonite and kaolinite modified with two surfactants - hexadecyltrimethylammonium bromide (H) and phenyltrimethylammonium bromide (PTMA) was studied by Alkaram et al. [7]. They reported that both clays modified with surfactants were much more effective in phenol removal than unmodified samples.

The aim of this work is to modify the natural kaolin, non-swelling clay with low cation exchange capacity (CEC) with two different amounts of surfactant (H) and to investigate if obtained materials would be efficient to remove IBU (as representative of NSAIDs) from aqueous solution.

METHODS

Starting material used in this study was a sample of the natural kaolin (Rgotina, Serbia) - KR. XRD analysis showed that the main mineral in KR is kaolinite with smaller amounts of quartz and mica [8,9]. The raw material was used without any further purification for the preparation of the organokaolins and subsequent IBU adsorption experiments. The total CEC of KR is 6 meq/100g [9].

Two organokaolins were prepared by mixing of KR suspensions with two different amounts of surfactant H (Sigma-Aldrich Co) solution that is equivalent to 50 % and 90 % of KR cation exchange capacity. Suspensions were stirred at 5000 rpm for 10 min at 50°C, then filtered, rinsed with distilled water and dried. Organokaolins were denoted as HKR-50 and HKR-90.

IBU (Sigma-Aldrich Co) standard solution was prepared in methanol with concentration of 1000 mg/L. In order to obtain isotherms, stock solutions of the drug in the concentration range from 2 to 20 mg/L in phosphate buffer at pH 7 were prepared. Experiments were performed by shaking 5 mg of HKR-50 or HKR-90 with 10 mL of each drug solution for 30 min at room temperature. Then mixtures were centrifuged and supernatants were collected for analysis. The concentrations of the IBU before and after adsorption were determined by HPLC.

RESULTS AND DISCUSSION

IBU is hydrophobic molecule, practically insoluble in water, freely soluble in acetone, methanol and methylene chloride. It dissolves in dilute solutions of alkali hydroxides and carbonates (Ph. Eur.). Adsorption experiments were performed at pH 7, at which IBU exists in anionic form (IBU pKa=4.4). Natural KR has a negative hydrophilic surface and hydrated inorganic cations, therefore it is not efficient in removal of hydrophobic molecules. In the preliminary experiment, it was confirmed, that the KR has no affinity to adsorb IBU. The results of adsorption of IBU by HKR-50 and HKR-90 are presented in Figure 2. It can be noticed, that adsorption of IBU increased with increasing of the amount of surfactant in the organokaolins. Also, adsorption of IBU by both adsorbents increased with increasing of the initial drug concentration.

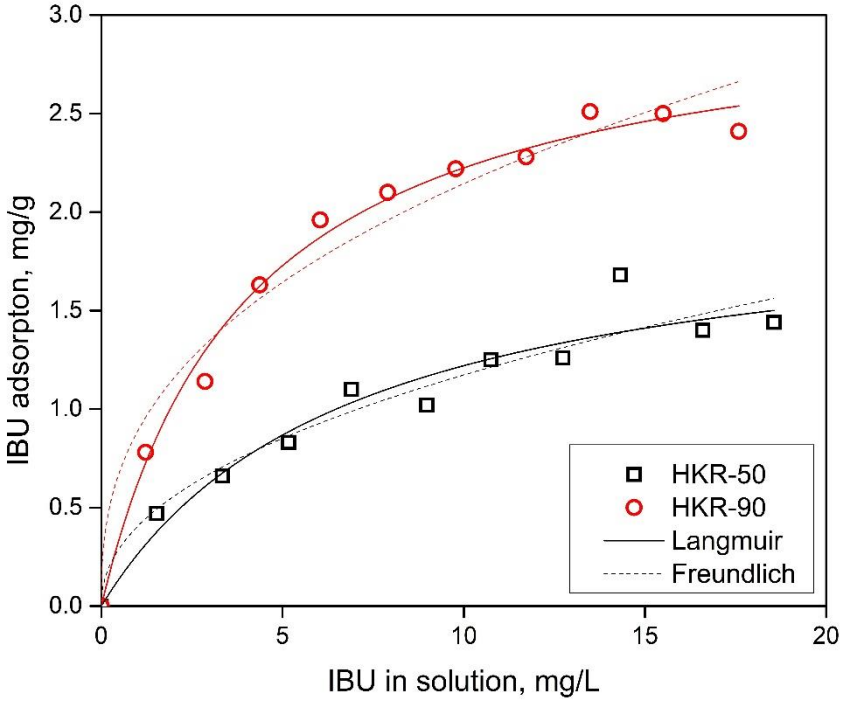

Figure 2. IBU adsorption by HKR-50 and HKR-90 at pH 7

The results showed that the presence of hydrophobic surfactant molecules in organokaolins increased IBU adsorption, indicating that surfactant molecules at the organokaolins surface are active sites responsible for drug adsorption.

For both adsorbents, nonlinear isotherms were obtained, thus Langmuir and Freundlich isotherm models were used to fit the equilibrium adsorption data. Parameters of the Langmuir and Freundlich isotherms are presented in Table 1. A better fit of experimental data was obtained with the Langmuir model. From the Langmuir model, the calculated values for IBU maximum adsorption capacities were 2.5 mg/g for HKR-50 and 3.12 mg/g for HKR-90. The low values of K_L (0.147 L/mg for HKR-50 and 0.248 L/mg for HKR-90) implied that binding between IBU and organokaolins was strong. Nonlinear isotherms obtained for adsorption of IBU by two organokaolins suggest complex adsorption mechanism which probably includes partitioning of the hydrophobic part of IBU into the surfactant alkyl chains as well as interactions between positive “heads” from H molecules at the kaolin surface and negatively charged IBU.

Table 1. Characteristic parameters of IBU adsorption isotherms

	Langmuir			**Freundlich**		
	q_m (mg/g)	K_L (L/mg)	r^2	n	K_F (L/mg)	r^2
HKR-50	2.05	0.147	0.937	2.161	0.404	0.935
HKR-90	3.12	0.248	0.989	2.608	0.887	0.964

CONCLUSION

Results reported in this paper demonstrated that modification of the KR with surfactant H improved adsorption of IBU, a representative of NSAIDs. Two amounts of surfactant were used for modification of KR. Adsorption of IBU increased with increasing amounts of surfactant in the organokaolins and also with increasing of the initial drug concentration. The presence of hydrophobic surfactants at the KR surface increased IBU adsorption, thus these adsorbents may be suitable materials for removal of IBU from contaminated water.

Acknowledgement

These experiments were funded by the Ministry of Education, Science and Technological Development of Republic of Serbia Contact numbers: 451-03-68/2020-14/200023 and 451-03-9/2021-14/200161. Ibuprofen adsorption experiments were done at the Vet. Med. Diag. Lab., University of Missouri, Columbia, USA.

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