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Bentonite Modified with Surfactants—Efficient Adsorbents for the Removal of Non-Steroidal Anti-Inflammatory Drugs

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Abstract: Organobentonites have been applied for the removal of two common non-steroidal anti-inflammatory drugs, ibuprofen (IBU) and diclofenac sodium (DS), from aqueous solutions. Two surfactants, one with and the other without benzyl group (octadecyldimethylbenzylammonium chloride, ODMBA, and hexadecyltrimethylammonium bromide, HDTMA), in amounts equivalent to 50, 75, and 100% of the cation exchange capacity of bentonite were used for the preparation of organobentonites. Successful modification of bentonite was confirmed by several methods: X-ray powder diffraction (XRPD), point of the zero charge (pH_{PZC}), determination of exchanged inorganic cations in bentonite, determination of textural properties, and scanning electron microscopy (SEM). Kinetic and thermodynamic data on the adsorption of IBU and DS showed that drug adsorption was controlled by the type and the amount of surfactant incorporated into the bentonite and by their arrangement in the interlayer space and at the surface of organobentonites. The adsorption of both drugs increased with an increase in the amount of both surfactants in organobentonites. The presence of the benzyl group in organobentonites enhanced the adsorption of IBU and DS and was more pronounced for IBU. Drug adsorption fits the pseudo-second-order kinetic model the best. The thermodynamic data revealed that the adsorption process was endothermic in nature and with increase of the amount of both surfactants drug adsorption processes were more spontaneous. The results obtained from this study revealed that adsorbents based on surfactants modified bentonite are promising candidates for IBU and DS removal from contaminated water.

Keywords: bentonite; surfactants; removal; pharmaceuticals; ibuprofen; diclofenac sodium

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1. Introduction

Water is the most fundamental substance for life on Earth. Therefore, its increasing contamination represents a great danger to water quality and health. In the last few decades, in water bodies, the presence of new chemicals has been detected. Chemicals, such as pharmaceuticals, personal care products and their metabolites, artificial sweeteners, endocrine-disrupting chemicals, and antibiotic-resistance genes, are called emerging contaminants (ECs) [1,2]. ECs are often present in water and wastewater, which represents a considerable problem that could have potential risks to human and aquatic life, even in small concentrations [3]. Wastewater treatment plant outlets are the primary cause of pharmaceutical presence in water [4,5]. Pharmaceuticals, especially non-steroidal anti-inflammatory drugs (NSAIDs), due to their wide analgesic, anti-inflammatory, and antipyretic applications, are among numerous ECs that are often detected in different water systems [6]. Thus, researchers all over the world are trying to find appropriate methods for the removal of NSAIDs in order to prevent their release into the aquatic

environment and, consequently, their impact on ecosystems and human health. Several techniques, such as photocatalytic degradation, microextraction, chlorination, biofiltration, electrocoagulation–flotation, electrochemical, oxidation, and adsorption (summarized in a review paper by Ahmed [7]), have been applied for the removal of NSAIDs from water. Compared to other techniques, adsorption is considered an efficient, economical, and simple method for the removal of these pollutants from water [8]. Clay minerals (bentonite, kaolin, illite, etc.) are a good choice for this application since they are recognized as being abundant in nature and are affordable and efficient adsorbents [9].

Clays contain hydrated inorganic cations (Na^+, K^+, Ca^{2+}, and Mg^{2+}) in interlayers and/or at the external surface, which balance negative charges caused by the isomorphic substitution of Si^{4+} with Al^{3+} in tetrahedral and Al^{3+} with Mg^{2+} in octahedral sheets. These charge-balancing cations are exchangeable, and their amount represents cation exchange capacity (*CEC*). Due to this property, clays are excellent adsorbents for the removal of cationic contaminants [10]. In many cases, natural clays, due to their hydrophilic nature, have no affinity for low polar molecules (like NSAIDs); thus, for the adsorption of these molecules, their modification with organic cations (surfactants) is necessary [9,11]. Among surfactants, cationic surfactants (quaternary ammonium salts) are commonly used since they possess a polar "head"—a quaternary ammonium ion and long hydrocarbon chain(s) containing between 8 and 24 carbon atoms. The chemical modification of clays with surfactants, in amounts below or equal to the *CEC* value of clay, creates a hydrophobic environment supported by an inorganic matrix suitable for retaining organic pollutants. Furthermore, clay modification with cationic surfactants, in amounts above the *CEC* value, in addition to a hydrophobic environment, provide a permanent positive charge from the polar "head", which additionally makes anion adsorption possible through ion exchange with counterions [12].

In our previous study [13], the adsorption of ibuprofen (IBU) and diclofenac sodium (DS), under the same experimental conditions, was investigated by zeolite (clinoptilolite), kaolin (kaolinite), and bentonite (yellow clay—montmorillonite) modified with octadecyldimethylbenzyl ammonium (ODMBA) chloride. The amount of surfactant used for modification was 100% of the *ECEC* value of zeolite (OZ), 90% of the *CEC* value of kaolin (OK), and 100% of the *CEC* value of bentonite (OB). These three raw materials are structurally, chemically, and mineralogically different, and they consequently showed different affinities for the adsorption of ODMBA and, subsequently, the adsorption of both IBU and DS. A comparison of the amounts of surfactant in organomodified minerals with adsorbed amounts of IBU and DS indicated that adsorption of both drugs was dependent on the ODMBA amount and its surface configuration on the mineral, pointing out that surfactant ions are active sites at which adsorption of both drugs occurred. It was reported that for OK and OZ, adsorption sites for IBU or DS were located at their external surfaces, and a higher adsorption of both drugs was observed for OZ. For these adsorbents, it was also noticed that the adsorption of DS was higher than the adsorption of IBU, which might be a consequence of the higher hydrophobicity of the DS molecule. The highest adsorption of IBU and DS was reported for OB, which contained the highest amount of ODMBA surfactant [13]. Thus, the proposed material (OB) was prepared through simple surfactant functionalization of naturally abundant and available clay. The literature often discusses the challenges associated with complex synthesis processes, including high costs and technical difficulties. In contrast, the proposed material offers a distinct advantage by featuring an easy, fast, and affordable synthesis process. This aligns with the growing interest in cost-effective synthesis methods [14,15], making the proposed material a practical and accessible choice.

Since surfactant ions in organomodified minerals are responsible for the adsorption of drugs, for the specific mineral, drug adsorption may be dependent on the type (structure) of surfactant—the presence of different functional groups and different alkyl chain lengths and their amounts used for the modification. Especially, surfactants modified clays containing an aromatic ring in their structure have improved the adsorption of different pollutants,

such as phenolic compounds [16], aniline [17], and bisphenol A [18]. Nevertheless, for the adsorption of NSAIDs by bentonites modified with different surfactants, reported data are contradictory. For example, França et al. [11] treated bentonite (swelling clay) with 1-dodecylpyridinium chloride hydrate and cetylpyridinium chloride - CP (surfactants with different alkyl chain lengths and the same aromatic functional group) in amounts equal to 100 and 200% of the *CEC* value of bentonite, and tested them for the removal of DS. They suggested that organobentonites have different characteristics depending on the amount of surfactant, as well as on the size of the surfactant alkyl chain, which, consequently, influenced the adsorption of DS. The highest adsorption of the drug was reported for organobentonite with a longer alkyl chain (CP) in the amount of 200% of its *CEC*. On the other side, De Oliveira et al. [19] studied organobentonites modified with two surfactants (benzyldimethyltetradecyl ammonium and hexadecyltrimethyl ammonium—HDTMA) (first containing benzyl group, two methyl groups, and a C-14 alkyl chain, and the other containing a C-16 alkyl chain and three methyl groups), in an amount equal to 400% of their *CEC* value, as adsorbents for DS. The authors pointed out that both organobentonites showed a good affinity toward DS, and the chemical structure of surfactants played a minor role [19].

Our results reported previously showed that OB containing ODMBA (a surfactant with two methyl groups, a benzyl group, and a C-18 alkyl chain), in the amount of 100% of the *CEC* value of bentonite, was the best adsorbent for DS and IBU [13]. The aim of this research was to compare the behavior of organobentonites modified with different amounts of two surfactants that contain different functional groups and similar alkyl chain lengths, ODMBA and HDTMA, toward the adsorption of IBU and DS. The starting bentonite (yellow clay—montmorillonite) was modified with three levels of HDTMA bromide (50, 75 and 100% of the bentonite *CEC*) and an additional two levels of ODMBA chloride (50 and 75% of the bentonite *CEC*). Synthesized samples were used for the first time for the adsorption of IBU and DS, and kinetic and thermodynamic parameters were determined and discussed. New insights into the arrangement of both surfactants in prepared samples and their influence on IBU and DS adsorption were suggested based on the characterization of adsorbents by various methods.

2. Materials and Methods

Natural bentonite clay (B) from the Šipovo deposit (Bosnia and Herzegovina) was used as a starting material. Mineralogical and chemical compositions of B were reported in our previous study [13]. Briefly, a qualitative XRPD analysis ascertained that the mineralogical composition of the B was primarily montmorillonite, with carbonates and quartz as accessory minerals. The specific surface area of B, determined by the nitrogen adsorption method (S_{BET}), was 88.6 m^2/g [13]. The chemical composition (wt %) of B was as follows: 56.01% SiO_2, 22.07% Al_2O_3, 3.75% CaO, 1.78% MgO, 3.16% Fe_2O_3, 0.25% K_2O, 0.05% Na_2O, 0.34% TiO_2, and 12.46% loss of ignition [13]. The cation exchange capacity of bentonite determined by methylene blue adsorption was 98 meq/100 g [13].

2.1. Bentonite Modification

Starting bentonite was modified with different amounts of two surfactants, HDTMA bromide and ODMBA chloride, their chemical structure is given in Figure 1. ODMBA (purity of 75%) and HDTMA (purity of ≥99%) were supplied by Hoechst AG (Frankfurt am Main, Germany) and Sigma Aldrich (St. Louis, MO, USA), respectively. The amounts of surfactants used for bentonite modifications were equivalent to 50, 75, and 100% of the *CEC* value of bentonite, determined by the methylene blue adsorption.

Modified bentonite samples were obtained according to the procedure previously described by Obradović et al. [13]. The scheme of the modification process is presented in Figure 2. Shortly, the predetermined amount of each surfactant was dissolved in distilled water at 60 °C and added slowly to previously prepared bentonite suspension under continuous stirring. The bentonite and surfactant suspensions were mixed at 9000 rpm

using a digital homogenizer (T-18 Digital Homogenizer Ultra-Turrax, IKA-Werke GmbH, Staufen, Germany). After contact time (15 min), suspensions were filtered, and supernatants were saved for further analysis. The concentrations of released inorganic cations (Na^+, K^+, Ca^{2+}, and Mg^{2+}) from B during the preparation of organobentonites in supernatants were determined by atomic absorption spectrophotometry—AAS (Analytic Jena Spekol 300, Jena, Germany). After filtration, the obtained products were rinsed with distilled water and dried at 60 °C. Prepared organobentonites (OrgBents) containing HDTMA were denoted as HB-50, HB-75, and HB-100, and when ODMBA was used for modification, products were OB-50 and OB-75. OB-100 was synthesized previously using the same procedure [13]. OrgBents obtained using HDTMA (HB-50, HB-75, and HB-100) and ODMBA (OB-50, OB-75, and OB-100) were denoted as HBs and OBs, respectively.

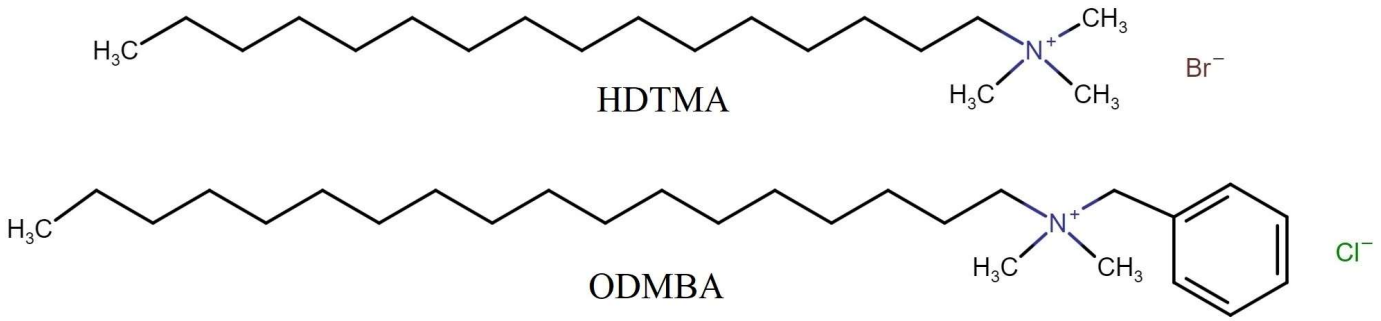


Figure 1. Chemical structure of surfactants.

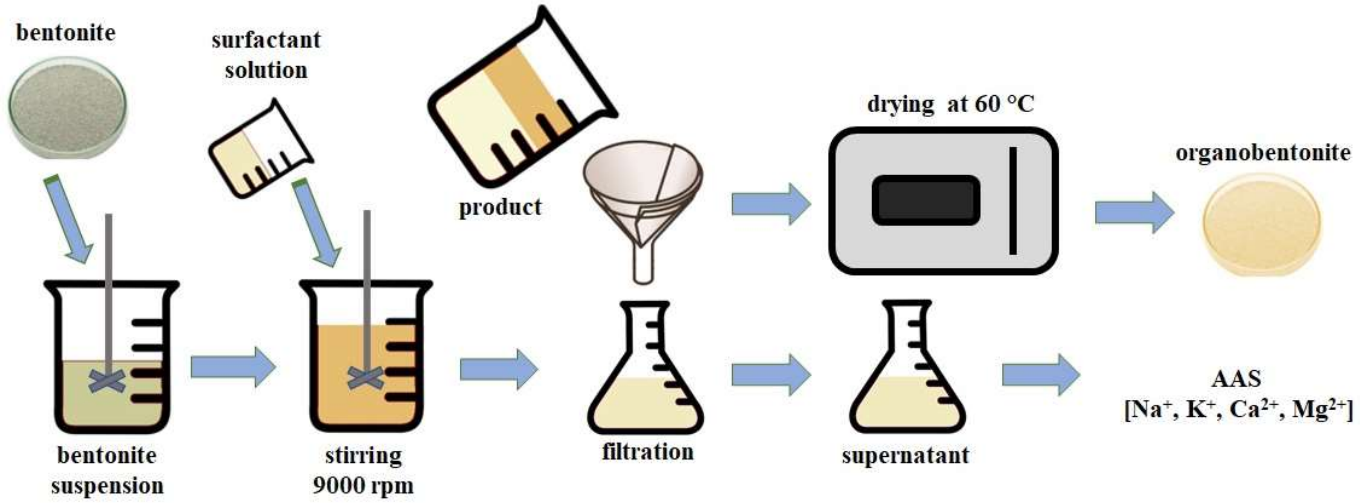


Figure 2. Bentonite modification process.

2.2. Characterization

Adsorption–desorption isotherms of all samples were obtained by nitrogen adsorption at 77 K using a gas sorption analyzer (Thermo Finnigan Sorptomatic 1990, Thermo Scientific, Waltham, MA, USA). Prior to adsorption, OrgBents were degassed first for 1 h at room temperature under a vacuum and then for 16 h at 313 K at the same residual pressure. Values of the total pore volume (V_{tot}) and the specific surface area (S_{BET}) of the samples were determined by applying Gurevitsch's rule at a relative pressure $p/p_0 = 0.98$ (p and p_0 represent the equilibrium and saturation pressures of nitrogen at the temperature of adsorption), and according to the Brunauer–Emmet–Teller (BET) method, from the part of the adsorption isotherms selected by Rouquerol criteria [20]. The specific volume of mesopores (V_{meso}) was determined based on the adsorbed volume of N_2 for the relative pressure ($0.18 \leq p/p_0 \leq 0.96$) corresponding to the mesopore region (pore width 2 nm

to 50 nm), while the Dubinin–Radushkevich (DR) equation was applied to the nitrogen adsorption isotherms to obtain the micropore volume (V_{mic}) [21].

Electron micrographs of B and OrgBents were acquired using a JEOL JSM-7001F field emission scanning electron microscope, SEM (JEOL Ltd., Tokyo, Japan), at an accelerating voltage of 30 kV, a probe current of approx. 1 nA, and a working distance of 6 mm. The samples were coated with gold prior to the SEM analysis, producing a 15 nm thick electrically conductive coating.

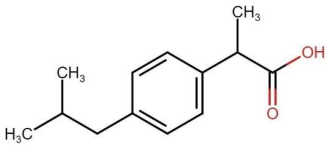
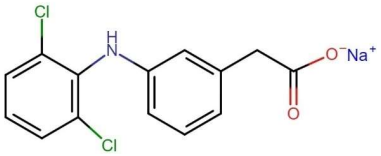
X-ray powder diffraction (XRPD) patterns of OrgBents were recorded on an X-ray powder diffractometer (PW 1710, Philips Instrument, Eindhoven, The Netherlands) with a Cu anticathode (λ = 0.154178 nm). Samples were scanned over the interval 4–65° 2θ at scanning speeds of 0.02°/s.

The point of zero charge (pH_{PZC}) was determined by the batch equilibration method [22]. KNO_3 (0.001; 0.01; 0.1 mol/L) was used as the background electrolyte. The initial *pH* values (pH_i) of 50 mL water solutions were adjusted in the range of 2–12 using 0.1 M KOH or 0.1 M HNO_3. The *pH* values of the solutions were measured using a pH meter (pH/Ion Meter 781, Metrohm, Herisau, Switzerland). Then, 100 mg of each sample was added to KNO_3 solutions. After shaking (150 rpm, Unimax 1010 Shaker with an incubator, Heidolph, Schwabach, Germany) for 24 h at room temperature solutions were filtered and the *pH* of each supernatant was measured (pH_f). The pH_{PZC} was determined as the plateau of the curve $pH_f = f(pH_i)$.

2.3. Drug Adsorption Experiments

DS was supplied by Sigma-Aldrich, and IBU was obtained from Galenika a.d. The experiments were performed at *pH* = 7 in a phosphate buffer solution. The chemical structure and basic physicochemical characteristics of the drugs are presented in Table 1.

Table 1. Chemical structure and physicochemical characteristics of IBU and DS.

Drug	Structure	*M* (g/mol)	pK_a	$log\ K_{ow}$
IBU		206.29	4.4 [1]	3.5 [2]
DS		318.13	4.1 [3]	4.5 [3]

[1] [23]; [2] [24]; [3] [25].

Kinetic experiments were performed at 298 K by mixing 25 mg of each adsorbent with 25.0 mL of IBU or DS at the initial concentration of 50 mg/L. All experiments were carried out in 100 mL Erlenmeyer flasks (with ground glass stoppers) using a rotary shaker (250 rpm, Unimax 1010 Shaker with incubator, Heidolph, Schwabach, Germany). Suspensions were filtered after 2, 5, 10, 20, 30, 40, 50, 60, 70, 80, and 90 min. Thermodynamic experiments were performed at 298, 308, and 318 K by mixing 25 mg of each adsorbent with 25.0 mL of each drug at an initial concentration of 50 mg/L. Suspensions in thermodynamic experiments were filtered after 60 min.

After the chosen reaction time, solutions were filtered, and the concentrations of non-adsorbed drugs were determined in supernatants. The concentrations of drugs before and after adsorption were determined using UV-Visible Spectrophotometry (UV-VIS 1800, Shimadzu, Kyoto, Japan), at a maximum wavelength of 222 nm for IBU and 276 nm for DS. The amounts of adsorbed drugs *q* (mg/g) were calculated from the difference between

the initial concentration of the drug and its concentration in the supernatant after the equilibrium using the following equation:

$$q = \frac{(c_0 - c_e)V}{m}, \quad (1)$$

where V (L) is the volume of the solution, m is the weight of the adsorbent (g), and c_0 (mg/L) and c_e(mg/L) are the concentrations of drugs in the initial solution and at the equilibrium, respectively. The adsorption index was calculated by the following equation:

$$adsorption\ index = \frac{(c_o - c_e)}{c_o} \times 100. \quad (2)$$

3. Results and Discussion

3.1. OrgBents Characterization

3.1.1. The Content of Exchangeable Cations

The amounts of surfactants, organic cations (OC), used in this study were below or equal to the *CEC* value of B. The modification of B with OC occurred via the ion exchange of inorganic cations in the interlayer space and at the surface of B with surfactant ions. In order to confirm this mechanism, the amounts of inorganic cations released from B during preparation (Σ_{total}) were determined and compared with the amounts of each surfactant used for modification (OC_{added}). The *CEC* value of starting B and amounts of released inorganic cations in supernatants after preparation of OrgBents are presented in Table 2.

Table 2. Content of exchangeable cations in the starting B and supernatants after the modification of B with surfactants.

Sample	OC_{aded}	Na^+	K^+	Mg^{2+}	Ca^{2+}	Σ_{total}	*Exchanged* (%) [2]
			(meq/100 g)				
B						98.0 [1]	
HB-50	49.0	0.5	0.7	6.0	43.9	51.1	100.0
HB-75	73.5	0.5	0.9	8.0	56.9	66.3	90.2
HB-100	98.0	0.7	0.9	9.4	74.9	85.9	87.7
OB-50	49.0	0.4	0.8	6.1	45.3	52.6	100.0
OB-75	73.5	0.6	1.0	7.8	63.9	73.3	99.7
OB-100	98.0	1.1 [3]	1.0 [3]	8.2 [3]	84.0 [3]	94.3	96.2

[1] Total *CEC* determined by the methylene blue adsorption method. [2] The ion exchange ratio, *Exchanged* = $\Sigma_{total}/OC_{aded} \times 100\%$; if $\Sigma_{total} \geq OC_{aded}$, then *Exchanged* = 100%. [3] Previously reported in Obradovic et al. [13].

A comparison of the amounts of inorganic cations released from B with the amount of OC used for modification showed that for all OrgBents containing ODMBA, quantitative ion exchange occurred. In our previous study [13], quantitative ion exchange for OB-100 was confirmed by comparing the Fourier-transform infrared spectrum of a water solution of ODMBA containing the amount of ODMBA as used for the preparation of OB-100, with the spectrum of the supernatant collected after preparation of this OrgBent. It was reported that characteristic bands of ODMBA at 2923 cm^{-1} and 2853 cm^{-1} were not visible in supernatants.

For OrgBent containing the lowest amount of HDTMA (50% of *CEC*), the ion exchange was quantitative (no differences between Σ_{total} and OC_{added}), while in OrgBents with higher amounts of HDTMA (75 and 100% *CEC*), the ion exchange occurred with high efficiency, but was incomplete. The differences in ion exchange behavior during the preparation of OBs and HBs may be the consequence of the different structures of HDTMA and ODMBA molecules and their different arrangements in the interlayer space and at the outer surface of OrgBents.

3.1.2. XRPD Analysis of B and OrgBents

XRPD patterns of B [13] and OrgBents are presented in Figure 3 in the 2θ range from 4 to 10°. After modification with surfactants, the basic structure of B remains unchanged, while the interlayer space (d_{001}) of B at 15.3 Å (the peak at 2θ equal to 5.79°) increased to around 17.0 Å (the peak at 2θ equal to 5.03°) for OrgBents obtained by the modification of B with ODMBA ions. For OrgBents containing HDTMA, the interlayer space increased to 16.7 Å (the peak at 2θ equal to 5.46°) for HB-50, 17.8 Å (the peak at 2θ equal to 4.96°) for HB-75, and 19.1 Å (the peak at 2θ equal to 4.61°) for HB-100. The shift toward lower 2θ angular values, which corresponds to the 001 reflection (i.e., increase in the interlayer spacing) for OrgBents compared to B, confirmed the presence of ODMBA or HDTMA ions in the interlayer space of B [26]. In the case of OrgBents modified with HDTMA, the d_{001} value increased significantly with an increase in the amount of surfactant in the interlayer space of B (from 16.7 Å for HB-50 to 19.1 Å for HB-100), while only a slight increase was observed for OrgBents modified with ODMBA (16.8 Å for OB-50 to 17.6 Å for OB-100). The obtained results are consistent with the XRPD results of Son et al. for organoclays modified with different amounts (n = 0.5, 1.0, 1.5, and 2.0; 100% *CEC* represents n = 1) of two surfactants, one without the benzyl group (HDTMA bromide), H-Bt, and the other with the benzyl group (benzyldimethylhexadecylammonium chloride), B-Bt [27]. Namely, they reported the calculated interlayer spacing of the organoclays H-Bt–n (n = 0.5, 1.0, 1.5, and 2.0) of 1.48, 1.81, 1.90, and 1.84 nm, respectively, and around 1.77 nm for all B-Bt samples. The authors pointed out that the reason for these differences may be the size of the benzene ring (8.29 Å), which is 2.3 times the width of the alkyl group (3.65 Å) of the surfactants, which leads to steric hindrance within the interlayer spaces of bentonite and caused the basal spacing of B-Bt to be smaller than H-Bt. Thus, in our study, an increase in the d_{001} values was less for OrgBents modified with ODMBA, and the results of XRPD analysis confirmed the presence of both surfactants in OrgBents and evidenced that surfactant ions in OrgBents with ODMBA are positioned at the outer surface and in the interlayer space, while for OrgBents modified with HDTMA ions, surfactants are mainly located in the interlayer space, and low amount of these ions is adsorbed at the outer surface.

3.1.3. Textural Properties of B and OrgBents

Low-temperature nitrogen physisorption at 77 K was used to determine the textural properties of B and OrgBents. Nitrogen adsorption–desorption isotherms for all investigated samples are given in Figure 4.

As previously reported [13], the isotherm of B and OrgBent modified with ODMBA in an amount of 100% of *CEC* can be classified as type II, which is typical for non-porous and macroporous materials. The isotherms of all OrgBents studied in this research can also be classified as type II. The reversible part of the isotherm occurs at low equilibrium pressures, while above $p/p_0 \approx 0.4$, a hysteresis loop of type H3 occurs, which is characteristic for aggregates of plate-shaped particles [28] and is particularly pronounced in the starting bentonite sample, and it still occurs in the isotherm of HB-50 and OB-50. From the data of adsorption measurements, the textual parameters of the materials were calculated and presented in Table 3. Changes in these parameters show the influence of B modification with different amounts of surfactants.

Table 3. Textural parameters of B and OrgBents.

Sample	S_{BET} (m^2/g)	V_{tot} (cm^3/g)	V_{meso} (cm^3/g)	V_{mic} (cm^3/g)
Bentonite [1]	88.6	0.170	0.106	0.036
HB-50	10.3	0.047	0.029	0.005
HB-75	3.0	0.033	0.010	0.001
HB-100	2.3	0.041	0.008	0.001
OB-50	4.3	0.036	0.016	0.002

Table 3. *Cont.*

Sample	S_{BET} (m^2/g)	V_{tot} (cm^3/g)	V_{meso} (cm^3/g)	V_{mic} (cm^3/g)
OB-75	3.5	0.063	0.009	0.002
OB-100 [1]	7.2	0.055	0.023	0.003

[1] Previously reported in Obradovic et al. [13].

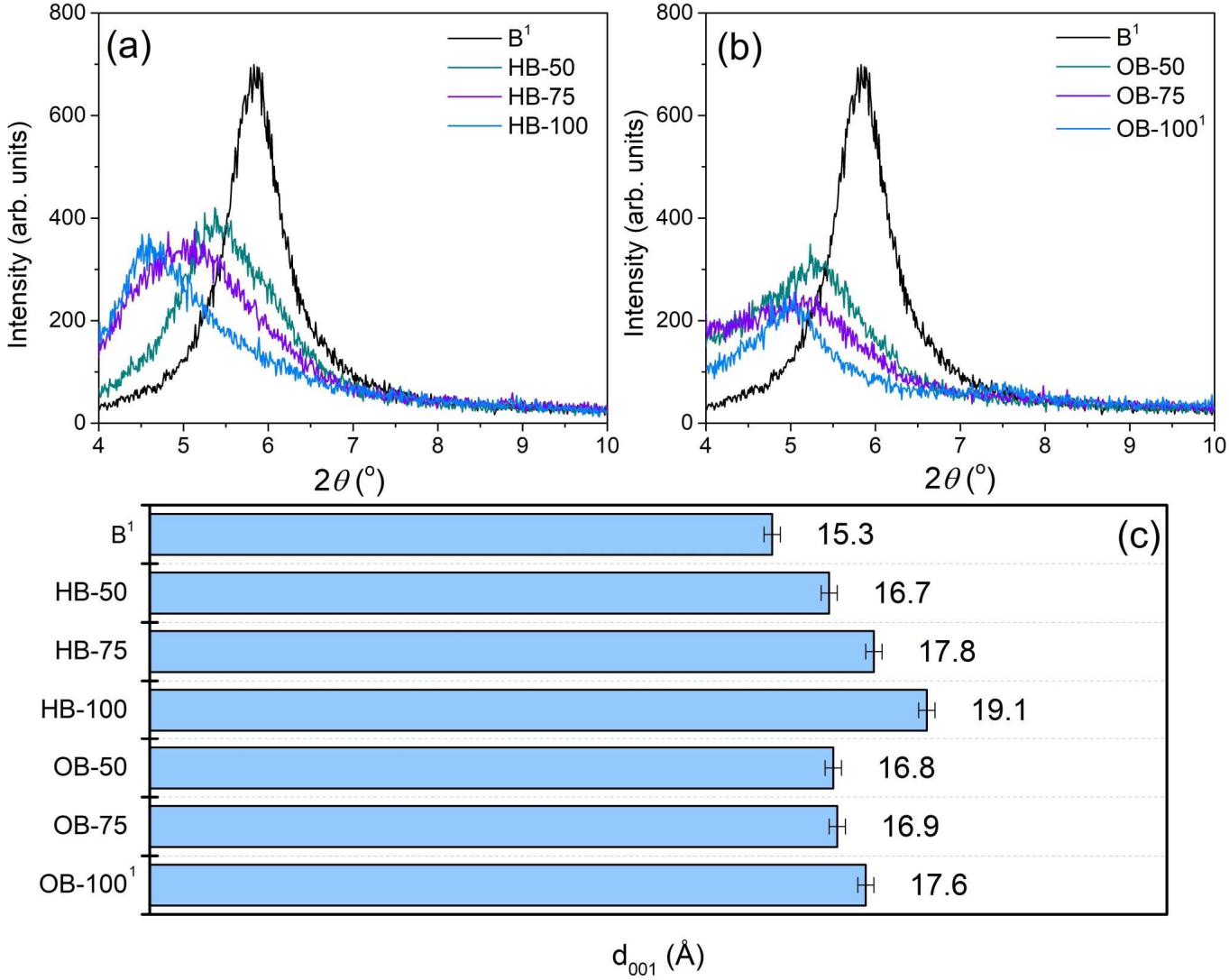


Figure 3. XRPD patterns of (**a**) B and HBs, (**b**) B and OBs, and (**c**) interlayer spacing d_{001} values of B and OrgBents. [1] Previously reported in Obradovic et al. [13].

The data in Table 3 indicate that compared to the starting B, all textural parameters of OrgBents are significantly reduced. The organomodification of B decreased the specific surface area and meso- and micropore volume in comparison to B, indicating substantial blockage of most B pores by the intercalated surfactant ions within the interlayer space. Modifications with HDTMA or ODMBA, however, result in a reduction in textural parameters in a slightly different manner. Interestingly, while there was not a significant variance in textural properties between HBs and OBs, in OBs, a marginal increase in textural parameters with functionalization degree was observed. This may indicate a potential steric hindrance to intercalation due to the benzyl group present in ODMBA and the small but recognizable contribution of the organic phase to the overall texture of the organomodified

bentonite as organic content increased. On the contrary, in the case of HB samples, there is a noticeable trend of a decrease in S_{BET} and V_{meso} with an increase in surfactant content.

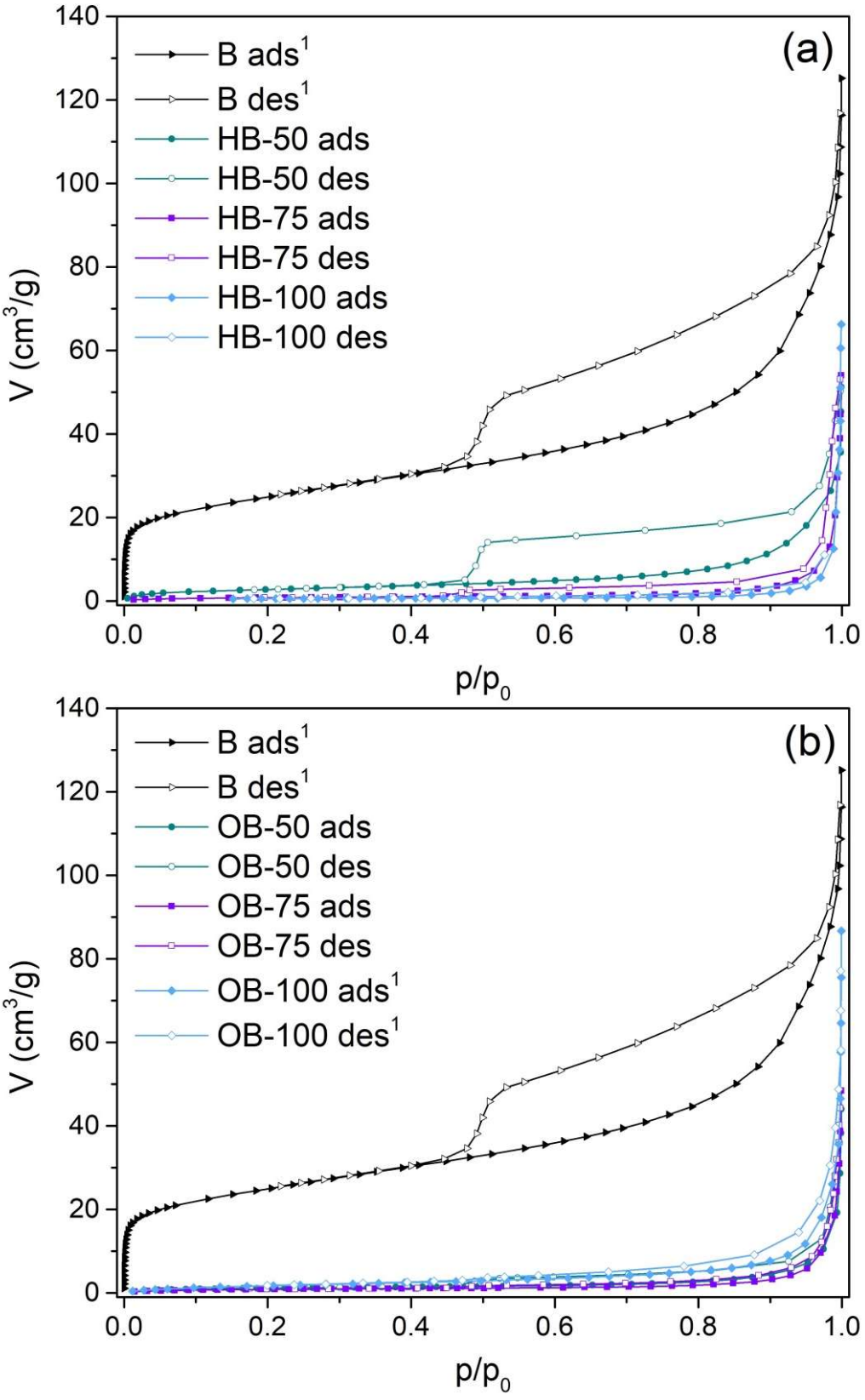


Figure 4. Nitrogen isotherms of (**a**) B and HBs and (**b**) B and OBs. [1] Previously reported in Obradovic et al. [13].

In other words, the successful exchange of inorganic cations up to the level of 50% of *CEC* by HDTMA, due to its slightly shorter chain compared to ODMBA, supported by the proper distribution of HDTMA ions at the available surface of B and its partial entry into the interlamellar space of B, which results in a smaller reduction in S_{BET} and all other textural parameters compared to its ODMBA-modified counterpart. A further increase in the HDTMA content ends with a decrease in textural sizes to a level typical for non-porous materials as a consequence of the complete wrapping of the native bentonite particles by the organic modifier. Additionally, the explanation regarding interlayer spacing is given in the XRPD section (please see Section 3.1.2, XRPD analysis of B and OrgBents), where it was suggested that the benzene ring leads to steric hindrance within the interlayer space of bentonite, causing a smaller shift of the basal spacing of OBs in comparison to HB samples [27].

3.1.4. SEM Analysis of B and OrgBents

Typical surface morphologies of B and OrgBents, acquired by SEM analysis, are presented in Figure 5. The starting material is absolutely dominated by irregular scale-like or flaky aggregates of B and is generally up to 1 μm in diameter and highly compacted. The modification with HDTMA showed a tendency to produce expanded, flattened aggregates of HBs with flat, plate-like (branched and non-coalescent) deposits of HDTMA on their surface, with a mean radius of around 20 nm for HB-50. A higher concentration of the surfactant promoted further growth of the deposits, to around 80 nm for HB-75, as well as their coalescence into rod-like, Y-shaped, and irregular forms. The concentration of HDTMA equivalent to 100% of the *CEC* value of B did not promote any significant growth but rather a further coalescence of deposits into branched and irregular forms (Figure 5d). The surface coverage of B with HDTMA was around 20, 35, and 45% for HB-50, HB-75, and HB-100, respectively. Considering the characteristic behavior of surfactants in excess on clay minerals or zeolites [29] through a micelle or bilayer formation, these aggregates are expected to be thin layers.

On the other hand, the modification with ODMBA at the level of 50% of the *CEC* value showed only a certain expansion of B aggregates, with no distinguishable surface deposits. An increase to 75% of the *CEC* value produced a thin, discontinuous film, with a surface coverage of over 70%, further increasing the ODMBA concentration, produced a more continuous film with a coverage of the clay surface of nearly 90% (compared to only 35% for HB-75 and 45% for HB-100).

Moreover, taking into account the efficiency of the cation exchange of clay minerals (please see Section 3.1.1, the content of exchangeable cations) in ODMBA-modified samples, a higher number of cations are exchanged. The exchange of cations with the surfactant ions leads to the formation of deposition centers, where the binding of additional surfactant ions occurs through hydrophobic interactions. Since the cation exchange of inorganic cations in B with ODMBA is more efficient than the exchange with HDTMA, there are initially more deposition centers at the surface of OBs. Additionally, ODMBA contains a benzene ring in the structure, enabling additional π-π bonding with other surfactant ions, resulting in the formation of a continuous film on the surface of OBs. Thus, SEM analysis confirmed the incorporation of the surfactants into the interlayer space of B, as well as a tendency of ODMBA to concentrate on the outer surface of B, to a much greater extent than applied to HDTMA, as discussed in detail in Section 3.1.1.

3.1.5. Point of Zero Charge of B and OrgBents

Point of zero charge (pH_{PZC}) is the pH value where the adsorbent surface has the same amount of positive and negative active sites, and the total net charge of the surface is zero. At *pH* values below pH_{PZC}, the adsorbent surface is positively charged and favors the uptake of anions. At *pH* values above pH_{PZC}, the adsorbent surface is negatively charged and is able to interact with positively charged species [30]. The pH_{PZC} was determined in order to investigate if the type and the amount of surfactants in OrgBents have an influence

on their surface charge. The results of the determination of the pH_{PZC} for starting B and OrgBents are presented in Figure 6.

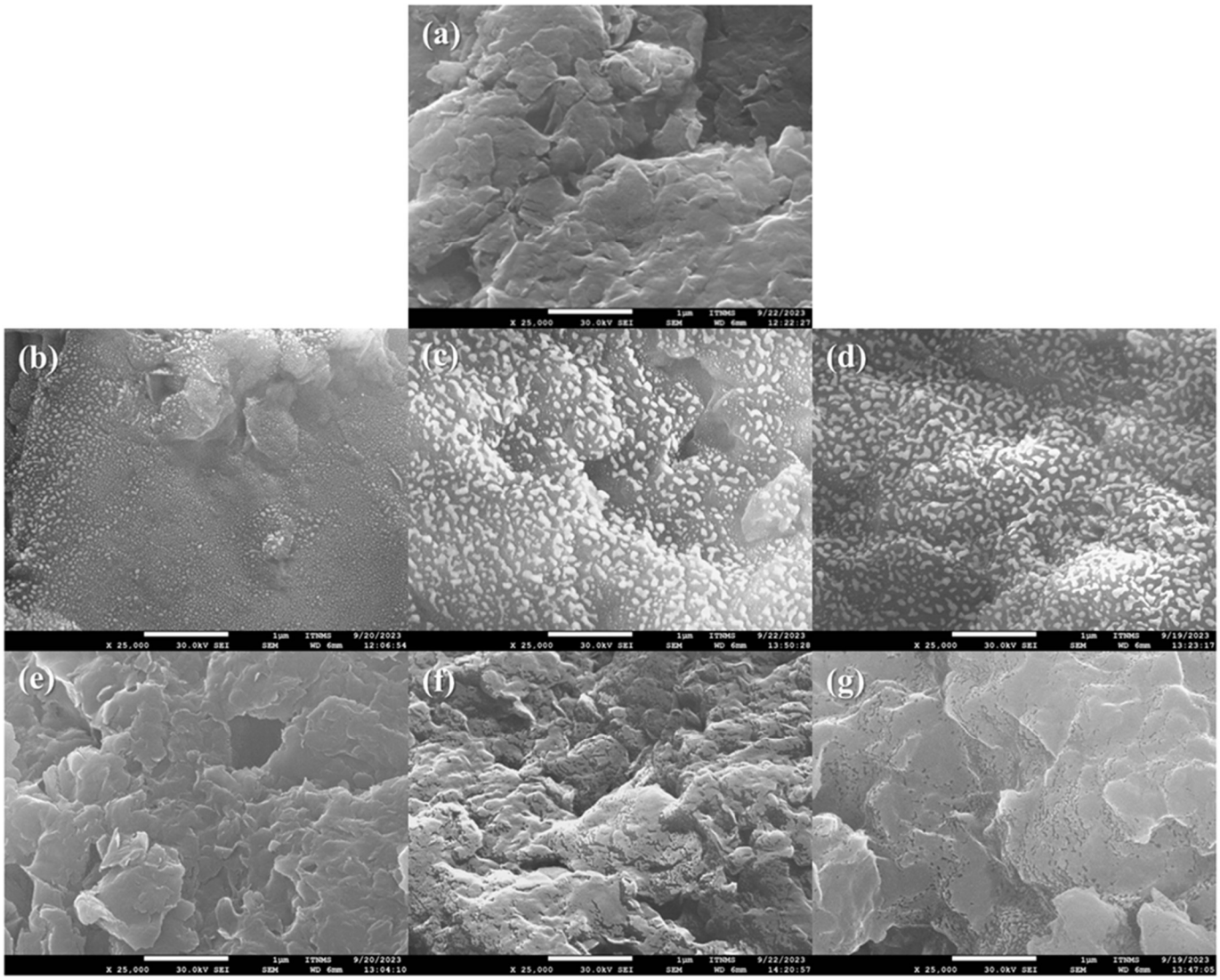


Figure 5. SEM images: (**a**) B; (**b**) HB-50; (**c**) HB-75; (**d**) HB-100; (**e**) OB-50; (**f**) OB-75; (**g**) OB-100, at the magnification of 25,000×, scale bar 1 µm.

The plotted curves have the same shape for all samples. The obtained pH_{PZC} values of all OrgBents are similar, and they do not differ from the pH_{PZC} value of B (pH_{PZC} = 7.3). The *pH* range of the plateau is the range of *pH*, where the buffering effect of the adsorbent surface takes place. The plateau for all samples was in a wide range (from about *pH* = 3 to *pH* = 10), where these adsorbents tend to remain at the same equilibrium pH value. Similar obtained pH_{PZC} values for all OrgBents are indications that pH_{PZC} is not dependent on the type and the amount of both surfactants in OrgBents. It was also observed that the pH_{PZC} determined in KNO_3 solutions of different concentrations was practically the same for all samples. Thus, the pH_{PZC} of all adsorbents does not depend on the used background electrolyte's ionic strength, and the specific adsorption of K^+ or NO_3^- did not occur [30,31].

The overall characterization results of OrgBents confirmed their successful synthesis by the modification of bentonite with surfactants via the ion exchange of inorganic cations in B. Results confirmed the presence of both surfactants in OrgBents. The difference in the structures of HDTMA and ODMBA molecules led to their different arrangement in the interlayer space and at the outer surface of B. The results showed that surfactant ions in

OrgBents modified with ODMBA are positioned at the outer surface and the interlayer space, while for OrgBents modified with HDTMA ions, surfactants are mainly located in the interlayer space, and lower amounts of these ions are positioned at the outer surface.

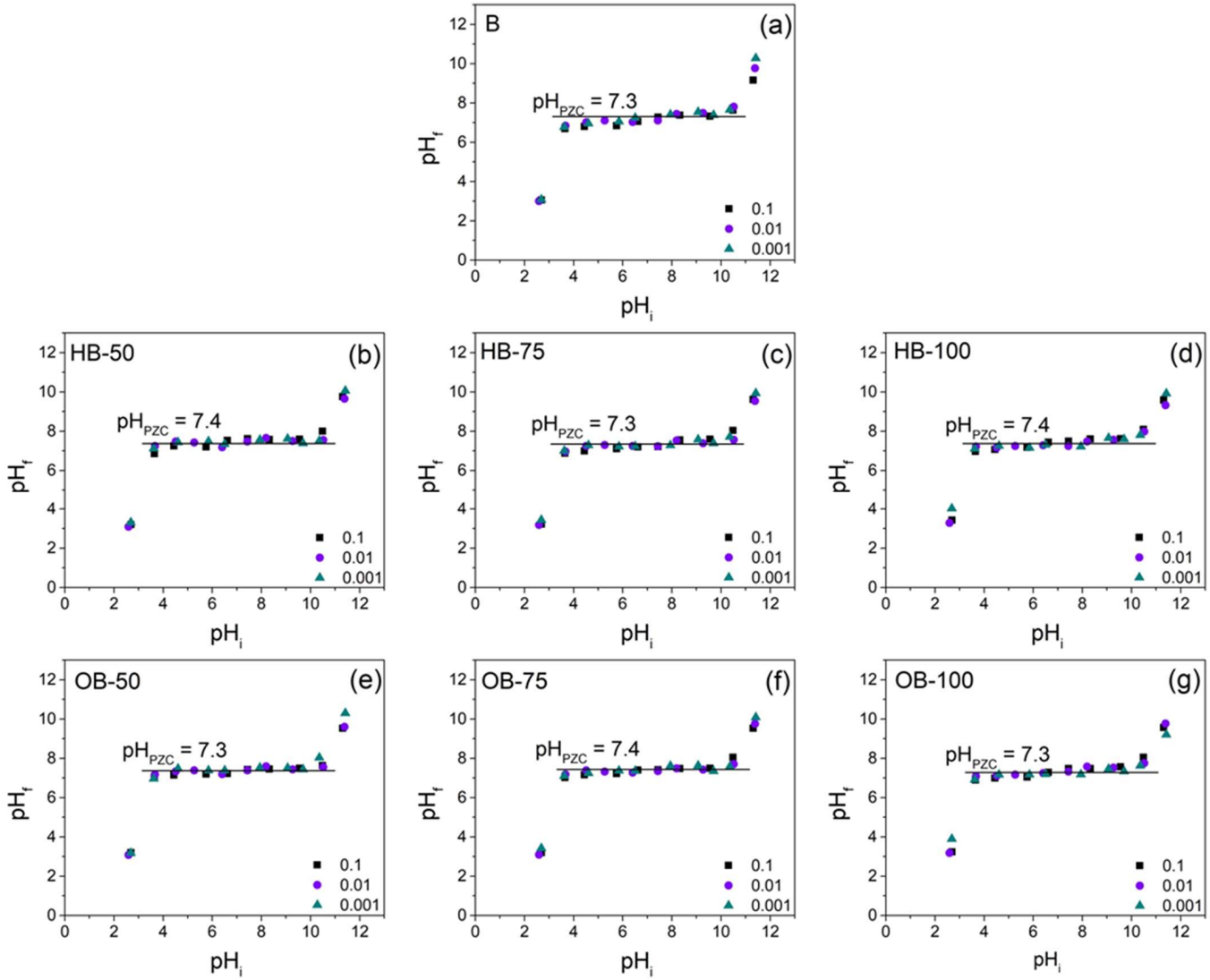


Figure 6. Determination of the point of zero charge of (**a**) B; (**b**) HB-50; (**c**) HB-75; (**d**) HB-100; (**e**) OB-50; (**f**) OB-75; (**g**) OB-100.

3.2. Kinetic and Thermodynamic Studies

3.2.1. Kinetic Study

The importance of kinetic studies for the adsorption process is essential for understanding the adsorption behavior of pollutants in relation to time. The effect of contact time on the adsorption of IBU and DS on OrgBents was studied, and the results are presented in Figure 7. Graphs showed that the adsorption of both drugs increased with time and attained equilibrium.

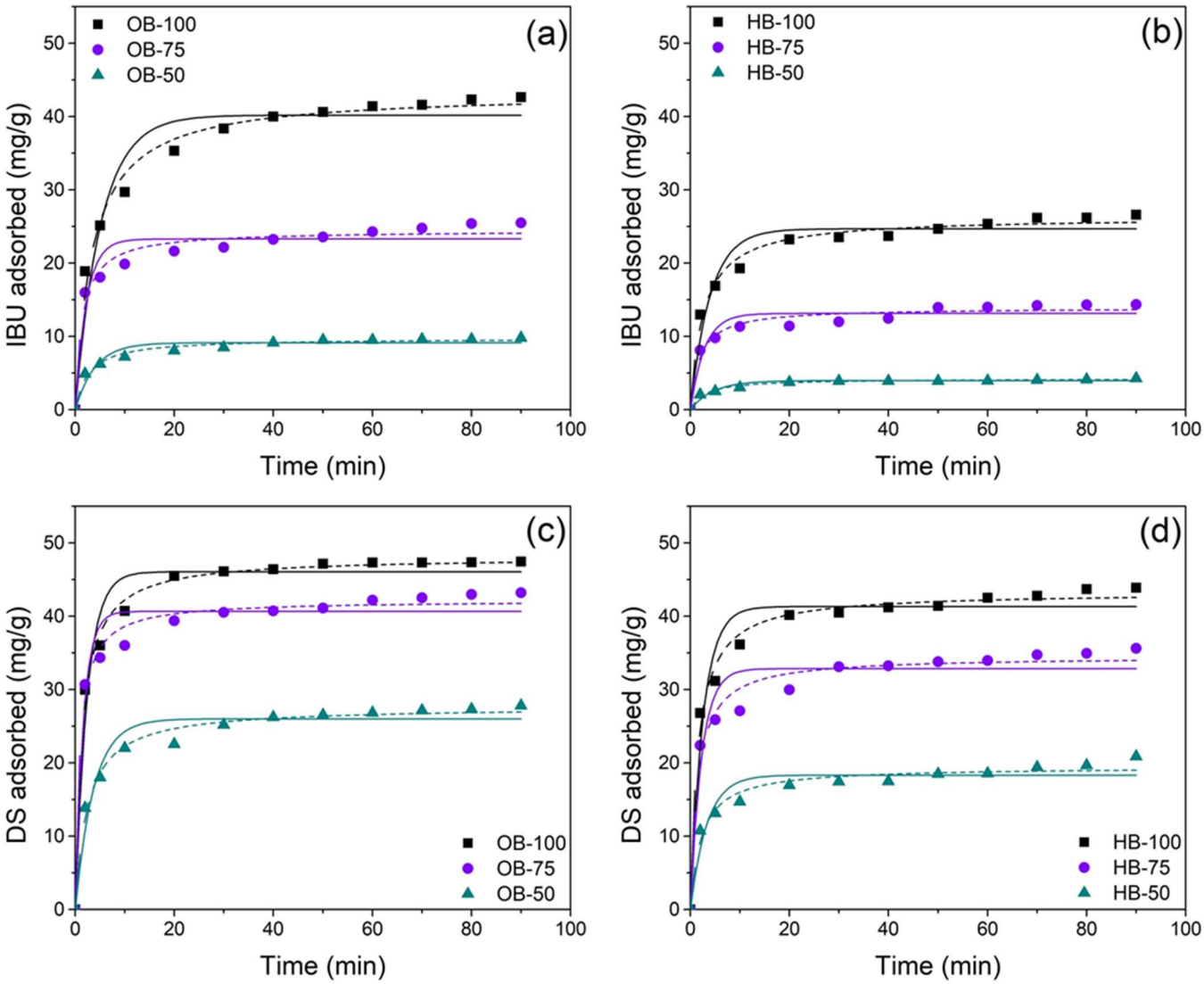


Figure 7. The impact of contact time on (**a**) IBU adsorption on OBs; (**b**) IBU adsorption on HBs; (**c**) DS adsorption on OBs; and (**d**) DS adsorption on HBs. The PFO model is represented by a solid line and the PSO model is represented by a dashed line.

The obtained data were fitted with nonlinear pseudo-first-order (PFO) and pseudo-second-order (PSO) kinetic models since these models have been commonly used for data analysis on drug adsorption on organomodified minerals [11].

The Lagergren PFO equation is generally expressed as follows:

$$q_t = q_e\left(1 - e^{-k_1 t}\right), \tag{3}$$

while the PSO equation is expressed as:

$$q_t = \frac{{q_e}^2 k_2 t}{q_e k_2 t + 1}, \tag{4}$$

where q_e (mg/g) is the equilibrium amount and q_t (mg/g) is the adsorbed amount of drugs at the adsorption time t (min). The k_1 (1/min) and k_2 (g/(mg·min)) are the kinetic constants of the PFO and PSO kinetic models. In the PSO model, the initial adsorption rate, h, can be defined as [32]:

$$h = k_2 {q_{e2}}^2. \tag{5}$$

The fitting curves using the PFO and PSO kinetic models are shown in Figure 7, while the values of the kinetic constants calculated by the nonlinear models are listed in Table 4.

Table 4. Kinetic parameters for IBU and DS adsorption on OrgBents.

Model	Parameter	IBU					
		HB-50	**HB-75**	**HB-100**	**OB-50**	**OB-75**	**OB-100**
Experimental data	q_e^{exp}	4.3	14.3	26.6	9.8	25.5	42.6
PFO	k_1	0.22	0.36	0.25	0.25	0.45	0.19
	q_{e1}	4.0	13.1	24.7	9.1	23.3	40.2
	r^2	0.95	0.91	0.94	0.93	0.92	0.94
PSO	k_2	0.08	0.04	0.01	0.04	0.03	0.01
	q_{e2}	4.2	13.9	26.3	9.7	24.4	43.3
	h	1.4	7.7	6.9	3.8	17.9	18.7
	r^2	0.98	0.96	0.99	0.98	0.97	0.99
Model	**Parameter**	**DS**					
		HB-50	**HB-75**	**HB-100**	**OB-50**	**OB-75**	**OB-100**
Experimental data	q_e^{exp}	20.9	35.6	43.9	27.8	43.2	47.4
PFO	k_1	0.30	0.45	0.39	0.27	0.62	0.42
	q_{e1}	18.3	32.8	41.3	26.0	40.7	46.1
	r^2	0.92	0.92	0.95	0.95	0.96	0.97
PSO	k_2	0.02	0.02	0.02	0.02	0.03	0.02
	q_{e2}	19.4	34.5	43.3	27.7	42.2	48.1
	h	8.7	23.8	37.5	15.3	53.4	46.3
	r^2	0.97	0.98	0.99	0.99	0.99	0.99

q_e^{exp}, q_{e1}, q_{e2}(mg/g), k_1(1/min), k_2(g/(mg·min)), h (mg/(g·min)).

As presented in Figure 7, the adsorption of both drugs by OrgBents with the lowest amount of HDTMA or ODMBA showed a steady increase for the first 10 min, and then slowly increased and attained equilibrium within 60 min. With an increase in the amount of both surfactants in OrgBents, the adsorption of IBU and DS was initially fast and increased within the first 30–40 min, achieving equilibrium after 60 min.

Based on the higher correlation coefficients (r^2), as well as lower deviations between calculated (q_{e1} and q_{e2}) and experimentally determined adsorbed amounts (q_{exp}), the PSO model showed better fits of the experimental data for all OrgBents (Table 4). The fact that the calculated q_{e2} values were very close to those of the measured results for PSO kinetics indicated that the IBU and DS adsorption behavior was controlled by several processes and that the chemical adsorption could be the primary interaction mechanism controlling drug adsorption.

In Table 4, it can be also seen in the PSO model that for the adsorption of IBU by OrgBents, the calculated rate constants decreased with an increase in the amount of either HDTMA or ODMBA (from 0.08 g/(mg·min) for HB-50 to 0.01 g/(mg·min) for HB-100 and from 0.04 g/(mg·min) for OB-50 to 0.01 g/(mg·min) for OB-100). For the adsorption of DS by OrgBents, the calculated rate constants were similar for all OBs and HBs (around 0.02 g/(mg·min)). The highest rate constants observed for IBU adsorption by adsorbents with the lowest amount of surfactants may be related to the existence of a certain number of active sites, which, with an increase in reaction time, are totally occupied within a short period of time, and then no more IBU molecules could be adsorbed by these adsorbents due to their saturation. When the amount of surfactants increases, a longer time is necessary for IBU to reach the active sites until equilibrium is achieved, so the adsorption rates decrease. For the adsorption of DS by all OrgBents, similar but lower values of rate constants suggest a slightly slower adsorption of this molecule by OrgBents. Additionally, the initial rates for IBU and DS adsorption increased with an increase in the amount of ODMBA and HDTMA

in OrgBents. The highest calculated initial rates were observed for adsorbents with the highest amounts of both surfactants, and for IBU adsorption, higher initial rates were observed for OBs than HBs (18.7 mg/(g·min) for OB-100 and 6.9 mg/(g·min) for HB-100). Compared to IBU, for the adsorption of DS, similar but much higher initial rates were noticed for both adsorbents with the highest amount of both surfactants (37.5 mg/(g·min) for HB-100 and 46.3 mg/(g·min) for OB-100). This may be additional evidence that an increase in the amount of surfactant in OrgBents increases the number and availability of active sites at which both drugs are adsorbed.

The obtained results are in agreement with the results reported by other researchers. Sun et al. [33] studied the kinetics of the adsorption of DS on illite and bentonite modified by HDTMA in an amount equal to 200% of the *CEC* of minerals. They reported that the adsorption of the drug was almost instantaneous, particularly on illite, and that the PSO model fit the adsorption experimental data the best. The authors suggested that a higher initial rate constant for DS adsorption on organomodified illite indicates surface adsorption of the investigated drug. Furthermore, the lower rate constant observed for DS removal by HDTMA-modified bentonite suggested that the adsorption of the drug occurred at the adsorption sites positioned in the interlayer space of organomodified bentonite instead of the surface, which could be due to DS diffusion from the bulk solution into the interlayer space. In our previous study [13], PSO fit the experimental data on the adsorption of IBU and DS on kaolin, zeolite, and bentonite modified with ODMBA (OK, OZ, and OB) the best. In the PSO model, rate constants for IBU adsorption by organomodified minerals decreased in the following order: OK (0.982 g/(mg·min)) > OZ (0.116 g/(mg·min)) > OB (0.069 g/(mg·min)). For the adsorption of DS on organomodified minerals, the rate constants were 2.463 g/(mg·min) (OK), 0.077 g/(mg·min) (OZ), and 0.250 g/(mg·min) (OB) [13]. A one order of magnitude lower rate constant observed for the adsorption of IBU and DS on OB additionally confirmed that the adsorption of drugs occurred not only at the surface but also in the interlayer space of OB, while for the adsorption of DS and IBU, active sites are located only at the external surfaces of OK and OZ. The PSO model was also successful in describing the kinetics of IBU adsorption on octadecylamine/montmorillonite [34], the adsorption of DS on decylpyridinium chloride or HDTMA chloride/bentonite [11], and the adsorption of IBU and DS on HDTMA/bentonite [9].

Supernatants were collected at the end of the kinetics experiments and used for the determination of the non-adsorbed amount of both drugs. The adsorbed amount of each drug was calculated by Equation (1). The adsorbed amounts of IBU and DS under applied experimental conditions were calculated in μmol/g and compared with the amounts of ODMBA and HDTMA in OrgBents expressed in μmol/g (calculated based on the value Exch. (%) presented in Table 1). The results are presented in Figure 8.

As can be seen, at the initial concentration of 243 μmol/g for IBU and 157 μmol/g for DS for adsorbents with the lowest amounts of surfactants, the maximum adsorbed amounts of IBU were 21 μmol/g for HB-50 and 48 μmol/g for OB-50. For the adsorption of DS, the following adsorbed amounts of the drug were observed: 66 μmol/g for HB-50 and 87 μmol/g for OB-50. An increase in the amount of surfactant in OrgBents increased the adsorbed amount of each drug. The maximum adsorbed amount of IBU was 129 μmol/g at HB-100 and 207 μmol/g at OB-100, while the maximum adsorbed amounts of DS were 138 μmol/g and 149 μmol/g at HB-100 and OB-100, respectively.

The results indicate that although adsorbents with the lowest amount of surfactants (HB-50 and OB-50) contain enough active sites at which drugs can be adsorbed, these sites are not equally available for adsorption of IBU and DS. Namely, the adsorption of IBU was 9% for HB-50 and 20% for OB-50, while much higher adsorption was observed for DS (42% at HB-50 and 56% for OB-50). An increase in the amount of both surfactants in OrgBents (HB-100 and OB-100) led to an increase not only in the number but also in the availability of active sites for the adsorption of IBU and DS. The adsorption of IBU was 53% for HB-100 and 85% for OB-100, while the adsorption of DS was 88% for HB-100 and 95% for OB-100. Also, the results suggested that the presence of the benzyl group

in adsorbents (OBs) enhanced the adsorption of both drugs, and the adsorption of IBU was more dependent on the type of organic cation used for modification of B than the adsorption of DS. Compared to IBU, the DS molecule, although bigger than IBU and more hydrophobic ($logK_{ow}$ values of IBU and DS are 3.5 and 4.5, respectively), easily reached hydrophobic active sites created by surfactants at the surface and interlayer space of both OrgBents. These results explained the results of adsorption kinetics (rate constants and initial rates). Namely, it was previously mentioned in the XRD analysis that organic cations in HBs are mainly positioned in the interlayer space, while in Obs, they are adsorbed at the external surface and interlayer space. The differences in the adsorption of both drugs, which is especially visible for adsorbents with the lowest amount of organic cations (HB-50 and OB-50), may be explained by the fact that in these adsorbents, there are some parts of the surface and in the interlayer space that contain inorganic cations at which anionic DS or IBU cannot be adsorbed. These inorganic cations may prevent IBU and DS from easily penetrating into the interlayer space of OrgBents and reaching active sites created by surfactants. Thus, the adsorption of both drugs occurs mainly at the active sites at HB-50 and OB-50 surfaces. Since OB-50 contains a higher number of surfactants at the external surface, a higher adsorption of both drugs was observed. With an increase in the amount of either HDTMA or ODTMA in adsorbents, the availability of active sites consisting of surfactants in the interlayer space and external surface increased and, consequently, the adsorption of IBU and DS increased.

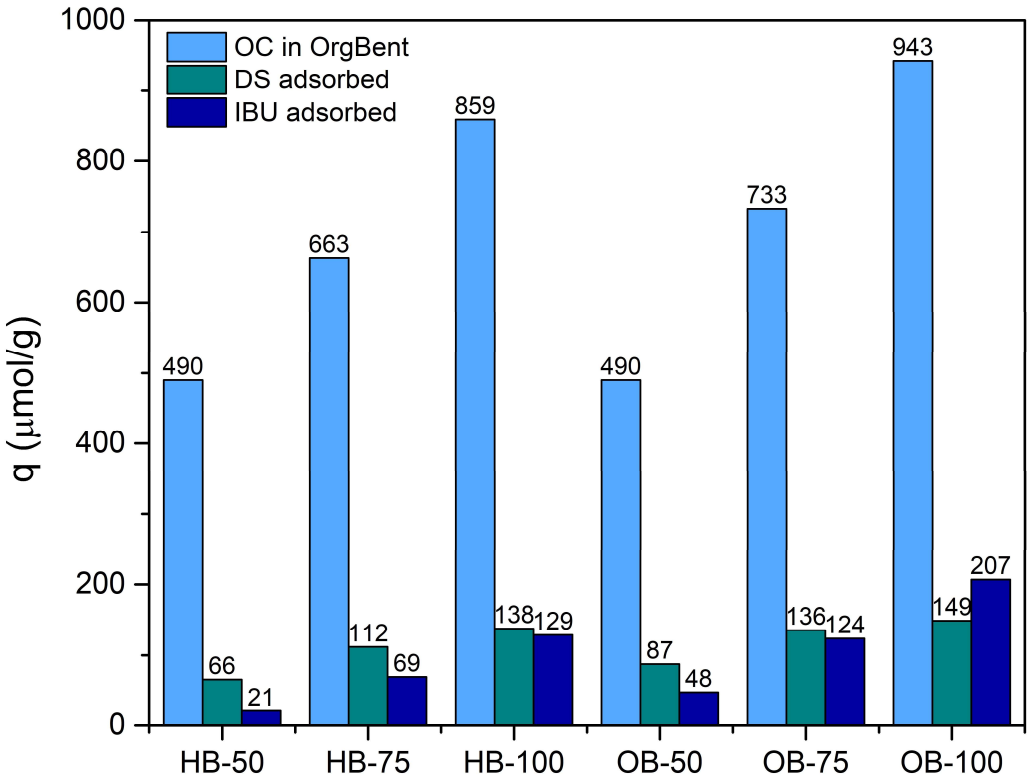


Figure 8. Adsorbed amounts of DS and IBU from the kinetic data versus amounts of surfactants in OrgBents.

It can be also noticed that the DS retention performance of OB-100 and HB-100 observed in this study reached up to 95%, exceeding the drug adsorption data reported for commercially available organoclay [35], organozeolite [13,36,37], and organokaoline [13]. Although IBU removal efficiency by the same adsorbents was somehow lower (approximately up to 85%), it still outperformed previously studied materials, such as biochar [38–40], inorganic nanocomposites [41], and organomodified silicates [13,34,42]. The efficiency in these particular systems originates from higher kinetic constants compared to other materi-

als with reported lower k_2 values, such as organonozeolite [36], functionalized chitosan [43], highly porous MOF [44], and activated carbons [45]. However, the results obtained in this study are hard to compare with the results reported in the literature for different adsorbents since experiments were performed under different experimental conditions.

3.2.2. Thermodynamic Study

Thermodynamic parameters, including the standard Gibbs free energy of adsorption (ΔG°), the standard enthalpy (ΔH°), and the entropy (ΔS°), can be calculated by the following equations:

$$\Delta G^\circ = -RTln\ K_e\ , \quad (6)$$

$$ln\ K_e = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT}, \quad (7)$$

where R is the universal gas constant (8.314 J/(mol·K)), T (K) is the absolute temperature, and K_e is the equilibrium constant at the temperature T, calculated as the ratio of the equilibrium concentrations of IBU or DS onto the adsorbent in a solution. ΔG° was calculated by Equation (6). The values of ΔH° and ΔS° can be found from the slopes and intercepts of the plotting $ln\ K_e$ vs. 1/T (Equation (7)). The values of the thermodynamic parameters for the adsorption of IBU and DS on OrgBents are presented in Table 5.

Table 5. Thermodynamic parameters for IBU and DS adsorption on OrgBents.

Adsorbent		**HB-50**			**HB-75**			**HB-100**		**Drug**
T	298	308	318	298	308	318	298	308	318	**IBU**
ΔG°	6.03	6.15	6.31	2.38	2.39	2.40	−0.17	−0.26	−0.37	
ΔH°		1.85			2.11			2.92		
ΔS°		−13.97			−0.91			10.31		
Adsorbent		**OB-50**			**OB-75**			**OB-100**		
T	298	308	318	298	308	318	298	308	318	**IBU**
ΔG°	3.42	3.51	3.53	−0.02	−0.07	−0.18	−3.95	−4.15	−4.45	
ΔH°		1.73			2.49			3.44		
ΔS°		−5.74			8.40			24.78		
Adsorbent		**HB-50**			**HB-75**			**HB-100**		
T	298	308	318	298	308	318	298	308	318	**DS**
ΔG°	1.24	1.23	1.23	−1.89	−2.00	−2.15	−4.89	−5.19	−5.47	
ΔH°		1.43			2.01			3.86		
ΔS°		0.67			13.05			29.35		
Adsorbent		**OB-50**			**OB-75**			**OB-100**		
T	298	308	318	298	308	318	298	308	318	**DS**
ΔG°	−0.39	−0.50	−0.53	−4.37	−4.60	−4.84	−8.17	−8.55	−8.98	
ΔH°		1.68			2.61			3.92		
ΔS°		6.98			23.45			40.57		

T (K), ΔG° (kJ/mol), ΔH° (kJ/mol), ΔS° (J/(mol·K)).

The standard Gibbs free energies for the adsorption of IBU by OrgBents modified with HDTMA ions were positive for the adsorbent with the lowest amount of surfactant (HB-50 and HB-75), while for the adsorbent with the highest amount of HDTMA (HB-100), ΔG° became negative. For the adsorption of DS by these OrgBents, ΔG° values were positive for HB-50 and negative for HB-75 and HB-100. The standard Gibbs free energies (ΔG°) for the adsorption of IBU by OrgBents containing ODMBA ions were positive for adsorbents with the lowest amount of surfactant (OB-50) and negative for adsorbents with higher amounts of surfactant (OB-75 and OB-100), while for the adsorption of DS, ΔG° values were negative for all adsorbents. Generally, the negative values of ΔG° of adsorption indicate that the adsorption of solute is feasible and spontaneous. This means that for the adsorption of IBU and DS by OrgBents, at higher amounts of both surfactants, their adsorption was

more spontaneous, while at lower amounts of surfactants, the adsorption of drugs was less spontaneous. In addition, ΔG° values become more negative as the temperature increases, suggesting that the adsorption of IBU and DS is more favorable at higher temperatures. Also, it is observed that ΔG° values were less positive or more negative for the adsorption of IBU and DS by OrgBents modified with ODMBA ions, indicating a higher affinity of these materials for both drugs and the enhanced adsorption of both drugs by the presence of the benzyl group in OBs. The change in adsorption standard enthalpy ΔH° was positive, showing the adsorption of either IBU or DS by all OrgBents is endothermic in nature. It is observed that ΔH° values increased with an increase in the amount of both surfactants in OrgBents, which indicates that the IBU and DS adsorption process may be attributed to the increased interactions between the OrgBents and drug molecules as surfactant amounts increased. The standard entropy change (ΔS°) was negative for the adsorption of IBU by OB-50 (−5.74 J/(mol·K)), HB-50 (−13.97 J/(mol·K)), and HB-75 (−0.91 J/(mol·K)), and positive for all other OrgBents. The ΔS° values become less negative or more positive with an increase in the amount of surfactant in OrgBents. An increase in ΔS° values with an increase in the amount of either ODMBA or HDTMA in OrgBents suggests an increased randomness at the solid/solution interface during drug adsorption [46–48].

In general, the characterization of OrgBents, kinetics, and thermodynamic data on the adsorption of IBU and DS by these composites confirmed that surfactant ions are responsible for the adsorption of both drugs. Their adsorption increased with an increase in the amount of both surfactants used for the preparation of OrgBents, confirming that the amount of surfactant influenced the adsorption of drugs. The adsorption of IBU and DS by OrgBents occurs mainly in the interlayer space of HBs, while for OBs, the adsorption of IBU and DS occurs at active sites created by surfactants that are mainly located at the surface of OBs and also in the interlayer space. The results evidenced that the adsorption of both drugs was influenced by the type of surfactant used for modification of B, and the presence of the benzyl group in OBs enhanced the adsorption of either IBU or DS (especially visible for IBU).

4. Conclusions

Bentonite was modified with different amounts (50, 75, and 100% of its *CEC* value) of two surfactants, one without (HDTMA) and the other with the benzyl group (ODMBA), and the obtained materials (OrgBents) were tested for the removal of two drugs, IBU and DS. The characterization of OrgBents showed that ODMBA ions are mainly positioned at the outer surface and interlayer space, while for materials modified with HDTMA ions, surfactants are mainly located in the interlayer space and outer surface in a lower amount.

The results on the adsorption of IBU and DS by OrgBents showed that their adsorption increased with an increase in amount of each surfactant in OrgBents, pointing out that surfactant ions were the active sites at which both drugs were adsorbed, and that the adsorption of drugs was influenced by the amount of surfactant used for modification. Among the surfactants, a much higher adsorption of IBU and DS was achieved by OrgBents modified with ODMBA ions. The results suggested that type of surfactant, as well as its configuration in the interlayer space and the OrgBents surface, influence drug adsorption.

The kinetics of IBU and DS adsorption on OrgBents showed the best fit of the experimental data to the pseudo-second-order kinetic model, indicating that drug adsorption was controlled by multiple processes. Thermodynamics data indicated that with an increase in the amount of surfactants in OrgBents, the adsorption of drugs becomes more spontaneous and generally endothermic in nature. Kinetics and thermodynamics data confirmed that the presence of the benzyl group in the ODMBA surfactant enhanced the adsorption of IBU and DS. The high capacities of OrgBents for IBU and DS and the simple modification process for the preparation of OrgBents, together with the availability and low cost of raw bentonite, make these materials suitable for a potential application in the purification of contaminated waters.

Author Contributions: Conceptualization, A.D.; methodology, M.O. (Milena Obradović), M.M. and D.S.; formal analysis, M.O. (Milena Obradović), D.S. and M.M.; investigation, M.O. (Milena Obradović), J.K., N.V. and M.O. (Milica Ožegović); resources, A.D. and J.K.; writing—original draft preparation, M.O. (Milena Obradović) and A.D.; writing—review and editing, A.D., M.M.-R., N.V. and J.K.; visualization, M.O. (Milena Obradović); supervision, A.D. All authors have read and agreed to the published version of the manuscript.

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Data Availability Statement: The data presented in this study are available upon request from the corresponding author.

Conflicts of Interest: The authors declare no conflicts of interest.

References

1. Noguera-Oviedo, K.; Aga, D.S. Lessons Learned from More than Two Decades of Research on Emerging Contaminants in the Environment. *J. Hazard. Mater.* **2016**, *316*, 242–251. [CrossRef] [PubMed]
2. Tran, N.H.; Reinhard, M.; Gin, K.Y.H. Occurrence and Fate of Emerging Contaminants in Municipal Wastewater Treatment Plants from Different Geographical Regions-a Review. *Water Res.* **2018**, *133*, 182–207. [CrossRef] [PubMed]
3. Sophia, C.A.; Lima, E.C. Removal of Emerging Contaminants from the Environment by Adsorption. *Ecotoxicol. Environ. Saf.* **2018**, *150*, 1–17. [CrossRef] [PubMed]
4. Gros, M.; Petrović, M.; Ginebreda, A.; Barceló, D. Removal of Pharmaceuticals during Wastewater Treatment and Environmental Risk Assessment Using Hazard Indexes. *Environ. Int.* **2010**, *36*, 15–26. [CrossRef] [PubMed]
5. Petrie, B.; Barden, R.; Kasprzyk-Hordern, B. A Review on Emerging Contaminants in Wastewaters and the Environment: Current Knowledge, Understudied Areas and Recommendations for Future Monitoring. *Water Res.* **2015**, *72*, 3–27. [CrossRef] [PubMed]
6. Loos, R.; Gawlik, B.M.; Locoro, G.; Rimaviciute, E.; Contini, S.; Bidoglio, G. EU-Wide Survey of Polar Organic Persistent Pollutants in European River Waters. *Environ. Pollut.* **2009**, *157*, 561–568. [CrossRef]
7. Ahmed, M.J. Adsorption of Non-Steroidal Anti-Inflammatory Drugs from Aqueous Solution Using Activated Carbons: Review. *J. Environ. Manag.* **2017**, *190*, 274–282. [CrossRef]
8. Jun, L.Y.; Mubarak, N.M.; Yee, M.J.; Yon, L.S.; Bing, C.H.; Khalid, M.; Abdullah, E.C. An Overview of Functionalised Carbon Nanomaterial for Organic Pollutant Removal. *J. Ind. Eng. Chem.* **2018**, *67*, 175–186. [CrossRef]
9. Ghemit, R.; Makhloufi, A.; Djebri, N.; Flilissa, A.; Zerroual, L.; Boutahala, M. Adsorptive Removal of Diclofenac and Ibuprofen from Aqueous Solution by Organobentonites: Study in Single and Binary Systems. *Groundw. Sustain. Dev.* **2019**, *8*, 520–529. [CrossRef]
10. Sahnoun, S.; Boutahala, M.; Tiar, C.; Kahoul, A. Adsorption of Tartrazine from an Aqueous Solution by Octadecyltrimethylammonium Bromide-Modified Bentonite: Kinetics and Isotherm Modeling. *Comptes Rendus Chim.* **2018**, *21*, 391–398. [CrossRef]
11. França, D.B.; Trigueiro, P.; Silva Filho, E.C.; Fonseca, M.G.; Jaber, M. Monitoring Diclofenac Adsorption by Organophilic Alkylpyridinium Bentonites. *Chemosphere* **2020**, *242*, 125109. [CrossRef] [PubMed]
12. Xi, Y.; Mallavarapu, M.; Naidu, R. Preparation, Characterization of Surfactants Modified Clay Minerals and Nitrate Adsorption. *Appl. Clay Sci.* **2010**, *48*, 92–96. [CrossRef]
13. Obradović, M.; Daković, A.; Smiljanić, D.; Ožegović, M.; Marković, M.; Rottinghaus, G.E.; Krstić, J. Ibuprofen and Diclofenac Sodium Adsorption onto Functionalized Minerals: Equilibrium, Kinetic and Thermodynamic Studies. *Microporous Mesoporous Mater.* **2022**, *335*, 111795. [CrossRef]
14. Guedidi, H.; Reinert, L.; Soneda, Y.; Bellakhal, N.; Duclaux, L. Adsorption of Ibuprofen from Aqueous Solution on Chemically Surface-Modified Activated Carbon Cloths. *Arab. J. Chem.* **2017**, *10*, S3584–S3594. [CrossRef]
15. Raupp, Í.N.; Filho, A.V.; Arim, A.L.; Muniz, A.R.C.; da Rosa, G.S. Ibuprofen Adsorption onto Olive Pomace Activated Carbon. *Chem. Eng. Technol.* **2023**, *46*, 2395–2403. [CrossRef]
16. Luo, Z.; Gao, M.; Yang, S.; Yang, Q. Adsorption of Phenols on Reduced-Charge Montmorillonites Modified by Bispyridinium Dibromides: Mechanism, Kinetics and Thermodynamics Studies. *Colloids Surfaces A Physicochem. Eng. Asp.* **2015**, *482*, 222–230. [CrossRef]
17. Gu, Z.; Gao, M.; Luo, Z.; Lu, L.; Ye, Y.; Liu, Y. Bis-Pyridinium Dibromides Modified Organo-Bentonite for the Removal of Aniline from Wastewater: A Positive Role of π-π Polar Interaction. *Appl. Surf. Sci.* **2014**, *290*, 107–115. [CrossRef]
18. Yang, Q.; Gao, M.; Luo, Z.; Yang, S. Enhanced Removal of Bisphenol A from Aqueous Solution by Organo-Montmorillonites Modified with Novel Gemini Pyridinium Surfactants Containing Long Alkyl Chain. *Chem. Eng. J.* **2016**, *285*, 27–38. [CrossRef]
19. De Oliveira, T.; Guégan, R.; Thiebault, T.; Le Milbeau, C.; Muller, F.; Teixeira, V.; Giovanela, M.; Boussafir, M. Adsorption of Diclofenac onto Organoclays: Effects of Surfactant and Environmental (pH and Temperature) Conditions. *J. Hazard. Mater.* **2017**, *323*, 558–566. [CrossRef]

20. Rouquerol, J.; Llewellyn, P.; Rouquerol, F. Is the BET Equation Applicable to Microporous Adsorbents? *Stud. Surf. Sci. Catal.* **2007**, *160*, 49–56. [CrossRef]
21. Dubinin, M.M. Physical Adsorption of Gases and Vapors in Micropores. *Prog. Surf. Membr. Sci.* **1975**, *9*, 1–70. [CrossRef]
22. Milonjić, S.K.; Ruvarac, A.L.; Šušić, M.V. The Heat of Immersion of Natural Magnetite in Aqueous Solutions. *Thermochim. Acta* **1975**, *11*, 261–266. [CrossRef]
23. Krajišnik, D.; Daković, A.; Malenović, A.; Kragović, M.; Milić, J. Ibuprofen Sorption and Release by Modified Natural Zeolites as Prospective Drug Carriers. *Clay Miner.* **2015**, *50*, 11–22. [CrossRef]
24. Liu, Z.H.; Ma, Q.G.; Dai, L.; Dang, Z. Occurrence, Removal and Risk Evaluation of Ibuprofen and Acetaminophen in Municipal Wastewater Treatment Plants: A Critical Review. *Sci. Total Environ.* **2023**, *891*, 164600. [CrossRef]
25. De Oliveira, T.; Guégan, R. Coupled Organoclay/Micelle Action for the Adsorption of Diclofenac. *Environ. Sci. Technol.* **2016**, *50*, 10209–10215. [CrossRef]
26. Xi, Y.; Frost, R.L.; He, H. Modification of the Surfaces of Wyoming Montmorillonite by the Cationic Surfactants Alkyl Trimethyl, Dialkyl Dimethyl, and Trialkyl Methyl Ammonium Bromides. *J. Colloid Interface Sci.* **2007**, *305*, 150–158. [CrossRef]
27. Son, Y.; Kim, Y.; Bae, S.; Kim, T.H.; Hwang, Y. Investigation of Chromate Adsorption Efficacy on Organo-Bentonite as Potential in-Situ Adsorbent for Groundwater Remediation. *J. Environ. Chem. Eng.* **2022**, *10*, 108778. [CrossRef]
28. Rouquerol, F.; Rouquerol, J.; Sing, K. *Adsorption by Powders and Porous Solids*; Academic Press: San Diego, CA, USA, 1999.
29. Li, Z.; Gallus, L. Surface Configuration of Sorbed Hexadecyltrimethylammonium on Kaolinite as Indicated by Surfactant and Counterion Sorption, Cation Desorption, and FTIR. *Colloids Surfaces A Physicochem. Eng. Asp.* **2005**, *264*, 61–67. [CrossRef]
30. Gulicovski, J.J.; Čerović, L.S.; Milonjić, S.K. Point of Zero Charge and Isoelectric Point of Alumina. *Mater. Manuf. Process.* **2008**, *23*, 615–619. [CrossRef]
31. Smiljanić, D.; Daković, A.; Obradović, M.; Ožegović, M.; Izzo, F.; Germinario, C.; de Gennaro, B. Application of Surfactant Modified Natural Zeolites for the Removal of Salicylic Acid—A Contaminant of Emerging Concern. *Materials* **2021**, *14*, 7728. [CrossRef]
32. Kragović, M.; Daković, A.; Marković, M.; Krstić, J.; Gatta, G.D.; Rotiroti, N. Characterization of Lead Sorption by the Natural and Fe(III)-Modified Zeolite. *Appl. Surf. Sci.* **2013**, *283*, 764–774. [CrossRef]
33. Sun, K.; Shi, Y.; Chen, H.; Wang, X.; Li, Z. Extending Surfactant-Modified 2:1 Clay Minerals for the Uptake and Removal of Diclofenac from Water. *J. Hazard. Mater.* **2017**, *323*, 567–574. [CrossRef] [PubMed]
34. Martín, J.; del Mar Orta, M.; Medina-Carrasco, S.; Santos, J.L.; Aparicio, I.; Alonso, E. Evaluation of a Modified Mica and Montmorillonite for the Adsorption of Ibuprofen from Aqueous Media. *Appl. Clay Sci.* **2019**, *171*, 29–37. [CrossRef]
35. Maia, G.S.; de Andrade, J.R.; da Silva, M.G.C.; Vieira, M.G.A. Adsorption of Diclofenac Sodium onto Commercial Organoclay: Kinetic, Equilibrium and Thermodynamic Study. *Powder Technol.* **2019**, *345*, 140–150. [CrossRef]
36. Smiljanić, D.; de Gennaro, B.; Izzo, F.; Langella, A.; Daković, A.; Germinario, C.; Rottinghaus, G.E.; Spasojević, M.; Mercurio, M. Removal of Emerging Contaminants from Water by Zeolite-Rich Composites: A First Approach Aiming at Diclofenac and Ketoprofen. *Microporous Mesoporous Mater.* **2020**, *298*, 110057. [CrossRef]
37. Smiljanić, D.; Daković, A.; Obradović, M.; Ožegović, M.; Marković, M.; Rottinghaus, G.E.; de Gennaro, B. Influence of the Type and the Amount of Surfactant in Phillipsite on Adsorption of Diclofenac Sodium. *Catalysts* **2022**, *13*, 71. [CrossRef]
38. Baccar, R.; Sarrà, M.; Bouzid, J.; Feki, M.; Blánquez, P. Removal of Pharmaceutical Compounds by Activated Carbon Prepared from Agricultural By-Product. *Chem. Eng. J.* **2012**, *211–212*, 310–317. [CrossRef]
39. Essandoh, M.; Kunwar, B.; Pittman, C.U.; Mohan, D.; Mlsna, T. Sorptive Removal of Salicylic Acid and Ibuprofen from Aqueous Solutions Using Pine Wood Fast Pyrolysis Biochar. *Chem. Eng. J.* **2015**, *265*, 219–227. [CrossRef]
40. Shin, J.; Kwak, J.; Lee, Y.G.; Kim, S.; Choi, M.; Bae, S.; Lee, S.H.; Park, Y.; Chon, K. Competitive Adsorption of Pharmaceuticals in Lake Water and Wastewater Effluent by Pristine and NaOH-Activated Biochars from Spent Coffee Wastes: Contribution of Hydrophobic and π-π Interactions. *Environ. Pollut.* **2021**, *270*, 116244. [CrossRef]
41. Lin, L.; Jiang, W.; Bechelany, M.; Nasr, M.; Jarvis, J.; Schaub, T.; Sapkota, R.R.; Miele, P.; Wang, H.; Xu, P. Adsorption and Photocatalytic Oxidation of Ibuprofen Using Nanocomposites of TiO_2 Nanofibers Combined with BN Nanosheets: Degradation Products and Mechanisms. *Chemosphere* **2019**, *220*, 921–929. [CrossRef]
42. Smiljanić, D.; de Gennaro, B.; Daković, A.; Galzerano, B.; Germinario, C.; Izzo, F.; Rottinghaus, G.E.; Langella, A. Removal of Non-Steroidal Anti-Inflammatory Drugs from Water by Zeolite-Rich Composites: The Interference of Inorganic Anions on the Ibuprofen and Naproxen Adsorption. *J. Environ. Manag.* **2021**, *286*, 112168. [CrossRef] [PubMed]
43. Liang, X.X.; Omer, A.M.; Hu, Z.H.; Wang, Y.G.; Yu, D.; Ouyang, X. kun Efficient Adsorption of Diclofenac Sodium from Aqueous Solutions Using Magnetic Amine-Functionalized Chitosan. *Chemosphere* **2019**, *217*, 270–278. [CrossRef] [PubMed]
44. Karami, A.; Sabouni, R.; Ghommem, M. Experimental Investigation of Competitive Co-Adsorption of Naproxen and Diclofenac from Water by an Aluminum-Based Metal-Organic Framework. *J. Mol. Liq.* **2020**, *305*, 112808. [CrossRef]
45. Nourmoradi, H.; Moghadam, K.F.; Jafari, A.; Kamarehie, B. Removal of Acetaminophen and Ibuprofen from Aqueous Solutions by Activated Carbon Derived from Quercus Brantii (Oak) Acorn as a Low-Cost Biosorbent. *J. Environ. Chem. Eng.* **2018**, *6*, 6807–6815. [CrossRef]
46. Su, J.; Lin, H.F.; Wang, Q.P.; Xie, Z.M.; Chen, Z.L. Adsorption of Phenol from Aqueous Solutions by Organomontmorillonite. *Desalination* **2011**, *269*, 163–169. [CrossRef]

47. Senturk, H.B.; Ozdes, D.; Gundogdu, A.; Duran, C.; Soylak, M. Removal of Phenol from Aqueous Solutions by Adsorption onto Organomodified Tirebolu Bentonite: Equilibrium, Kinetic and Thermodynamic Study. *J. Hazard. Mater.* **2009**, *172*, 353–362. [CrossRef]
48. Garmia, D.; Zaghouane-Boudiaf, H.; Ibbora, C.V. Preparation and Characterization of New Low Cost Adsorbent Beads Based on Activated Bentonite Encapsulated with Calcium Alginate for Removal of 2,4-Dichlorophenol from Aqueous Medium. *Int. J. Biol. Macromol.* **2018**, *115*, 257–265. [CrossRef]