



ORIGINAL ARTICLE

Enhanced accessibility of active sites in hierarchical ZSM-5 zeolite for removal of pharmaceutically active substances: Adsorption and microcalorimetric study



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Abstract The possibility of removal of pharmaceutically active substances, atenolol, diclofenac sodium and salicylic acid, from water solutions using hierarchical form of zeolite ZSM-5 is investigated in this paper. Mesopore formation in ZSM-5 was achieved using alkaline treatment. Zeolitic samples were characterized by X-ray diffraction, low temperature nitrogen adsorption, solid-state ²⁷Al MAS NMR, point of zero charge determination and microcalorimetry – volumetry of ammonia adsorption. Adsorption isotherms of pharmaceutically active substances were obtained and liquid calorimetric experiments were used to evaluate the strength of interactions. The capacity for salicylic acid adsorption measured for the mesoporous sample did not significantly differ from the results obtained for the parent ZSM-5. However, in the case of atenolol and diclofenac sodium, mesoporous ZSM-5 exhibited increased adsorption capacities. Calorimetric data revealed higher heats of atenolol adsorption on mesoporous ZSM-5, compared to the parent. Based on similar acidity and surface charge determined for the two samples, our results show that geometry and

Abbreviations: PAC, pharmaceutically active compound; CEC, contaminants of emerging concern; SA, salicylic acid; ATL, atenolol; DFC, diclofenac-Na; pH_{pzc}, point of zero charge; Q_{diff}, differential heat of adsorption

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dimensions of both zeolite pores and adsorbing molecules play a crucial role in the studied adsorption processes and that tailoring ZSM-5 porosity by desilication can be used to expand its applicability in depollution processes.

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1. Introduction

Pharmaceutically active compounds (PACs) are substances commonly used in medicine, human and veterinary. During their manufacture and use they can arrive in soil, surface waters and even in drinking water and are now considered an important environmental threat (Wang and Wang, 2016; Kyzas et al., 2017; Daughton, 2016; Vasquez et al., 2014). The most important source of contamination is the pharmaceutical industry; however, excretions from humans and animals are also considered significant (Zhou et al., 2017; Corcoran et al., 2010; Khetan and Collins, 2007; Prasse et al., 2010). Although the concentrations of PACs found in the environment are sometimes very low (Tambosi et al., 2010; Carballa et al., 2004; Garcia-Ac et al., 2009; Hollender et al., 2008), long-term exposure can lead to harmful effects. PACs are even classified as “contaminants of emerging concern” – CECs (Daughton, 2004) or “emerging pollutants”. Development of appropriate methods for water pollution abatement caused by PACs is currently a topic which receives great scientific attention (Glassmeyer et al., 2008; Rivera-Utrilla et al., 2013). Commonly used, filtration-based procedures are not completely suitable for removal of PAC molecules, which are usually polar and of small dimensions. Since the pore sizes of either micro- or ultra filters are 100–1000 times larger, they allow pollutants to “slip” through the membranes or filters (Deegan et al., 2011). Therefore, it is not surprising that some of them can be found in drinking water from filtration plants (Khetan and Collins, 2007). Advanced oxidation processes (AOP) (Feng et al., 2013; Mohapatra et al., 2014; Marco-Urrea et al., 2010; Giri et al., 2010; Klavarioti et al., 2009) have been studied, but AOPs can be expensive and energy consuming. Therefore, until processes leading to environmentally benign products are perfected, probing and improving different adsorbents will remain in scientific focus (Papageorgiou et al., 2017; Lin et al., 2015; Sathishkumar et al., 2015; Kyzas et al., 2013; Ayranci and Duman, 2006; Polakovic et al., 2005). Our own research (Rakić et al., 2015), concerning activated carbons as adsorbents for PACs removal, revealed that the dominant factor influencing their adsorptive capacities was the magnitude of their surface, while the strength of adsorbate, adsorbent interactions was determined by the acidity/basicity of both the carbon surfaces and the pollutant molecules. Hence, another type of materials, zeolites, which possess both acidic properties and high surfaces, are the obvious choice for further investigations.

In this work, the results related to adsorptive properties of synthetic zeolite ZSM-5 (in microporous and microporous/mesoporous forms) for the removal of three PACs (salicylic acid, diclofenac sodium and atenolol) from aqueous solutions are reported. Zeolites are well known for their adsorptive capabilities and their use for removal of pharmaceuticals from water solutions has been studied (Martucci et al., 2012; De Ridder et al., 2012; González-Ramos et al., 2014). Zeolites are

hydrated aluminosilicates, which are well ordered in all three dimensions: their cage-like structures usually have very high internal and external surface areas of up to several hundred square meters per gram. They possess specific active sites that might be active in adsorption. ZSM-5 zeolite is a medium-pore zeolite with a three-dimensional interconnected channel system and 10-membered openings ($5.1 \text{ \AA} \times 5.5 \text{ \AA}$ and $5.3 \text{ \AA} \times 5.6 \text{ \AA}$). The size of the channels intersection is close to $8.5\text{--}9.0 \text{ \AA}$ (Ashtekar et al., 2000). Since the adsorptive capacities of zeolites can be limited by their pore sizes, the adsorption of the three pollutants on hierarchical ZSM-5 has been investigated in this work. Hierarchical zeolites are zeolites which, besides their inherent microporosity, also possess mesopores (Serrano et al., 2013; Schwieger et al., 2015). ZSM-5 zeolite with hierarchical structure used in this investigation was obtained by desilication procedure (Xiao et al., 2015; Mitchell and Pérez-Ramírez, 2011). Thus formed mesopores can be expected to be accessible to larger guest species, which might extend the usability of the zeolite as an adsorbent. For that reason, the adsorption capabilities of microporous and hierarchical ZSM-5 zeolites toward salicylic acid, diclofenac sodium and atenolol were compared in this work. The adsorption of pollutants from aqueous solutions were studied by isothermal batch experiments and, additionally, using microcalorimetry of adsorption in order to obtain both adsorption capacities and evaluate the corresponding strengths of adsorbate – adsorbent interactions. Changes in adsorptive properties were discussed with respect to modifications of zeolite’s structure and acidity, which are induced by the introduction of mesopores to its initially purely microporous structure. To the best of our knowledge, such an investigation, which combines textural and surface characterization, quantitative acidity determination, batch adsorption investigation and, especially, liquid

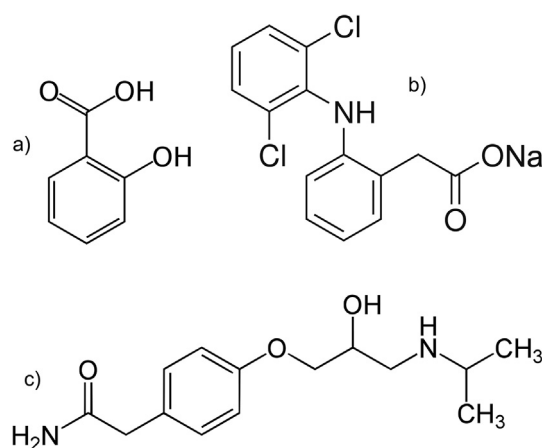


Fig. 1 Chemical structures of the investigated molecules: (a) salicylic acid, (b) diclofenac sodium and (c) atenolol.

phase microcalorimetry of adsorption is applied for the first time in hierarchical zeolite – PACs interaction studies.

All chemicals chosen to be adsorbed on ZSM-5 zeolite are recognized as emerging contaminants of water: salicylic acid (SA), diclofenac-sodium (DFC), a frequently used non-steroidal anti-inflammatory drug and atenolol (ATL), a beta-blocker drug. The reasons for the choice of these PACs are: (1) their presence in industrial wastewaters, (2) their molecular structures: different molecular sizes of the three molecules (Fig. 1) and their acidic/basic properties, which enable the investigation of the influence of both mesopore formation in ZSM-5 and the zeolite's acidity on its adsorptive capabilities towards selected PACs.

2. Experimental section

2.1. Materials

Parent ZSM-5 zeolite, with SiO₂/Al₂O₃ ratio of 50, was supplied by Zeolyst (CBV5524G). Salicylic acid (SA) and atenolol (ATL) were supplied by pharmaceutical company "Galenika", Belgrade, Serbia, and diclofenac-Na (DFC) was purchased from Sigma, Aldrich.

Mesopore formation in ZSM-5 zeolite was achieved via alkaline treatment, using the method of Groen et al. (2004a, 2004b). Zeolite samples (5 g) were subjected to NaOH solution (0.2 M, 150 ml) during 30 min at the temperature of 333 K. Subsequently, the samples were filtrated, thoroughly washed with deionized water until a neutral pH was reached and dried at 393 K overnight. Following the alkaline treatment, an acidic treatment was preformed, using hydrochloric acid (0.1 M, 150 ml) for 6 h at room temperature. The samples were then filtered, washed and dried again. Both parent and modified ZSM-5 were afterwards converted to their ammonium form by three-fold ion-exchange (150 ml, 0.1 M ammonium nitrate at 363 K during 1 h). As prepared materials were filtered, washed with deionized water and dried in an oven at 393 K. The resulting samples were calcined in air at 773 K, for 5 h.

2.2. Characterization

Powder X-ray diffraction patterns were recorded on a Bruker (Siemens) 5005 diffractometer at room temperature using Cu K_α radiation (0.154 nm), from 3 to 80 2θ in 0.02° steps, with 1 s per step. Nitrogen adsorption was performed at 77 K; zeolite samples were pretreated in vacuum at 673 K for 4 h. BET and t-plot methods were used to calculate the textural properties. Transmission electron Microscopy (TEM) was carried out in a JEOL JEM-1400 Plus microscope operated at 120 kV. The sample was dispersed from ethanol onto a carbon-coated copper grid which was subsequently dried at room temperature. Solid-state ²⁷Al MAS NMR spectra were acquired on a Bruker MSL-400 (9.39 T) spectrometer upgraded with Apollo console (Tecmag, USA) operating at 104.27 MHz. MAS probes (7 mm) were used and the spinning speeds were 4.7 kHz. Single-pulse excitations of 2 μs were used for the ²⁷Al MAS NMR experiments. All the spectra were accumulated with a 3 s recycle time. Obtained chemical shift was determined in ppm relative to AlCl₃ 6H₂O solution as an external standard. Point of zero charge for both samples was evaluated using batch equilibrium method (Dakovic et al., 2010). Two series

of KNO₃ solutions (0.1 M and 0.01 M) were prepared, each solution having a different pH value (pH_i), which was adjusted by addition of 0.1 M HNO₃ or 0.1 M KOH. 100 mg of a zeolitic sample was added to 50 ml of each solution and the mixtures were then stirred for 24 h at room temperature. The solid was separated from the solutions by centrifugation at 13,400 rpm during 20 min and the final pH values (pH_f) of the solutions were measured. The point of zero charge was determined as the pH value at which a plateau is obtained on the graph pH_f = f(pH_i). Acidity of the samples was investigated by microcalorimetric – volumetric measurements of ammonia adsorption. The heats of ammonia adsorption were measured in a heat-flow Tian-Calvet calorimeter (Setaram), linked to a glass volumetric line. Heats of adsorption and adsorption isotherms were determined, using a well-established method (Solinas and Ferino, 1998).

2.3. Adsorption measurements and liquid phase microcalorimetry

Adsorption of salicylic acid, diclofenac-Na and atenolol was studied using batch method (Damjanovic et al., 2010): approximately 50 mg of a sample was mixed with an appropriate volume of adsorbate solution in a sealed container using a magnetic stirrer during 1 h at 303 K. Solid adsorbent was subsequently separated from aqueous solution by centrifugation (Minispin, Eppendorf, 13,400 rpm, 0.5 h). Equilibrium adsorbate concentrations were measured using spectrophotometry (Shimadzu UV-1650PC). The adsorbed amounts (mol per gram of zeolite) were determined as the difference between the initial and equilibrium concentrations. Every point of an isotherm was obtained from a separate experiment. Measurements were done in triplicates. Initial solution concentrations were in the range 10⁻⁵ M to 10⁻³ M. The one hour equilibrium adsorption time was determined experimentally: for a fixed dose of an investigated adsorbate, adsorbed amounts were measured for different solid-liquid contact durations (15 min, 30 min, 1 h, 2 h and 6 h). The values of concentrations that were found remaining in solutions after 2 h or 6 h of stirring were found to be the same as in the case of 1 h long contact time.

Experimental data were fitted to the Langmuir, Freundlich, Sips and Toth equations using Microcal Origin 8 software; the corresponding constants were calculated. Eqs. (1)–(4) present Langmuir, Freundlich, Sips and Toth equations, respectively (Jaroniec and Marczewski, 1984):

$$S_e = \frac{S_m K_L c_{eq}}{1 + K_L c_{eq}} \quad (1)$$

$$S_e = K_F c_{eq}^n \quad (2)$$

$$S_e = \frac{S_m (K_S c_{eq})^n}{1 + (K_S c_{eq})^n} \quad (3)$$

$$S_e = \frac{S_m K_T c_{eq}}{[1 + (K_T c_{eq})^n]^{1/n}} \quad (4)$$

where c_{eq} is the equilibrium concentration of adsorbate (mol L⁻¹) and S_e is the adsorbed amount at equilibrium (mol g⁻¹). In Langmuir, Sips and Toth equation S_m is the maximum amount of adsorbate bonded (mol g⁻¹) and K_L ,

K_S and K_T are constants related to the energy of adsorbent – adsorbate bonding. Constant n in Sips and Toth models is related to the heterogeneity of the adsorption sites. If $n = 1$ Eqs. (3) and (4) reduce to Langmuir model, for which an energetically homogeneous surface is postulated.

The heats of adsorption of investigated adsorbates were determined using liquid calorimetric measurements. A differential heat flow reaction calorimeter (TITRYS, from Setaram) equipped with a stirring system was used. The calorimeter was linked by capillary tubes to a system for liquid injection (a programmable syringe pump PHD 2000, from Harvard Apparatus). Successive pulse injections of 0.2 ml of adsorbate solutions were sent to the sample in 2 h time intervals. The temperature of the calorimetric cell was maintained at 303 K. Furthermore, each dose of the liquid was equilibrated at the same temperature in a preheating furnace prior to being injected in order to avoid enthalpy effects due to mixing phenomena. All liquids used in this investigation were previously purged with flowing nitrogen as this procedure, based on experimental experience, prevents formation of air bubbles in the capillary tubes. At the beginning of the experiment, the reference and measurement cells contained water (1.5 cm³) and water with a weighted amount of the solid sample (ca. 50 mg), respectively. Initial solution concentrations of atenolol, diclofenac sodium and salicylic acid were the same as in the previously described adsorption experiments. Hence, the calorimetric experiments were used to directly measure the heats which evolved due to adsorption (expressed as J g⁻¹ of solid), for each admitted dose. Using previously determined corresponding adsorbed amounts, differential heats of adsorption (Q_{dif} , expressed in kJ mol⁻¹) were calculated.

3. Results and discussion

3.1. Characterization

The alterations of pore structure of zeolite ZSM-5, caused by the alkaline treatment, were investigated using low temperature nitrogen adsorption (Fig. 2). The modified sample shows a more than two-fold increase in the total amount of nitrogen adsorbed compared to the parent zeolite. The isotherm of the parent sample consists of an adsorption branch of type I and a H4 type hysteresis, typical for microporous materials (Sing et al., 1985). The modified sample exhibits an isotherm of type IIb, with a steep slope at higher values of p/p^0 , and a H3 hysteresis, which is in accordance with the results obtained by other authors for hierarchical zeolites (Fernandez et al., 2010; Wu et al., 2012). Alkaline treatment of ZSM-5 resulted in an increase of the total pore volume (from 0.236 to 0.449 cm³ g⁻¹), mesopore volume (from 0.085 to 0.380 cm³ g⁻¹), BET surface (from 365 to 470 m² g⁻¹) and external surface (65 to 173 m² g⁻¹), which is attributed to mesopore formation (Groen et al., 2004b). Microporosity of the zeolite was preserved to a high degree: only a slight decrease of the micropore volume was measured (from 0.144 to 0.138 cm³ g⁻¹). The pore size distribution of both samples is presented in Fig. 2 (inset). The modified ZSM-5 sample exhibits a fairly broad peak centered at 14 nm. Formed mesopores and differences in pore structure between parent and modified zeolite are clearly visible in TEM micrographs (Fig. 3).

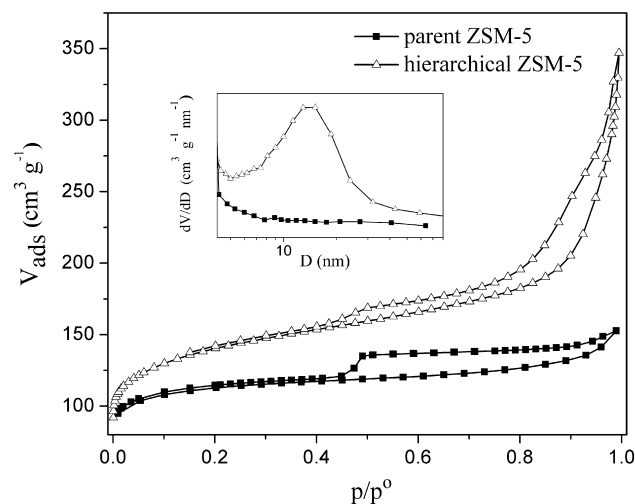


Fig. 2 Isotherms of nitrogen adsorption and pore size distributions of parent and modified ZSM-5 zeolite.

The influence of the alkaline treatment on the acidity of the zeolite structure was investigated by coupled microcalorimetry and volumetry of ammonia adsorption. Fig. 4 presents the site strength distributions for the investigated samples. The results show that the shapes of distributions are generally the same for both samples, consisting of two major domains, centered at ~150 and 75–80 kJ mol⁻¹. Compared to the parent zeolite, there is a slight decrease of the number of strong (~150 kJ mol⁻¹) and weak (~75 kJ mol⁻¹) acid sites for the hierarchical sample, while an increase of the number of sites with intermediate strength (85–125 kJ mol⁻¹) is also noticeable. The observed changes in the distribution of strength of the acid sites are not drastic and it can be concluded that the acidity of ZSM-5 remained unaffected to a large extent by the modification procedure. A detailed analysis of the obtained calorimetric results is presented elsewhere (Rac et al., 2013).

The coordination state of Al in both zeolite samples was estimated by solid-state ²⁷Al MAS NMR spectra (not presented here). The obtained results show that both the parent and the modified sample predominantly contain tetrahedral Al (peak at 54 ppm), which is attributed to framework aluminum. Some extraframework Al species, octahedrally coordinated (peak at 0 ppm), were also found in the spectra of both samples. These results indicate that desilication did not result in significant extraframework Al buildup. It is here important to point out that the total SiO₂/Al₂O₃ ratio, measured by chemical analysis, changed from 50 to 43 after the alkaline treatment, but its value was restored to 50 again, after the subsequent acid wash. This is in accordance with data obtained by Mitchell and Pérez-Ramírez (2011), who emphasized the importance of acid wash treatment, which removes non-framework aluminum resulting from alkaline treatment and recovers Si/Al composition similar to that of the starting material.

The point of zero charge (PZC) for both parent and mesoporous sample was determined by batch equilibrium method (Fig. 5). The obtained results show that the PZC value is 2.95 ± 0.05 for parent and 3.05 ± 0.05 for mesoporous ZSM-5, indicating that the introduction of mesoporosity in ZSM-5 did not lead to any significant change in surface charge.

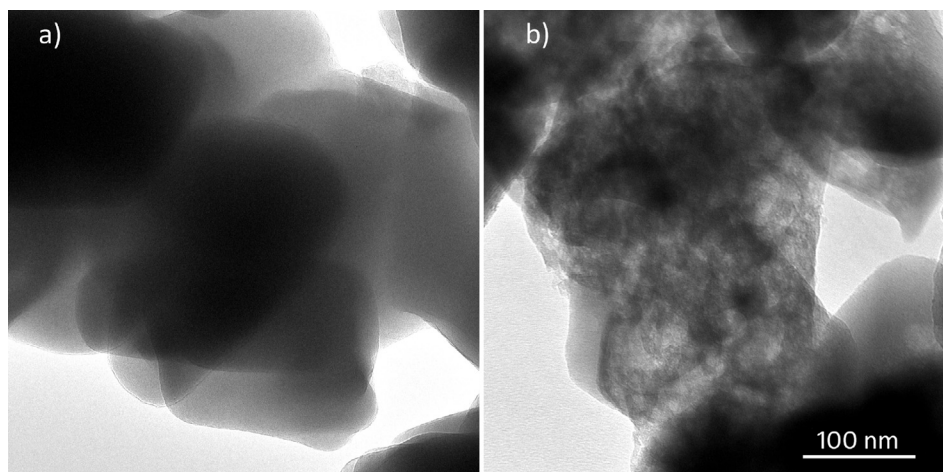


Fig. 3 TEM micrographs of (a) microporous and (b) hierarchical ZSM-5.

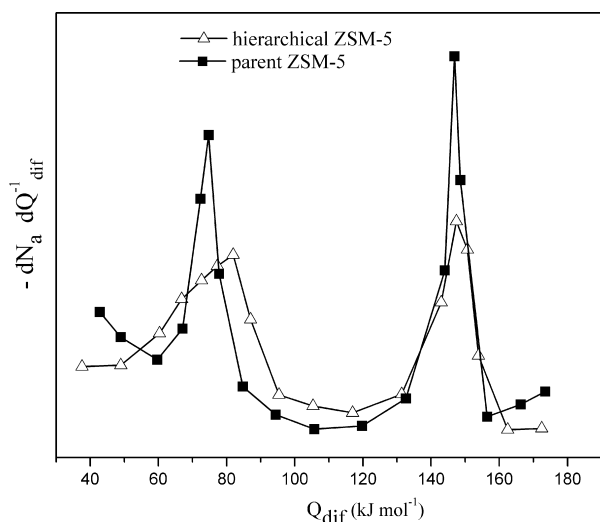


Fig. 4 Distribution of strength of acid sites in parent and modified ZSM-5 zeolite.

XRD patterns were recorded in order to estimate the influence of desilication on the crystallinity of ZSM-5. The results (not presented here) show that the diffraction patterns typical for ZSM-5 structure were recorded for both samples and that the desilicated sample preserved its crystalline structure. However, the degree of crystallinity was altered in the modified zeolite. The variation in crystallinity of the modified zeolite was calculated as proposed in literature (Martinez et al., 2013; Auroux et al., 1996), from the intensities of the reflection at $23^\circ 2\theta$, taking the crystallinity of the parent sample to be 100%. The crystallinity of the mesoporous ZSM-5 was found to be 76%.

3.2. Adsorption measurements and liquid phase microcalorimetry

Adsorption experiments revealed a distinct difference in the way mesopore creation in ZSM-5 affected its adsorptive

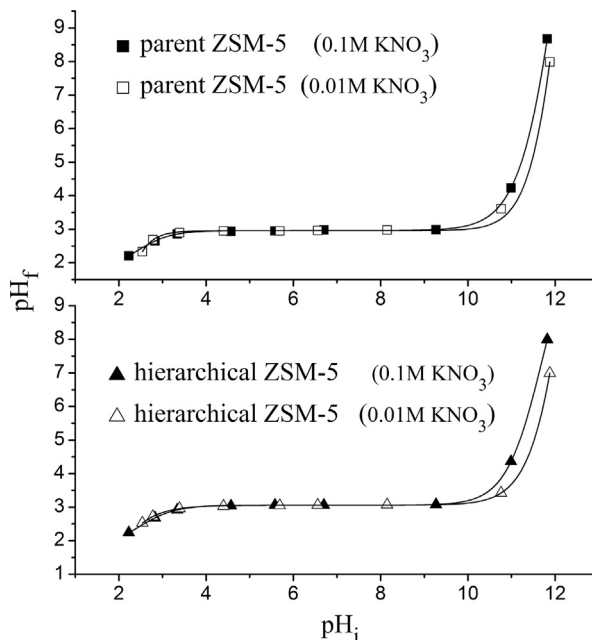


Fig. 5 pH_f versus pH_i for parent and modified ZSM-5 zeolite; PZC determination.

behavior towards salicylic acid, atenolol and diclofenac. In the case of salicylic acid there is a slight decrease of the overall adsorptive capability for the mesoporous sample, compared to the parent one (Fig. 6). However, this decrease is more pronounced in the region of lower equilibrium concentrations while maximal amounts of SA adsorbed on microporous and hierarchical samples, calculated using Langmuir, Sips and Toth models are similar (Table 1). The best fit of the experimental values was obtained using Toth equation and, in this case, the extrapolated maximal adsorptive capacities for parent and modified sample are almost the same, $0.00021 \text{ mol g}^{-1}$ and $0.00022 \text{ mol g}^{-1}$, respectively. These results are in accordance with the fact that the molecular diameter of SA molecules, 4.6 \AA (Kirumakki et al., 2003), enables them to enter into the micropores of ZSM-5. Consequently, no positive effect of mesopore existence in the structure on the adsorption

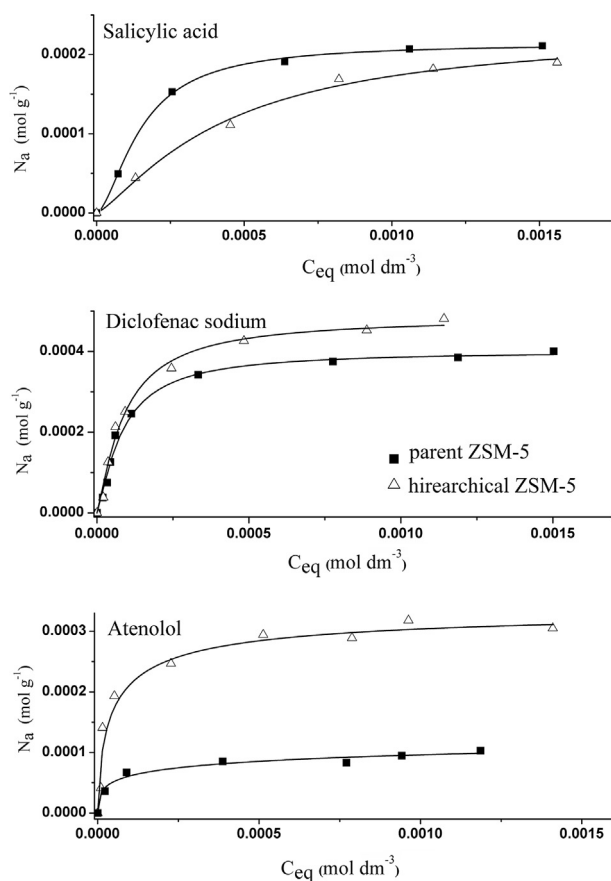


Fig. 6 Adsorption isotherms of salicylic acid, diclofenac sodium and atenolol.

capacity for SA should be expected. In fact, our results indicate that bonding of salicylic acid to zeolitic inner surface is somewhat favored in narrow micropores.

In the case of atenolol and diclofenac sodium adsorption, the effect of mesopore formation is quite opposite: an increase of the maximum adsorbed amount of both molecules is observed for the alkaline treated sample compared to the parent (Fig. 6). This effect is moderate for diclofenac sodium and very pronounced for atenolol, where there is a more than threefold increase of the maximal adsorbed amount. Obviously, the existence of mesopores in the desilicated sample enables more of the adsorbate molecules to enter the zeolite structure and interact with the active sites to a much larger extent than in the case of the parent sample. The difference in the enhancement of the adsorption capability towards diclofenac and atenolol is probably caused by the structure and shape of the molecules in question. The difference in dimension between the two molecules ($7 \times 18.2 \text{ \AA}$ for ATL (Fagerholm et al., 1999) and $3.5 \times 8.3 \times 7.0 \text{ \AA}$ for DFC (Xie et al., 2012)) can also play an important role, considering the zigzag channel structure of ZSM-5 zeolite. Since the acidity of the zeolite was only mildly affected by the mesopore formation process and the surface charge remained unchanged, the presumption that the geometry of the pores and molecules is a crucial factor can be expressed.

Hence, the observed increases in adsorption capabilities toward atenolol and diclofenac seem to be the result of the availability of the adsorption sites to the adsorbing molecules, which was the parameter that was actually changed by the mesopore formation process. The molecules in the hierarchical zeolite are able to bond to the adsorption sites which are inaccessible to them in the parent sample. The extent of the adsorption capability enhancement depends on the shape and the diameter of both mesopores and the adsorbing molecules. Fitting of the experimental isotherms to theoretical models showed that the use of Toth equation resulted in best agreement, for all adsorbent – adsorbate combinations (Table 1). However, in some cases, Sips and Langmuir models also adequately fitted empirical data. It is, at this point, important to emphasize that good agreement between experimental values

Table 1 Isotherm parameters for adsorption of pharmaceuticals on parent and modified ZSM-5.

	Microporous ZSM-5			Hierarchical ZSM5		
	SA	DFC	ATL	SA	DFC	ATL
<i>Fitted Freundlich equation</i>						
$K_F ((\text{mol g}^{-1})(\text{dm}^3 \text{mol}^{-1})^n)$	0.00198	0.00330	0.00044	0.00519	0.00515	0.00166
n	0.33	0.31	0.21	0.50	0.34	0.24
R^2	0.81121	0.85829	0.93729	0.91924	0.88849	0.87151
<i>Fitted Langmuir equation</i>						
$S_m (\text{mol g}^{-1})$	0.00025	0.00043	0.00001	0.00028	0.00052	0.00032
$K_L (\text{dm}^3 \text{mol}^{-1})$	5080	10,242	23,276	1616	12,352	29,582
R^2	0.95994	0.97496	0.96456	0.97776	0.98033	0.92088
<i>Fitted Sips equation</i>						
$S_m (\text{mol g}^{-1})$	0.00021	0.00039	0.00011	0.00023	0.00048	0.00035
$K_S (\text{dm}^3 \text{mol}^{-1})$	6880	13,146	17,612	2336	13,590	20,960
n	1.63	1.47	0.69	1.28	1.22	0.74
R^2	0.99651	0.98837	0.97010	0.97827	0.98177	0.91202
<i>Fitted Toth equation</i>						
$S_m (\text{mol g}^{-1})$	0.00021	0.00039	0.00011	0.00022	0.00051	0.00036
$K_T (\text{dm}^3 \text{mol}^{-1})$	3801	8806	53,852	1525	9799	134,709
n	1.88	1.49	0.60	1.65	1.05	0.51
R^2	0.99620	0.99152	0.97155	0.99477	0.99512	0.98589

and a given model is very useful for interpretation and analysis of the results, but should not be used as definite proof of the theoretical postulates the model is based upon (Adamson, 1990). Nevertheless, further analysis of the results obtained using Toth equation allowed us to easily evaluate and compare adsorptive capabilities of the investigated zeolites at low concentrations. Toth equation reduces to linear shape in the region of low concentrations. Indeed, this is a property that adequately depicts the real situation: when the concentration of the adsorbate is very small, the available concentration of adsorption sites within the zeolite is, relatively, so large that it can be regarded as “infinite” in the sense that its change during the adsorption process is negligible. Hence, at these conditions, the adsorbed amount becomes solely dependent of the adsorbate concentration and the isotherm is theoretically expected to be linear. Toth equation becomes linear when $K_T c_{eq} \ll 1$, which reduces Eq (4) to

$$S_e = S_m K_T c_{eq} \quad (5)$$

Using Eq (5) and data in Table 1, it can be shown that, for a given c_{eq} , S_e of hierarchical sample is approximately 8 times larger than S_e of microporous sample, in the case of atenolol adsorption. Hence, superior adsorptive capabilities of modified ZSM-5 towards atenolol are expected to be even more pronounced in low concentration situations.

Aside from Eq (5), which is specific for a given adsorbate – adsorbent couple, another mathematical relation between adsorbed amount (S_e) and equilibrium concentration (c_{eq}) exists:

$$S_e = \frac{V}{m} (c_0 - c_{eq}) \quad (6)$$

where V is the total volume of the solution, m is the mass of zeolite used and c_0 is the initial concentration of the adsorbate. This equation gives all possible pairs of S_e and c_{eq} values which are theoretically possible for given V , m and c_0 . Combining Eqs. (5) and (6) yields:

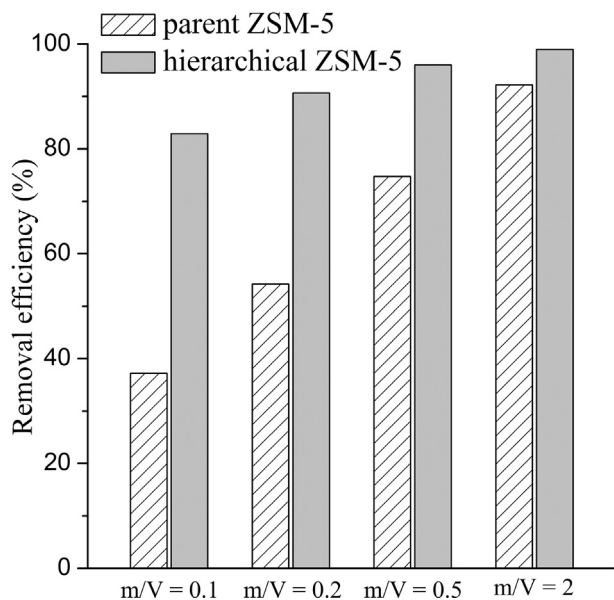


Fig. 7 Removal efficiencies for atenolol at low initial concentrations for different m/V .

$$\frac{c_0 - c_{eq}}{c_0} 100 = \left[1 - \frac{1}{1 + k \frac{m}{V}} \right] 100 \quad (7)$$

where $\frac{c_0 - c_{eq}}{c_0} 100$ (%) is the relative decrease of adsorbate concentration due to adsorption, i.e. the efficiency of the process and $k = S_m K_T$. Eq. (7) can be used to calculate V and m values which are needed in order to obtain a desired adsorption efficiency or to compare efficiencies of different adsorbents for given V and m . Fig. 7 presents atenolol removal efficiencies for the investigated microporous and hierarchical ZSM-5 samples, for different m/V values. The results show that enhanced adsorptive capability of modified ZSM-5 becomes more pronounced with decreasing m/V ratio.

To further investigate the interaction between the active sites of the zeolite samples and the adsorbing molecules, liquid calorimetry measurements were conducted. For each of the molecules, calorimetric experiments were performed in the concentration range corresponding to the part of the isotherm before the saturation plateau, where the strongest binding is expected. In the case of atenolol adsorption, a remarkable increase of the strength of interaction was detected for the hierarchical sample compared to the parent zeolite (Fig. 8). The heats of adsorption in the initial regions of the two calorimetric curves show almost a 30 kJ mol^{-1} difference. Considering the previously described distribution of strength of the active sites of the two zeolite samples, this increase of the atenolol – hierarchical ZSM-5 interactions can be interpreted as a result of enhanced accessibility of strong adsorption sites within the zeolite structure to atenolol molecules. However, this increase is limited to the initial region of the calorimetric curve after which the strength of the interaction becomes equal to that detected for the parent sample. It seems that, in the case of parent microporous sample, atenolol can be adsorbed only at its surface; since the dimensions of its molecules prevent them from entering three-dimensional interconnected channel system of ZSM-5 zeolite. Evidently, the formation of mesopores enabled ATL molecules to reach adsorption sites stronger than those existing at the surface of zeolite.

For the two other investigated molecules, such a drastic change in the strength of interactions with the zeolite samples (microporous and hierarchical) was not detected. The measured heats of adsorption for diclofenac sodium were approximately 45 kJ mol^{-1} . The calorimetric effects for salicylic acid adsorption were below detection limit, since in this case, we did not obtain signals which differed significantly from the baseline of the calorimeter. Generally, the existence of basic or acidic groups in the adsorbing molecules determines their strength of interaction with ZSM-5. Evidently, the interactions between zeolitic acid sites and basic groups of atenolol molecules result in the strongest bonds. The values of differential heats of DFC adsorption indicate somewhat weaker interaction with ZSM-5 structure, which is in agreement with weakly basic character of the molecule. In the case of salicylic acid, it is reasonable to assume that its acidity ($\text{pK}_a = 2.97$) prevents strong adsorption. Obviously, salicylic acid interacts with ZSM-5 structure forming very weak bonds so the heats of adsorption could not be detected.

It has to be underlined here that the charge of an adsorbate in a solution (i.e. whether the molecules are dissociated, protonated or not) as well as the surface charge of the adsorbent are expected to be important factors in adsorption processes.

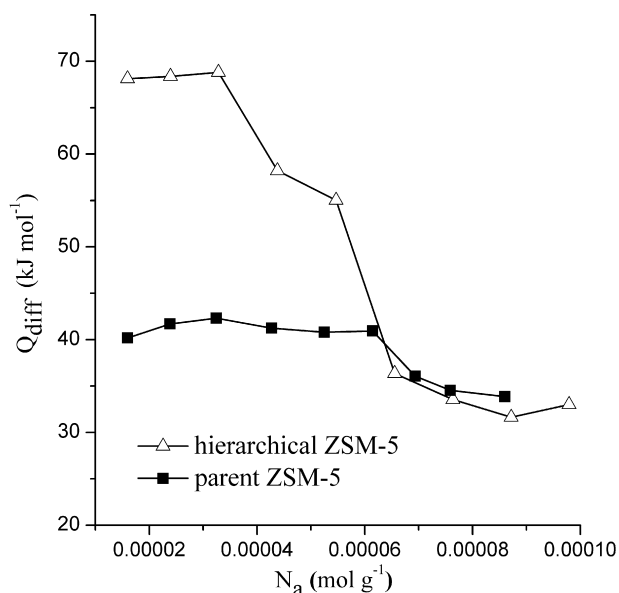


Fig. 8 Differential heats of adsorption of atenolol obtained by liquid calorimetry.

However, although the state of a molecule in a solution is defined by its pK_a value and the pH of the solution, the situation is not as straightforward when conditions within the zeolite are concerned, where we can have no certainty about the local pH (Chen and Sachtler, 1998). Yousef and El-Eswed (2009) have even found increasing capacities for phenol adsorption on natural zeolite with increasing pH, even though the phenolate anion and the zeolite surface were both negatively charged. Considering the previously discussed results obtained for PZC values of the investigated samples, it can be concluded that the differences in adsorption capacities measured for the two zeolitic samples cannot be attributed to changes in total surface charge of the solid. Since the PZC values of both zeolites are almost identical, it is safe to state that the adsorbing molecules are exposed to the same surface charge during adsorption on either parent or hierarchical ZSM-5. Hence, electrostatic attraction/repulsion cannot be considered to be the reason behind the observed differences in adsorption capacities between the two samples. The work presented in this paper shows that the presence and strength of basic groups in a pollutant molecule and its size and geometry are the main factors governing adsorption on ZSM-5 zeolite and that induced mesoporosity can significantly improve ZSM-5 usability in depollution processes, when molecules with diameters comparable to or larger than micropore openings are concerned.

4. Conclusion

In this work, the possibility of adsorptive capability improvement of ZSM-5 towards selected pharmaceuticals via mesopore formation was investigated. In comparison with the parent microporous sample, the obtained hierarchical zeolite expressed just slightly diminished acidity, as determined by microcalorimetry of ammonia adsorption, and no change in point of zero charge value. The adsorption of pharmaceuticals, which was probed from the aqueous solutions, seems to be governed by (1) the affinity of acid sites that can be found

on ZSM-5 surface toward specific pharmaceutical molecules and (2) dimensions of both the adsorbing molecules and the pore structure of the zeolite. The results presented here give evidence about the importance of steric effects: among the probed pharmaceuticals, atenolol and diclofenac were more effectively adsorbed on mesoporous than on microporous zeolite. It was shown that, in the case of atenolol, superior adsorptive capabilities of hierarchical ZSM-5 can be expected to be even more pronounced at low initial concentrations. Hence, it is to be underlined that forming of mesopores can significantly improve the accessibility of active sites inside the ZSM-5 structure. In view of the fact that microporosity of zeolites presents their major drawback for their application as adsorbents in the domain of environmental protection and remediation, results presented in this work clearly show that the applicability of these materials can be improved by mesopore formation.

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References

- Adamson, A.W., 1990. *Physical Chemistry of Surfaces*. Wiley, New York, p. 646.
- Ashtekar, S., McLeod, A.S., Mantle, M.D., Barrie, P.J., Gladden, L. F., Hastings, J.J., 2000. Determining the adsorption sites for binary mixtures of p-xylene and n-heptane in silicalite using FT-Raman spectroscopy and temperature-programmed desorption. *J. Phys. Chem. B* 104, 5281–5287.
- Auroux, A., Huang, M., Kaliaguine, S., 1996. Decrystallization process of HNaY zeolites upon mechanical milling: a microcalorimetric and thermokinetic study. *Langmuir* 12, 4803–4807.
- Ayranci, E., Duman, O., 2006. Adsorption of aromatic organic acids onto high area activated carbon cloth in relation to wastewater purification. *J. Hazard. Mater.* 136, 542–552.
- Carballa, M., Omil, F., Lema, J.M., Llompart, M., Garcia-Jares, C., Rodriguez, I., Gomez, M., Ternes, Th., 2004. Behavior of pharmaceuticals, cosmetics and hormones in a sewage treatment plant. *Water Res.* 38, 2918–2926.
- Chen, H.-Y., Sachtler, W., 1998. Activity and durability of Fe/ZSM-5 catalysts for lean burn NOx reduction in the presence of water vapor. *Catal. Today* 42, 73–83.
- Corcoran, J., Winter, M.J., Tyler, Ch.R., 2010. Pharmaceuticals in the aquatic environment: a critical review of the evidence for health effects in fish. *Crit. Rev. Toxicol.* 40, 287–304.
- Dakovic, A., Kragovic, M., Rottinghaus, G., Sekulic, Z., Milicevic, S., Milonjic, S., Zaric, S., 2010. Influence of natural zeolitic tuff and organozeolites surface charge on sorption of ionizable fumonisin B1. *Colloids Surf. B* 76, 272–278.
- Damjanovic, Lj, Rakic, V., Rac, V., Stosic, D., Auroux, A., 2010. The investigation of phenol removal from aqueous solutions by zeolites as solid adsorbents. *J. Hazard. Mater.* 184, 477–484.
- Daughton, C.G., 2016. Pharmaceuticals and the Environment (PiE): evolution and impact of the published literature revealed by bibliometric analysis. *Sci. Total Environ.* 562, 391–426.
- Daughton, Ch.G., 2004. Non-regulated water contaminants: emerging research. *Environ. Impact. Asses.* 24, 711–732.
- De Ridder, D.J., Verberk, J.Q.J.C., Heijman, S.G.J., Amy, G.L., van Dijk, J.C., 2012. Zeolites for nitrosamine and pharmaceutical removal from demineralised and surface water: mechanisms and efficacy. *Sep. Purif. Technol.* 89, 71–77.

- Deegan, A.M., Shaik, B., Nolan, K., Urell, K., Oelgemöller, M., Tobin, J., Morrissey, A., 2011. Treatment options for wastewater effluents from pharmaceutical companies. *Int. J. Environ. Sci. Tech.* 8, 649–666.
- Fagerholm, U., Nilsson, D., Knutson, L., Lennernas, H., 1999. Jejunal permeability in humans *in vivo* and rats *in situ*: investigation of molecular size selectivity and solvent drag. *Acta Physiol. Scand.* 165, 315–324.
- Feng, L., van Hullebusch, E.D., Rodrigo, M.A., Esposito, G., Oturan, M.A., 2013. Removal of residual anti-inflammatory and analgesic pharmaceuticals from aqueous systems by electrochemical advanced oxidation processes. A review. *Chem. Eng. J.* 228, 944–964.
- Fernandez, C., Stan, I., Gilson, J.-P., Thomas, K., Vicente, A., Bonilla, A., Perez-Ramirez, J., 2010. Hierarchical ZSM-5 zeolites in shape-selective xylene isomerization: role of mesoporosity and acid site speciation. *Chem. Eur. J.* 16, 6224–6233.
- Garcia-Ac, A., Segura, P.A., Gagnon, Ch., Sauve, S., 2009. Determination of bezafibrate, methotrexate, cyclophosphamide, orlistat and enalapril in waste and surface waters using on-line solid-phase extraction liquid chromatography coupled to polarity-switching electrospray tandem mass spectrometry. *J. Environ. Monit.* 11, 830–838.
- Giri, R.R., Ozaki, H., Ota, S., Takanami, R., Taniguchi, S., 2010. Degradation of common pharmaceuticals and personal care products in mixed solutions by advanced oxidation techniques. *Int. J. Environ. Sci. Tech.* 7, 251–260.
- Glassmeyer, S.T., Kolpin, D.W., Furlong, E.T., Focazio, M.J., 2008. In: *Fate of Pharmaceuticals in the Environment and in Water Treatment Systems*. CRC Press, Boca Raton, pp. 3–51.
- González-Ramos, K.M., Fernández-Reyes, B., Román, F.R., Hernández-Maldonado, A.J., 2014. A hierarchical porous carbon – Mn + [FAU] (Mn + = Ni²⁺ or Cu²⁺) adsorbent: synthesis, characterization and adsorption of salicylic acid from water. *Micropor. Mesopor. Mater.* 200, 225–234.
- Groen, J.C., Jansen, J.C., Moulijn, J.A., Pérez-Ramirez, J., 2004a. Optimal aluminum-assisted mesoporosity development in MFI zeolites by desilication. *J. Phys. Chem. B* 108, 13062–13065.
- Groen, J.C., Peffer, L.A.A., Moulijn, J.A., Pérez-Ramirez, J., 2004b. Mesoporosity development in ZSM-5 zeolite upon optimized desilication conditions in alkaline medium. *Colloids Surf. A* 241, 53–58.
- Hollender, J., Singer, H., Mcardell, Ch.S., 2008. Polar organic micropollutants in the water cycle. In: Hlavinek, P., Bonacci, O., Marsalek, J., Mahrikova, I. (Eds.), *Dangerous Pollutants (Xenobiotics) in Urban Water Cycle*, NATO Science for Peace and Security Series C: Environmental Security. Springer, Dordrecht, pp. 103–116.
- Jaroniec, M., Marczewski, A.W., 1984. Physical adsorption of gases on energetically heterogeneous solids I. Generalized Langmuir equation and its energy distribution. *Monatsh. Chem.* 115, 997–1012.
- Khetan, S.K., Collins, T.J., 2007. Human pharmaceuticals in the aquatic environment: a challenge to green chemistry. *Chem. Rev.* 107, 2319–2364.
- Kirumakki, S., Nagaraju, N., Chary, K., Narayanan, S., 2003. Kinetics of esterification of aromatic carboxylic acids over zeolites H β and HZSM5 using dimethyl carbonate. *Appl. Catal. A* 248, 161–167.
- Klavarioti, M., Mantzavinos, D., Kassinos, D., 2009. Removal of residual pharmaceuticals from aqueous systems by advanced oxidation processes. *Environ. Int.* 35, 402–417.
- Kyzas, G.Z., Bikiaris, D.N., Lambropoulou, D.A., 2017. Effect of humic acid on pharmaceuticals adsorption using sulfonic acid grafted chitosan. *J. Mol. Liq.* 230, 1–5.
- Kyzas, G.Z., Kostoglou, M., Lazaridis, N.K., Lambropoulou, D.A., Bikiaris, D.N., 2013. Environmental friendly technology for the removal of pharmaceutical contaminants from wastewaters using modified chitosan adsorbents. *Chem. Eng. J.* 222, 248–258.
- Lin, K.-Y.A., Yang, H., Lee, W.-D., 2015. Enhanced removal of diclofenac from water using a zeolitic imidazole framework functionalized with cetyltrimethylammonium bromide (CTAB). *RSC Adv.* 5, 81330–81340.
- Marco-Urrea, E., Radjenovic, J., Caminal, G., Petrovic, M., Vicent, T., Barcelo, D., 2010. Oxidation of atenolol, propranolol, carbamazepine and clofibrac acid by a biological Fenton-like system mediated by the white-rot fungus *Trametes versicolor*. *Water Res.* 44, 521–532.
- Martinez, C., Verboekend, D., Perez-Ramirez, J., Corma, A., 2013. Stabilized hierarchical USY zeolite catalysts for simultaneous increase in diesel and LPG olefinicity during catalytic cracking. *Catal. Sci. Technol.* 3, 972–981.
- Martucci, A., Pasti, L., Marchetti, N., Cavazzini, A., Dondi, F., Alberti, A., 2012. Adsorption of pharmaceuticals from aqueous solutions on synthetic zeolites. *Micropor. Mesopor. Mater.* 148, 174–183.
- Mitchell, S., Pérez-Ramírez, J., 2011. Mesoporous zeolites as enzyme carriers: synthesis, characterization, and application in biocatalysis. *Cat. Today* 168, 28–37.
- Mohapatra, D.P., Brar, S.K., Tyagi, R.D., Picard, P., Surampalli, R. Y., 2014. Analysis and advanced oxidation treatment of a persistent pharmaceutical compound in wastewater and wastewater sludge-carbamazepine. *Sci. Total Environ.* 470–471, 58–75.
- Papageorgiou, M., Nanaki, S.G., Kyzas, G.Z., Koulouktsi, C., Bikiaris, D.N., Lambropoulou, D.A., 2017. Novel isocyanate-modified carrageenan polymer materials: preparation, characterization and application adsorbent materials of pharmaceuticals. *Polymers* 9, 595–615.
- Polakovic, M., Gorner, T., Villieras, F., de Donato, Ph., Bersillon, J. L., 2005. Kinetics of salicylic acid adsorption on activated carbon. *Langmuir* 21, 2988–2996.
- Prasse, C., Schlusener, M.P., Schulz, R., Ternes, Th.A., 2010. Antiviral drugs in wastewater and surface waters: a new pharmaceutical class of environmental relevance? *Environ. Sci. Technol.* 44, 1728–1735.
- Rac, V., Rakić, V., Miladinović, Z., Stošić, D., Auroux, A., 2013. Influence of the desilication process on the acidity of HZSM-5 zeolite. *Thermochim. Acta* 567, 73–78.
- Rakić, V., Rac, V., Krmar, M., Otman, O., Auroux, A., 2015. The adsorption of pharmaceutically active compounds from aqueous solutions onto activated carbons. *J. Hazard. Mater.* 282, 141–149.
- Rivera-Utrilla, J., Sánchez-Polo, M., Ferro-García, M.A., Prados-Joya, G., Ocampo-Pérez, R., 2013. Pharmaceuticals as emerging contaminants and their removal from water. A review. *Chemosphere* 93, 1268–1287.
- Sathishkumar, P., Arulkumar, M., Ashokkumar, V., Yusoff, A.R.M., Murugesan, K., Palvannan, T., Salam, Z., Anic, F.N., Hadibarát, T., 2015. Modified phyto-waste *Terminalia catappa* fruit shells: a reusable adsorbent for the removal of micropollutant diclofenac. *RSC Adv.* 5, 30950–30962.
- Schwieger, W., Machoke, A.G., Weissenberger, T., Inayat, A., Selvam, T., Klumpp, M., Inayat, A., 2015. Hierarchy concepts: classification and preparation strategies for zeolite containing materials with hierarchical porosity. *Chem. Soc. Rev.* 45, 3353–3376.
- Serrano, D.P., Escola, J.M., Pizarro, P., 2013. Synthesis strategies in the search for hierarchical zeolites. *Chem. Soc. Rev.* 42, 4004–4035.
- Sing, K.S.W., Everett, D.H., Haul, R.A.W., Moscou, L., Pierotti, R. A., Rouquerol, J., Siemieniowska, T., 1985. Reporting physisorption data for gas/solid systems with special reference to the determination of surface area and porosity. *Pure Appl. Chem.* 57, 603–619.
- Solinas, V., Ferino, I., 1998. Microcalorimetric characterisation of acid–basic catalysts. *Catal. Today* 41, 179–189.
- Tambosi, J.L., Yamanaka, L.Y., José, H.J., Moreira, R.F.P.M., 2010. Recent research data on the removal of pharmaceuticals from sewage treatment plants (STP). *Quim. Nova* 33, 411–420.
- Vasquez, M.I., Lambrianides, A., Schneider, M., Kümmerer, K., Fatta-Kassinos, D., 2014. Environmental side effects of pharma-

- ceutical cocktails: what we know and what we should know. *J. Hazard. Mater.* 279, 169–189.
- Wang, J., Wang, S., 2016. Removal of pharmaceuticals and personal care products (PPCPs) from wastewater: a review. *J. Environ. Manage.* 182, 620–640.
- Wu, Y., Tian, F., Liu, J., Song, D., Jia, C., Chen, Y., 2012. Enhanced catalytic isomerization of α -pinene over mesoporous zeolite beta of low Si/Al ratio by NaOH treatment. *Micropor. Mesopor. Mater.* 162, 168–174.
- Xiao, W., Wang, F., Xiao, G., 2015. Performance of hierarchical HZSM-5 zeolites prepared by NaOH treatments in the aromatization of glycerol. *RSC Adv.* 5, 63697–63704.
- Xie, M., Nghiem, L.D., Price, W.E., Elimelech, M., 2012. Comparison of the removal of hydrophobic trace organic contaminants by forward osmosis and reverse osmosis. *Water Res.* 46, 2683–2692.
- Yousef, R., El-Eswed, B., 2009. The effect of pH on the adsorption of phenol and chlorophenols onto natural zeolite. *Colloids Surf. A* 334, 92–99.
- Zhou, H., Zhang, Z., Wang, M., Hu, T., Wang, Z., 2017. Enhancement with physicochemical and biological treatments in the removal of pharmaceutically active compounds during sewage sludge anaerobic digestion processes. *Chem. Eng. J.* 316, 361–369.