ZSM-5 ZEOLITES AS AGENTS FOR TREATMENT OF WATERS POLLUTED BY PHARMACEUTICALLY ACTIVE COMPOUNDS

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ABSTRACT

The removal of chosen pharmaceutically active substances (PACs) from aqueous solutions using microporous and hierarchical (microporous/mesoporous) zeolites of ZSM-5 type is reported. Mesopore formation was achieved through desilication by alkaline treatment. Zeolitic samples were fully characterized by appropriate methods. Adsorption isotherms of PACs were obtained and fitted to common mathematical models. It was found that Sips' method has the highest level of agreement with experimental data, and fits well all experimentally obtained isotherms. The influence of zeolites' acidities, textural properties and the adsorbing molecules' structures on the measured adsorption capacities was evaluated.

Keywords: ZSM-5, adsorption, pharmaceutically active compounds, hierarchical zeolites.

INTRODUCTION

The presence of PACs in the aquatic environment is nowadays considered as a relevant and very important topic. PACs are often classified as "contaminants of emerging concern", since some of these compounds, after their discard in the environment become ubiquitous in natural aquatic systems [1,2]. The most important contamination of environment comes from pharmaceutical companies, but also by excretion from humans or animals [1,2]. Although their concentrations in the environment are sometimes very low (often detected in ng/L) the long-term exposure may impose risks both for aquatic and terrestrial organisms [3,4]. Therefore, the launch of appropriate procedures that could enable the remediation of water polluted by PACs became a subject of permanent interest. However, technologies widely used for water remediation (commonly based on filtrations) are not suitable for removal of small polar molecules [2]. The same stands for treatment technologies based on advanced oxidation processes (AOP) [5]. Hence, there is still continuous need for solid adsorbents that can achieve high efficacy and good selectivity in the removal of PACs from polluted waters.

The adsorptive capabilities of zeolites toward specific molecules are limited by the sizes of their internal channels and channels intersections. In our previous contribution, we reported preliminary results related to the adsorption capabilities of mesoporous ZSM-5 (Si/Al = 26) for removal of the selected PACs, in comparison to those of the unmodified ZSM-5 zeolite [6]. Here, the adsorptions of chosen pollutants: salicylic acid (2-Hydroxybenzoic acid), atenolol ((*RS*)-2-{4-[2-Hydroxy-3-(propan-2-ylamino)propoxy]phenyl}acetamide) and diclofenac-sodium (Na salt of 2-(2-(2,6-dichlorophenylamino)phenyl)acetic acid) on so-called hierarchical (microporous/mesoporous) zeolites which recently have been obtained by desilication procedures and have attracted great attention since they express improved ability as carriers for large active species [7], have been investigated in details.

EXPERIMENTAL

Parent ZSM-5 zeolites (SiO_2/Al_2O_3 = 23, 50 and 80) were supplied by Zeolyst. Salicylic acid (SA) and atenolol (ATL) were supplied by pharmaceutical company "Galenika", Belgrade, Serbia, while diclofenac-Na (DFC) has been purchased from Sigma, Aldrich. Mesopore formation in ZSM-5 zeolite was performed through silicon extraction by NaOH solution, using the procedure proposed by Groen *et al.* [8]. The investigated solids were

denoted as ZxP and ZxM, where x denotes SiO_2/Al_2O_3 ratio while P and M are marks for the parent and the mesoporous HZSM-5, respectively. The crystallinity of parent and alkaline treated samples was checked by X-ray diffraction; while the total surface area, the total pore volume and the volumes occupied by micropores and mesopores were determined from nitrogen adsorption isotherms measured at 77 K after pretreatment at 673 K for 4 h under vacuum, as explained elsewhere [9].

Adsorption of SA, DFC and ATL from aqueous solutions (0.002 M) was studied using a previously established procedure [10]: typically, ca. 50 mg of zeolite was added to an appropriate amount of adsorbate solution and the suspension was mixed in a sealed flask using a magnetic stirrer during 30 minutes at 303 K. The solid and liquid phases were separated by centrifugation (Minispin from Eppendorf, 13400 rotations per minute, duration of centrifugation 1 hour). Equilibrium adsorbate concentrations were determined by Shimadzu UV-1650PC spectrophotometer and the adsorbed amounts, expressed as moles of the adsorbed substance per gram of zeolite, were calculated from the difference between the initial and equilibrium concentrations of the adsorbate. Each point of an isotherm was collected in a separate experiment. The duration of stirring which is necessary to achieve equilibrium concentrations at a given temperature was determined in a separate set of experiments: the same doses of the investigated substances as mentioned previously were admitted to the same amount of adsorbent and stirred during different times (15 min, 30 min, 1 h, 2 h and 6h). The adsorption duration of 30 minutes was established.

The obtained isotherms were fitted to the Langmuir, Freundlich and Sips equations [10] using Microcal Origin 8 software.

RESULTS AND DISCUSSION

The pore structure changes of ZSM-5 zeolites which took place as a result of the desilication process can be observed from the low-temperature nitrogen adsorption isotherms. while XRD patterns were recorded in order to estimate the influence of desilication on their crystallinities. Desilicated samples did preserve their crystalline structure, since XRD patterns typical for ZSM-5 structure were recorded. However, the alkaline treatment did influence the degree of crystallinity in the hierarchical mesopores containing samples (see Table 1).

Table 1. Textural properties and crystallinity of parent and modified Z23, Z50 and Z80 zeolites [9].

Sample	V_{pore} $(cm^3 g^{-1})^a$	V_{micro} $(cm^3 g^{-1})^b$	V_{meso} $(cm^3 g^{-1})^c$	S_{meso} $(m^2 g^{-1})^b$	S_{BET} $(m^2 g^{-1})^d$	Cristallinity (%)	SiO_2/Al_2O_3
Z23P	0.221	0.147	0.058	71	377	100	23
Z23M	0.253	0.139	0.095	103	392	91	22
Z50P	0.236	0.144	0.085	65	365	100	50
Z50M	0.449	0.138	0.380	173	470	76	50
Z80P	0.256	0.148	0.083	112	426	100	80
Z80M	0.493	0.145	0.324	214	521	84	78

[a] Volume mesured at p/p^0=0.98, [b] t-plot method, [c] BJH method, [d] BET method

Figure 1 presents the adsorption isotherms of DFC, ATL and SA obtained using microporous and mesoporous ZSM-5 zeolites. Experimental results are presented by symbols. Solid lines present calculated isotherms obtained as a result of mathematical harmonization of Sips' equation to experimental data, since this model has shown the highest level of agreement with them. It can be seen that the adsorption capacities for DFC adsorption lie in ~ 0.3–0.5 mmol/g range. Furthermore, it can be noticed that the amounts of adsorbed DFC are higher for parent samples containing more alumina. It is also obvious that for DFC adsorption mesoporous Z23M exhibits lower capacity than Z23P; Z50M exhibits higher capacity than Z50P, while similar capacities for parent and mesoporous samples were found for Z80.
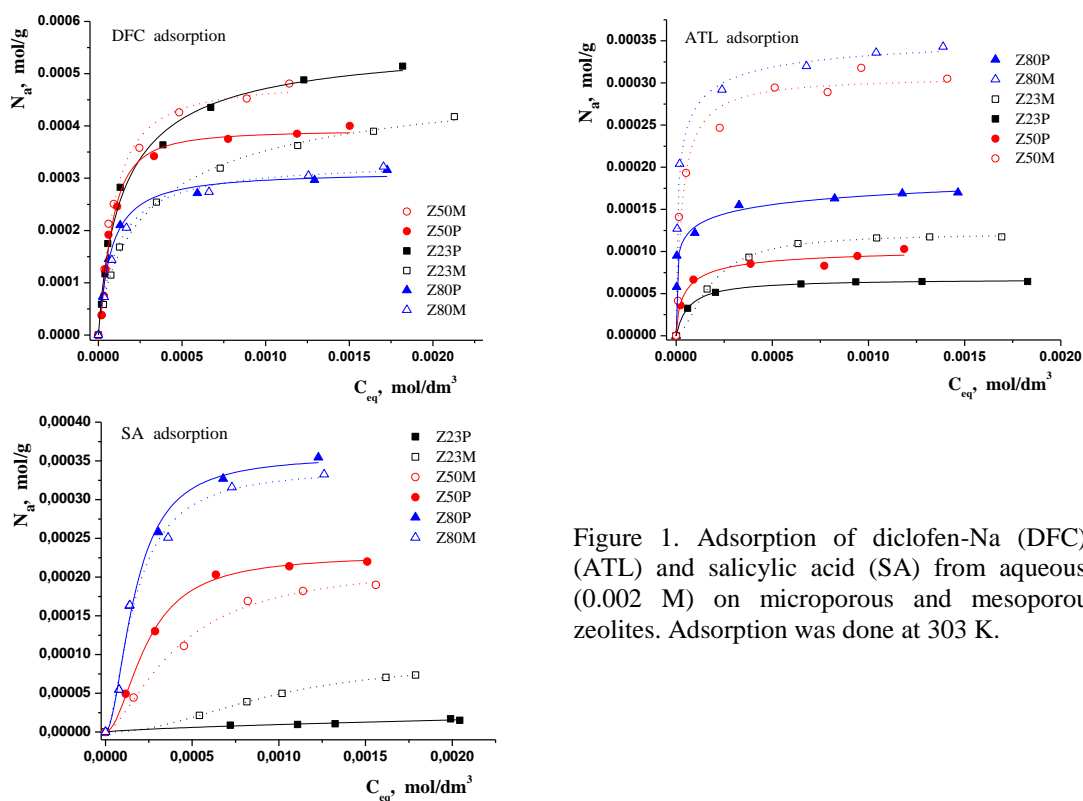
Figure 1. Adsorption of diclofen-Na (DFC), atenolol (ATL) and salicylic acid (SA) from aqueous solutions (0.002 M) on microporous and mesoporous ZSM-5 zeolites. Adsorption was done at 303 K.

The adsorption capacities for ATL are in ~ 0.050 – 0.32 mmol/g range. It is evident that significantly higher amounts of ATL are adsorbed on mesoporous forms of all investigated ZSM-5 samples. The capacities for the adsorption of SA are in a broad range from very low ~ 0.01 mmol/g found for Z23 samples, up to ~ 0.35 mmol/g determined for Z80. Evidently, more silicious ZSM-5 samples express higher affinity for SA adsorption. It is worth noticing that, except for Z23 zeolite, parent (microporous) Z50 and Z80 samples have slightly higher affinities to adsorb SA, in comparison with hierarchical, mesopores containing samples.

The acidity of all solids was previously estimated using the adsorption of ammonia [10]. Apart from the known fact that zeolites rich in aluminium are more acidic then those with the high content of Si, these results have shown that, as a result of desilication process, important diminishing of acidity appeared only in the case of Z23 sample, while in Z50 and Z80 acidity was preserved in spite of important increase of intracristalline mesoporosity.

To interpret the results presented in Figure 1, acidity and porosity of solids have to be taken into account, but also acidity-basicity of adsorbate molecules, as well as their dimensions. DFC and ATL molecules possess basic groups; therefore more effective adsorption could be expected on more acidic surfaces. Indeed, in the case of DFC, it is evident that Z23P adsorbs higher amount of DFC than Z50P, while this zeolite adsorbs more DFC then Z80P. However, although mesoporous Z50M is slightly less acidic then parent one, its higher ability for DFC adsorption was found. Therefore, it has to be inferred that active cites for DFC adsorption are more available in mesopore-containing samples. Evidently, the pore entrances of microporous ZSM-5 (6.2x6.3 Å, as calculated with Norman's corrections [11]) hinder the entrance of DFC molecule (3.54x8.29x7.00 Å [12]). In the case of ATL adsorption, the most important factor seems to be the availability of active sites, which is greater for mesoporous samples, since the dimensions of ATL molecules are estimated to be 7x18.2 Å [13]. The most important factor for adsorption of SA is acidity – the most effective retention of this PAC was noticed on the least acidic samples. Mesopore creation was found to have

little influence on the interaction of this small molecule (diameter estimated as 4.6 Å [14]) with ZSM-5 structure.

CONCLUSION

The adsorption of pharmaceuticals from the aqueous solutions seems to be governed by affinities of acid sites present in ZSM-5 structure. The results presented here give also evidence about the importance of steric effects, since certain PACs were more effectively adsorbed on mesoporous then on parent microporous zeolite. Evidently, mesopore creation in zeolite structures can improve zeolite applicability for pollutants removal from waters.

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