ADSORPTION OF PHARMACEUTICALLY ACTIVE COMPOUNDS FROM AQUEOUS SOLUTION BY MESOPOROUS HZSM-5 ZEOLITE

Vladislav Rac[1], Vesna Rakić[1], Vera Dondur[2], Aline Auroux[3]
[1]Faculty of Agriculture, Department of Chemistry, University of Belgrade, 11000 Belgrade, Serbia;
[2]Faculty of Physical Chemistry, University of Belgrade, 11000 Belgrade, Serbia;
[3]Institut de Recherches sur la Catalyse et l'Environnement de Lyon (IRCELYON), UMR 5256 CNRS/Université Lyon1, 2 av. Albert Einstein, 69626 Villeurbanne Cedex, France.
E-mail: vrac@ffh.bg.ac.rs

ABSTRACT

Introduction of mesopore regions into initially micropore zeolite structures incresases the range of molecules zeolite can potentialy interact with, while presearving its active sites. In recent years, a novel route for mesopore formation via silicon extraction by hydroxides has been proposed. In this work zeolite ZSM-5, a material well known for its selective adsorbing and catalytic properties was modified by desilication for the purpose of removal of pharmaceutically active compounds (atenolol, diclofenac sodium, salicylic acid and phenol) from aqueous solutions. The samples were fully characterized. The obtained ZSM-5 zeolite containing mesopore regions preserved its crystalline structure and acidity distribution upon modification. The adsorption capabilities of mesoporous ZSM-5 for removal of the selected pharmaceutically active molecules were compared to those of the parent, unmodified ZSM-5 zeolite.

Keywords: mesoporous zeolite, adsorption, atenolol, diclofenac, salicylic acid.

INTRODUCTION

Nowadays, the presence of pharmaceutically active compounds as pollutants in the aquatic environment is considered a relevant and very important topic [1]. Pharmaceuticals have physiological effects on humans and animals in very low concentrations. Today, we are aware that certain discarded pharmaceuticals can persist in the environment and make their way back to us either via the food chain or via drinking water. Some members of eminent prescription-drug groups are ubiquitous in natural aquatic systems, since they are polar molecules and hence soluble in water [1]. Therefore, their detection, the investigation of their effects and discovery of versatile possibilities to remove them from the environment impose challenges for researchers.

Recently, mesoporous zeolites, obtained by desilication procedures, have attracted attention since they express improved ability as carriers for large active species [2, 3]. In this work, we report results concerning adsorption of salicylic acid, a non-steroidal anti-inflammatory drug – diclofenac Na, a β blocker – atenolol and phenol from aqueous solution, using mesoporous HZSM-5 zeolite.

EXPERIMENTAL

Mesopore formation in HZSM-5 zeolite (Zeolyst, Si/Al = 26) has been done through silicone extraction by sodium hydroxide (0.2 M), using procedure reported in reference 2. The surface pore volumes and pore sizes were measured by nitrogen adsorption at 78 K on a Micromeritics 2010 apparatus, after pre-treatment at 673 K during 4 hours. XRD measurements were performed on a Bruker D5005 powder diffractometer scanning from 2° to 80° (2θ) at a rate of 0.02° s^{-1} using a Cu Kα radiation. Salicylic acid (SA) and atenolol (ATL) were supplied by pharmaceutical company "Galenika", Belgrade, Serbia, and diclofenac-Na (DFK) and phenol (PH) have been purchased from Sigma, Aldrich. Adsorption was studied using a previously established procedure [4]: typically, 50 mg of zeolite was added to an appropriate amount of adsorbate solution and the suspension was mixed using a magnetic

stirrer during 1 h at 303 K. Initial solution concentrations were 0.002 M for atenolol, diclofenac sodium and salicylic acid and 0.02 M for phenol. Equilibrium adsorbate concentrations were determined by Shimadzu UV-1650PC spectrophotometer. In order to estimate the population and strength of acid sites, ammonia adsorption (done at 423 K) on both parent and mesoporous zeolite has been studied by means of microcalorimetry. These experiments gave evidence that desilication procedure did not influence importantly the acidity of ZSM-5 zeolite.

RESULTS AND DISCUSSION

Desilication of parent HZSM-5 (Si/Al = 26) resulted in development of mesoporosity, which is evident from the profiles of isotherms of low-temperature nitrogen adsorption, presented in Figure 1 (left). Table 1 summarizes the textural properties of both zeolites. XRD measurements, Figure 1 (right) show that MFI structure has been preserved after desilication procedure.

Table 1. Textural properties of parent and mesoropous HZSM-5 zeolite.

HZSM-5 zeolite	V_{pore} [$cm^3\ g^{-1}$], at P/Po = 0.98	V_{micro} [$cm^3\ g^{-1}$], t-plot method	S_{meso} [$m^2\ g^{-1}$], t-plot method	S_{BET} [$m^2\ g^{-1}$], BET method
Parent	0.24	0.14	64	365
Mesoporous	0.45	0.14	173	470

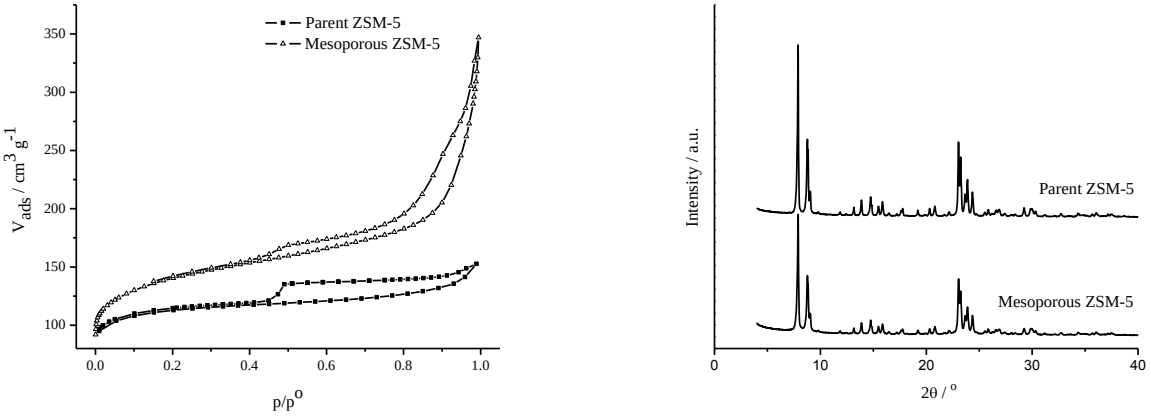

Figure 1. Textural properties (left) and XRD patterns (right) of parent and mesoporous HZSM-5 zeolite.

Both parent and mesoporous HZSM-5 express affinity toward adsorption of investigated pollutants. The adsorption capacities of mesoporous zeolite towards SA and PH are comparable to those of the parent zeolite (approximately 0.2 mmol/g for both molecules, Figure 2). The amount of adsorbed phenol is in accordance with our previous results obtained on ZSM-5 zeolites [4]. In the case of larger molecules, DFK an ATL, mesoporous samples show increased adsorption capabilities (Figure 3). The maximal adsorbed amounts of DFK were found to be 0.5 and 0.4 mmol/g, and of ATL 0.3 and 0.1 mmol/g, for mesoporous and parent ZSM-5, respectfully.

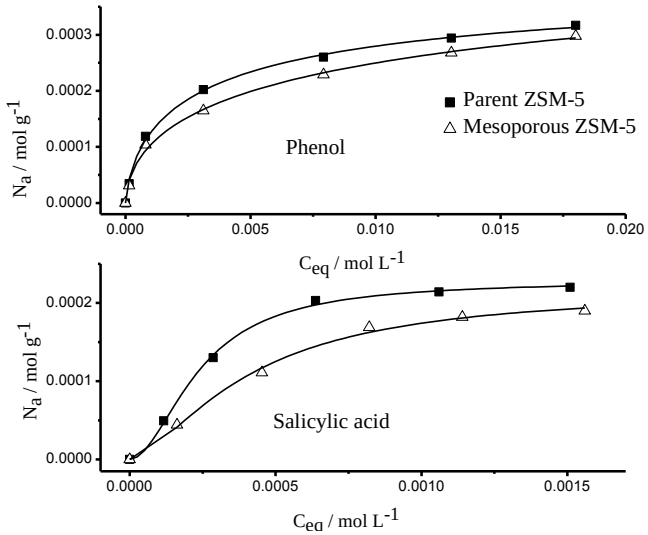

Figure 2. Isotherms of salicylic acid and phenol adsorption on parent and mesoporous HZSM-5 zeolite.

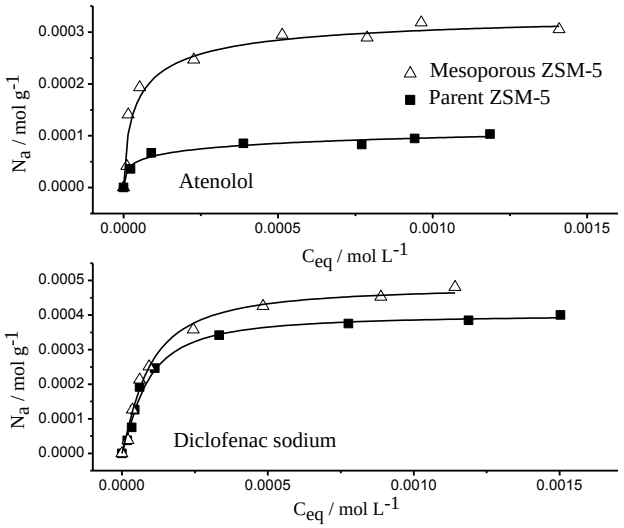

Figure 3. Isotherms of diclofenac-Na and atenolol adsorption on parent and mesoporous HZSM-5 zeolite.

CONCLUSION

The results obtained in this work show that desilication procedure improves mesoporosity and increases free volume inside the structure of MFI type zeolites. Mesoporous ZSM-5 zeolite shows greater capacities for adsorption of atenolol and diclofenac-Na from aqueous solutions compared to the parent, all-microporous ZSM-5. From the results obtained in this work, it can be inferred that improving mesoporosity offers the possibility to use these materials as effective adsorbents for pollutants of water.

REFERENCES

[1] S. K. Khetan, T. J. Collins, *Chem. Rev.*, 2007, **107**, 2319–2364.

[2] S. Mitchell, J. Pérez-Ramírez, *Cat. Today*, 2011, **168**, 28-37.

[3] D. Verboekend, J. Pérez-Ramírez, *Chem. Eur. J.*, 2011, **171**, 137 – 1147.

[4] Lj. Damjanovic, V. Rakic, V. Rac, D. Stosic, A. Auroux, *Journal of Hazardous Materials*, 2010, **184**, 477–484.