Experimental report

24/05/2019

Proposal: **1-04-128** **Council:** 4/2017

Title: Location of pharmaceuticals adsorbed from water on Y organophilic zeolite by neutron powder diffraction

Research area: Materials

This proposal is a new proposal

Main proposer: **Annalisa MARTUCCI**

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Samples: (Na2,Ca,Mg)3.5[Al7Si17O48]Â·32(H2O)

Instrument	Requested days	Allocated days	From	To
D1B	6			
D2B	6	3	22/06/2018	25/06/2018

Abstract:

In the last decade, it was demonstrated that domestic wastewaters contain a variety of organic contaminants such as pharmaceuticals and personal care products. Most of these compounds undergo both incomplete removal in wastewater treatment plants and slow natural degradation, consequently they are found in surface waters receiving effluent from treatment plants [1]. Pharmaceuticals can also be found in surface waters due to their veterinary use, in such cases they enter the environment via manure dispersion and animal excretion onto soils [2]. Studies on conventional biological drinking-water treatment processes such as biofiltration have shown that they are largely ineffective in removing pharmaceuticals [3].

In literature, several works focused on advantages of zeolites as adsorbents, such as high selectivity, rapid kinetics, reduced interference from salt and humic substances [4], excellent resistance to chemical, biological, mechanical and thermal stress [5-7 and references therein]. Even if zeolites are more expensive with respect to other adsorbents, they offer the possibility to be regenerated without loss of performances at relatively low temperatures [8-10].

In this work

EXPERIMENTAL REPORT

EXPERIMENT N° 1-04-128
DATES OF EXPERIMENT: FROM 22/06/2018 TO 25/06/2018
TITLE: LOCATION OF PHARMACEUTICALS ADSORBED FROM WATER ON Y ORGANOPHILIC ZEOLITE BY NEUTRON POWDER DIFFRACTION.

EXPERIMENTAL TEAM: ANNALISA MARTUCCI, GIADA BELTRAMI, ELISA RODEGHERO

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LOCAL CONTACT: Emmanuelle SUARD, Vivian NASSIF

In the last decade, it was demonstrated that domestic wastewaters contain a variety of organic contaminants such as pharmaceuticals and personal care products. Most of these compounds undergo both incomplete removal in wastewater treatment plants and slow natural degradation, consequently they are found in surface waters receiving effluent from treatment plants [1]. Pharmaceuticals can also be found in surface waters due to their veterinary use, in such cases they enter the environment via manure dispersion and animal excretion onto soils [2]. Studies on conventional biological drinking-water treatment processes such as biofiltration have shown that they are largely ineffective in removing pharmaceuticals [3].

In literature, several works focused on advantages of zeolites as adsorbents, such as high selectivity, rapid kinetics, reduced interference from salt and humic substances [4], excellent resistance to chemical, biological, mechanical and thermal stress [5-7 and references therein]. Even if zeolites are more expensive with respect to other adsorbents, they offer the possibility to be regenerated without loss of performances at relatively low temperatures [8-10].

At present, pharmaceuticals removing from water systems through adsorption on synthetic microporous zeolites is considered the best compromise in terms of cost-effectiveness and eco-sustainability [11-12]. In this work, two samples of Y zeolite (*i.e.*, Si/Al ratio=30) loaded with two different pharmaceutical compounds (*ibuprofen*, $C_{13}H_{18}O_2$ and *atenolol*, $C_{14}H_{22}N_2O_3$) were studied through neutron powder diffraction to determine zeolite sorption capacity and highlight host-guest interactions. The sample to be used in this project is a synthetic commercial zeolite Y (code HSZ-390HUA) with 30 and 200 SiO_2/Al_2O_3 (mol/mol) ratio, purchased in its protonated form from the Tosoh Corporation (Japan). We have collected three samples for each zeolite Y (SAR equal to 30 and 200) powders (Atenolol-Y, diclofenac-Y and ketoprofen-Y, respectively). In particular, all samples were obtained by the ion exchanging the as-synthesized form with deuterated drugs in aqueous solution for ≈140 h at room temperature and then washed with D_2O. All samples were packed in our laboratory in an argon-flushed glove-bag into a vanadium container sealed with a rubber gasket to ensure humidity-free transport to the neutron source. Diffraction data were collected at the D2B beamline (ILL; Grenoble) at 4 K. Rietveld refinements were performed using the GSAS software [13] whereas extra-framework sites were located by difference Fourier maps and then optimized using EXPO2014 [14]) software to obtain reasonable bond lengths and angles and calculate the H atoms position.

Results obtained from the cell parameters analysis confirmed the presence of extraframework molecules within the zeolite pores, which were located within the *supercage* through the difference Fourier maps analysis. Contrariwise, no coadsorbed water molecules were detected. Refinement of extraframework occupancies revealed the presence of higher amount of ibuprofen (33.68%) than atenolol (*atn*=11.55%) within the zeolite pores. According to bond distances analysis, both molecules directly interact with the zeolite framework, thus guaranteeing the molecule immobilization and preventing from uncontrolled release phenomena. The analysis of structural parameters allowed calculating both ellipticity and Crystallographic Free Area (CFA), which highlighted strong differences among the two drug-zeolite systems. Compared to the bare zeolite (unloaded-Y=46.26), CFA values after molecules adsorption increase: *ibu*-Y=56.58 and *atn*-Y=48.16. On the contrary, after loading no evident differences in channel shape and geometry were detected, thus confirming the high flexibility of zeolite framework. Based on the obtained results, the Y zeolite efficiency in ibuprofen and atenolol adsorption has been proved and its possible exploitation as sorbent materials in water remediation treatments can be assumed.

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