



## Removal of sulfonamide antibiotics from water: Evidence of adsorption into an organophilic zeolite Y by its structural modifications

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### ABSTRACT

Sulfonamide antibiotics are persistent pollutants of aquatic bodies, known to induce high levels of bacterial resistance. We investigated the adsorption of sulfadiazine, sulfamethazine, and sulfachloropyridazine sulfonamides into a highly dealuminated faujasite zeolite (Y) with cage window sizes comparable to sulfonamide dimensions. At maximal solubility the antibiotics were almost completely (>90%) and quickly ( $t < 1$  min) removed from the water by zeolite. The maximal amount of sulfonamides adsorbed was 18–26% DW of dry zeolite weight, as evidenced by thermogravimetric analyses and accounted for about one antibiotic molecule per zeolitic cage. The presence of this organic inside the cage was revealed by unit cell parameter variations and structural deformations obtained by X-ray structure analyses carried out using the Rietveld method on exhausted zeolite. The most evident deformation effects were the lowering of the  $Fd-3m$  real symmetry in the parent zeolite to  $Fd-3$  and the remarkable deformations which occurred in the 12-membered ring cage window after sulfadiazine or sulfachloropyridazine adsorption. After sulfamethazine adsorption, zeolite deformation caused a lowering in symmetry up to the monoclinic  $P2_1/m$  space group. The effective and irreversible adsorption of sulfonamides into organophilic Y zeolite makes this cheap and environmentally friendly material a suitable candidate for removing sulfonamides from water.

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### 1. Introduction

In recent years, the occurrence and fate of pharmaceutically active compounds in the aquatic environment has been recognized as one of the emerging issues in environmental chemistry [1]. The occurrence of antibiotics in hospital effluents and waste or surface waters may present two kinds of risks. Firstly, after supply, antibiotics select for resistant bacteria in the treated individuals themselves. Secondly, the presence of antibiotics in streams, lakes and water supplies encourages the growth of resistant bacteria in humans and wildlife [2]. Growing resistance means that what were once effective and cheap antibiotics may become unsuitable for treating infections.

Sulfonamide antibiotics comprise a class of synthetic sulfanilamide derivatives, widely used for the treatment of bacterial, protozoal and fungal infections in human therapy, livestock production and aquaculture [3]. They act as competitive inhibitors of p-aminobenzoate in folate biosynthesis. Sulfonamides are known

to induce high levels of resistance using a bypass mechanism—the metabolic step which is inhibited by the antibiotic may be replaced (bypassed) by an alternative metabolic step [4]. They are sufficiently stable in manure to maintain significant residual activity until field application [5]. In liquid manure, N-aniline acetyl sulfonamides conjugates can be cleaved back to parent compounds [6]. They may reach the soil through the faeces of treated grazing livestock and/or the spreading of manure as fertilizer on agricultural soils where they may persist in an unmetabolized form for months [7]. In non-acidic soils, sulfonamides may exist mainly in anionic form due to the  $pK_a$  value of the sulfonamide group ( $pK_a$  5.0–7.5 [8,9]) and therefore be potentially highly mobile and thus, pollute water bodies [10]. In fact, the presence of a net negative charge on soil surfaces makes this environmental compartment ineffective in the retention of negative compounds. The adsorption of sulfonamide antibiotics in soil organic matter is reported to be a time-dependent process [11], while on clay components it exhibits pronounced acidic pH dependence [12]. Sulfonamides may also directly reach water bodies through hospital and fish farming wastewaters [1] bypassing soil filtering and depuration activity. Furthermore, in municipal sewage treatment plants, sulfonamides may not be effectively eliminated owing to their anionic character. In fact, pollutant biodegradation is largely achieved by sorption on activated sludge, which is partly mediated through hydrophobic

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interactions [13]. Approximately 20 years after industrial aquaculture began, evidence has emerged on the transfer of antibiotic resistance between aquatic bacteria and human pathogens [14]. A number of important studies indicate that the bacterial flora in the environment surrounding aquaculture sites contain an increased number of antibiotic-resistant bacteria [15].

Despite the need to clean up wastewaters which have been highly polluted with sulfonamide antibiotics, no sorbents with specific adsorption potential and favourable kinetics have been identified to date. The aim of this study is to verify the efficiency of sorbents such as zeolitic materials in removing sulfonamide antibiotics from water bodies.

Zeolites are crystalline aluminosilicates, characterized by three-dimensional networks containing channels and cavities whose dimensions are comparable with small organic molecules. Such networks of well-defined micropores may act as adsorption and reaction sites whose selectivity and activity can be modulated by acting on their structure and chemical composition. The three-dimensional framework, consisting of nanometre-sized channels and cages, imparts high porosity and a large surface area to these materials. One of their defining features is that the shape of their internal pore structure can strongly affect their adsorption selectivity with respect to host molecules. The most fundamental consideration regarding the adsorption of chemical species by zeolites is molecular sieving. The pores, or rather the active sites within the pores, exclusively process molecules that fit them, so that species with a kinetic diameter which makes them too large to pass are effectively “sieved”.

Zeolites are commonly used in areas as diverse as laundry detergents, gas separation, oil refining and the petrochemical industries, agriculture, wastewater and sewage treatment. The ability of zeolites with a low Si/Al ratio to remove cations by ionic exchange has been largely demonstrated and utilized in water treatment plants which produce drinking water [16]. On the contrary, zeolites characterized by a high Si/Al ratio are hydrophobic and organophilic materials widely used in adsorption-related applications. To date, studies and applications on organic pollutant adsorption in these microporous materials from aqueous media are scarce [17–19]. Moreover, their purpose is the remediation of non-polar hydrocarbons pollutants which are frequently found in refineries and gasoline station groundwater [20] and not of negatively ionisable and polar compounds, such as sulfonamide antibiotics.

In this study, a Y faujasite hydrophobic zeolite is presented due to its ability to specifically adsorb high amounts of sulfonamide antibiotics inside its cavities with very favourable kinetics. These findings were supported by X-ray analyses which demonstrated the accommodation of antibiotic molecules inside the zeolite cage.

## 2. Experimental

### 2.1. Materials

Sulfadiazine (4-amino-2-N-pyrimidinyl-benzene sulfonamide, SD), sulfamethazine (4-amino-N-(4,6-dimethyl-2-pyrimidinyl) benzene sulfonamide, SM), and sulfachloropyridazine (4-amino-N-(6-Cl-3-pyridazinyl)benzene sulfonamide, SC) were purchased as analytical standards by Dr. Ehrenstorfer GmbH (Germany) with a purity of 98.7%, 99.5%, and 98.0%, respectively. These antimicrobial agents have been chosen because of their widespread consumption and predominant occurrence in water bodies and soils [21–23]. The chemical structures of sulfonamides are shown in Table 1. Stock solutions of antibiotics at maximal solubility were prepared by adding SD, SM and SC antibiotics to distilled water in amounts exceeding those required to saturate the solution. The suspensions

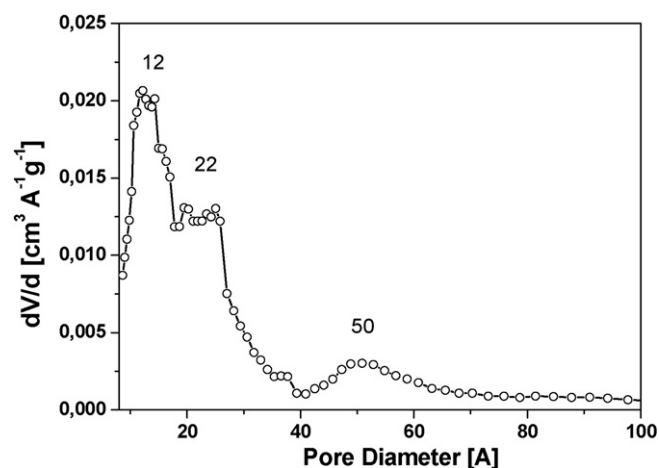


Fig. 1. Pore size distribution of zeolite Y determined by nitrogen adsorption isotherm at  $-196^{\circ}\text{C}$  using a cylindrical pore NLDFT method in the desorption branch.

were sonicated for 15 min, shaken at  $50^{\circ}\text{C}$  for 30 min and, after cooling at room temperature, filtered through  $0.45\ \mu\text{m}$  Durapore® membrane filters to eliminate the undissolved solute from the solutions. The solubility of the antibiotics, measured by means of high performance liquid chromatography (HPLC), was  $71.9 \pm 4.8$ ,  $135.8 \pm 3.9$  and,  $173.6 \pm 7.7\ \mu\text{M}$  for SD, SM and SC, respectively.

“Y” type faujasite zeolite powder (code HSZ-390HUA) with a 200  $\text{SiO}_2/\text{Al}_2\text{O}_3$  (mol/mol) ratio, a  $7.0\ \text{\AA} \times 7.1\ \text{\AA}$  dimension and a 12-membered ring window diameter was purchased in its protonated form from the Tosoh Corporation (Japan). The specific surface area was measured by means of nitrogen adsorption at liquid nitrogen temperature ( $-196^{\circ}\text{C}$ ) in the pressure range  $5 \times 10^{-6}$  to 760 torr (1 Torr = 133.33 Pa) using an Autosorb-1-MP (Quantachrome Instruments) (Fig. S-1 in Supporting Information). Prior to adsorption, the samples were outgassed for 1 h at  $90^{\circ}\text{C}$ , 1 h at  $130^{\circ}\text{C}$ , and finally 16 h at  $300^{\circ}\text{C}$  under high vacuum conditions (final pressure  $1 \times 10^{-9}$  Torr). The specific zeolite Y area, determined by the Brunauer–Emmett–Teller approach and using 0.01 as the value of maximum relative pressure, was  $853\ \text{m}^2\ \text{g}^{-1}$  (Table 2). The pore size distribution was calculated by applying the cylindrical pore NLDFT method in the desorption branch (Fig. 1). A total specific surface area of ca.  $850\ \text{m}^2\ \text{g}^{-1}$ , most of which related to the presence of structural micropores ( $616\ \text{m}^2\ \text{g}^{-1}$ ), was determined (Table 2). As expected, zeolite Y shows structural 12 Å micropores whose related volume is  $0.21\ \text{cm}^3\ \text{g}^{-1}$ . The presence of 22 Å (related volume =  $0.12\ \text{cm}^3\ \text{g}^{-1}$ ) and 50 Å pores (related volume =  $0.08\ \text{cm}^3\ \text{g}^{-1}$ ) were also found.

### 2.2. Adsorption screening

A preliminary study of the adsorption properties of zeolite Y from distilled water towards a mixture of sulfonamide antibiotics was conducted. The adsorption screening was performed at room temperature and  $65^{\circ}\text{C}$ , by adding the zeolite to a solution containing SD, SM, and SC (ca.  $40\ \mu\text{M}$  each, prepared by diluting antibiotics stock solutions) with a zeolite:antibiotic solution ratio of 1 mg:2 mL in polyallomer centrifuge tubes (Nalgene, NY, USA). Suspensions were shaken for 24 h and then centrifuged at  $20,000 \times g$  for 15 min. Finally, an aliquot of the supernatant was withdrawn and analyzed by HPLC. The amount of antibiotics adsorbed by zeolite was calculated by the difference between the initial and final concentrations. A control was run in the absence of zeolites in order to check the stability of the antibiotics and the adsorption properties of the centrifuge tube. No decrease in sulfonamides concentration was recorded after 24 h.

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