

Removal of sulfamethoxazole sulfonamide antibiotic from water by high silica zeolites: A study of the involved host–guest interactions by a combined structural, spectroscopic, and computational approach



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ABSTRACT

Sulfonamide antibiotics are persistent pollutants present in surface and subsurface waters in both agricultural and urban environments. Sulfonamides are of particular concern in the environment because they are known to induce high levels of bacterial resistance. Adsorption of sulfamethoxazole sulfonamide antibiotic into three high silica zeolites (Y, mordenite, and ZSM-5) with pore opening sizes comparable to sulfamethoxazole dimensions is reported. Sulfamethoxazole was almost completely removed from water by zeolite Y and MOR in a few minutes. Adsorption onto ZSM-5 showed an increased kinetics with increasing temperature. Antibiotic sorption was largely irreversible with little antibiotic desorbed. Sulfamethoxazole incorporation and localization into the pore of each zeolite system was defined along with medium-weak and cooperative host–guest interactions in which water molecules play a certain role only in zeolite Y and mordenite.

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1. Introduction

Sulfamethoxazole (SMX) is a broad spectrum antibiotic used in human and veterinary therapy which belongs to the sulfonamide family (sulfa drugs). Like other sulfonamides, SMX is a competitor of p-aminobenzoic acid in the biosynthesis of tetrahydrofolic acid. In studies on humans it was found that 20% of SMX daily dose was excreted via urine/feces in its original form, 50–60% was transformed to acetylated derivative (N1-acetylsulfamethoxazole, see Fig. 1) and 15–20% to glucuronide conjugate [30,31,13].

The inefficiency of sewage treatment plants to degrade sulfonamides and the practice to land apply sulfonamide-containing manure for agronomic purpose contribute to the spreading of antibiotics in the environment. As reported by Michael et al. [36], SMX concentrations in urban wastewater treatment plants depend on its consumed amount and the type of wastewater treatment

employed. Using biological treatment with activate sludge, SMX removal efficiency ranged between 100% and <25% [36]. Two reasons for the high variability could have been the reconversion of the N1-acetyl derivate in the parent compound, which would have underestimated SMX removal efficiency, and to its anionic nature ($pK_{a2} = 5.7$ [26]) that limits sorption on activate sludge resulting in lower efficiency [38]. As a result, wastewater treatment plants represent potential reservoirs of sulfonamides that may contribute to the evolution and spread of antibiotic resistance [33]. Owing to its anionic nature, SMX is not strongly retained by soils containing organic carbon and clays [15,16] and moves through the soil profile accumulating in the aquatic environment [7]. The most important consequence of antibiotic release in natural environments is the development of resistant bacteria [18].

Several techniques have been developed to degrade and remove antibiotics from water and wastewater [34]. Among these, adsorption on activated carbon is one of the most efficient; however, the high cost of the adsorbent, their susceptibility of pore blocking, and the difficulties of regeneration are disadvantages [9]. As an alternative low-cost adsorbent, this study evaluated the mechanisms of SMX removal efficiency from water using several commercial high silica (HS) zeolites.

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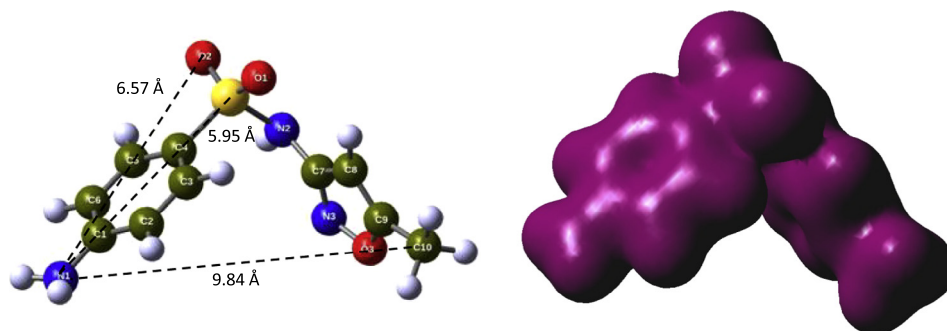


Fig. 1. DFT optimized stick and ball (left) and electron density (right) structure of sulfamethoxazole. Geometry optimization with GGA functional BLYP. Plot of total electron density with isosurface at $8 \times 10^{-3} \text{ \AA}^3$.

Zeolites are microporous crystalline aluminosilicates extensively used because of their high surface area, adsorption capacity and cationic exchange capacity. Moreover, the sorption of hydrophobic and hydrophilic solutes can be modulated by control of zeolite $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio. Of particular interest in this study is the relation between the molecular dimensions of the zeolite pores relative to the size of SMX.

Studies on the use of high silica (HS) zeolites (high $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio) adsorbents for pharmaceutical compounds from water are limited [37,4,12,19,20,6,24,25]. HS zeolite Y has been tested for the adsorption of sulfa drugs from soil solution containing salts and dissolved organic matter with excellent results (ca. 20% zeolite dry weight – DW [4,5]). In the light of these recent findings, we believed interesting to investigate the adsorption of SMX from water by a series of HS zeolites and the effect of water on the host–guest interactions between zeolite and antibiotic.

2. Materials and methods

2.1. Chemicals

Sulfamethoxazole (4-amino-*N*-(5-methylisoxazol-3-yl)benzenesulfonamide (DFT optimized structure in Fig. 1); MW 253.3 g mol^{-1} ; K_{ow} 0.4; [27]; pK_{a2} 5.7), was purchased as analytical standard by Dr. Ehrenstorfer GmbH (Germany) with a purity of 99%.

Because SMX contains ionizable functional groups, its solubility depends on solution pH [23]. A SMX stock solution at the maximal solubility was prepared by adding the antibiotic to distilled water in equilibrium with the atmospheric CO_2 (ca. pH 6.0), in amount exceeding that required to saturate the solution. The suspension was sonicated for 15 min, shaken at 50°C for 30 min and, after cooling at room temperature (RT), filtered through $0.45 \mu\text{m}$ Durapore® membrane filters to eliminate the undissolved solute. SMX solubility, measured by means of high performance liquid chromatography (HPLC), was $202.3 \pm 4.2 \mu\text{M}$ at RT.

Three different HS zeolites have been chosen: Y, mordenite (MOR), and ZSM-5. Powders of zeolites Y and MOR (code HSZ-390HUA and HSZ-690 HOA, respectively) were purchased in their protonic form from Tosoh Corporation (Japan). ZSM-5 (code TSP-3022) was supplied in its ammonium form (<0.04%) by Tricat (USA).

2.2. Temperature effect on adsorption

Adsorption experiments were performed at both RT and 65°C by adding each zeolite to a $30 \mu\text{M}$ antibiotic solution (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 20,000g for 15 min. Finally, an aliquot of the

supernatant was withdrawn and analyzed by HPLC. The amount of adsorbed antibiotics was calculated by the difference between the initial and final concentration. Controls run in the absence of zeolites allowed to verify the stability of SMX and any possible adsorption of the drug onto the centrifuge tubes. The experiments were carried out in triplicate.

2.3. Adsorption kinetics

Kinetics were performed at RT on zeolite Y and MOR and at 65°C on ZSM-5 with a zeolite:antibiotic solution ratio of 1 mg:2 mL. SMX was weighted on a Mettler Toledo AT21 Comparator balance (weigh limit = $1 \mu\text{g}$). The concentration of adsorbed antibiotic was obtained by HPLC as reported in Section 2.2. The experiments were conducted in triplicate. Control experiments were conducted to verify the SMX stability for the entire duration of the kinetics.

2.4. Adsorption and desorption isotherms

Owing to the moderate SMX solubility and to the high adsorption capacity of the selected zeolites, the adsorption isotherms were built by mean of subsequent adsorption cycles with zeolite:antibiotic solution ratio of 1 mg:2 mL as follows: suspensions of zeolites Y or MOR in the antibiotic solution at maximal solubility were shaken for 30 min, whereas ZSM-5 for 24 h. Then the suspensions were centrifuged and the supernatant analyzed by HPLC. The supernatant was then completely removed and substituted by fresh antibiotic solution. Several subsequent adsorption steps were performed until the zeolites reached the maximum adsorption capacity (from here on called exhausted/loaded zeolites). All experiments were conducted in triplicate.

Adsorption data were expressed as C_e (μM) – the antibiotic concentration in aqueous phase at equilibrium – and C_s ($\mu\text{mol g}^{-1}$ adsorbent) – the amount of antibiotics adsorbed onto zeolite (i.e. the sum of adsorbed antibiotic after each adsorption step) – calculated by the difference between the initial and final (C_e) concentrations.

Desorption isotherms were performed on loaded zeolites obtained after the last adsorption step by substituting one SMX solution half-volume with distilled water. The new suspension was shaken for 24 h, centrifuged and the supernatant analyzed by HPLC. Then, a supernatant second half-volume was again removed and substituted with distilled water. The dilution step was repeated several times, until no decrease was detected in the SMX equilibrium concentration.

2.5. Chromatographic analysis

SMX concentration was determined by a Jasco HPLC-Diodarray. The system was assembled with the detector set at 267 nm , Jasco

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