



Effect of humic monomers on the adsorption of sulfamethoxazole sulfonamide antibiotic into a high silica zeolite Y: An interdisciplinary study



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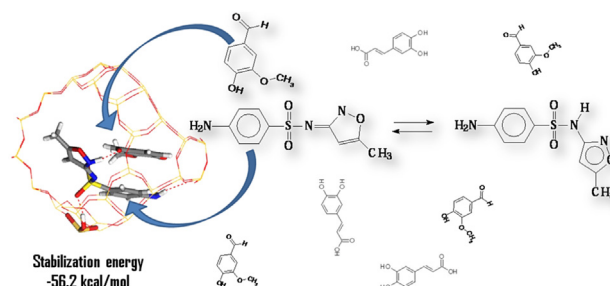
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HIGHLIGHTS

- Reversible and pH-dependent adsorption of vanillin by HS zeolite Y.
- Negligible adsorption of caffeic acid by HS zeolite Y at any pH.
- Irreversible and pH-dependent adsorption of sulfamethoxazole by HS zeolite Y.
- Evidence of a vanillin-sulfamethoxazole adduct into the zeolite pores.
- Guest-guest interactions into zeolite pores and computation of stabilization energy.

GRAPHICAL ABSTRACT



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ABSTRACT

The adsorption efficiency of a high silica zeolite Y towards sulfamethoxazole, a sulfonamide antibiotic, was evaluated in the presence of two humic monomers, vanillin and caffeic acid, representative of phenolic compounds usually occurring in water bodies, owing their dimension comparable to those of the zeolite microporosity. In the entire range of investigated pH (5–8), adsorption of vanillin, as a single component, was reversible whereas it was irreversible for sulfamethoxazole. In equimolar ternary mixtures, vanillin coadsorbed with sulfamethoxazole, conversely to what observed for caffeic acid, accordingly to their adsorption kinetics and pKa values. Lower and higher adsorptions were observed for sulfamethoxazole and vanillin, respectively, than what it was observed as single components, clearly revealing guest-guest interactions. An adduct formed through H-bonding between the carbonyl oxygen of vanillin and the heterocycle NH of sulfamethoxazole in amide form was observed in the zeolite pore by combined FTIR and Rietveld analysis, in agreement with Density Functional Theory calculations of the adduct stabilization energies. The formation of similar adducts, able to stabilize other naturally occurring phenolic compounds in the microporosities of hydrophobic sorbents, was proposed.

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1. Introduction

The release of antibiotics in the environment has been

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associated to chronic toxicity and the onset of the antibiotic resistance phenomena in bacteria (Gao et al., 2012). For these reasons, the removal of antibiotics from water bodies has become a public health issue which should be urgently addressed. Sulfonamides (sulfa drugs) were the first group of synthetic antimicrobials systematically used to treat/prevent bacterial infections. (Sweetman, 2011). Due to the beneficial effect on production efficiency in poultry and swine, sulfonamides are usually administered as growth promoters in livestock (Dibner and Richards, 2005; Neu and Gootz, 1996). Owing to their pH-dependent anionic nature, sulfonamides accumulate in water bodies, being neither completely retained by soils (Pan and Chu, 2016) nor by activated sludge in biological treatment plants (Manaia et al., 2016). Sulfamethoxazole (SMX) is one of the top-selling sulfonamide antibiotic used in human and veterinary therapy. Several studies report about its occurrence in aquatic ecosystems such as surface and drinking water, as well as wastewater treatment plants and hospital effluents (Kummerer, 2001; Brown et al., 2006; Tamtam et al., 2008; Watkinson et al., 2009). Above all, hospital and breeding farm outputs represent point source pollution which requests special consideration.

High silica (HS) zeolites have been recently tested to remove pharmaceutical from waters (de Ridder et al., 2012; Martucci et al., 2012; Grieco and Ramarao, 2013). In this contest, several model studies have indicated HS zeolites to quickly remove high amount of sulfonamide antibiotics from water (Braschi et al., 2010, 2013; Fukahori et al., 2011; Blasioli et al., 2014; Martucci et al., 2014) and to be easily regenerated (Leardini et al., 2014). Possible effect of dissolved organic matter (DOM), naturally present in water bodies, on sulfonamide adsorption into these zeolites has been ruled out, owing to the dimensions of its main components which are higher than those of the zeolite microporosities (Braschi et al., 2010), but no investigation on the effect of organic components of molecular size comparable with their pore window diameter has been addressed. This aspect is of utmost importance in order to exploit the zeolite microporosities to reduce the sulfonamide point source pollution as breeding farm effluents.

Natural and wastewaters contain plenty of low molecular weight organic molecules (Hem, 1987; Kordel et al., 1997). Among them, the phenolic component, which is formed by compounds like catechol, caffeic, ferulic, and *p*-coumaric acids, as well as *p*-hydroxybenzaldehyde, vanillin, and other more, can be simultaneously found. The tendency of these compounds to aggregate through biotic and abiotic oxidative coupling in soils to form humic substances, where their chemical structures can be resembled, is the reason for calling them humic monomers (Nyanhongo et al., 2006; Tossel, 2009; Nuzzo and Piccolo, 2013). Due to the different structure of phenolic compounds and their coexistence in natural water compartments (Muscolo et al., 2013), two of them were identified as a model to evaluate their effect on the adsorption of sulfonamide antibiotics into a HS zeolite Y and, of more general knowledge, their ability to clog eventually the microporosities of siliceous hydrophobic sorbents. Vanillin and caffeic acid were selected as representative of humic monomers because of their different chemical nature (an aldehyde the former and an hydroxycinnamic acid the latter) and reactivity in water. Their adsorption competition against SMX, as a sulfonamide antibiotic model, was tested into a large pH range to embrace that of natural, artificial and wastewaters.

2. Materials and methods

2.1. Chemicals

Sulfamethoxazole (4-amino-*N*-(5-methylisoxazol-3-yl)-

benzenesulfonamide, SMX), was obtained from Dr. Ehrenstoffer GmbH (Germany) with 99% purity. Vanillin (4-hydroxy-3-methoxybenzaldehyde, VNL) and caffeic acid (3-(3,4-dihydroxyphenyl)-2-propenoic acid, CA) were supplied by Sigma Aldrich Co LLC (USA) with 95 and 99% purity, respectively. Their chemical structures and *pKa* values are reported in Table 1.

The water solubility of SMX and the two phenols at room temperature (RT) was determined by adding each compound to MilliQ water in amount exceeding that required to saturate the solution. The suspensions were sonicated (15 min) and filtered at 0.45 μm (Durapore[®] membrane filters) to eliminate undissolved particles. The solubility measured by HPLC was $203 \pm 2.7 \mu\text{M}$ for SMX, 9.46 ± 1.03 and 2.53 ± 0.31 mM for VNL and CA, respectively.

HS zeolite Y with $\text{SiO}_2/\text{Al}_2\text{O}_3 = 200$ and surface area of $750 \text{ m}^2 \text{ g}^{-1}$ was purchased from Tosoh Corporation (Japan).

In the experiments conducted in the presence of zeolite, the desired pH values were achieved and kept constant by addition of 0.1 N HCl/NaOH to avoid any possible coadsorption of buffering components. The pH was controlled for the entire duration of the trial.

2.2. Persistence of humic monomers in water

Aqueous solutions of VNL or CA (50 μM each) were prepared in polyallomer centrifuge tubes (Nalgene, NY, USA) dissolving the compounds in media buffered at pH 5 and 6 (10 mM CH_3COONa , Carlo Erba Reagents, Milano, Italy) and at pH 7 and 8 (10 mM Na_2HPO_4 , Carlo Erba Reagents, Milano, Italy). The persistence of the two phenols was followed over 48 h at RT by HPLC. Each experiment was conducted in triplicate.

2.3. Adsorption kinetics

Several aliquots of zeolite Y (1 mg) pre-equilibrated at the desired pH in the 5–8 range were placed into polyallomer centrifuge tubes where 2 mL of SMX, VNL or CA solutions (50 μM each) at the same pH were added. The suspensions were then placed on a horizontal shaker at RT and, at different times, the supernatants were separated from the pellet by centrifugation and analyzed by HPLC. To guarantee the pH stability, the pH of each suspension was checked and eventually adjusted by a few drops of 10 mM HCl/NaOH solution for the entire experiment duration. The experiment was conducted in duplicate.

2.4. Adsorption-desorption isotherms

Adsorption isotherms of SMX or VNL on zeolite Y were performed at RT in the 5–8 pH range (zeolite:solution = 1 mg:2 ml). Each suspension was shaken for 1 h, then centrifuged and the supernatants analyzed by HPLC. The pH of the suspensions was monitored and adjusted during the entire experiment.

Owing to the high SMX adsorption capacity of zeolite Y and the low SMX solubility at RT ($203 \pm 2.7 \mu\text{M}$), the isotherm data points at high concentrations were obtained as described in Blasioli et al. (2014). The desorption trials were conducted with the dilution method as reported in Blasioli et al. (2014). All adsorption-desorption experiments were conducted in duplicate.

The concentration of antibiotic and humic monomers in aqueous phase at equilibrium was expressed as Ce (μM) whereas the amount adsorbed by the zeolite, expressed as Cs ($\mu\text{mol g zeolite}^{-1}$), was calculated by the difference between the initial and final concentrations.

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