



Removal of salicylic acid and carbamazepine from aqueous solution with Y-zeolites modified with extraframework transition metal and surfactant cations: Equilibrium and fixed-bed adsorption

Wilman A. Cabrera-Lafaurie^a, Félix R. Román^b, Arturo J. Hernández-Maldonado^{a,*}

^a Department of Chemical Engineering, University of Puerto Rico-Mayagüez Campus, Mayagüez 00681-9000, Puerto Rico

^b Department of Chemistry, University of Puerto Rico-Mayagüez Campus, Mayagüez 00681-9000, Puerto Rico

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ABSTRACT

A synthetic zeolite (Na⁺-Y; Si/Al ~ 2.8) was modified through incorporation of both a transition metal (Co²⁺, Ni²⁺ or Cu²⁺) and a surfactant (cetylpyridinium; CPY⁺) to develop adsorbents with tailored selectivity and uptake capacity for pharmaceutical and personal care products (PPCPs) present in water. Two PPCPs were targeted in this study, namely salicylic acid and carbamazepine, due to their reported recurrence in water sources. In general, the zeolite modifications increased the equilibrium salicylic acid adsorption capacities, from 0.03 up to 3.9 mg g⁻¹ in the 0.1–10 ppm PPCP concentration range (pH range 6–11). The salicylic acid equilibrium adsorption capacities increased as follows: Ni²⁺ < Na⁺ < Co²⁺ < Cu²⁺. A remarkable selectivity toward salicylic acid was evident in all cases, but the capacity for carbamazepine also varied upon modification of the zeolite. Fixed-bed adsorption studies were performed on (Cu²⁺, CPY⁺)-Y for single- and multi-component PPCP feeds at pH ~ 6 and ambient temperature, and indicated that the uptake was not limited by diffusion and that most of the bed depth was used efficiently. The multi-component tests revealed a ca. 55% increase in adsorption capacity for salicylic acid when compared against the single-component results.

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Introduction

Pharmaceuticals and personal care products (PPCPs) have emerged during the last decade as a group of contaminants of considerable concern. PPCPs are compounds designed for human and veterinary medical consumption (including some endocrine disrupting chemicals) as well as active and inert ingredients present in personal care products [1–4]. Furthermore, the ever-increasing consumption of these compounds due to an explosive increase in human population and demand for water has resulted in significant concentrations in groundwater, surface water, and treated wastewater effluents [5–10]. Although there are few statutory maximum levels for these contaminants in water sources or even wastewater, there is a sense of urgency to develop novel treatment strategies due to the chemical complexity of the contaminant matrix (including metabolites) and to avoid or minimize unwanted or transformation products. Much work will

be certainly required since the options employed today at water treatment plants are not suitable for complete and efficient removal of many PPCPs [11–13].

Adsorption-based technologies used for water treatment in general have evolved considerably during the last few decades, with most of emphasis placed around the use of activated carbon adsorbents. A similar trend has been observed in a number of research reports focused on adsorption strategies for the removal of PPCPs [12,14–19]. Although activated carbons are not expensive and are readily available, they are not a suitable platform for selectivity enhancement via surface functionalization or appropriate porosimetry tailoring. There have been some efforts in order to tackle this quandary, including studies involving mesoporous silica [20–22], clays [23–26], metal organic frameworks [27,28], and zeolites [18,26,29–35]. Among these materials, zeolites could be considered ideal adsorbents for separation of complicated matrices because of their combined regenerability (thermal), surface and porosimetry characteristics. The only major drawback with these materials is their inherent high level of hydrophilicity.

Zeolites are aluminosilicate frameworks that possess well-defined microporosity (pore size between 0.5 and 2.0 nm). This serves to achieve separations based on size-exclusion principles,

* Corresponding author. Tel.: +787 832 4040x3748; fax: +787 834 3655.

E-mail addresses: arturoj.hernandez@upr.edu, arturojh@me.com (A.J. Hernández-Maldonado).

which is ideal to deal with mixtures where the larger adsorbates block the access of smaller adsorbates to surface sites. The zeolite framework chemistry also permits effective functionalization via simple ion exchange processes in which extra-framework metal cations that counterbalance the zeolite anionic surface can be replaced with other charged species that produce enhanced interactions the adsorbates that are able to access the porous structure [36]. This permits fine-tuning of selectivity toward particular compounds, which could be suitable for the removal of targeted PPCPs. Furthermore, if the charged species being exchanged are surfactants such approach will deal effectively with the hydrophilicity of these aluminosilicates [34,37–40]. Access of cationic surfactants to the micropores is usually limited to due to their large size, but they are able to occupy the zeolite crystals external surface. This in turn stops the access of bulk hydrophilic species to the micropores.

The main objective of the present work is the development of a transition metal, surfactant containing Y-type (Faujasite; FAU) zeolite for single- and multi-component PPCPs adsorption from water. A FAU type zeolite (see Fig. S1) containing a silicon-to-aluminum ratio (Si/Al) of 2.8 was chosen for the study due to its relative large cation exchange capacity (CEC \sim 50 charges per unit cell). In addition, this zeolite contains relative large micropores (\sim 8 Å) suitable for transport of certain PPCPs even when decorated with surfactant cationic moieties. The transition metals incorporated onto the zeolite where Co^{2+} , Ni^{2+} or Cu^{2+} in an attempt to induce complexation-like PPCP-adsorbent interactions at ambient conditions [20,22,24,25]. Studies related to the transformation of pharmaceuticals into new drugs suggest that transition metals (e.g., Cu^{2+} , Ni^{2+} , Co^{2+} , Fe^{2+} , and Zn^{2+}) could form complexes with those drugs [41–43] and, when combined with a solid surface (this work), this phenomenon may pave the way for the development of a new class of adsorbents for water treatment. For the tests involving the adsorption of single- and multi-component PPCPs, we have chosen salicylic acid and carbamazepine (see Table S1, supplementary data) since they are among the most frequently detected PPCP residues in aquatic environments. The consumption of salicylic acid based on use of aspirin is more than 12,000 tons in United States and more than 30,000 tons in China each year [44,45]. Carbamazepine, on other hand, is consumed at a rate of 1000 tons per year [46].

Experimental

Materials

The Y-type zeolite (FAU: Na^+ -Y; Si/Al = 2.8) sample used in the present study was purchased from Sigma-Aldrich and the chemical composition of the unit cell is shown in Table S2. The chemicals used for modification of the zeolite were: cetylpyridinium bromide hydrate (98.0% purity), cobalt(II) nitrate (98%), nickel(II) sulfate hexahydrate (99%), and copper(II) nitrate (99.99%). Chemicals used for the adsorption experiments were salicylic acid (99%), and carbamazepine. All of these were also obtained from Sigma-Aldrich and used without further modification. The water used for all the experiments described or discussed below was both distilled and deionized.

Na^+ -Y modification

Zeolites containing transition metals (M^{2+} -Y; M: Co, Ni or Cu) were prepared by exchanging Na^+ -Y (5 g; total CEC \sim 15 meq) with a metal nitrate or sulfate salt aqueous solution (0.15 mol L^{-1} ; 300 ml) at 70 °C for at least 24 h. The amount of salt used in the exchanges provided a 6-fold excess amount of cations over the

zeolite CEC. Ion exchanged samples were washed with copious amounts of water to remove excess salt residue and dried in a forced convection oven at 80 °C overnight. These materials will be referred to henceforward as Co^{2+} -Y, Ni^{2+} -Y, and Cu^{2+} -Y, respectively. Surfactant-modified zeolites were prepared using a cationic surfactant (cetylpyridinium bromide; CPY^+Br^-). Aqueous samples containing 5 g of Na^+ - or M^{2+} -Y and 100 ml of surfactant were stirred for 4 h at room temperature and the solids recovered via centrifugation. The solids were then washed multiple times with copious amounts of water to remove the extra surfactant material. The resulting new product was dried in a forced convection oven at 80 °C overnight. These materials will be referred to as (Na^+ , CPY^+)-Y, (Co^{2+} , CPY^+)-Y, (Ni^{2+} , CPY^+)-Y, and (Cu^{2+} , CPY^+)-Y.

Adsorbent characterization methods

Thermal gravimetric analysis (TGA) tests were performed using a high-resolution TA-Q500 TGA unit operating under a constant gas flow of air of 60 ml min^{-1} (carrier gas), while heating from room temperature to 900 °C at a rate of 10 °C min^{-1} . TGA measurements provided information about water and surfactant content. The rest of unit cell chemical composition was estimated using inductively coupled plasma mass spectroscopy (ICP-MS) analysis. Galbraith Laboratories, Inc. in Knoxville, TN, USA performed these tests.

The surface area, pore volume and pore size of the as-received and modified zeolites were estimated using nitrogen adsorption isotherms gathered at -196 °C (77 K) in a Micromeritics ASAP 2020 static volumetric adsorption unit fitted with turbomolecular drag pumps. Samples were first degassed in vacuum at high temperature (350 °C for Na^+ -Y or M^{2+} -Y; 150 °C for the surfactant containing zeolites) for at least 4 h. Specific total pore volumes were evaluated from nitrogen uptake at $P/P_0 = 0.99$. The corrected Horvath Kawazoe method was employed to estimate the pore volumes and size [47].

The surface charge behavior of the as-received and modified materials was analyzed using zeta potential data gathered with a Brookhaven Instruments ZetaPlus unit. The zeolites were suspended in water (0.2%, w/v) at pH values ranging from 2 to 12. A constant ionic strength based on KCl concentration of 0.001 M was maintained during the tests.

PPCPs equilibrium adsorption

Because of the reliability and simplicity of the method, single-point salicylic acid or carbamazepine adsorption experiments were carried out to evaluate the adsorption capacity of the zeolites at different equilibrium pH conditions. The pH was varied in the 2–12 range for an initial PPCP concentration (C_0) of ca. 14 mg L^{-1} . The initial pH of the working solutions was adjusted by adding either diluted HCl or NaOH (0.1 M). Changes in pH during adsorption were minimal, with deviations of ± 0.3 in the mid (pH \sim 6) and ± 0.1 in the upper (pH \sim 12) ranges. Adsorbed amounts were estimated based on the aqueous phase PPCP concentration difference after 48 h and normalized using the adsorbent mass (ca. 50 mg). The PPCP concentration remaining in the aqueous phase was measured using high performance liquid chromatography (HPLC) at the corresponding characteristic wavelength (298 and 286 nm for salicylic acid and carbamazepine, respectively). The HPLC module system was fitted with a diode array detector (DAD), a deuterium lamp and a temperature control unit. Separation of the adsorbate from the aqueous media was performed using a Zorbax Eclipse XDB Column C8. An acetonitrile/(water 1% folic acid) isocratic mixture was used at a flow rate of 1.0 ml min^{-1} and at a composition of 30:70. A detection limit of 0.1 mg L^{-1} was found for all the PPCPs tested. All experiments were conducted in triplicates.

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