# Adsorption of pharmaceutical compounds in aqueous solution on natural clays and carbon nanomaterials

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# **Objective and Novelty**

increasing presence of pharmaceutical The contaminants in water requires innovative adsorption technologies beyond conventional fixed-bed systems, which often suffer from channeling, pressure drop, and inefficient mass transfer. This thesis presents, for the first time, the design and fabrication of 3D-printed carbon monoliths with precisely engineered porosity and complex channel geometries for liquid-phase adsorption. By integrating sol-gel polymerization with 3D printing, this approach overcomes the structural limitations of traditional monoliths, which often exhibit uncontrolled porosity and limited straightchannel configurations. The optimized textures and tailored channel architectures of these integral carbon monoliths improve fluid distribution, maximize contact between the fluid and adsorption sites, and improve mass transfer properties, resulting in higher adsorption capacities, lower pressure drops, and scalability in water treatment applications.

In addition, this study explores natural and hybrid claybased materials as adsorbents. Their tunable surface chemistry, high surface area, and swelling properties make them promising candidates for pharmaceutical adsorption. While their direct integration into 3D-printed monoliths has not been implemented, they represent a strategic functionalization approach for future hybrid adsorption systems, enabling improved surface chemistry and selective contaminant interactions.

The main objectives of this thesis are i) to synthesize and characterize novel 3D-printed carbon monoliths with tailored porosity and complex channel geometries, ii) to evaluate their adsorption performance for pharmaceutical contaminants, iii) to analyze the effects of synthesis conditions, activation methods, and channel design on adsorption, and iv) to optimize performance through CFD modeling of fluid dynamics. In addition, v) synthesize and characterize natural and hybrid clay-based materials for pharmaceutical adsorption, and vi) assess the influence of their structural properties on the adsorption capacity and the mass transfer mechanisms governing the overall adsorption rate.

# Results

Novel 3D-printed carbon monolith adsorbents with precisely tailored channel geometries and porous textures have been successfully fabricated for the removal of sulfamethoxazole (SMX), a hazardous antibiotic commonly found in water. The synthesis combined sol-gel polymerization of resorcinol (R) and formaldehyde (F), catalyzed by Cs<sub>2</sub>CO<sub>3</sub> (Cs), with 3D printing of templates representing the desired channel geometries. Fig. 1a shows the meticulously designed 3D-printed template, which flawlessly replicates the original CAD model. After polymerization and curing processes, the organic monolith (Fig. 1b) exhibits seamless integration of the template within the organic gel-matrix, with no detectable interfacial gaps or detachment. This strong adhesion is indicative of the excellent compatibility between the template and the organic gel, ensuring precise structural control and optimal mechanical integrity in the final monoliths. Following carbonization, the template is then removed, and the final 3D-printed carbon monolith (Fig. 1c) shows a well-preserved, structurally intact channel morphology. In order to assess the influence of channel architecture on adsorption, three additional channel geometries: hexagonal (Fig. 1d), rhomboidal (Fig. 1e), and straight (Fig. 1f), were also designed and fabricated.

The R/Cs ratio was systematically varied at 100, 500, 1000, and 2000, significantly influencing the morphological, textural, chemical, and mechanical properties of the monoliths. These characteristics directly influence SMX adsorption [1]. It was observed that higher R/Cs ratios resulted in the presence of larger spherical primary particles, which in turn led to a modulating mean pore diameter in the macropore region (95.1-157.1 nm). This increased macroporosity, reduced flow resistance, and enhanced adsorption performance. The composition R/Cs = 1000 exhibited the best results, with longer breakthrough times and shorter mass transfer zone heights. The study found that adsorption was primarily driven by  $\pi$ - $\pi$  stacking and electrostatic attractions.

The monoliths were further activated using steam and CO<sub>2</sub>, significantly enhancing their porosity and adsorption capacity. Both methods effectively removed residual carbon deposits from the channel surfaces, remnants of the 3D template, preventing macropore blockage and increasing SBET values beyond 1000 m<sup>2</sup>/g.  $CO_2$  activation gradually enlarged micropores, increasing microporous surface area, while steam activation generated larger pores, shifting pore size distribution toward narrow mesopores. These structural modifications improved adsorption. Adsorption isotherms revealed a drastic increase in adsorption capacity with longer activation times. The highest adsorption capacities were 379.1 mg/g for the 8-hour CO<sub>2</sub>-activated monolith and 488.6 mg/g for the 2-hour steam-activated monolith, surpassing

most reported values. Breakthrough curves showed that extended activation prolonged breakthrough times due to a more open and accessible porous texture facilitating SMX adsorption.

Channel geometry significantly influenced breakthrough curves. The complex network of interconnected channels exhibited the longest breakthrough times across different flow rates (Fig. 1g). In contrast, hexagonal (Fig. 1h), rhomboidal (Fig. 1i), and straight (Fig. 1j) channels led to earlier breakthrough without reaching saturation, indicating partial adsorption. In these geometries, some SMX molecules exited unadsorbed, while mass transfer effects contributed to partial adsorption over time. The network of interconnected channels promoted intricate flow patterns and turbulence, enhancing fluid mixing and distribution (Fig. 1k). In contrast, the other geometries exhibited laminar flow, causing preferential pathways, channeling effects, and limited fluid-adsorbent interaction (Figs. 1I to 1n).



Figure 1. Schematic of 3D-printed carbon monolith synthesis (a-f), breakthrough curves for SMX adsorption on different channel geometries (g-j), and velocity profiles (k-n).

The adsorption capacity of raw clays for tetracycline (TC), trimethoprim (TMP), chlorphenamine (CPA), and SMX were strongly influenced by their structural arrangement, swelling capability, interlayer cations, and the molecular size of pharmaceuticals. Among the studied clays, bentonite showed the highest adsorption capacity for TC, TMP, and CPA, but lower for SMX [2]. Adsorption occurred on both the external surface and within interlayer spaces, primarily driven by cation exchange and electrostatic attractions. Diffusional model analysis indicated that TMP and TC adsorption was governed by both surface and pore volume diffusion, while CPA adsorption was controlled solely by pore volume diffusion [3].

To enhance SMX adsorption, hexadecyltrimethylammonium bromide-modified organobentonite was synthesized. The surfactant intercalated within the interlayer space, forming a double molecular layer. Adsorption isotherms demonstrated significantly higher SMX adsorption capacities than raw bentonite, as pharmaceutical ionic charge and adsorbent surface charge influenced adsorption. Electrostatic attractions and hydrophobic partitioning were the dominant mechanisms, with fast adsorption rates controlled by external mass transport [4]. These properties make organobentonite a promising functionalization agent for 3D-printed carbon monoliths.

### Conclusions

This thesis presented a novel framework for the development of structured adsorbents, transforming fixed bed adsorbers into high performance, scalable 3D-printed carbon monolithic beds. By integrating computational design, 3D printing, and sol-gel polymerization, porosity and channel geometry were precisely tailored to optimize fluid dynamics and maximize adsorption of pharmaceutical contaminants. The results showed adsorption capacities surpassing those in the literature, demonstrating the superiority of 3D-printed monoliths over traditional adsorbents. activation Tailored channel architecture and methods enhanced adsorption, reduced pressure drops, mitigated flow channeling, and extended breakthrough times, offering a scalable and customizable alternative to conventional systems. Additionally, this work highlights hybrid clay-based

materials as promising adsorbents. Organobentonite synthesis and characterization revealed improved hydrophobic interactions and adsorption capacity for SMX.

#### **Related publications**

<sup>[1]</sup> Ortiz-Ramos U, Bailón-García E, Pérez-Cadenas AF, Leyva-Ramos R, Carrasco-Marín F. Synthesis of porous carbon xerogel adsorbents with tailored hierarchical porosity and morphology for the selective removal of sulfamethoxazole from water. Environ Sci Pollut Res 2024; 31:67105-67120.

<sup>[2]</sup> Ortiz-Ramos U, Leyva-Ramos R, Mendoza-Mendoza E, Aragón-Piña A. Removal of tetracycline from aqueous solutions by adsorption on raw Ca-bentonite. Effect of operating conditions and adsorption mechanism. Chem Eng J 2022; 432:134428.

<sup>[3]</sup> Ortiz-Ramos U, Leyva-Ramos R, Mendoza-Mendoza E, Carrasco-Marín F, Bailón-García E, Villela-Martínez DE, Valdez-García GD. Modeling adsorption rate of trimethoprim, tetracycline and chlorphenamine from aqueous solutions onto natural bentonite clay. Elucidating mass transfer mechanisms. Chem Eng J 2024; 493:152666.

<sup>[4]</sup> Leyva-Ramos R, Villela-Martínez DE, Ortiz-Ramos U, Valdez-García GD, Ortiz-Anaya I, Carrales-Alvarado DH. Fundamentos de cinética de adsorción en sistemas líquidosólido. Desarrollo y aplicación de modelos difusionales. In: Fundamentos de adsorción aplicados a la eliminación de compuestos tóxicos presentes en solución acuosa. Chapter 7. Ediciones Uniandes, 2024.

Full Thesis can be downloaded from: https://hdl.handle.net/10481/97437