

Simulating Transport and Adsorption of Organic Contaminants in 3D Porous Activated Carbon Block Media

Jun Kim^{1,2,3,*}, Amanda Morgott³, Ziqi Wu³, Liane Hopaluk³, Michael Miles³, William Stoner³, Qilin Li^{1,2}

1. Department of Civil and Environmental Engineering, Rice University, Houston, TX 77025, USA

2. Nanosystems Engineering Research Center for Nanotechnology-Enabled Water Treatment, Houston, TX 77025, USA

3. Access Business Group, LLC, Ada, MI 49355, USA

*Corresponding author: jun.newt@rice.edu

Abstract

To evaluate the organic contaminants removal performance of hollow cylindrical block-shaped porous activated carbon media, COMSOL Multiphysics[®] simulation software with Chemical Engineering module was used. The study clearly demonstrates how each organic compound in a steady-state fluid is dynamically transported in the three-dimensional porous media and removed by adsorption. The simulated adsorption results are compared to the experimental test data for validation. Axisymmetric geometry in COMSOL gives better simulation accuracy and faster computation than full three-dimensional geometry due to higher element quality and lower volume/area ratio. Based on 5% breakthrough (95% removal) line, the COMSOL simulations have only 0.9-2.9% discrepancy from the actual data, while a classical two-dimensional rapid-small-scale column test (RSSCT) model method has 39.8-782.2%. The COMSOL Multiphysics[®] model used in this transport/adsorption study successfully demonstrated not only flow patterns in the modulated reactor but also chemical concentration changes in the full-scale porous adsorbent structure.

Keywords: Porous media, flow analysis, chemical adsorption, filtration, activated carbon

Introduction

Granular and powdered activated carbons have been widely used for purification/filtration in air and water as catalysts or organic adsorbents (Aljeboree, Alshirifi, & Alkaim, 2017; Chen, Dussert, & Suffet, 1997; Chiang, Chiang, & Huang, 2001; Cotoruelo et al., 2010; Crittenden, Hand, Arora, & Benjamin Jr, 1987; HUMPola, Odetti, Fertitta, & Vicente, 2013; Inal et al., 2009; Ruddy & Carroll, 1993); Shih, Wangpaichitr, and Suffet (2003); (Shim, Lee, & Moon, 2003; Summers & Laura, 1992; Tsai, Chiang, Huang, & Chiang, 2008; Yu, Zhang, Deng, Huang, & Yu, 2009). To obtain mechanical filtration capacity and inorganic reduction performance, activated carbon can be formed into a block-shaped porous media as in Figure 1, demonstrating excellent removal of waterborne contaminants, such as particulate, heavy metals, and organic compounds. Some examples of these types of contaminants would be asbestos, lead, mercury, volatile/semi-volatile organic compounds (VOCs), and emerging organic contaminants like Disinfection by-Products (DBPs), Pharmaceuticals, Endocrine Disrupting Compounds (EDCs), Per/Polyfluoroalkyl Substances (PFAs), etc. (Kuennen, Taylor, Van Dyke, & Groenevelt, 1992; Kuennen, Van Dyke, Crittenden, & Hand, 1989);

Performance Data Sheet, eSpring Water Purifier 2019).

To evaluate the performance of adsorbent media, rapid small-scale column test (RSSCT) models such as homogeneous surface diffusion model (HSDM) and pore surface diffusion model (PSDM) have been widely used to estimate breakthrough curves of different organic species in a closed system (Crittenden et al., 1991; Hand, Crittenden, Arora, Miller, & Benjamin Jr, 1989). Both RSSCT models are based on the two-dimensional ideal plug-flow systems, thus more suitable for column-shaped packed bed reactors. However, it does not accurately represent the system performance of materials in other complex reactor designs, especially in hollow cylindrical block-shape. The incoming mass flux to the porous media is determined by the flow both outside and inside porous media. The contaminant mass flux greatly depends on system design and often has large spatial variations when the fluid flux is not evenly distributed inside the reactor. In this case, a specific portion of the media saturates faster than the rest, leading to effluent concentration increase at that point which impacts the overall performance. Thus, it is especially challenging to precisely simulate both transport and reaction phenomena of each contaminant at the same time.

Adsorption isotherms of the adsorbents should be simultaneously considered with kinetic parameters determined by the mass balances in the reactor (Crittenden et al., 1991; Shih et al., 2003).



Figure 1. An example of an activated carbon block for the removal of organic contaminants in water.

Therefore, this case study demonstrates how organic contaminants in a steady-state fluid are dynamically transported in the three-dimensional porous media (activated carbon block) and removed by chemical reaction (adsorption) using COMSOL Multiphysics® simulation software.

Model Definition

Two different types, a full three-dimensional (3D) component and an axisymmetric component which allows 3D analysis, were used as in Figure 2. Like most block type media applications, the outside-in flow was considered in both components. The actual flow patterns are determined by operating conditions (e.g. working pressure, temperature, test cycles, etc.) and external structural design of the reactor (e.g. inlet/outlet, pressure vessel, endcaps, wrapping materials, etc.) that holds the active media. Due to confidential reasons, the inner/outer parts of the original structure are not shown in the figure. In this study, the entire media is surrounded by simplified fluid geometry.

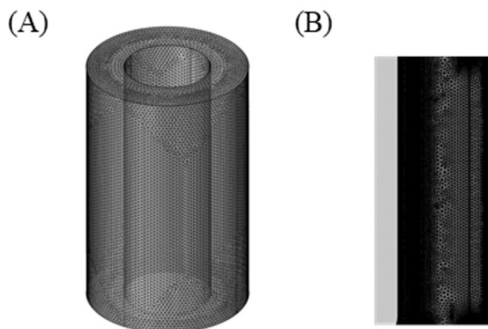


Figure 2. Model component; (A) full three-dimensional and (B) Axisymmetric mesh geometry.

Model Equations

This study focused more on macroscopic convection-diffusion reaction occurring simultaneously inside the three-dimensional porous media. First, the freely moving fluid movement outside the block media and permeable flow inside the porous block were solved at a steady-state condition in the *Free and porous media flow (fp)* physics interface. Second, the mass transport of the chemical species in the porous media is modeled with the *Transport of Diluted Species in Porous Media (tds)* interface with a time-dependent study step. Diluted species model was chosen since most contaminants tested for drinking water are in the concentration range from ng/L (or parts per trillion, ppt) to µg/L (parts per billion, ppb) (Keller; Stocking, Suffet, McGuire, & Kavanaugh, 2001). The overall process diagram is illustrated in Figure 3.

The RSSCT models use the Freundlich adsorption model (Freundlich & Heller, 1939) to express the adsorbed amount of organic compounds as

$$q_{e,A} = K_{f,A} c_{e,A}^{1/n}$$

where

- $q_{e,A}$ is the adsorbed amount at equilibrium (mg/g)
- $K_{f,A}$ is the Freundlich constant [mg/g (L/mg)ⁿ]
- $c_{e,A}$ is the aqueous concentration of chemical species, A (mg/L)

On the other hand, COMSOL models used in this study adopt Langmuir adsorption model (Hall, Eagleton, Acrivos, & Vermeulen, 1966; McKay, El Geundi, & Nassar, 1987) for the simulation of particle concentration of species A , $c_{p,A}$ in the media as

$$c_{p,A} = \frac{c_{p,max,A} K_{L,A} c_A}{1 + K_{L,A} c_A}$$

where

- $c_{p,max,A}$ is the Langmuir adsorption maximum (mol/kg)
- $K_{L,A}$ is the Langmuir constant (m³/mol)
- c_A is the aqueous concentration of chemical species, A (mol/m³)

Further, the transport of a chemical species, A in the porous media is described by a convection-diffusion equation:

$$\frac{\partial(\epsilon_p c_A + \rho c_{p,A})}{\partial t} + \nabla \cdot (-D_{e,A} \nabla c_A) + u \cdot \nabla c_A = 0$$

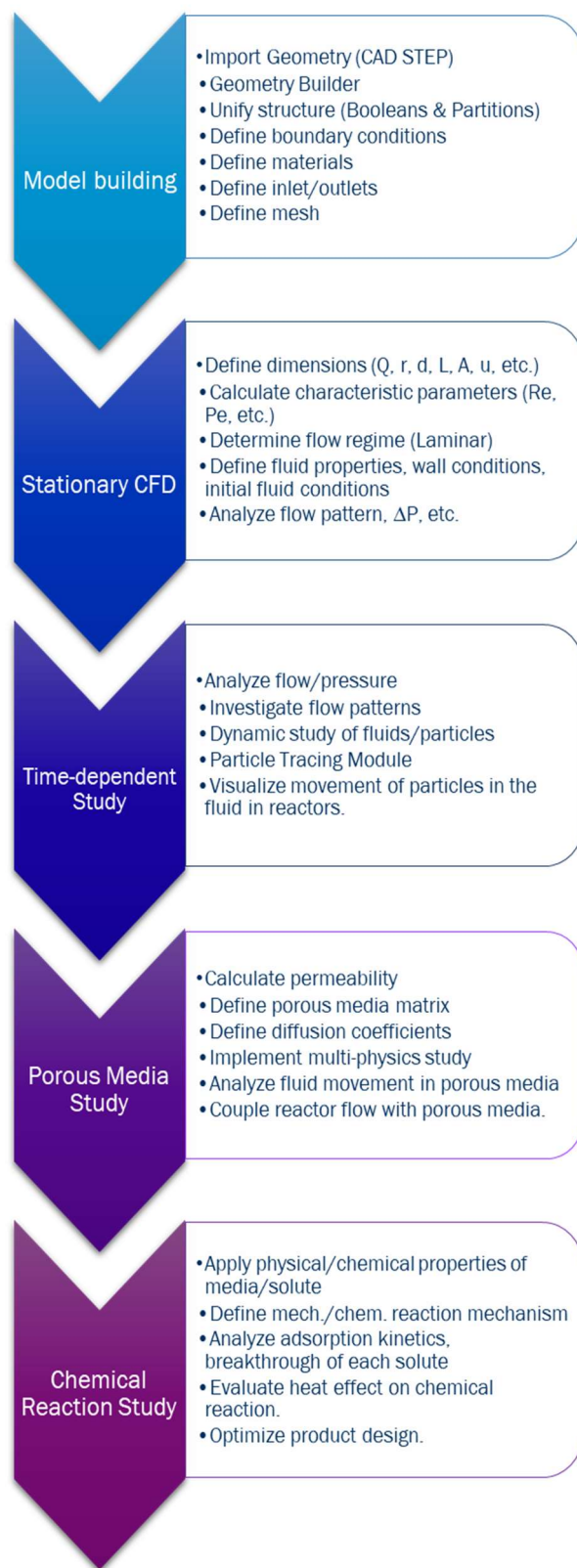


Figure 3. Process diagram.

where

- ϵ_p and ρ is the porosity and the density (kg/m^3) of the porous media, respectively
- c_A and $c_{p,A}$ is the aqueous and particle concentration of chemical species, A (mol/m^3)
- u is the fluid velocity determined by the reactor design (m/s)
- $D_{e,A}$ is the effective diffusivity of the chemical species, A (m^2/s)

The boundary condition at the inlet is fixed to product flow rate, $q_0=0.9$ gpm (3.41 L/min). The pressure boundary condition at the outlet was also fixed to dynamic pressure, $P=60$ psi (0.41 MPa), in accordance with the NSF International/American National Standards Institute (NSF/ANSI) Standard 53 - 2018: Drinking Water Treatment Units — Health Effects. The NSF/ANSI Standard 53 states specific influent water concentrations for each organic compound, e.g. 300 $\mu\text{g/L}$ Chloroform as VOCs surrogate testing, 1.5 $\mu\text{g/L}$ total combined Perfluoro-octane Sulfonate (PFOS) and Perfluoro-octanoic Acid (PFOA) concentration. For most organic contaminants, the NSF/ANSI 53 requires more than 95% reduction from the influent concentration. No-slip boundary condition was applied to all surfaces.

- Inlet flow rate: $q_0=0.9$ gpm (fully developed)
- Inflow concentration: $c_{A,0}, c_{B,0}$
- Outlet pressure: $P = P_0 - \Delta P = 60$ psi
- Wall conditions: no slip

Results and Discussion

The COMSOL's *fp* physics interface allows simulating both the free flow in the bulk fluid (outside of the block) and the passing-through flow inside the porous media at a steady state. As shown in Figure 4, there is a higher flow velocity in the top, especially the outlet, due to the outside-in directional flow and the location of inlet/outlet. The pressure is evenly distributed throughout the entire volume of the reactor. Due to the flow rate of 0.9 gpm, the Reynolds number is $\sim 2,100$, still in the laminar flow regime. However, due to the faster flow rate inside the porous media, the retention time for organics in water is less than 1 minute, this requires large capacity and fast adsorption kinetics for adsorbents to achieve $> 95\%$ removal performance.

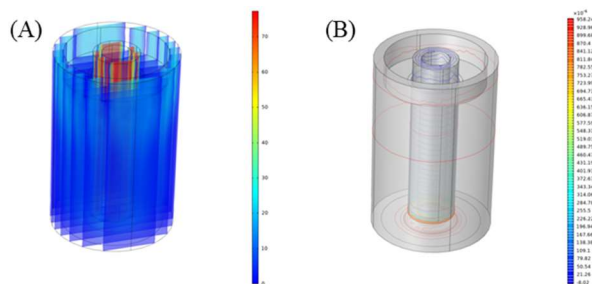


Figure 4. Steady-state computational fluid dynamics analysis; (A) flow velocity ($fp.U$), (B) pressure (p).

Time-dependent fluid dynamics analysis of fp provide an in-depth understanding of flow movement in and out of the porous media, especially when it is combined with *Particle Tracing for Fluid Flow (fpt)* physics interface. As illustrated in Figure 5, the initial flow velocity slows down after released from the inlet to the bottom. The flow gets faster in the inner part of the block and shows maximum velocity at the inner outlet.

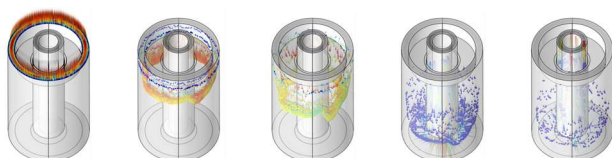


Figure 5. Time-dependent fluid dynamics analysis using *Particle Tracing for Fluid Flow (fpt)* interface.

Figure 6 shows the macroscopic concentration change of chemical species, A , in the block media over time (time can be converted to volume treated using flow rate). The outside-in directional flow causes the media on the exterior of the block to saturate first. The saturation then gradually travels inward until the entire block is saturated. Thus, the effluent concentration from the inner core remained close to 0 until the breakthrough capacity and then rapidly increased by transported chemical species. The amount of volume treated at a fixed flow rate is differed by the isotherm parameters ($c_{p,max,A}$, $K_{L,A}$) of each contaminant.

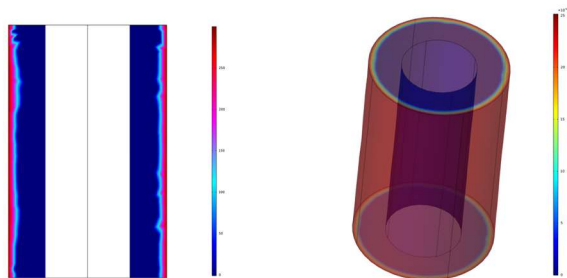


Figure 6. Transport study (tds) of chemical species A , after 100 gallons volume treatment.

Figure 7 shows averaged effluent concentration of a VOC surrogate species A from three different simulations, a two-dimensional packed-bed RSSCT model (RSSCT-HSDM), a full three-dimensional COMSOL model (COMSOL full 3D), and an axisymmetric COMSOL model (COMSOL AS). All three simulations are compared to the experimental data from actual product testing. Both RSSCT and COMSOL AS represent a sharp break-through curve of chemical species A . However, the simulated curve from the COMSOL full 3D shows more gradual breakthrough, unlike the experimental data and other simulations.

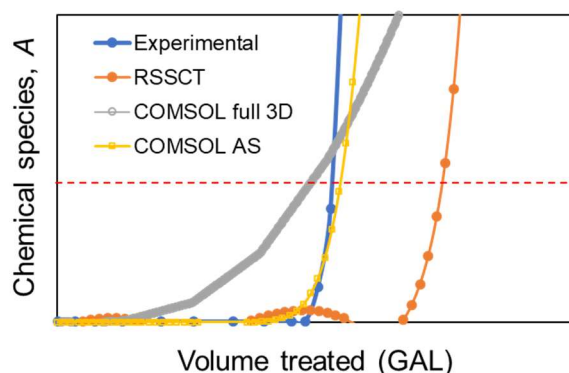


Figure 7. The averaged effluent concentration of species A from RSSCT and COMSOL simulations with respect to volume treated compared to the actual experimental result. The horizontal red dashed line: 5% breakthrough (95% reduction).

The gradual curve is possibly caused by the limited number of mesh in the full three-dimensional model. The predefined mesh size applied to the main body (except boundaries) was limited due to much longer computation time (> several days). Limited mesh size and excessive computation time can be overcome by applying the axisymmetric (AS) approach. As summarized in Table 1, the AS geometry has higher element quality (0.9335) and lower volume/area ratio (0.0362) compared to the full 3D, allowing faster computing time within a few minutes.

Table 1. Statistics of % element in COMSOL, full three-dimensional (Full 3D) vs. axisymmetric (AS) mesh.

	Full 3D	AS
Predefined mesh	Coarse	Finer
Number of Elements	14,852	16,854
Element quality	0.6741	0.9335
Volume/area ratio	0.1048	0.0362

As shown in Figure 7, the COMSOL AS estimates the most accurate breakthrough curve among three models which can be contributed to the smaller mesh size. The RSSCT also shows the rapid breakthrough pattern, but estimates the capacity to be relatively far from the experimental result. This inaccuracy could be due to RSSCT's plug-flow and column-shape based model. In the RSSCT curve, there is an unexpected small peak before the main breakthrough. Because most RSSCT models use the Freundlich isotherm model which has relatively large truncation error in its exponential function for small numbers (concentration less than 10^{-6} g/L). All COMSOL models discussed in this study use the Langmuir adsorption isotherm, which does not have the secondary peak problem.

As summarized in Table 2, estimated treated water volume capacity from the COMSOL AS is only +2.4% different from the experimental result at 5% breakthrough point (95% reduction, red line). However, the RSSCT model overestimated the capacity by +42%. This represents that it is important to take the flow movement in the media into model simulations, especially for block-shaped porous media.

Table 2. Simulation % difference at 5% breakthrough point compared to experimental data (+: overestimated, -: underestimated)

Model Name	Chemical A	Chemical B
RSSCT-HSDM	+42.0%	+782.2%
COMSOL full 3D	-3.5%	N/A
COMSOL AS	+2.4%	-0.9%
RSSCT-modified	N/A	-39.8%

Another breakthrough curve of a hydrophilic organic compound *B* is represented in Figure 8 (the COMSOL full three-dimensional model is not included in the later studies). The result supports the previous conclusion that the COMSOL AS has the highest resolution and accuracy. The difference from the COMSOL AS to the experimental result is only -0.9% in contrast to +782.2% from the RSSCT model. The much greater discrepancy found in the RSSCT mainly came from overestimated Freundlich isotherm parameters using the Polanyi Isotherm Estimation (PIE) method (Crittenden et al., 1987) in low (ppb-level) concentration influent. The Adjusted RSSCT model (RSSCT-modified) using experimental isotherm parameters gives better estimation with lower % difference, compared to the PIE-based RSSCT model. However, as summarized in Table 2,

the RSSCT-modified simulation underestimated the capacity by 39.8%.

Further, simulated comparison studies on 15 different major organic compounds study including 50 additional surrogate organics showed the same result regardless of chemical species. Computation Fluid Dynamics (CFD) analysis using COMSOL with the Langmuir isotherm can significantly improve existing Freundlich isotherm-based plug-flow RSSCT models. To accurately simulate the adsorption phenomena in different reactors, both adsorption isotherm and fluid movement should be considered and computed simultaneously.

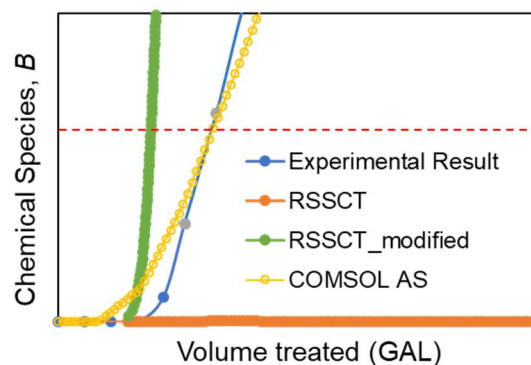


Figure 8. The averaged effluent concentration of species *B* with respect to volume treated from unmodified/modified RSSCT and COMSOL simulation, compared to the actual experimental result. The horizontal red line: 5% breakthrough (95% reduction).

Conclusions

The COMSOL Multiphysics® model used in this transport and adsorption study successfully demonstrated not only flow patterns in the modulated reactor but also chemical concentration changes in the full-scale hollow cylindrical porous adsorbent structure. The results are critically important to enhance contaminant reduction performance by optimizing design parameters in similar reactor applications. In addition, the transport/adsorption model can be used as a platform estimating the performance of other numerous chemical species and emerging contaminants with different physical and chemical properties. The use of model simulations can make product development cycles much faster and less expensive than full-scale media testing.

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