COMSOL CONFERENCE

2020 NORTH AMERICA

COMSOL CONFERENCE 2020 NORTH AMERICA

Amway RESEARCH & DEVELOPMENT

Equation-Based Adsorption Modeling for Aqueous Inorganic Species in Cylindrical Porous Media

Jun Kim*, Amanda Morgott, Ziqi Wu, Amy Puroll, Michael Miles, William Stoner, Qilin Li

Access Business Group, LLC
Department of Civil and Environmental Engineering, Rice University

In 2019…

COMSOL CONFERENCE 2019 BOSTON

Amway RESEARCH & DEVELOPMENT

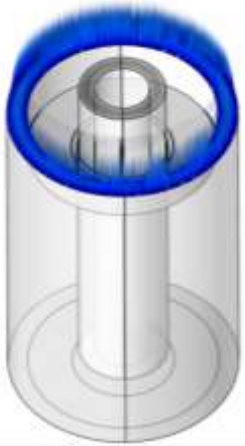
Simulating Transport and Adsorption of Organic Contaminants in 3D Porous Activated Carbon Block Media

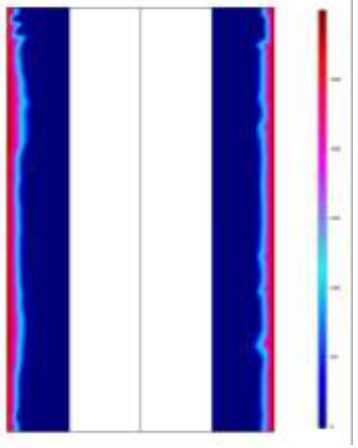
Jun Kim, Amanda Morgott, Ziqi Wu, Liane Hopaluk, Michael Miles, William Stoner, Qilin Li

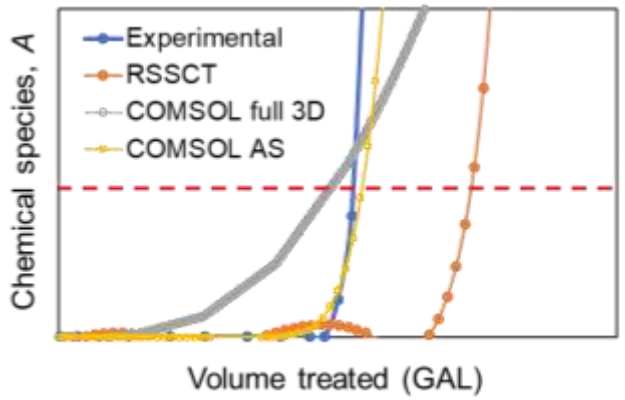
NSF ERC for Nano-technology Enabled Water Treatment (NEWT), Rice University
Access Business Group/Amway

RICE NEWT

We have completed simulations for ORGANIC SPECIES (covering 64 total compounds) in 2019.







Kim et al., 2019

COMSOL CONFERENCE 2019 BOSTON

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

Jun Kim[1,2,3,*], Amanda Morgott[1], Ziqi Wu[1], Liane Hopaluk[3], Michael Miles[3], William Stoner[3], 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. (Knennen, Taylor, Van Dyke, & Groenevelt, 1992; Knennen, 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.

1

https://doi.org/10.25611/fmxp-ff31

2019 COMSOL Conference Best Paper Award

Amway
RESEARCH & DEVELOPMENT

- Dr. Jun Kim from Durable PD – Water, presented new research findings at the 2019 COMSOL Conference.
- The proceedings entitled "*Simulating Transport and Adsorption of Organic Contaminants in 3D Porous Activated Carbon Block Media*" was awarded the ***Best Paper Award***.
- Authors:
  Dr. Jun Kim, Amanda Morgott, Ziqi Wu, Liane Hopaluk, Michael Miles, William Stoner, Qilin Li

Svante Littmarck (left), Founder/CEO of COMSOL and Dr. Jun Kim (right), Product Development Engineer in Durables PD. (Image credit: COMSOL)

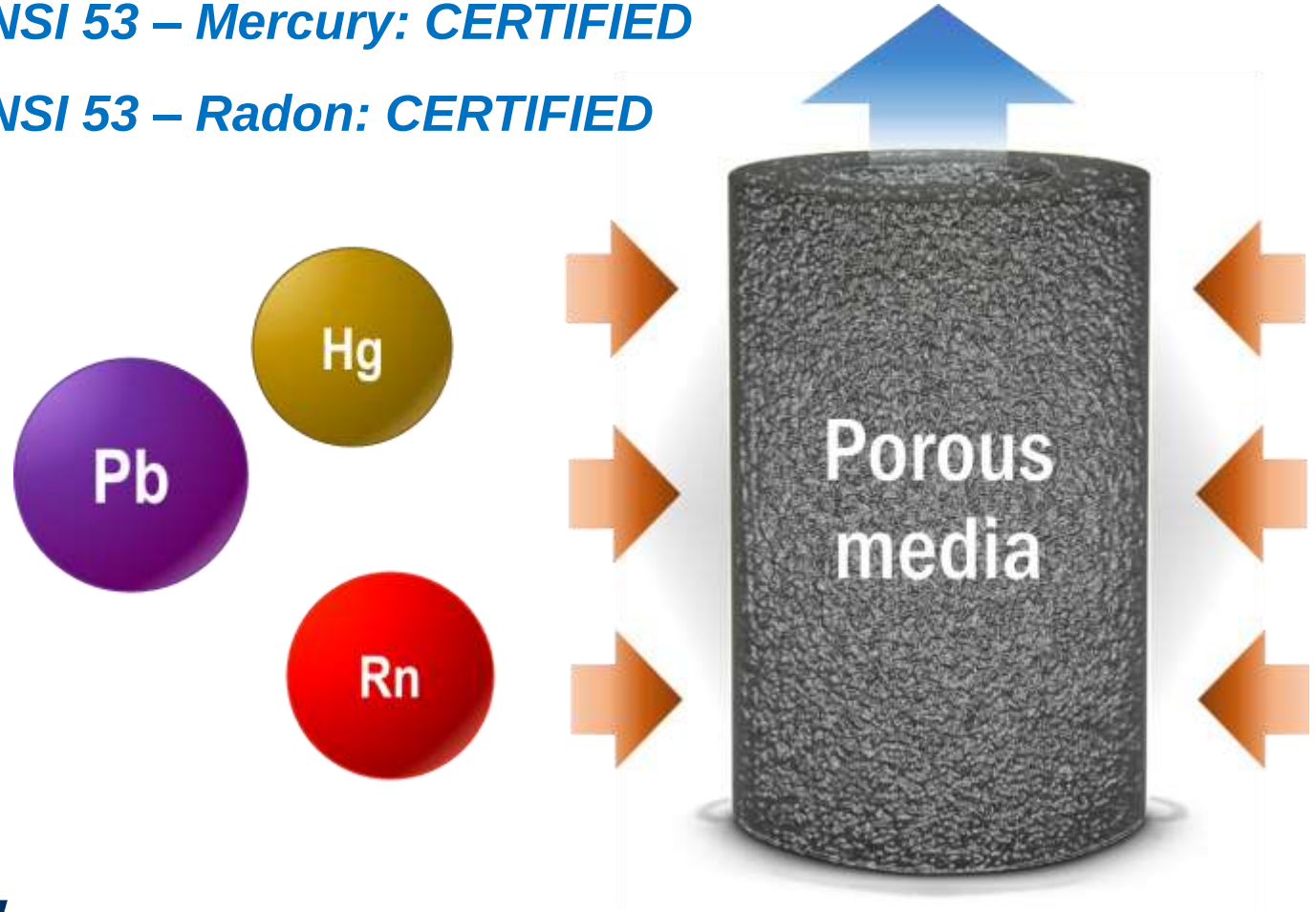
Inorganic Contaminants

COMSOL CONFERENCE 2020 NORTH AMERICA

NSF/ANSI 53 – Lead: CERTIFIED

NSF/ANSI 53 – Mercury: CERTIFIED

NSF/ANSI 53 – Radon: CERTIFIED



- Lead
  - US EPA primary drinking water pollutant
  - US EPA Action Level: 15 ppb
  - Damage to brain, kidneys, nervous system.

Source:
Water Quality Association (WQA) Fact Sheet

Figure 1. *Heterogeneous porous media and contaminants in water.*

Amway
RESEARCH & DEVELOPMENT

Process Diagram

COMSOL CONFERENCE 2020 NORTH AMERICA

Model building → Stationary CFD → Time-dependent Study → Porous Media Study → Chemical Reaction Study

Amway RESEARCH & DEVELOPMENT

Full 3D vs. Axisymmetric

COMSOL CONFERENCE 2020 NORTH AMERICA

Computation time
~1 day

Computation time
~2 min

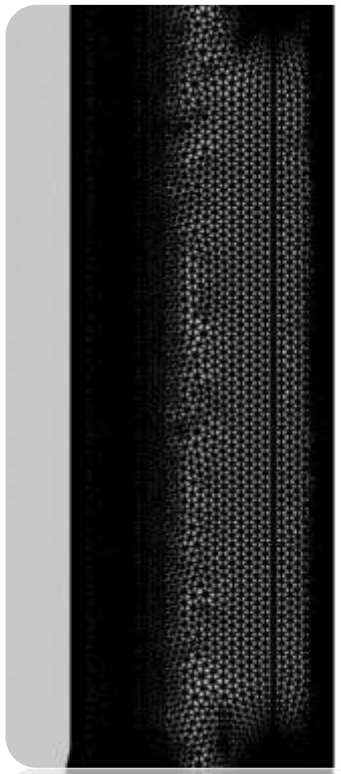


Table 1. Statistics of % element in COMSOL, full three-dimensional (Full 3D) vs. axisymmetric (AS) mesh.

	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

Kim et al., 2019

https://doi.org/10.25611/fmxp-ff31

Amway
RESEARCH & DEVELOPMENT

Model Equations

COMSOL CONFERENCE 2020 NORTH AMERICA

- Model Equations for Inorganic Contaminants
  - Based on Langmuir model
  - Transport and reaction on the surface (source term, *f*)

$$f = r_a - r_d = k_{ads,A} c_A \left(\Gamma_{p,A} - c_{p,A}\right) - k_{des,A} c_{p,A}$$

where
r_a, r_d is the rate of adsorption and desorption, respectively (mol/m^3-min)
$k_{ads,A}$ and $k_{des,A}$ is the rate constant for the adsorption (m^3/mol-min) and desorption (1/min), respectively
$\Gamma_{p,A}$ is the total volume concentration of active sites in particle pores (mol/m^3)

  - Assume chemical reaction (r_a >> r_d)
  - Rate of adsorption: numerically solving surface mass balance using **PDE**

Amway
RESEARCH & DEVELOPMENT

Model Equations

COMSOL CONFERENCE 2020 NORTH AMERICA

- Model Equations for Inorganic Contaminants
  - PDE based modeling (*General Form PDE Interface*)
  - Source term: adsorption rate, r_a (assume $r_a >> r_d$)

$$e_{a,A}\frac{\partial^2 c_{p,A}}{\partial t^2} + d_{a,A}\frac{\partial c_{p,A}}{\partial t} + \nabla \cdot \left(-D_{p,A}\nabla c_{p,A}\right) = k_{ads,A}c_A\left(\Gamma_{p,A} - c_{p,A}\right)$$

where
$e_{a,A}$ and $d_{a,A}$ is the mass coefficient and the damping coefficient, respectively
$D_{p,A}$ is the surface diffusivity of the chemical species, A (m^2/s)
$k_{ads,A}$ is the rate constant for the adsorption (m^3/mol-min)
$\Gamma_{p,A}$ is the total volume concentration of active sites in particle pores (mol/m^3)

  - Conservative laws (diffusive mass transfer)
    - Coordinate system (Cartesian vs. Curvilinear)
      - Cylindrical $\nabla\cdot(\kappa\nabla T) = \frac{\partial}{\partial x}(\kappa\frac{\partial T}{\partial x})+\frac{\partial}{\partial y}(\kappa\frac{\partial T}{\partial y})+\frac{\partial}{\partial z}(\kappa\frac{\partial T}{\partial z}) = \frac{1}{r}\frac{\partial}{\partial r}(r\kappa\frac{\partial T}{\partial r})+\frac{1}{r}\frac{\partial}{\partial \phi}(\frac{\kappa}{r}\frac{\partial T}{\partial \phi})+\frac{\partial}{\partial z}(\kappa\frac{\partial T}{\partial z}).$
      - Axisymmetric $\nabla \cdot \Gamma = \frac{1}{r}\frac{\partial(r\Gamma_r)}{\partial r} + \frac{\partial \Gamma_z}{\partial z} = \frac{\partial \Gamma_r}{\partial r} + \frac{\partial \Gamma_z}{\partial z} + \frac{\Gamma_r}{r}.$

Amway RESEARCH & DEVELOPMENT

Model Equations

COMSOL CONFERENCE 2020 NORTH AMERICA

- Model Equations for Inorganic Contaminants
  - PDE based modeling (*General Form PDE Interface*)
  - Using an alternative source term for compensating the conservative flux term

$$\frac{\partial \Gamma_r}{\partial r} + \frac{\partial \Gamma_z}{\partial z} + \frac{\Gamma_r}{r} = f. \quad \rightarrow \quad \frac{\partial \Gamma_r}{\partial r} + \frac{\partial \Gamma_z}{\partial z} = -\frac{\Gamma_r}{r} + f.$$

  - For conservative flux, $\nabla \cdot \left(-D_{p,A} \nabla c_{p,A}\right)$

$$-D_{p,A} \frac{\partial c_{p,A}}{\partial \mathrm{r}}, -D_{p,A} \frac{\partial c_{p,A}}{\partial \mathrm{z}}$$

  - For source term, *f*

$$k_{ads,A} c_A \left(\Gamma_{p,A} - c_{p,A}\right) + D_{p,A} \frac{c_{p,A}}{\mathrm{r}}$$

https://www.comsol.com/blogs/guidelines-for-equation-based-modeling-in-axisymmetric-components/

Amway RESEARCH & DEVELOPMENT

Physics/Interface-selected

COMSOL CONFERENCE 2020 NORTH AMERICA

Fluid movement in the entire reactor:

Free and porous media flow (fp)

Mass transport of the chemical species in the porous media:

Transport of Diluted Species in Porous Media (tds)

interface with a time-dependent study step.

*contaminants level: ng/L (ppt) - μg/L (ppb)

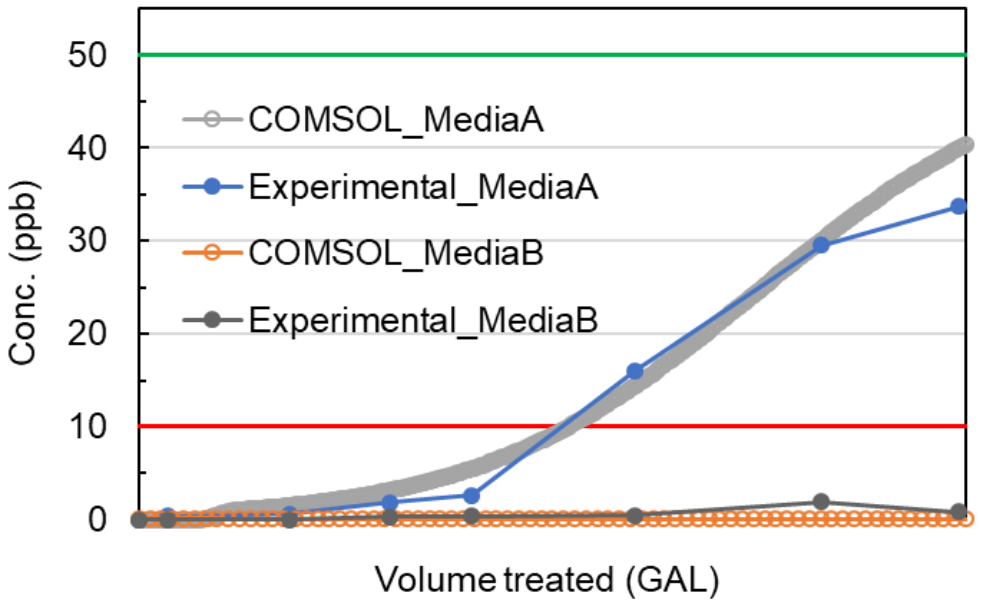
Chemical Engineering module: partial differential equation (PDE)

General Form PDE interface

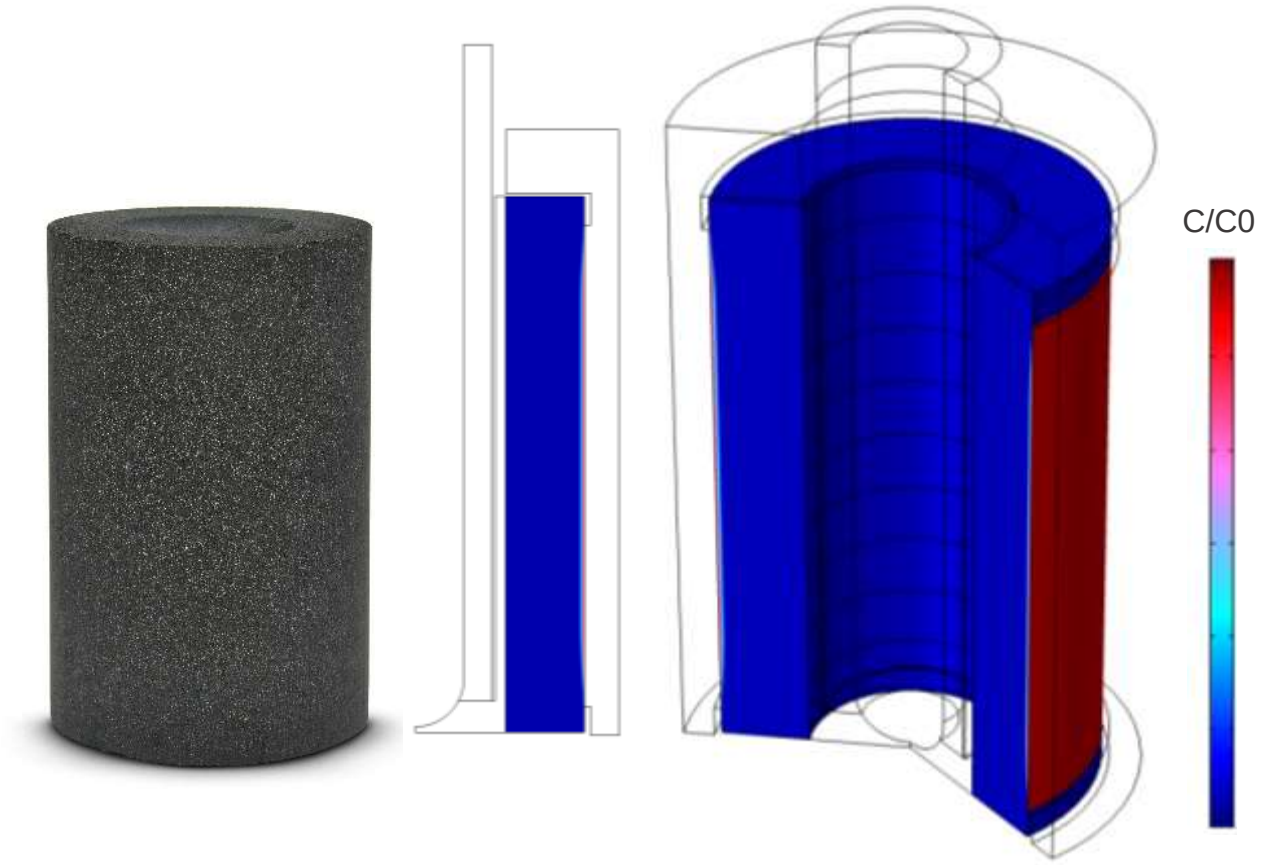
Amway RESEARCH & DEVELOPMENT

Chemical Adsorption Study

COMSOL CONFERENCE 2020 NORTH AMERICA



Media	+/- %
Media A	N/A
Media B	0.7%

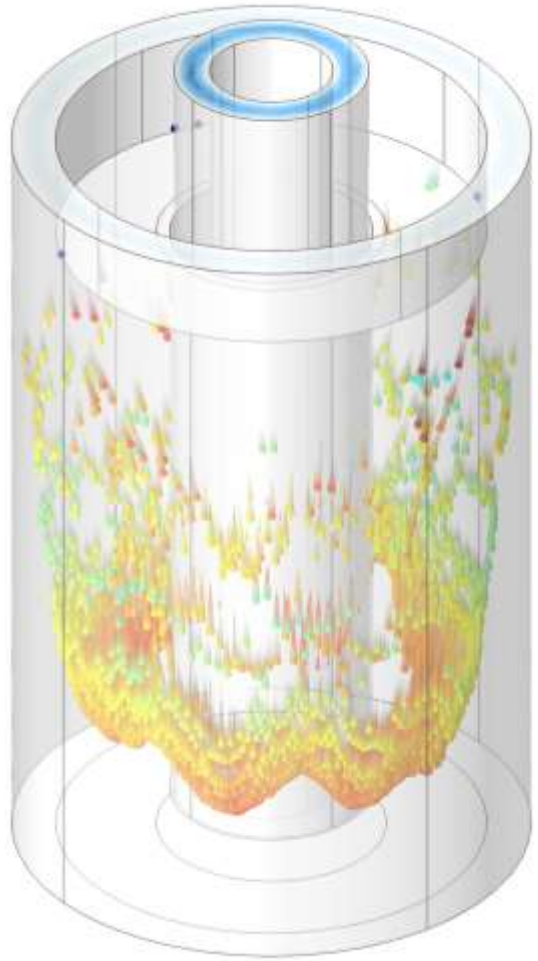


- Simulated result < 1% difference
- Same media weight, different kinetics (k_{ads})

Amway RESEARCH & DEVELOPMENT

Conclusions

1. A mass-transport equation describing the concentration of contaminant in the fluid (c_f) and on the adsorptive material surface (c_p) was solved numerically using the built-in **PDE interface**.
2. The simulated results successfully explain how material's embedded kinetic characteristic, in terms of **adsorption rate**, plays an important role in the filtration performance of adsorptive media.
3. The Chemical Engineering module in COMSOL can minimize lab-works and protect researchers from dangerous experiments, especially during pandemic situations.



Acknowledgement

COMSOL CONFERENCE 2020 NORTH AMERICA

RICE | ENGINEERING
Department of Civil and Environmental Engineering

Special thanks to Mr. William Luke, Director at Amway

Durables & Devices PD – Innovation & Science

Simulation Center of Excellence (CoE)

Amway
RESEARCH & DEVELOPMENT

eSpring™

Thank you!