Modeling transport and retention of graphene oxide in porous media

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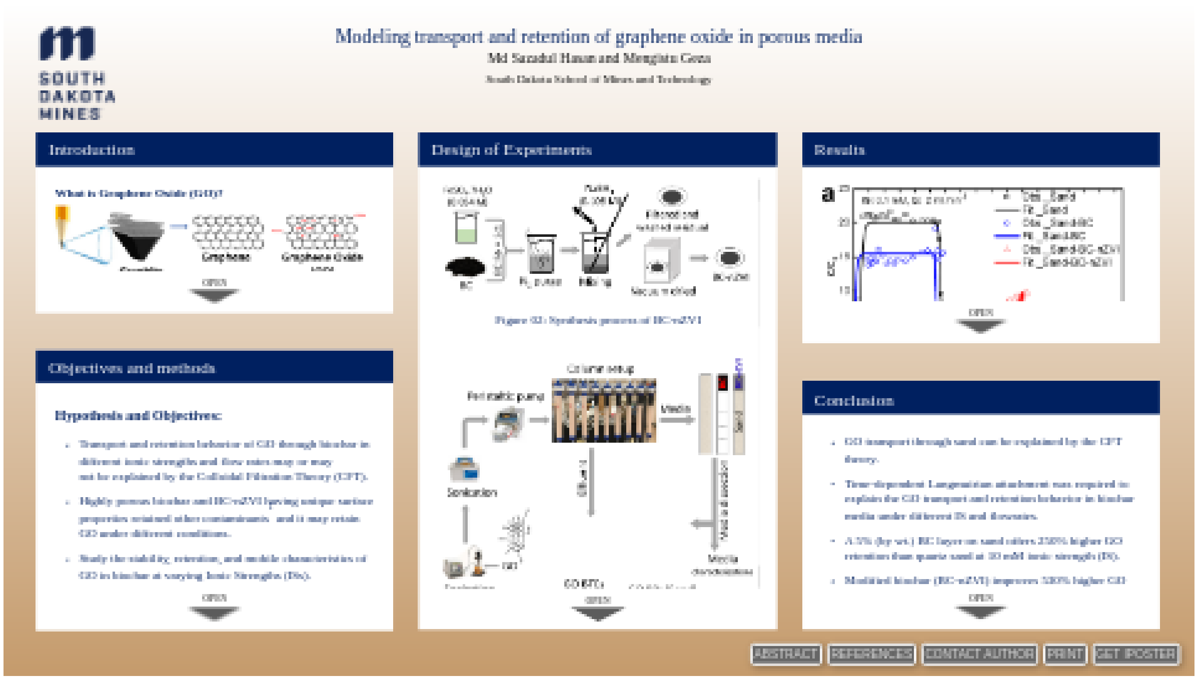
Abstract

Transport and retention behavior of Graphene Oxide (GO) is influenced by the physical and chemical properties of porous media under subsurface environmental conditions. Fixed-bed column studies using quartz sand and biochar (BC) in different configurations were conducted as a function of ionic strength and flowrate. Colloid filtration theory (CFT) was employed to develop mathematical models based on the one-dimensional convection-dispersion equation using experimental GO breakthrough curves (BTCs) and retention profiles (RPs) obtained from the experimental data. GO transport and retention behavior was modeled using BC and BC-nZVI (BC surface modified with nanoscale zero-valent iron) as filter media to understand the effect of media properties. It was demonstrated that the model can describe measured BTCs and RPs of GO in the sand, BC, and BC-nZVI. The inverse modeling approach was implemented to determine the attachment coefficient (Ka) and maximum solid-phase retention capacity (Smax) using GO BTCs for different experimental conditions. Higher Ka in BC at 10 mM IS indicated the influence of straining which agrees with the depth-dependent retention kinetics. Furthermore, pronounced GO aggregation at higher IS supports the higher Ka values at 10 mM compared to 0.1 mM. In contrast, higher Ka values were predicted in BC-nZVI at lower ionic strength (0.1 mM) primarily due to the attachment of GO onto nZVI where nZVI in BC pores was also favorable for the straining process. This study revealed that CFT including the attachment, straining, and blocking process can effectively describe the GO transport in BC and surface-modified BC-nZVI under subsurface environmental conditions.

Modeling transport and retention of graphene oxide in porous media



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INTRODUCTION

What is Graphene Oxide (GO)?

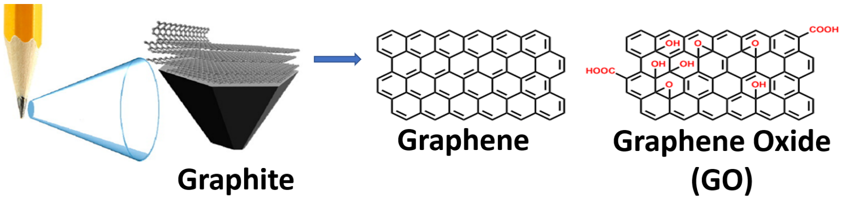


Figure 01: GO from graphite.

GO associated risk:

- Acute toxicity
- Lung granuloma
- Lower anti-bacterial resistance
- Limited metabolic rate

Extensive use and mass production of GO:

- Unique properties (Tensile, Mechanical, Electrical, etc.) make GO a unique material.
- Extensive use in Automobiles, Medical, Electronics, Agricultural, Food safety, Energy storage, Environmental application, etc.
- Expected market value/year: $1.05 billion by 2024.

Environmental release:

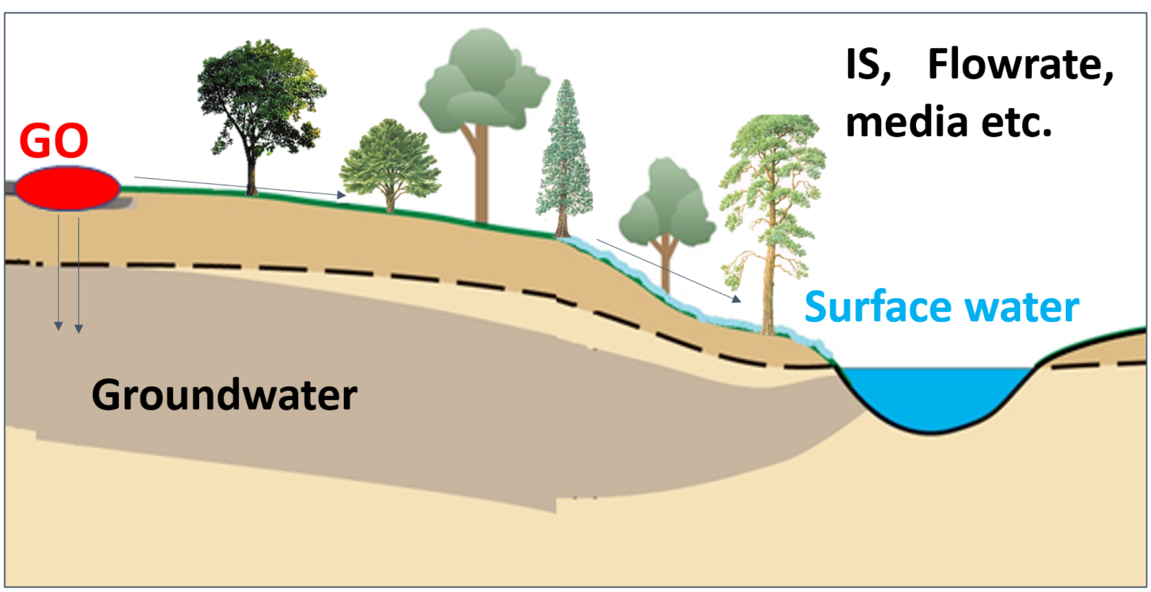


Figure 02: Release of GO under distinct environmental aquatic conditions.

OBJECTIVES AND METHODS

Hypothesis and Objectives:

- Transport and retention behavior of GO through biochar in different ionic strengths and flow rates may or may not be explained by the Colloidal Filtration Theory (CFT).
- Highly porous biochar and BC-nZVI having unique surface properties retained other contaminants [1] and it may retain GO under different conditions.
- Study the stability, retention, and mobile characteristics of GO in biochar at varying Ionic Strengths (ISs).
- Understand the effects of physicochemical factors on GO transport behavior in biochar media.
- Better prediction of GO transport parameters at the continuum scale and use the model parameters to model at field scale transport.

Numerical simulations:

GO transport in BC and BC-nZVI showed opposite retention behavior at varying IS [2]. Breakthrough curves (BTCs) of GO in columns under different experimental conditions were simulated using a one-dimensional convection-dispersion equation with one-site kinetic retention as follows:

Model 1: CFT considering with attachment:

Fitted parameter: K_a

$$\frac{\partial \theta C}{\partial t} + \rho_b \frac{\partial S}{\partial t} = \frac{\partial}{\partial x}\left(\theta D \frac{\partial C}{\partial x}\right) - \frac{\partial q C}{\partial x}$$

$$\rho_b \frac{\partial S}{\partial t} = \theta K_a C$$

Model 2: Considering time-dependent Langmuirian attachment:

Fitted parameter: K_a and S_{max}

$$\frac{\partial \theta C}{\partial t} + \rho_b \frac{\partial S}{\partial t} = \frac{\partial}{\partial x}\left(\theta D \frac{\partial C}{\partial x}\right) - \frac{\partial q C}{\partial x}$$

$$\rho_b \frac{\partial S}{\partial t} = \theta K_a \psi C$$

$$\psi = \left(1 - \frac{S}{S_{max}}\right)$$

Where, θ is the volumetric water content [−];

C is the nanohybrid concentration in aqueous phase [NL^{-3}, where N and L denote number and length, respectively];

t is time [T, where T denotes time];

ρ_b is the bulk density of porous media [ML^{-3}, where M denotes mass];

S is the nanohybrid concentration on solid phase [NM−1];

x is the spatial coordinate [L];

D is the hydrodynamic dispersion coefficient [−];

q is flow rate [LT^{-1}];

K_a and K_d are first-order attachment and detachment rate coefficients [T−1], respectively.

ψ is a dimensionless function considering both time- and depth-dependent retention.

S_{max} is the maximum solid phase retention capacity [NM^{-1}];

DESIGN OF EXPERIMENTS

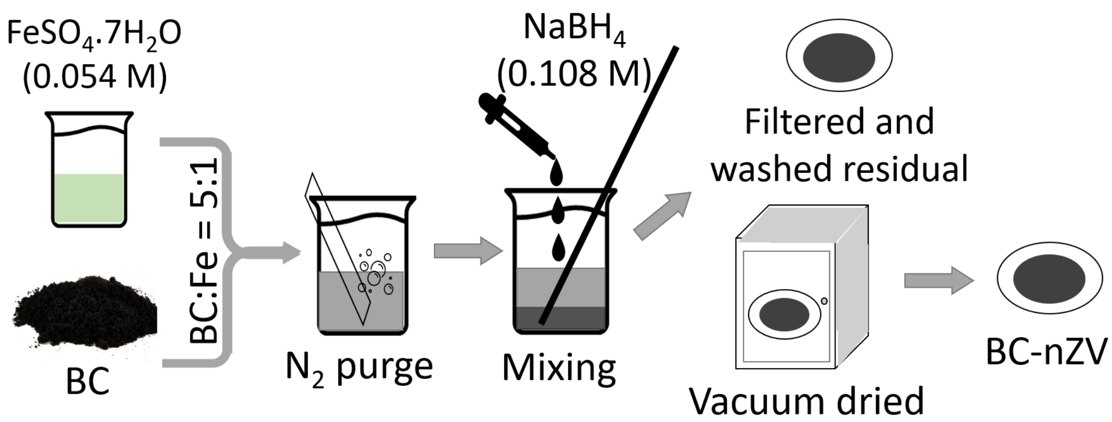


Figure 03: Synthesis process of BC-nZVI [2]

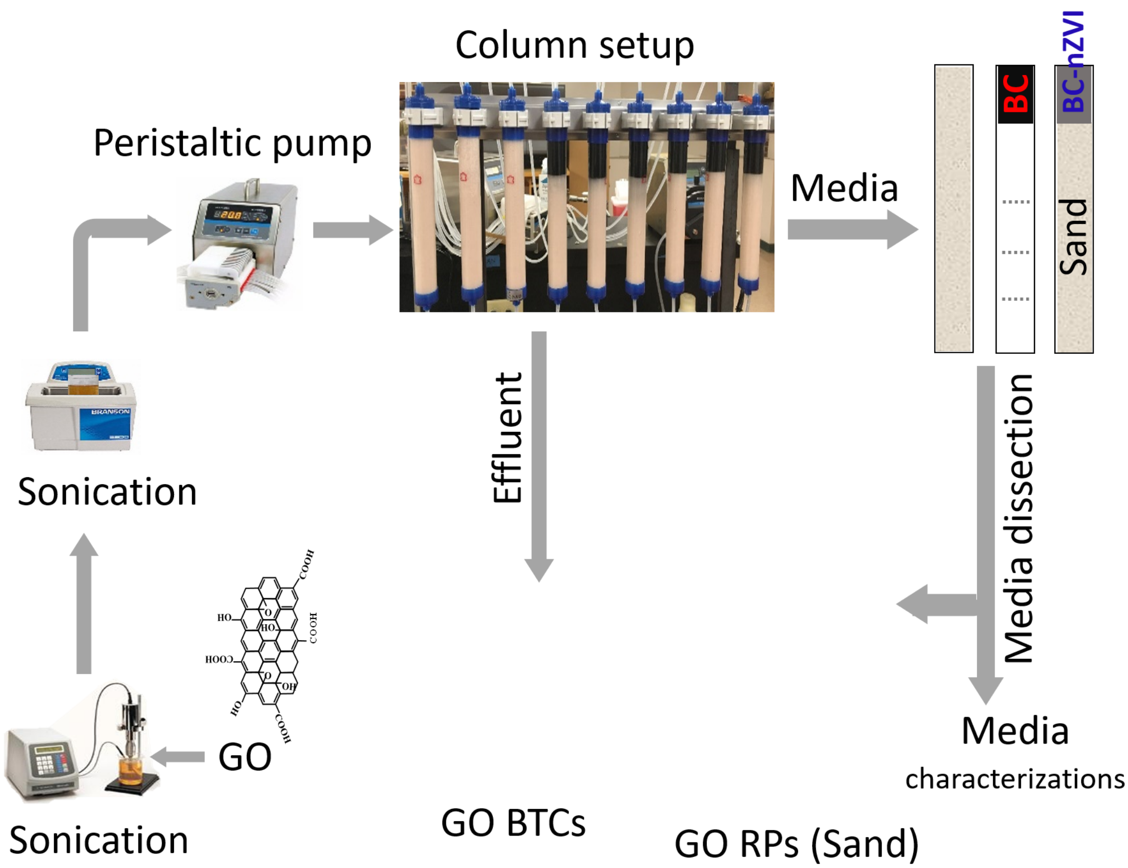


Figure 04: A schematic diagram of the experiment [2]

Characterization:

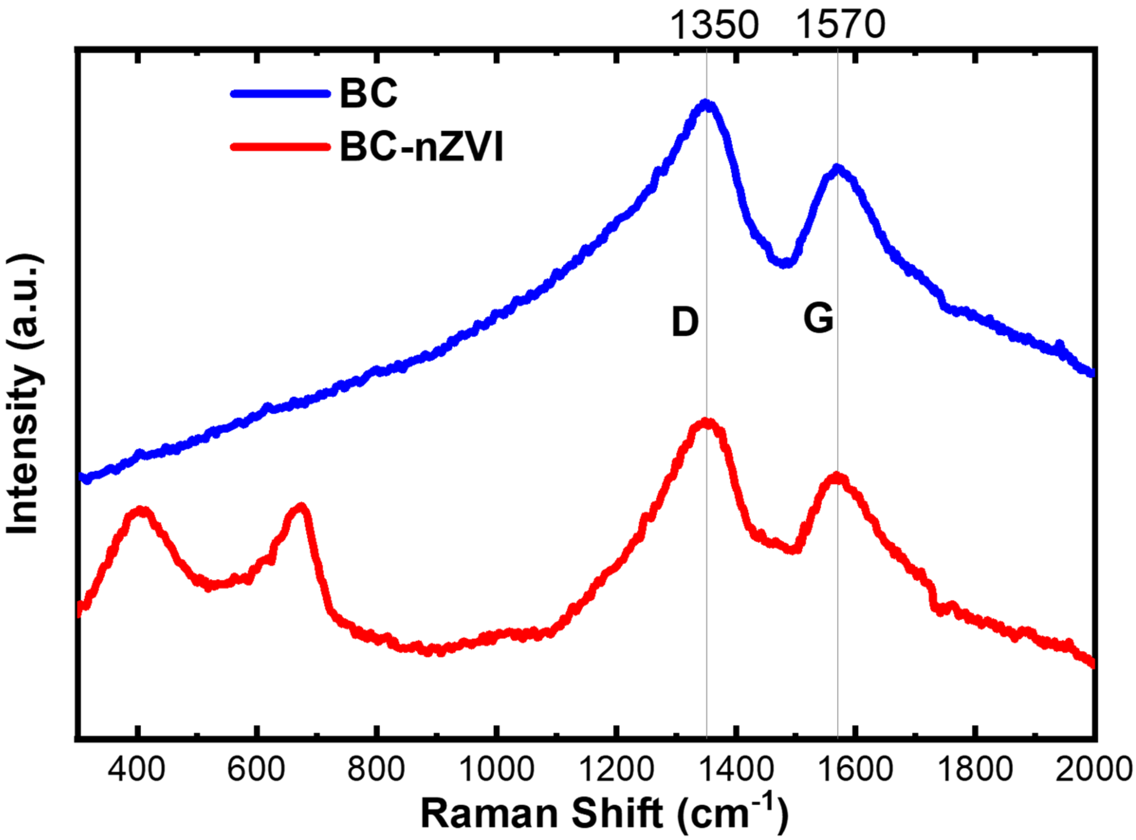


Figure 05: Raman spectra of BC and BC-nZVI [2]

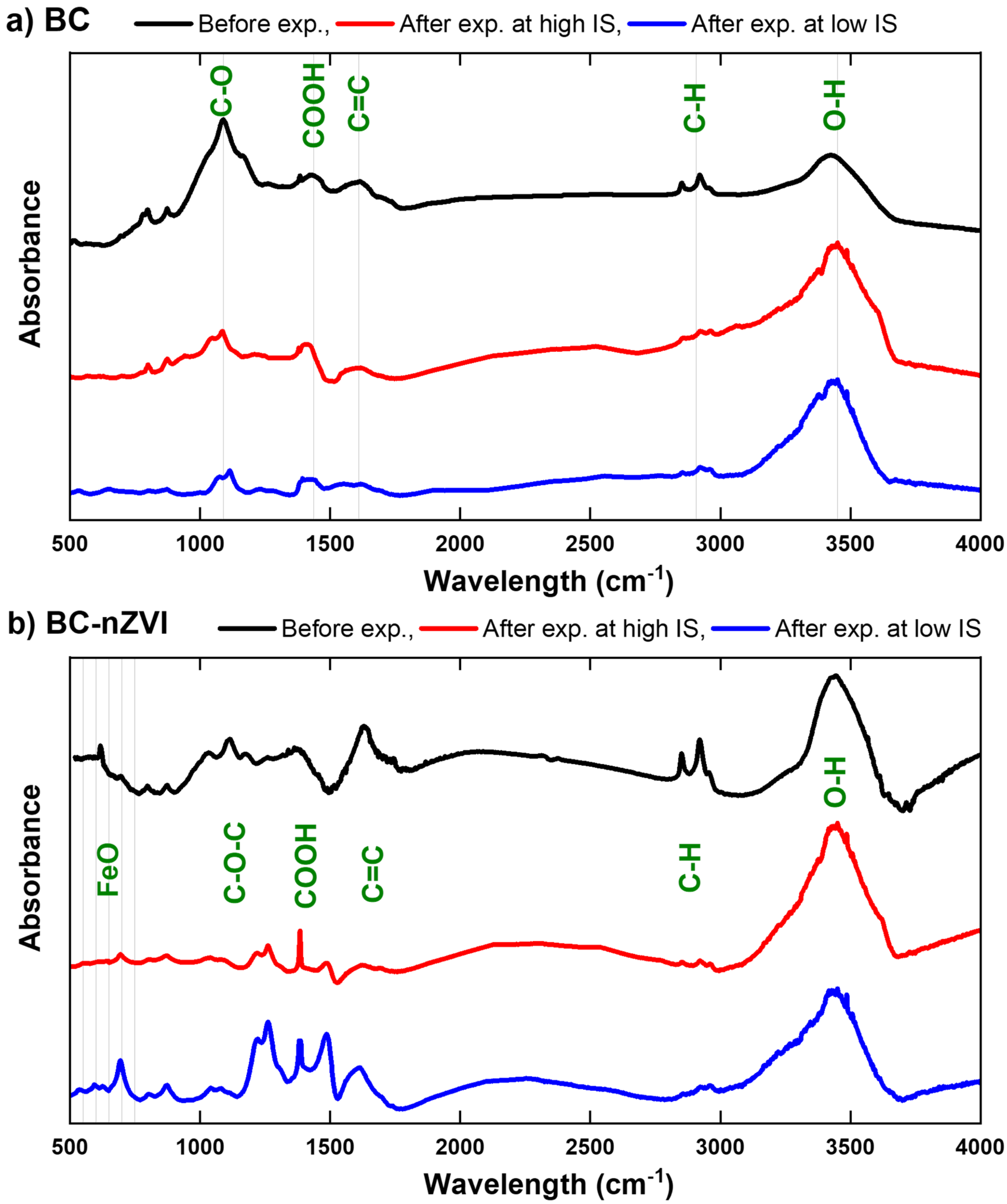
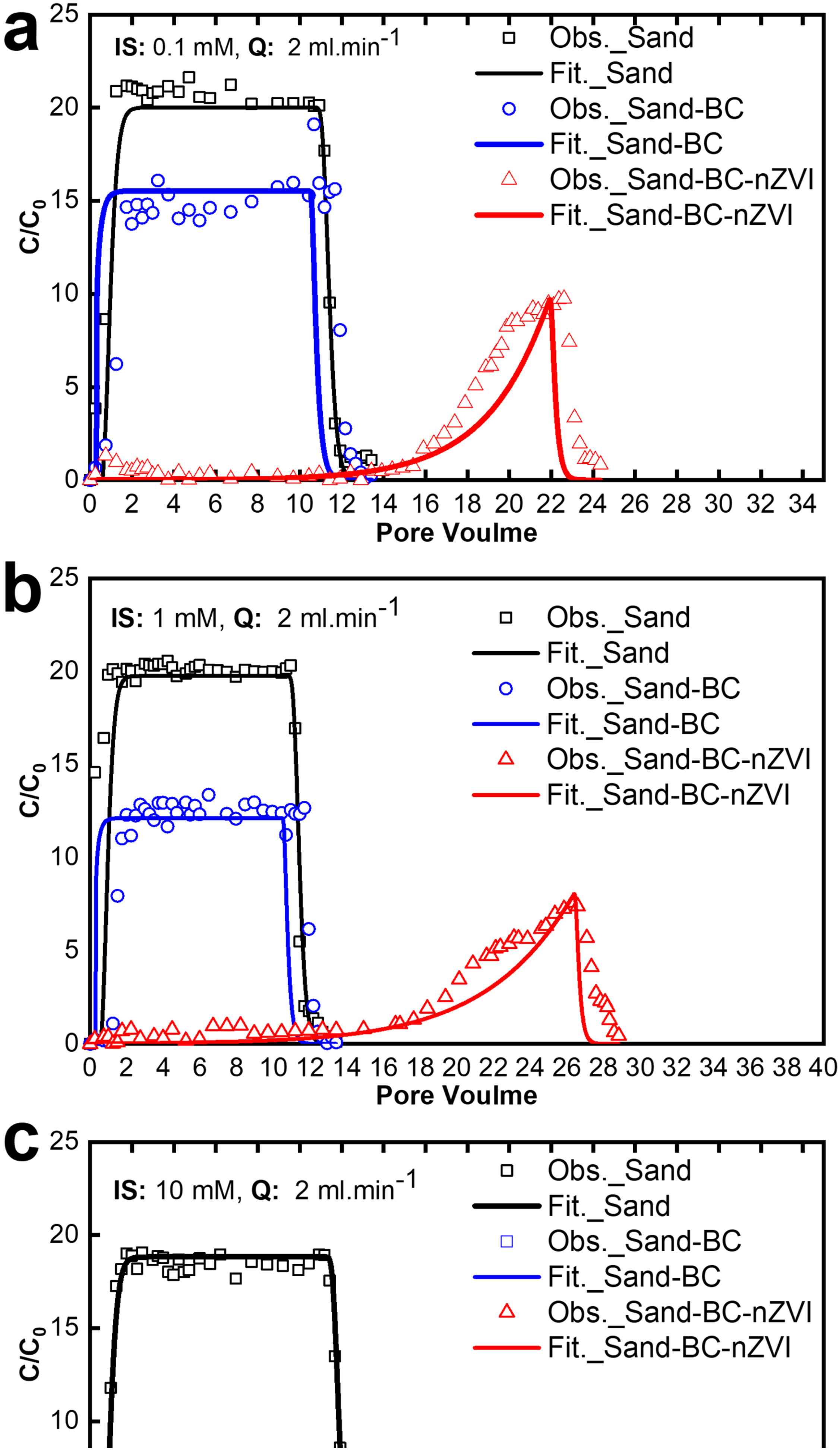


Figure 06: FTIR spectra before and after the column run [2]

RESULTS


a
IS: 0.1 mM, Q: 2 ml.min-1
Obs._Sand
Fit._Sand
Obs._Sand-BC
Fit._Sand-BC
Obs._Sand-BC-nZVI
Fit._Sand-BC-nZVI
C/C0
Pore Voulme
0 2 4 6 8 10 12 14 16 18 20 22 24 26 28 30 32 34
0 5 10 15 20 25
b
IS: 1 mM, Q: 2 ml.min-1
Obs._Sand
Fit._Sand
Obs._Sand-BC
Fit._Sand-BC
Obs._Sand-BC-nZVI
Fit._Sand-BC-nZVI
C/C0
Pore Voulme
0 2 4 6 8 10 12 14 16 18 20 22 24 26 28 30 32 34 36 38 40
0 5 10 15 20 25
c
IS: 10 mM, Q: 2 ml.min-1
Obs._Sand
Fit._Sand
Obs._Sand-BC
Fit._Sand-BC
Obs._Sand-BC-nZVI
Fit._Sand-BC-nZVI
C/C0
10 15 20 25

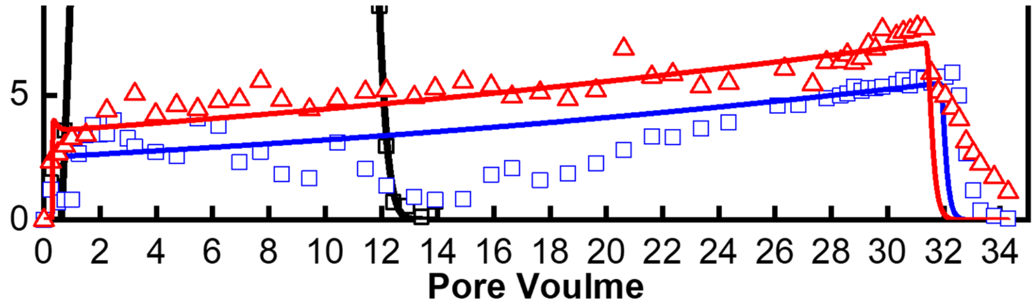
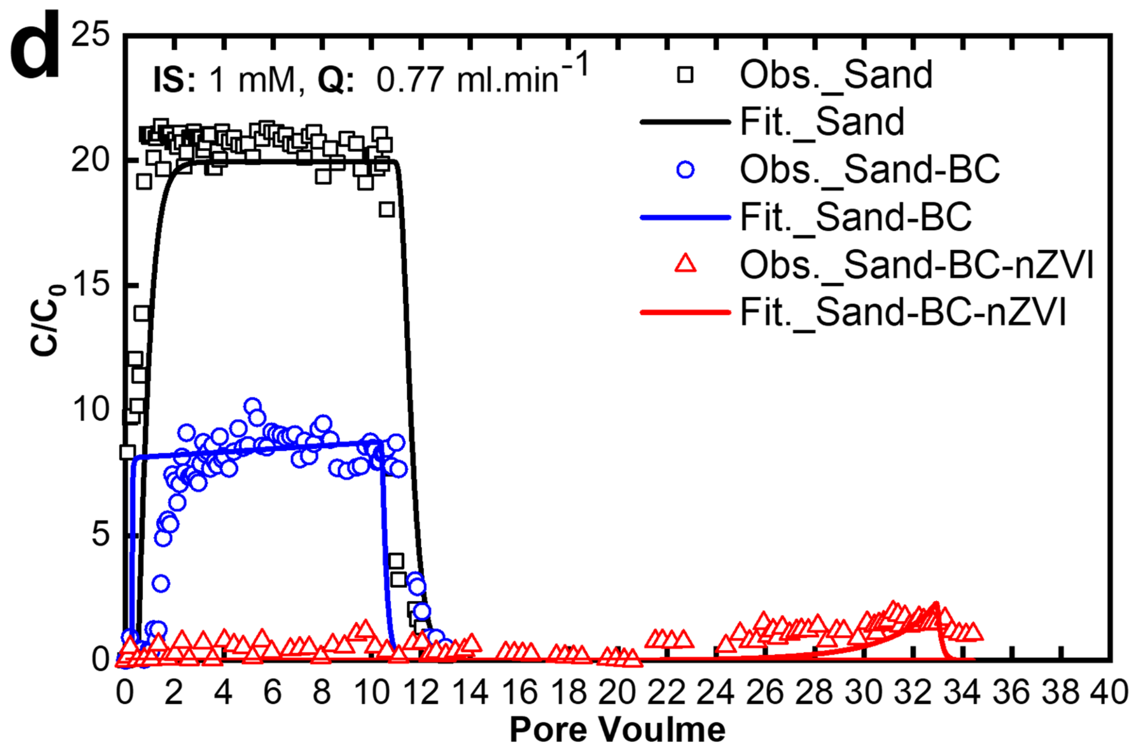
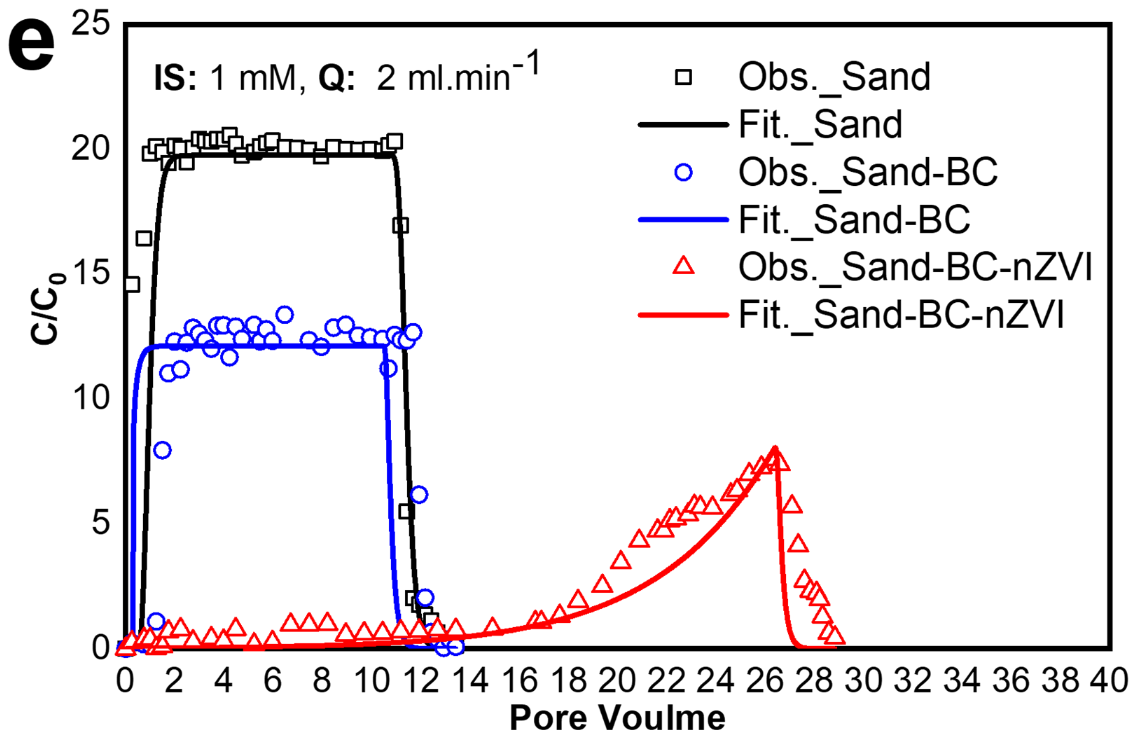


Figure 07: Effects of Ionic Strength.





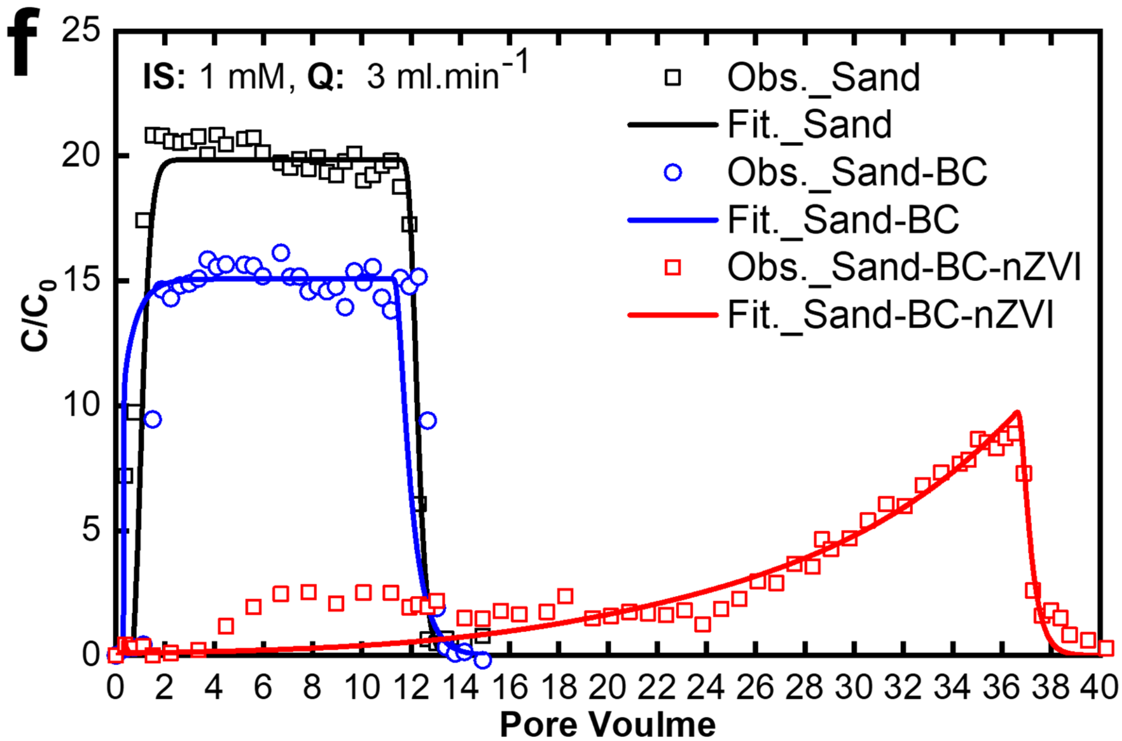


Figure 08: Effects of Flowrates.

Table 01: Model fitted parameters.

Ionic Strength	Flowrate	Sand		BC in Sand-BC		BC-nZVI in Sand-BC-nZVI	
		K_a	S_{max}	K_a	S_{max}	K_a	S_{max}
mM	$ml.min^{-1}$	min^{-1}	$mg.mg^{-1}$	min^{-1}	$mg.mg^{-1}$	min^{-1}	$mg.mg^{-1}$
0.1	2.0	0.000003	-	0.030	-	2.50	2.10
1.0	2.0	0.0006	-	0.053	-	1.75	2.55
10.0	2.0	0.003	-	0.325	5.85	0.26	5.01
1.0	0.77	0.000005	-	0.056	6.50	4.75	3.70
1.0	2.0	0.0006	-	0.053	-	1.75	2.55
1.0	3.0	0.0005	-	0.023	-	1.05	1.59

CONCLUSION

- Colloid filtration theory (CFT) and mathematical models based on the one-dimensional convection-dispersion equation were employed to describe the GO retention in biochar.

- A set of column experimental breakthrough data was employed to fit the maximum solid-phase retention capacities (S_{max}) and first-order attachment rate coefficients (K_a).

- Model outputs indicate that GO transport through sand can be explained by CFT whereas blocking function was significant to describe GO transport in biochar.

- Sand column models showed a range ($3x10^{-3}$ to $3x10^{-6}$ min^{-1}) of K_a which was increasing with increasing (0.1 to 10 mM) ionic strength.

- Numerical simulations suggest that the CFT considering time-dependent Langmuirian attachment can accurately explain the GO transport behavior in biochar media under environmental conditions.

- Fitted parameters (S_{max} = 1.5~6.5 $mg.mg^{-1}$ and K_a = 0.023~4.75 min^{-1}) were extracted from models simulated GO transport through BC and BC-nZVI layered columns.

- Aggregation, straining, and attachment at distinct IS controls GO transport and retention behavior in engineered media.

ABSTRACT

Transport and retention behavior of Graphene Oxide (GO) is influenced by the physical and chemical properties of porous media under subsurface environmental conditions. Fixed-bed column studies using quartz sand and biochar (BC) in different configurations were conducted as a function of ionic strength and flowrate. Colloid filtration theory (CFT) was employed to develop mathematical models based on the one-dimensional convection-dispersion equation using experimental GO breakthrough curves (BTCs) and retention profiles (RPs) obtained from the experimental data. GO transport and retention behavior was modeled using BC and BC-nZVI (BC surface modified with nanoscale zero-valent iron) as filter media to understand the effect of media properties. It was demonstrated that the model can describe measured BTCs and RPs of GO in the sand, BC, and BC-nZVI. The inverse modeling approach was implemented to determine the attachment coefficient (K_a) and maximum solid-phase retention capacity (S_{max}) using GO BTCs for different experimental conditions. Higher K_a in BC at 10 mM IS indicated the influence of straining which agrees with the depth-dependent retention kinetics. Furthermore, pronounced GO aggregation at higher IS supports the higher K_a values at 10 mM compared to 0.1 mM. In contrast, higher K_a values were predicted in BC-nZVI at lower ionic strength (0.1 mM) primarily due to the attachment of GO onto nZVI where nZVI in BC pores was also favorable for the straining process. This study revealed that CFT including the attachment, straining, and blocking process can effectively describe the GO transport in BC and surface-modified BC-nZVI under subsurface environmental conditions.

REFERENCES

1. Hasan, Md Sazadul, Mengistu Geza, Raul Vasquez, Govinda Chilkoor, and Venkataramana Gadhamshetty. "Enhanced Heavy Metal Removal from Synthetic Stormwater Using Nanoscale Zerovalent Iron–Modified Biochar." Water, Air, & Soil Pollution 231 (2020): 1-15.
2. Hasan, Md Sazadul, Mengistu Geza, Jacob B. Petersen, and Venkataramana Gadhamshetty. "Graphene oxide transport and retention in biochar media." Chemosphere 264 (2020): 128397.