

Dynamic interactions between cyclodextrin, an organic pollutant, and granular activated carbon in column studies

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In this study, the dynamic interactions between cyclodextrin (CD), an organic chemical and granular activated carbon (GAC) were investigated using column studies. Breakthrough curves of a chlorinated solvent, trichloroethylene (TCE) were obtained over a range of concentrations of 2-hydroxypropyl-beta-cyclodextrin (HPCD) (0, 20, and 50 g L⁻¹) and flow velocities (1.0, 4.0, and 10.2 mL min⁻¹). Important transport parameters (*i.e.* residence time, dispersion coefficient, retardation factor) were estimated using truncated temporal moment analysis. Our result shows that increasing CD concentration resulted in earlier TCE breakthrough, demonstrated by decreasing residence times which are 306.23, 151.26, and 102.24 pore volumes for 0, 20, and 50 g L⁻¹ CD respectively. Comparison of the original breakthrough curves (BTCs) under different CD concentrations to the solubility-enhancement-rescaled BTCs showed (1) the presence of CD decreases the relative degree of TCE sorption to GAC and (2) all 3 curves exhibited similar rescaled times at which they reach 50% of the input concentration. The lowest flow rate, (1.0 mL min⁻¹), resulted in a more symmetrical BTC, indicating more ideal conditions were achieved under the longer exposure time provided by this flow rate. As the flow rate increases the first appearance of TCE in the eluent occurs relatively earlier and exhibits comparatively greater delay in achieving full breakthrough, suggesting non-equilibrium processes are more significant at higher flow rates.

Introduction

Cyclodextrin (CD) molecules are polycyclic glucose oligomers derived from starch that have a hydrophobic interior and hydrophilic exterior, making CD a promising solubility enhancement agent.¹ There is a growing body of evidence²⁻⁹ suggesting that CD can greatly enhance the performance of *in situ* flushing of contaminated soil and aquifer sediments. To increase the efficacy of CD as an agent to enhance groundwater

remediation, post-aquifer flushing solutions must be treated to regulatory levels. Recent pilot-scale studies have demonstrated that pollutants separation from CD solutions can be accomplished by a combination of air stripping^{10,11} and granular activated carbon (GAC) adsorption.¹²

GAC has been widely used to remove of organic and inorganic contaminants from contaminated media.¹³⁻¹⁷ The association of chemicals and CD molecules can significantly alter the chemical partitioning behavior and therefore the efficiency of treatment might be affected.^{18,19} A previous study²⁰ which involved batch isotherm tests has shown that the presence of CD does lower the availability of trichloroethylene (TCE) for dissolution in water and adsorption to GAC, demonstrated by reduced TCE partitioning to GAC with increasing CD concentration. While this study was conducted under batch equilibrium conditions, further

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Environmental impact

This manuscript includes new experimental data and calculated transport parameters for the dynamic interactions between 2-hydroxypropyl-beta-cyclodextrin (CD), water and granular activated carbon (GAC) of a common organic chemical, trichloroethylene (TCE). TCE transport behavior was investigated over a range of concentrations of CD (0, 20, and 50 g L⁻¹) and flow velocities (1.0, 4.0, and 10.2 ml min⁻¹). This study provides important information to design GAC systems treating post-aquifer flushing CD solutions for environmental remediation. It may also have potential use for the design GAC purification systems for other common CD applications such as pharmaceuticals, food additives, and cosmetics industries.

research on the kinetic interaction between hydrophobic organic pollutants and GAC in the presence of CD is needed and the fate and transport mechanisms of chemicals in GAC systems must be studied in greater depth in order to optimize the design and assess the performance of GAC treatment systems containing CD solutions.

The objectives of the work presented in this paper are to: (1) assess the fate and transport behavior of TCE in GAC using column studies in the presence of 2-hydroxypropyl- β -CD; (2) evaluate the effect of pore-water velocity (1.0, 4.0, 10.0 mL min⁻¹) on TCE transport in CD solutions for these systems, and (3) investigate the effect of CD concentration (0, 20, 50 g L⁻¹) on the breakthrough of TCE in GAC columns. The findings of this study may provide important information on the design of GAC systems for treating post flushing CD solutions during environmental remediation. It may also have the extensive potential of using the transport parameters to design GAC purification systems for other common CD applications in the pharmaceutical, food additive, and cosmetics industries.

Materials and experimental methods

Chemicals

TCE (>99.5% purity), sodium azide (>99.5% purity), and calcium bromide hydrate (98% purity) were purchased from Sigma-Aldrich. Sodium nitrate (98%) was purchased from Fisher Scientific. HP β CD was donated by Wacker Chemie AG. NORIT C GRAN is a chemically activated granular carbon donated by Norit Americas Inc. (Marshall, TX). For the relevant properties of HP β CD and Norit C GRAN see our previous study (Gao and Blanford, 2011).

Column setup and experiments

Column setup. Bench-scale column tests were carried out to evaluate the interactions between chemicals and GAC in the presence of CD. The initial TCE-CD solutions were prepared in 4 L amber glass bottles. To minimize potential loss due to volatilization and provide consistent concentrations for the column studies, the TCE-CD solution was transferred to Teflon gas sampling bags (Jensen Inert Product, FL) with no headspace. For these tests, stainless steel columns, with an inside diameter of 2.54 cm and 25.0 cm long (Grace Alltech) was packed with Norit C GAC. A stainless steel distribution plate and a filter ($d = 0.22 \mu\text{m}$) were placed at each end of the columns to provide an even flow field and avoid potential clogging due to mobilization of fine grains. The columns were oriented vertically and fluid was introduced into the basal end using a piston pump with stainless steel fittings (LabAlliance Series I Pump, Fisher Scientific). Samples for TCE and Br-analysis were taken with 10 mL gas tight syringes with luer lock connectors (Swagelok). A gate valve (Swagelok) was incorporated in the effluent line of the column prior to the sampling port in order to decrease the potential back pressure caused by the gas-tight sampling syringe.

Experiment operation. Two primary variables, flux rate and CD concentration, which can influence the application of GAC for treatment of post-flushing solution, were evaluated in this study. A series of column tests were performed at flow rates

of 1.0, 4.0, and 10.2 mL min⁻¹ with the TCE concentration of 50 mg L⁻¹ in 50 g⁻¹ HPCD solutions. The effect of CD concentrations (0, 20, and 50 g L⁻¹) was investigated in columns supplied with a flow rate of 4.0 mL min⁻¹. Bromide was used as conservative tracer to evaluate the fate and transport behavior in this system.

Effluent flow rates were measured regularly *via* weighing samples and the effluent fluid passed between samples to verify that the flowrate remained constant. All column experiments were carried out at ambient room temperature ($23 \pm 1^\circ\text{C}$). The concentration of TCE in liquid samples entering and exiting the columns was determined *via* the gas chromatography method as described in Gao and Blanford (2011). A bromide ion-specific electrode (Cole-Parmer) coupled with an Orion Star pH/mV meter (Thermo Scientific) was used to measure the conservative tracer concentrations in influent and effluent samples.

Truncated temporal moment analysis

Contaminant transport through saturated porous media in a one-dimensional uniform flow field can be described by eqn (1).²¹⁻²³

$$R \frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial x^2} - v \frac{\partial C}{\partial x} \quad (1)$$

where, R is the retardation factor, dimensionless; C is contaminant concentration in aqueous phase, mg L⁻¹; D is the dispersion coefficient, cm² min⁻¹; v is the net transport velocity, cm min⁻¹; t is travel time, minute; and x is distance, cm.

Traditional temporal moment analysis often encounters difficulties when full breakthrough is not achieved. The truncated moment method as developed by Jawitz²⁴ and Luo *et al.*²⁵ was used for parameter estimation in this study. Consider a breakthrough curve is truncated at time T , the k^{th} truncated temporal moments, $m_k(T)$ is defined by eqn (2).

$$m_k(T) = \int_0^T t^k c(x, t) dt \quad (2)$$

A log-normal distribution was selected to parameterize the advective-dispersive transport at travel time τ and the solutions of truncated temporal moments are given by

$$m_0^\tau(T) = \frac{1}{2} \left[\text{erf} \left(\frac{\ln T - \mu_{\ln\tau}}{\sigma_{\ln\tau} \sqrt{2}} \right) + 1 \right] \quad (3)$$

$$m_1^\tau(T) = \frac{1}{2} \exp \left(\mu_{\ln\tau} + \frac{\sigma_{\ln\tau}^2}{2} \right) \times \left[\text{erf} \left(\frac{\ln T - \mu_{\ln\tau} - \frac{\sigma_{\ln\tau}}{\sqrt{2}}}{\sigma_{\ln\tau} \sqrt{2}} \right) + 1 \right] \quad (4)$$

$$m_2^\tau(T) = \frac{1}{2} \exp(2\mu_{\ln\tau} + 2\sigma_{\ln\tau}^2) \times \left[\text{erf} \left(\frac{\ln T - \mu_{\ln\tau} - \frac{2\sigma_{\ln\tau}}{\sqrt{2}}}{\sigma_{\ln\tau} \sqrt{2}} \right) + 1 \right] \quad (5)$$

In which $m_{0-2}^\tau(T)$ are zeroth, first, and second truncated moment respectively; $\mu_{\ln\tau}$ and $\sigma_{\ln\tau}$ are the mean and standard deviation of the log travel-time distribution. Detailed description of this distribution can be found in Jawitz²⁴ and Johnson *et al.*²⁶ The mean residence time, μ_τ , the variance of the log-normally

distributed breakthrough curves, σ_τ^2 , and the retardation factor, R , can be calculated according to Luo *et al.*²⁵

$$\mu_\tau = \exp(\mu_{\ln\tau} + \frac{1}{2}\sigma_{\ln\tau}^2) \quad (6)$$

$$\sigma_\tau^2 = \exp(2\mu_{\ln\tau} + 2\sigma_{\ln\tau}^2) - \exp(2\mu_{\ln\tau} + \sigma_{\ln\tau}^2) \quad (7)$$

$$R = \frac{\mu_\tau(\text{TCE})}{\mu_\tau(\text{Br})} \quad (8)$$

where $\mu_\tau(\text{TCE})$ and $\mu_\tau(\text{Br})$ are the mean residence times of TCE and Br, respectively.

Results and discussion

Bromide tracer results

Bromide was used as the conservative tracer in this study to track the fluid flow through the porous media because it has been shown that bromide does not undergo significant sorption or chemical transformations.^{27,28} Fig. 1 illustrates the normalized effluent concentration, C/C_0 , versus the numbers of pore volumes flushed at different CD concentrations (top) and flowrates (bottom). As can be seen, the BTCs were not axially symmetric and the time which took the BTCs to fully reach 100% was delayed. Transport parameters including residence time, variance of distribution, and dispersivity were obtained from truncated moment analysis.

Br exhibited good mass recovery (above 90%) (Table 1) for all tested column studies. The sources of unaccounted mass might be due to sorption and dilution of bromide to below measurable concentration (0.2 mg L^{-1}). Compared to the large adsorbed

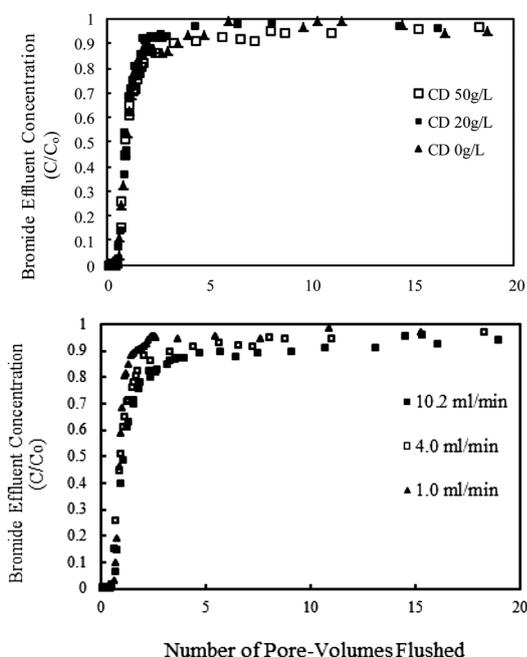


Fig. 1 Breakthrough curves (BTCs) of bromine under different CD concentrations (top) and different flow rates (bottom). (Note: the flow rate during the tests comparing the different CD concentrations was 4 mL min^{-1} and the CD concentration during the tests of different flow rates was 50 g L^{-1} .)

Table 1 Br transport parameters at different CD concentrations

CD concentration, g L^{-1}	0	20	50
Mass Recovery Fraction (MRF), %	0.99	0.99	0.95
Residence Time (RT), PV	1.11	1.14	1.16
Variance of distribution, PV	0.54	0.68	0.69
Dispersivity, $\text{cm}^2 \text{ min}^{-1}$	4.12	5.95	2.96

quantity of TCE, the comparatively small amount of Br loss can be ignored. Br showed similar breakthrough behaviors, in term of resident times (1.11, 1.14, and 1.16 PV) and variances of distribution (0.54, 0.68, and 0.69 PV) at the CD concentration of 0, 20, and 50 g L^{-1} respectively. There is no obvious trend in the calculated bromide dispersion coefficients for the column tests performed at the CD concentrations (Table 1). This might indicate that the CD did not have significant effect on Br's transport at the tested CD concentration range.

The parameters of Br transport are listed in Table 2. The variances (the third row in Table 2) of the best-fitting log-normal distribution quantitatively demonstrate the spans of the tracer's elution time. The calculated variances of distribution were 0.36, 0.69, and 1.32 pore volumes at the flowrates of 1.0, 4.0, and 10.2 mL min^{-1} , respectively. This indicates increasing non-equilibrium transport at higher flowrates, which can be explained that a higher flowrate provides insufficient exposure time for bromide to diffuse fully into porous media.²⁹ This is further confirmed by the residence times calculated from truncated moment analysis (Table 2). Br showed a longer residence time ($\text{RT} = 1.58 \text{ PV}$) at the higher flowrates (10.2 mL min^{-1}) compared to the value ($\text{RT} = 1.06 \text{ PV}$) at the lower flowrate (1 mL min^{-1}). For different flow rates at constant CD concentrations the dispersion coefficient, D , increased with increasing flow rate (Table 2). This is consistent with the common finding that D is a function of flow velocity when the aqueous diffusion is constant.³⁰

Effect of CD concentration on TCE transport

In order to determine the effect of CD concentration on TCE transport, column studies were conducted using a series of CD solutions (0, 20, and 50 g L^{-1}). Fig. 2 shows the normalized effluent concentration of TCE, C/C_0 , versus the numbers of pore volumes flushed. As can be seen in Fig. 2, increasing CD concentration resulted in earlier TCE breakthrough. This is shown quantitatively by the truncated moment analysis results (Table 3). The residence time and retardation factor inversely correlated with CD concentration. This can be explained by the apparent solubility enhancement of CD. To be more specific, TCE elution from GAC column depends on the relative aqueous solubility and the affinity between TCE and GAC. Because CD

Table 2 Br transport parameters at different flow rates

Flow rate, mL min^{-1}	1.0	4.0	10.2
Mass Recovery Fraction (MRF), %	0.98	0.95	0.93
Residence Time (RT), PV	1.06	1.16	1.58
Variance of distribution, PV	0.36	0.69	1.32
Dispersivity, $\text{cm}^2 \text{ min}^{-1}$	0.57	2.96	24.5

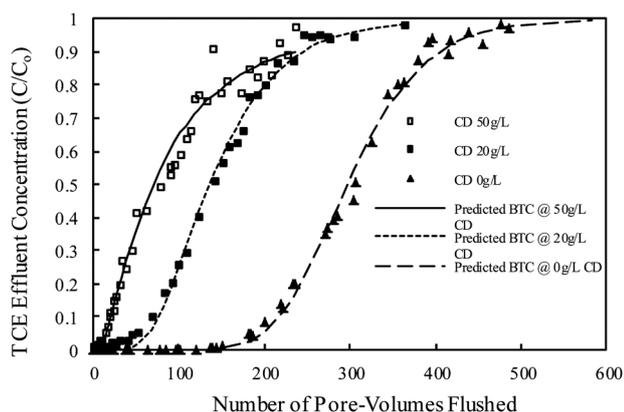


Fig. 2 Effects of CD concentration on breakthrough behaviour of trichloroethylene (TCE) in CD-GAC-water systems with the flowrate of 4.0 mL min^{-1} .

Table 3 Results of TCE truncated temporal moment analysis at different CD concentrations

CD concentration, g L^{-1}	0	20	50
Mass Recovery Fraction (MRF), %	0.50	0.60	0.61
Residence Time (RT), PV	306.2	151.3	108.7
Retardation factor, dimensionless	275.9	132.7	93.7
Variance of distribution, PV	75.0	72.6	130.1

can greatly enhance the apparent aqueous solubility, TCE elutes earlier at higher CD concentrations.

To draw a more direct comparison on the basis of the relative solubility for the varying CD concentrations, the pore volume axis can be rescaled by the apparent CD solubility enhancement factor (Fig. 3). Comparing the times at which TCE reach half their input concentration is often useful because the effects of non-ideal behaviors such as rate-limited dispersion and sorption are less pronounced. As can be seen, Fig. 3 exhibited similar scaled times at which they reach 50% of the input concentration. This is consistent with the batch results¹⁷ which found that TCE sorption isotherms to this GAC were statistically identical when rescaled for CD concentration. The rescaled data also shows different distribution variances of the rescaled BTCs, which can be explained by the

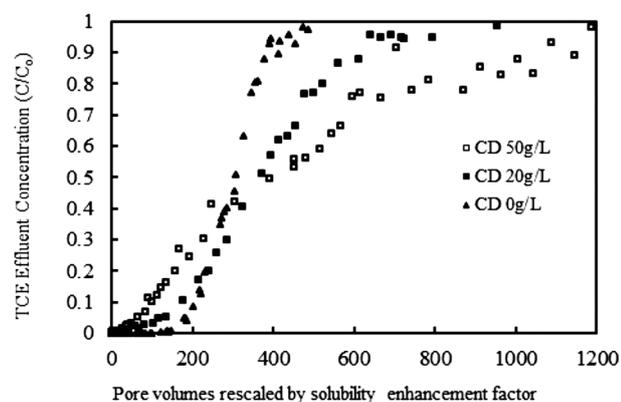


Fig. 3 Rescaled breakthrough curves of TCE under different CD concentrations.

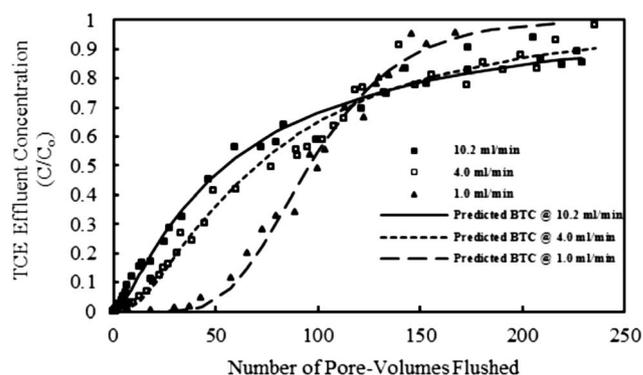


Fig. 4 Effects of flow rates on breakthrough behaviour of trichloroethylene (TCE) in CD-GAC-water systems with the CD concentration of 50 g L^{-1} .

Table 4 Results of TCE truncated temporal moment analysis at different flow rates

Flow rate, mL min^{-1}	1.0	4.0	10.2
Mass Recovery Fraction (MRF), %	0.55	0.61	0.63
Residence Time (RT), PV	102.2	108.7	122.7
Retardation factor, dimensionless	96.4	93.7	77.7
Variance of distribution, PV	38.2	130.1	246.2

effects of non-equilibrium dispersion and sorption. To be more specific, (1) the chosen flow rate for this system resulted in non-equilibrium condition such that TCE had insufficient contact time with the GAC to achieve equilibrium distribution and (2) diffusion processes were slower as CD concentration increased due to the greater viscosity of the CD solutions, indicating that the presence of CD increases the time needed for TCE to fully penetrate the intra-particle pores of the GAC grains.

Effect of flow rate on TCE transport

The normalized effluent TCE concentration, C/C_0 , versus pore volumes under different flow rates is shown in Fig. 4. The lowest flow rate, (1.0 mL min^{-1}), resulted in a more symmetrical BTC, indicating more ideal conditions were achieved under the longer exposure time provided by this flow rate. As the flow rate increases the first appearance of TCE in the eluent occurs relatively earlier and exhibits comparatively greater delay in achieving full breakthrough, suggesting non-equilibrium processes are more significant at higher flow rates.^{31–33}

Table 4 summarizes the TCE transportation parameters calculated *via* truncated moment analyses. Because lower flow rates provided more exposure time to diffuse into the intra-GAC particles, TCE showed a shorter residence time (102.2 PV), smaller distribution variance (38.2 PV), and greater retardation factor (96.4) at the lower flowrate (1.0 mL min^{-1}), which is consistent with the breakthrough behavior described in Fig. 4.

Conclusions

The purpose of this study was to collect experimental data and assess dynamic interactions between CD, an organic chemical and GAC. The key findings of this study are summarized as below:

Increasing CD concentration resulted in earlier TCE breakthrough, demonstrated by (1) shorter residence times, larger distribution variances, and lower retardation factors at higher CD concentrations. This can be explained by the apparent solubility enhancement of CD. Breakthrough curves can be rescaled using the TCE solubility enhancement factor and the rescaled curves show similar scaled times at which they reach 50% of the input concentration; this is consistent with the batch results. The flow rate can influence TCE transport behavior in CD–GAC system. Because lower flow rates provide more time for diffusion into the intra-particle pores of the GAC grains, TCE showed a shorter residence time, smaller distribution variance, and larger retardation factor at lower flowrates. The truncated moment method successfully evaluated TCE transport behaviour in the presence of CD. The important transport parameters including residence time, distribution variance, and retardation factor obtained from truncated temporal moment analysis can accurately describe breakthrough behaviors.

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