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Dynamics of Contaminant Flow Through Porous Media Containing Random Adsorbers

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1 Dynamics of contaminant flow through porous
2 media containing random adsorbers

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12 **Abstract**

13 Many porous media are mixtures of inert and reactive materials, manifesting
14 spatio-chemical heterogeneity. We study the evolution of scalar transport in a
15 chemically heterogeneous material that mimics a green roof soil substrate, frac-
16 tionally composed of inert and reactive adsorbing particles. These adsorbing
17 particles are equivalent to biochar within a real soil substrate. The scalar trans-
18 port evolution is determined using experiments and simulations calibrated from
19 experimental data. Experiment 1 is used to determine the equilibrium capacity
20 and adsorption rate of two biochar types when immersed in a methylene blue
21 solution. Breakthrough curves of a packed bed of glass beads with randomly
22 interspersed biochar are determined in experiment 2. Simulations are then run
23 to investigate the solute transport and adsorption dynamics at the pore-scale.
24 An analytical model is proposed to capture the behavior of the biochar adsorp-
25 tion capacity and the simulation results are compared with experiment 2. A
26 pore-scale analysis showed that uniformly sized beds are superior in contaminant
27 breakthrough reduction, which is related to the adsorptive surface area and the
28 rate at which adsorption capacity is reached. Cases using the adsorption capacity
29 model display a tight distribution of particle surface concentration at later simu-
30 lation times, indicating maximum possible adsorption. The beds with dissimilar

31 particle sizes create more channeling effects which reduce adsorptive particle effi-
32 ciency and consequently higher breakthrough concentration profiles. Comparison
33 between experiments and simulations show good agreement. Improved biochar
34 performance can be achieved by maintaining particle size uniformity along-
35 side high adsorption capacity and adsorption rates appropriate to the rainfall
36 intensity.

37 **Keywords:** biochar, lattice Boltzmann, experiment, adsorption, methylene blue

38 Article Highlights

- 39 • Experiments on biochar adsorption of methylene blue compared to simulations, with
40 good agreement.
- 41 • Simple analytical model proposed to capture biochar adsorption capacity, results
42 compared to experiments.
- 43 • Performance inferior in polydisperse beds due to underutilized particles and
44 inhomogeneous concentration front profile.

45 1 Introduction

46 Porous media containing a proportion of inert and chemically reactive elements can
47 found in biology in the form of biofilters, bioreactors, and organic tissue. They are
48 also found in geological elements such as rocks or soils, which are also highly chemi-
49 cally heterogeneous, containing a wide variety of chemically dissimilar minerals and/or
50 organic elements. Research into this type of porous media has formerly been primar-
51 ily driven by the petrochemical industry, however this has shifted in recent years to
52 a more environmental focus. Green roofs are one such example, consisting of living
53 greenery ranging from trees to grasses growing in a soil substrate whose composition
54 can vary widely, from crushed brick to manure to peat moss. The benefits of green
55 roofs in urban environments are well documented, such as their contributions to the
56 reduction in urban noise, air, and water pollution; their effects on the urban heat island

57 as well as building envelopes themselves; and urban rainwater runoff management
58 [Aguilar Fajardo et al. \(2022\)](#).

59 Green roofs require regular maintenance, including the administration of fertilizer
60 upon installation and potentially thereafter as the need arises. The fertilizer consists
61 of a fast-acting agent which gives the plants a boost to survive the initial period of
62 installation and establish themselves; and longer-acting nutrients which aim to keep
63 the additional required maintenance to a minimum. Excess fertilizer which cannot be
64 stored by the soil or used directly by the vegetation can be carried by rainwater from
65 the soil through the drainage system to locations where it acts as a contaminant [Wang
66 et al. \(2017\)](#). The addition of biochar to the soil to adsorb excess fertilizer (contaminant
67 or solute) is currently being put forth as viable solution to this problem.

68 **1.1 Biochar in green roofs**

69 Biochar is essentially any organic material that has been carbonized under high tem-
70 perature through a process known as pyrolysis and can vary in material properties
71 and morphology significantly. A thorough overview of the types of biochar in use
72 commercially can be found in [Novotný et al. \(2023\)](#).

73 Biochar is incorporated into green roof soil via three strategies; random application
74 to the top of the bedding material, thorough mixing into the substrate composition
75 prior to vegetation, and set as a layer at the bottom of the substrate. Thorough
76 mixing and layering at the soil base are considered the most effective, with the latter
77 shown to be effective for reducing the leaching of total nitrogen and total phosphorous
78 [Kuoppamäki et al. \(2016\)](#). The proportion of applied biochar varies, from 5% by
79 weight/volume up to about 40%, however excessive proportions of biochar will have
80 adverse effects on plant growth and contribute to increased contamination [Xiang et al.
81 \(2021\)](#).

82 There are few large-scale projects incorporating biochar use on green roofs though a
83 few exist, such as the NWE CASCADE project, in which France intends to implement
84 the use of biochar to enhance stormwater management within the Brittany region.
85 Other similar solutions will likely be implemented within a larger initiative led by
86 Bloomberg Philanthropies as touched upon in [Senadheera et al. \(2024\)](#).

87 The industrial-scale implementation is dependent upon several factors, such as the
88 ecological impact of large-scale biochar use and the release of additional contaminants
89 present within or on the surface of biochar as a result of its preparation and function.
90 For example, [Premarathna et al. \(2023\)](#) discusses the almost complete removal of
91 ammonia from the soil when excessive biochar is applied, which can be problematic
92 for soil health. Another key factor is availability of biochar itself, given the different
93 feedstock and treatment methods for its creation. A final major consideration is the
94 lifetime of the biochar as an adsorbent and its end-of-life handling. Little work has been
95 done on the effects of aging on biochar performance due to limited long-term projects
96 but what is known is that degrading performance is dependent upon the contaminant
97 and environmental conditions. For example, if the primary goal of the biochar is to
98 trap micro and nano-plastics (MPs and NPs) then both the aging of the biochar *and*
99 the plastics themselves play an important role in the removal efficiency [Ji et al. \(2024\)](#).
100 Physical degradation of the biochar also occurs during the aging process and leads
101 to biochar dust, which no longer serves its purpose of entrapping pollutants but can
102 act to spread captured plastics or heavy metals due to its increased mobility. It has
103 been shown the granulated biochar in particular is more resistant to this degradation
104 process, thus making it more suitable for applications such as green roofs where the
105 environmental exposure is high [Lee and Kwon \(2024\)](#).

106 Related to the issue of biochar disposal is the issue of regeneration, which heavily
107 depends upon the captured contaminants. It is possible to regenerate biochar that
108 has captured MPs/NPs using organic solvents such as acetone, however this is not

109 feasible in a green roof environment due to environmental concerns. Water rinsing
110 performs relatively poorly for removing carbon-based adsorbents but can be used [Ji
111 et al. \(2024\)](#). Adsorbed copper can be almost completely recovered [Bashir et al. \(2023\)](#),
112 as can cadmium [Cui et al. \(2022\)](#). Biochar regeneration over five adsorption-desorption
113 cycles was assessed with regard to volatile organic compounds (VOCs) with reported
114 88% to 96% regeneration [Rajabi et al. \(2021\)](#). While these reports are promising, the
115 scalability for some of the processes used for regeneration is in doubt as they are either
116 inappropriate for green roofs due to their open nature, or less efficient if alternatives
117 are used [Gupta et al. \(2020\)](#).

118 Biochar may raise the production costs of green roofs, resulting in higher final prices
119 for these products [Khan et al. \(2021\)](#). To evaluate its profitability for both producers
120 and end users, it is essential to compare its effects against using fertilizers alone or in
121 combination with fertilizers [Ye et al. \(2020\)](#). Additionally, given its environmental ben-
122 efits—such as minimizing nutrient leakage and boosting carbon sequestration—efforts
123 are underway to improve cost calculation models to include both private and soci-
124 etal costs and benefits [Campion et al. \(2023\)](#). However, these calculations are highly
125 case-specific, influenced by factors like location, feedstock, scale, pyrolysis conditions,
126 biochar pricing, and crop type. To promote greater adoption of biochar, [Campion
127 et al. \(2023\)](#) suggest developing standardized calculation models and emphasizing
128 additional societal benefits of biochar, such as improved water retention. While the
129 proposed model is comprehensive, it remains unclear how potential hazards associated
130 with biochar [Xiang et al. \(2021\)](#) will be addressed with it. Thus, the technoeconomic
131 benefits of biochar will be a focus of future research.

132 **1.2 Biochar adsorption capabilities**

133 Many variants of biochar have been employed for the purpose of removing contam-
134 inants in a soil or packed bed. [Afroze et al. \(2016\)](#) determined the adsorption of

135 methylene blue (MB) by eucalyptus bark biomass in a packed bed and found that it
136 performs well in the removal of dye-containing effluents. [Dawood et al. \(2019\)](#) ana-
137 lyzed the adsorption of MB in pine cone biochar in a packed bed column of Kaolin
138 clay and utilized several analytical models to determine breakthrough curves. These
139 curves were compared under varying experimental conditions and the biochar/clay
140 packed bed was found to perform best under low flow rates, high MB concentration,
141 and larger bed depth. [Zanin Lima et al. \(2023\)](#) analyzed competitive sorption and des-
142 orption of zinc, cadmium, and lead between compost, biochar, and peat. They found
143 that biochar had the highest adsorption capacity and lowest desorption rate, with lead
144 removal being the most effective. [Beesley et al. \(2010\)](#) examined the efficacy of biochar
145 and greenwaste compost on the reduction of zinc, cadmium, and copper within soils
146 and found them to be beneficial in the control of pollutants. [Pita et al. \(2024\)](#) provided
147 a review of the work associated with the use of biomass on the removal of pharma-
148 ceutical compounds and reported that biochar made from a variety of plants; such as
149 rice husks, corn, sawdust, and sugar cane, was the most effective in many industrial
150 applications, partly due to their high adsorption capacity. While the aforementioned
151 studies are valuable in understanding biochar as an adsorbent for a variety of contam-
152 inants, we are unable to identify the mechanisms by which it performs best, such as
153 available adsorbing surface area, effect on the flow field, or their pore storage capac-
154 ity. For this level of detail we must utilize numerical models which can describe such
155 systems and provide the level of detail we require.

156 The physical process of contaminant adsorption in a flow field is described mathe-
157 matically by the advection-diffusion of species, combined with adsorption/desorption;
158 a model which is present across many fields of application. This general model is used
159 to describe processes such as post-combustion CO₂ capture [Pröll et al. \(2016\)](#), deter-
160 mining optimal geometry of granular heat exchangers [Mitra et al. \(2018\)](#), analyzing
161 methane adsorption in subsurface shale deposits [Li et al. \(2016\)](#), and describing the

162 behavior of photocatalytic textiles [Robin et al. \(2016\)](#) to name a few. Investigations
163 into the dominant factors affecting adsorption rates and capacity have shown that
164 particle and pore morphology play an important role [Liapis et al. \(1999\)](#); [Jareteg
165 et al. \(2022\)](#). Adsorption rates themselves also strongly determine the process evolu-
166 tion [Marin et al. \(2014\)](#), with lower rates determining adsorption quantity by reaction
167 duration, and higher rates controlling quantity through reaction rate [Zakirov et al.
168 \(2023\)](#). Non-isothermal systems can result in high heterogeneity of concentration and
169 temperature, with performance suffering from regions of stagnant flow and increased
170 near-wall breakthrough [Verma and Mewes \(2009\)](#).

171 When one considers a transported reactive species adsorbed locally by reactive
172 elements within a porous matrix; understanding the underlying interactions which
173 determine the local concentration distribution is necessary. The mixing itself within
174 porous media has been shown to be complex at high Reynolds numbers (Re). As such,
175 the flow is characterized by an initial advection-dominated regime as the flow pene-
176 trates the pore network and is followed by a diffusion-dominated regime wherein the
177 molecular diffusion redistributes the scalar more effectively than the advection. The
178 advective regime consists of stretching of the scalar front in longer finger-like struc-
179 tures, particularly where the flow is strongest, and can be defined by by the plume's
180 concentration mean, variance, and probability distribution [Bonazzi et al. \(2023\)](#). A
181 thorough overview of current state of research and methods used to solve species
182 transport in porous media can be found in [Dentz et al. \(2023\)](#).

183 At low Re , over a short time these structures regress to a more uniform distribution
184 through molecular diffusion. However, even at low Re , the process of homogenization
185 by diffusion may be retarded by the presence of local chemical heterogeneities in the
186 form of solid adsorbing particles which affect the concentration field. The effect of
187 varying the quantity of uniformly distributed adsorbers within a porous medium was
188 undertaken previously, with two regimes in the evolution of the concentration field

189 identified and the rate at which one regime reaches the other is determined by the
190 number of adsorbing elements present [Maggiolo et al. \(2023\)](#).

191 The previous investigations cover primarily changes in adsorptivity, usually a static
192 value, with the values not necessarily reflecting realistic conditions. The geometries
193 generally tend to be regular, not reflecting in any way a realistic soil sample. We
194 will extend this characterization by introducing the presence of polydisperse particles
195 within the packed bed as well as an adsorption rate dependent upon a proposed adsorp-
196 tion capacity model for the biochar. In addition, we make use of experimental data to
197 correctly tune the simulations to realistic adsorption rates and determine how these
198 factors impact the previously identified regimes as well as report additional influences
199 on the biochar performance. The results are directly compared to experimental data
200 to assess the predictive accuracy of our model, quantified by breakthrough curves.

201 **2 Experiments**

202 The experiments outlined in this section have been undertaken for two purposes.
203 Experiment 1 was used calculate the adsorption capacity of the biochar which in turn
204 is an input in the numerical simulations used to compare against experiment 2. The
205 results for experiment 2 were directly compared to the numerical results to determine
206 the accuracy of the model used in this work. All experimental information is given in
207 this section, with the common materials introduced first, followed by each experiment
208 and its respective results.

209 The adsorption capabilities of two types of biochar were experimentally deter-
210 mined: wood-chip biochar (WCB) produced mainly from European spruce and
211 granulated biochar (GB) produced mainly from agricultural seed waste. The wood chip
212 biochar was produced by Hjelmsätters Fastigheter AB while the granulated biochar was
213 produced by Skånefrö AB; both companies being based in Sweden. [Figure 1](#) displays

214 the types of biochar used in the experiments. Alongside the types of biochar, acid-
215 washed glass beads were also used and acted both as an inert, transparent packing
material for the biochar and as a control case with minimal to no adsorption.

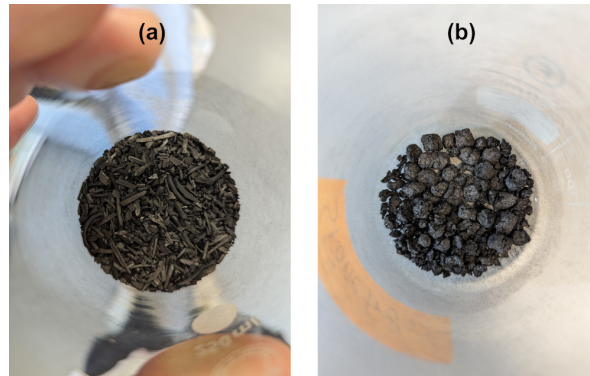


Fig. 1: Types of biochar (a) WCB (Hjelsåters Fastigheter AB) and (b) GB (Skånefrö AB).

216
217 MB, chemical formula $C_{16}H_{18}ClN_3S$, was used as the adsorbate; diluted to 6 mg/L
218 in a phosphate buffer solution containing 380 mg/L KH_2PO_4 and 300 mg/L K_2HPO_4 .
219 It is worth noting that due to its properties, methylene blue can be seen as an analog
220 for some organic pollutants however it is by no means representative of all possibilities.
221 Other compounds or the direct pollutant itself may be required for more accuracy and
222 the numerical model must be appropriately modified as well.

223 The MB concentration was measured using spectrophotometry with absorbance
224 measured at 680nm. Figure 2 shows the experimental setup that was used for
225 experiments 1 and 2.

226 2.1 Experiment 1

227 In experiment 1, a known mass of biochar or glass beads (1mm diameter) was placed
228 in a 5cm diameter Plexiglas column, as shown in Figure 3. The quantities of biochar

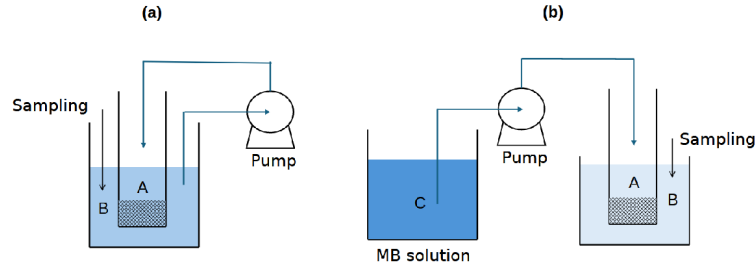


Fig. 2: Experimental setup for (a) experiment 1 and (b) experiment 2. A - Inner annular column containing porous medium, B - Outer annular beaker where MB sampling occurs, C - MB reservoir with original concentration c_0 used in experiment 2

229 were chosen such that differences in behavior would be evident while allowing for a
 steady-state to be reached within a reasonable time frame.

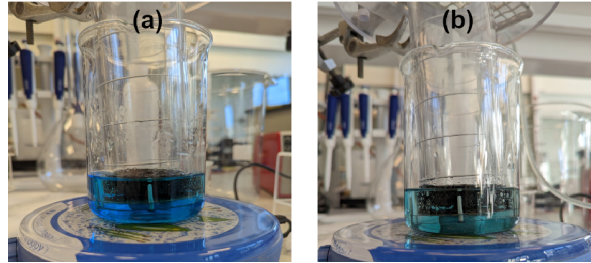


Fig. 3: Experiment 1 at (a) $t = 0$ min and (b) $t = 135$ min

230
 231 The bottom of the column was covered with a steel mesh which kept the biochar/
 232 glass beads within the column. The column was submerged in a glass beaker containing
 233 100mL of the MB solution, which was circulated through the biochar-packed column
 234 using a peristaltic pump operating at a flow rate of 4mL/min. The column is fully
 235 immersed in the MB solution to allow for the adsorption to occur at the maximum
 236 possible rate, which is a property of the biochar itself rather than a consequence of
 237 the local availability of adsorbent. Liquid samples from the solution being circulated
 238 through the Plexiglas column were collected regularly from the glass beaker. The quan-
 239 tity of biochar used in this experiment is determined such that the measured difference
 240 in adsorbance is clear as the quantity of biochar is increased.

241 Figure 4 shows the evolution of the normalized outflow concentration over time in
 242 experiment 1. Absorbance (A) is converted to concentration and normalized against
 243 the initial concentration c_0 . We define absorbance as $A = \log_{10}(I_0/I)$ where I_0 is the
 244 intensity of incident light at 680nm wavelength and I is the transmitted intensity.
 There is no large difference in the performance for the cases using WCB, even when

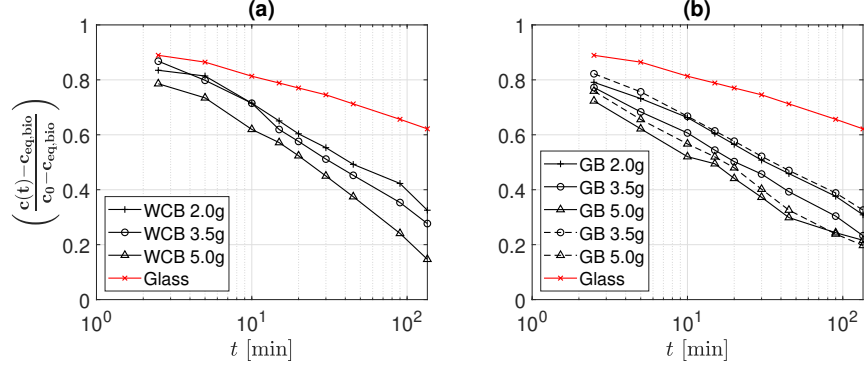


Fig. 4: Normalized outflow concentration for (a) Wood chip biochar (WCB), (b) Granulated biochar (GB)

245
 246 the quantity of biochar is increased to 5 grams; with the results for the GB being
 247 similar. To calculate the adsorption capacity of the biochar we employ the conservation
 248 equation

$$V_{bio}c_{eq,bio} = V_{liq}(c_0 - c(t_{end})) - V_{glass}c_{eq,glass}, \quad (1)$$

249 where V_{bio} , V_{glass} and V_{liq} are the biochar, glass and liquid volumes, c_0 is the initial
 250 concentration, c is the measured concentration, and $c_{eq,bio}$, $c_{eq,glass}$ are the measured
 251 adsorption capacities (equilibrium concentrations) within the biochar and glass, which
 252 is the quantity at which they cease to adsorb additional solute, at t_{end} . Table 1 gives
 253 the substrate composition for experiment 1 and the resultant calculated adsorption
 254 capacity (equilibrium concentration).

255 Equation (1) is ideal for calculating the maximum adsorption capacity and biochar
 256 equilibrium concentration given that experiment 1 runs until a steady-state is reached,

Table 1: Experiment 1, $Q = 4\text{mL}/\text{min}$ MB solution. WCB - wood-chip biochar, GB - granulated biochar. Calculated adsorption rate $k = 3.3e - 4. [\text{s}^{-1}]$

Material	Glass	WCB			GB				
Weight [g]	20.0	2.0	3.5	5.0	2.0	3.5	3.5	5.0	5.0
c_{eq}	0.24	0.42	0.45	0.52	0.43	0.47	0.42	0.48	0.49

257 however this equation is unsuitable for calculating the evolution of the concentration
 258 at the adsorbing surface over time. To this end we employ the formulation for the
 259 evolution of the concentration at the adsorber surface

$$-V_p \frac{dc}{dt} = S_p k (c(t) - c_{eq,bio}), \quad (2)$$

$$c(0) = c_0,$$

$$c(t \rightarrow \infty) = c_{eq,bio},$$

260 where the solution takes the form

$$c(t) = (c_0 - c_{eq,bio})e^{-S_p kt/V_p} + c_{eq,bio}, \quad (3)$$

261 where V_p, S_p are the reactive particle volume and surface area and the adsorption rate
 262 is calculated by solving (3) for k , as all other quantities are known. This formulation
 263 is based upon the assumption that the system is reaction-limited, which is valid since
 264 the biochar is initially fully immersed in the solution. Fully immersed biochar allows
 265 for the entire surface area of a reactive particle to contribute in the removal of the MB
 266 with maximum efficiency, hence reaction-limited. The calculated adsorption rate is
 267 used in the calibration of the simulations, as explained in section 3.2. It is important to
 268 mention that the above formulations cannot be used for the analysis of experiment 2 as
 269 it is mass-transport limited and thus we cannot make any assumption on the evolution
 270 of adsorption in time. Thus we are forced to model the rate at which the adsorption

271 capacity of the biochar is reached, and it's subsequent effect on the adsorption rate
 272 itself.

273 If one wishes to apply a simple capacity model to the system, the resulting bound-
 274 ary condition at the reactive particle surface will be as in equation (4). Note that this
 275 condition bears striking similarity to (2) but is distinct, supporting our claim equation
 276 (3) is not suitable for solving the mass-transport limited problem. In these equations
 277 D_m is the molecular diffusivity, Da the Damköhler number, and $f(c)$ the capacity
 278 model. This condition will be formalized in section 3.2 and is only presented here to
 279 demonstrate the differences in boundary condition between the experiments.

$$-V_p \frac{dc}{dt} = S_p D_m \frac{\partial c}{\partial n}, \quad (4)$$

$$\begin{aligned} \frac{S_p D_m}{Q} \frac{\partial c}{\partial n} &= \frac{k S_\zeta}{Q} f(c) c(t), \\ &= Da f(c) c^*|_{S_\zeta}. \end{aligned} \quad (5)$$

280 2.2 Experiment 2

281 In experiment 2, the Plexiglass column was filled with glass beads mixed with WCB to
 282 a height of 32mm. The biochar made up 15% of the column by volume and was either
 283 evenly mixed with the glass beads, placed as a layer at the bottom of the column, or
 284 placed as a layer at the top of the glass beads. The chosen fraction of 15% is motivated
 285 by the standard composition used in green roofs in industrial production, which varies
 286 but provides diminishing benefits beyond this fraction. The column was submerged in
 287 a beaker filled with approximately 100mL phosphate solution without MB. The MB
 288 solution was then fed to the top of the column at a flow rate of 8mL/min and the
 289 MB concentration in the solution surrounding the column was measured in regular
 290 time intervals. Table 2 outlines the cases shown in Figure 5, including variable particle
 291 distributions and the equivalent weight of the included biochar.

Table 2: Experiment 2, $Q = 8\text{mL}/\text{min}$ with MB solution. WCB - wood-chip biochar.

Material Type	%Biochar	Biochar [g]	Particle dist. [mm]
Glass Only	0.0	0.0	$\mu = 1.0$
Glass Only	0.0	0.0	$\mu = 1.0, \sigma = 0.5$
Glass + WCB	15.0	0.93	$\mu = 1.0, \sigma = 0.5$
Glass + WCB	15.0	0.93	$\mu = 1.0, \sigma = 0.5$
Glass + WCB	15.0	0.93	$\mu = 1.0$
Glass + WCB	15.0	0.93	$\mu = 1.0$

292 The results of experiment 2 are shown in Figure 5 in the form of normalized concen-
 293 tration outflow, also called breakthrough. Once again the data is normalized against
 an initial concentration. We see an initial period where little of the MB is adsorbed,

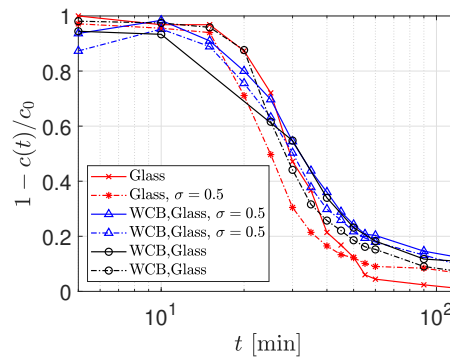


Fig. 5: Evolution of concentration breakthrough $1 - c(t)/c_0$

294
 295 whereafter the reaction rapidly reaches saturation within the biochar and little addi-
 296 tional MB solution is adsorbed, leading to a "steady state" in the breakthrough curve.
 297 These periods; the initial adsorption, the rapid saturation, and the ceasing of addi-
 298 tional adsorption can be characterized by the time intervals of i) $0 < t < 20$, ii)
 299 $20 < t < 70$, and iii) $t > 70$.

300 We see that the cases using only glass beads perform the worst, as expected. Inter-
 301 estingly these cases also adsorb some measure of MB, which means their behavior
 302 should be taken into account when examining the results of the cases which include
 303 biochar. Indeed, the inclusion of the quantities of biochar used in these experiments

304 show that they perform only marginally better than the glass beads themselves.
305 Another important point to note from Figure 5 is that there is little discernible dif-
306 ference between cases in which a variety of particle sizes are present and cases where
307 only a single particle size are used. This will be touched upon later in the numerical
308 simulation results, particularly when the concept of adsorption capacity of reactive
309 particles is present within the system.

310 **3 Numerical approach**

311 **3.1 Lattice Boltzmann method**

312 When one talks about solving the transport of a scalar, we formalize the concept using
313 the advection-diffusion equation

$$\frac{\partial c}{\partial t} = \nabla \cdot (D_m \nabla c) - \nabla \cdot (\mathbf{u}c) + R, \quad (6)$$

314 where c is a scalar (in our case concentration), t is time, D_m is the diffusion coeffi-
315 cient, \mathbf{u} is the advecting fluid velocity, and R is a sink/source term related to reactive
316 processes. At the micro-scale this equation can be represented using the Boltzmann
317 transport equation, which describes motion through particle streaming as well as
318 collisions.

319 It is an ideal choice for solving flows in porous media due to the complex geometry
320 involved and allows for detailed information of the flow dynamics to be extracted at
321 the pore scale. The system is solved on a lattice structure wherein each lattice element
322 consists of a centroid and nodes placed on a cubic convex hull. The fictive particles
323 travel along the lattice nodes governed by probabilities appropriate for the chosen
324 lattice geometry such that the macroscopic properties of the fluid are preserved [Succi](#)
325 [\(2001\)](#). A 3D regular cubic lattice with 19 degrees of freedom for movement (D3Q19)

326 is used and the solved equation is of the form

$$f_r(\mathbf{x} + \mathbf{c}_r \delta t, t + \delta t) - f_r(\mathbf{x}, t) = -\tau^{-1}(f_r(\mathbf{x}, t) - f_r^{eq}(\mathbf{x}, t)) + F_r \quad (7)$$

327 where $f_r(\mathbf{x}, t)$ is the distribution function at position \mathbf{x} and time t along the r -th
 328 direction; \mathbf{c}_r is the so-called discrete velocity vector along the r -th direction over time
 329 interval δt ; f_r^{eq} is the equilibrium distribution function; and τ is the mean collision time
 330 and is related to kinematic viscosity by $\nu = c_s^2(\tau - 0.5\delta t)$. The equilibrium distribution
 331 function $f_r^{eq}(\mathbf{x}, t)$ takes the form

$$f_r^{eq} = w_r \rho \left(1 - \frac{\mathbf{u} \cdot \mathbf{u}}{2c_s^2} \right), \quad r = 1 \quad (8)$$

$$f_r^{eq} = w_r \rho \left(1 + \frac{\mathbf{c}_r \cdot \mathbf{u}}{c_s^2} + \frac{(\mathbf{c}_r \cdot \mathbf{u})^2}{2c_s^4} - \frac{\mathbf{u} \cdot \mathbf{u}}{2c_s^2} \right), \quad r = 2 - 19 \quad (9)$$

332 where w_r is the appropriate weighting parameter for the D3Q19 lattice; ρ is the den-
 333 sity; c_s is the speed of sound; and \mathbf{u} is the velocity used for defining the equilibrium
 334 distribution functions, which can differ from the fluid hydrodynamic velocity, on the
 335 basis of the specific forcing scheme used.

336 The macroscopic flow quantities density and velocity, (ρ, \mathbf{u}) are thus related to the
 337 hydrodynamic moments as the following:

$$\rho = \sum_r f_r, \quad (10)$$

$$\rho \mathbf{u} = \sum_r \mathbf{c}_r f_r + \frac{\Delta t}{2} \left(\frac{\Delta P}{L} \right), \quad (11)$$

338 where $\Delta t = 1$ in our case. The force F_r as formulated by [Guo et al. \(2002\)](#) is applied
 339 to the fluid, which mimics the flow rate intensity during a rain event in our case as

340 described later in more detail, and is given by

$$F_r = \left(1 - \frac{1}{2\tau}\right) w_r \left(\frac{\mathbf{c}_r - \mathbf{u}}{c_s^2} + \frac{\mathbf{c}_r \cdot \mathbf{u}}{c_s^4} \mathbf{c}_r \right) \left(\frac{\Delta P}{L} \right). \quad (12)$$

341 **3.2 Solute adsorption implementation**

342 A solute adsorption rate is assigned to a percentage of chosen particles ζ such that
 343 their surfaces S follow the first-order kinetics given by:

$$-\frac{\partial c^*}{\partial \lambda_s^*} \Big|_{S_\zeta} = \text{Da } c^* \Big|_{S_\zeta}, \quad (13)$$

344 where Da is the Damköhler number, $c^* = c(\mathbf{x}, t)/c_0$ is the dimensionless concentration
 345 at position $\mathbf{x} = (x, y, z)$, and $\lambda_s^* = \lambda_S/d$ is the dimensionless direction pointing inward
 346 to the particle surface. The Damköhler number, a ratio of the reaction rate and the
 347 advective mass flow rate, is given by

$$\text{Da} = kS_\zeta/Q, \quad (14)$$

348 where k is the adsorption rate on the particle surface, S_ζ is the total reactive surface
 349 area expressed as a fraction ζ of the total particle surface area, and the flow rate is
 350 given by $Q = l_0^2 \varepsilon U$. Here l_0 is the porous domain width, ε is the porosity, and U is
 351 the mean streamwise velocity.

352 Numerically, the concentration field $c(\mathbf{x}, t)$ is solved using a second population
 353 which is transported by the fluid velocity \mathbf{u} . The solute is then initialized at the inlet
 354 of the porous media as a volume with concentration c_0 . The second lattice population,

355 denoted g_r , gives the local concentration field by

$$c(\mathbf{x}, t) = \sum_r g_r(\mathbf{x}, t). \quad (15)$$

356 We impose a Neumann boundary condition at the adsorbing surfaces for the scalar
 357 lattice Boltzmann quantity g_r . The distribution function at a fluid node \mathbf{x} in the
 358 proximity of an adsorbing surface placed at $(\mathbf{x} - \mathbf{c}_r)$ is corrected along the wall-normal
 359 direction r as

$$g_r(\mathbf{x}, t + 1) = \frac{-A_1 + A_2}{A_1 + A_2} g_r(\mathbf{x}, t) + \frac{2w_r A_3}{A_1 + A_2}, \quad (16)$$

360 where $A_1 = k$, $A_2 = D_m$, and $A_3 = 0$. This condition was developed by [Huang and](#)
 361 [Yong \(2015\)](#); [Huang et al. \(2016\)](#).

362 In order to limit the reactivity as the particle surface reaches high levels of concen-
 363 tration we apply a functional coefficient to the prescribed reaction rate. This limit is
 364 designed to act as an analog to the particles reaching a saturated state wherein they
 365 can no longer adsorb more of the solute, known as adsorption capacity. Several differ-
 366 ent functions were tested, including a triangular function as well as a sigmoid function
 367 however a simple linear function was chosen, of the form

$$f(c) = 1 - c/c_{eq}, \quad \forall c \leq c_{eq} \quad (17)$$

368 which allows for full reactivity at low values of concentration but reaches zero when the
 369 particle equilibrium concentration has been reached. This equilibrium concentration
 370 is set to $c_{eq} = 0.5$ and is based upon the results of experiment 1. This alteration is
 371 reflected in the adsorption boundary condition, becoming

$$-\frac{\partial c^*}{\partial \lambda_s^*}|_{S_\zeta} = \text{Da} f(c) c^*|_{S_\zeta}, \quad (18)$$

372 which is the equivalent of equation (4) presented in the previous section.

373 **3.3 Domain generation and operating conditions**

374 The pore structure used in the simulations is a packed bed generated by the applica-
375 tion of rigid body physics on falling spheres within a cylindrical container. Two such
376 cases are generated; i) a monodisperse case with a fixed particle diameter, and ii) a
377 polydisperse case with the mean diameter equal to that of the monodisperse case. The
378 particles are centered around a diameter of 1.0 with $2\sigma = \pm 0.82$ millimeters. A cubic
379 subdomain is then selected from the cylindrical container and the volume is discretized
380 into a binary matrix of $l_0^3 = 256^3$ computational nodes, giving the mean particle diam-
381 eter $d = 21.6$ nodes. The method by which the domain is generated and characterized
382 can be found in [Maggiolo et al. \(2023\)](#) such that domain integrity is assured and the
383 volumetric porosity is calculated to be $\varepsilon = 0.4, 0.36$ for the mono- and polydisperse
384 cases, respectively.

385 In order to simulate an intense rainfall event the Péclet number $Pe > 1$ and we
386 assume little inertial influence, thus $Re < 1$. We set the Damköhler number, $Da \approx 1$,
387 which represents equal magnitudes of molecular diffusion and reaction rates, as calcu-
388 lated in the experiment 2. By applying the conditions required above, the simulation
389 has $Re = 0.017$ and $Pe = 6.7$, which is representative of a rainfall event with intensity
390 of around 60mm/hr. The flow rate of experiment 2 is $Q = 8\text{mL}/\text{min}$, which converts
391 to about 600mm/hr, about double the world record rainfall intensity, with $Pe = 250$
392 and $Re = 0.17$. It is worthwhile to note that intensities higher than the record can be
393 reached when runoff is channeled to a porous surface, which is not naturally occur-
394 ring rainfall. While these values are higher than those chosen for the simulation, the
395 governing physics are identically balanced, as the originally defined conditions are all
396 satisfied, including $Da \approx 1$. With the above mentioned flow rates we have been able
397 to measure variations in concentration quantities in a few hours, which we found as a

398 good time lapse to minimize effects from changes in environmental conditions on the
399 measurements.

400 These conditions are used to tune $\Delta P/L$, the molecular diffusivity and viscosity
401 accordingly. It is worth mentioning that common rainfalls are between 3-8mm/hr,
402 however less common extreme events can reach 15-60 mm/hr or more. We can extrap-
403 olate the simulation conditions to lower rainfall intensities by accounting for the time
404 scale of the physical processes involved. The soil will not be as thin as that in the
405 simulations and no runoff infiltration front will be pure contaminant. Additionally,
406 one can alter the diffusivity to compensate such that the physically realistic process
407 is retained.

408 The resultant mean flow velocity is averaged over the entire domain, given by
409 $U = (\int_{j_0^3} u_z dl_0^3) / l_0^3 \varepsilon$. The Kozeny-Carman relationship stipulates that if the porosity
410 of a domain is altered the flow rate must be changed accordingly. Since in our cases
411 porosity is approximately unaltered, the resultant mean velocity for the polydisperse
412 case is the same. The biochar percentage is set to 30% in the simulations, double the
413 industry maximum recommendation, to improve statistical analysis on single particle
414 adsorption features without straying significantly from realistic conditions.

415 The initial concentration $c_0 = 1.0$ is applied to an inlet zone directly adjacent to
416 porous volume. The streamwise boundaries are assigned a periodic condition wherein
417 buffer zones are applied to the inlet and outlet boundaries to prevent any effect on the
418 flow within the porous zone. The lateral boundaries are assigned a free-slip condition.

419 The simulations are run in two steps; first the single phase velocity profile is solved
420 for each geometry and then the solute is added. In this way we solve only the steady-
421 state flow in the first stage and only the concentration profile in time in the second
422 stage. Six cases total are run on two different geometries, the details of which can be
423 found in Table 3.

Table 3: Case numbers corresponding to operating conditions. Adsorption rate, particle type, and adsorption capacity are altered between cases.

Case	k	Particle	Capacity
1	0.0	Mono	None
2	0.0	Poly	None
3	5.3e-6	Mono	Unlimited
4	5.3e-6	Poly	Unlimited
5	5.3e-6	Mono	Limited
6	5.3e-6	Poly	Limited

4 Results

4.1 Concentration profiles

We show a comparison of the concentration profile in the domain between the monodisperse and polydisperse geometries for all cases listed in Table 3.

Transverse cuts at $x/l_0 = 140/256$ are shown at the same timestep $t^* = 0.6$, given by $t^* = tU/l_0$, which corresponds to the time at which the majority of the reactive particles begin to reach their full capacity, in the cases with limited capacity. Particles marked with black stars indicate reactive particles. Figures 6(a), (c), and (e) display a more homogeneous front, all with the monodisperse geometry. We do see decreased homogeneity in figures 6(b), (d), and (f), where we have the polydisperse geometry. One can see clearly the difference in front homogeneity and indeed the formation of tendrils of higher concentration within these figures. We also observe a general trend of decreased homogeneity in the polydisperse cases with adsorption, (d) and (f), which we investigate in more detail in subsequent sections.

4.2 Average surface concentration and flux ratio comparison

The average surface concentration of all reactive particles is given in Figure 7. This quantity is calculated by summing the concentration on all particle surface nodes and dividing by the total amount of such nodes. In Figure 7(a) there is a great similarity

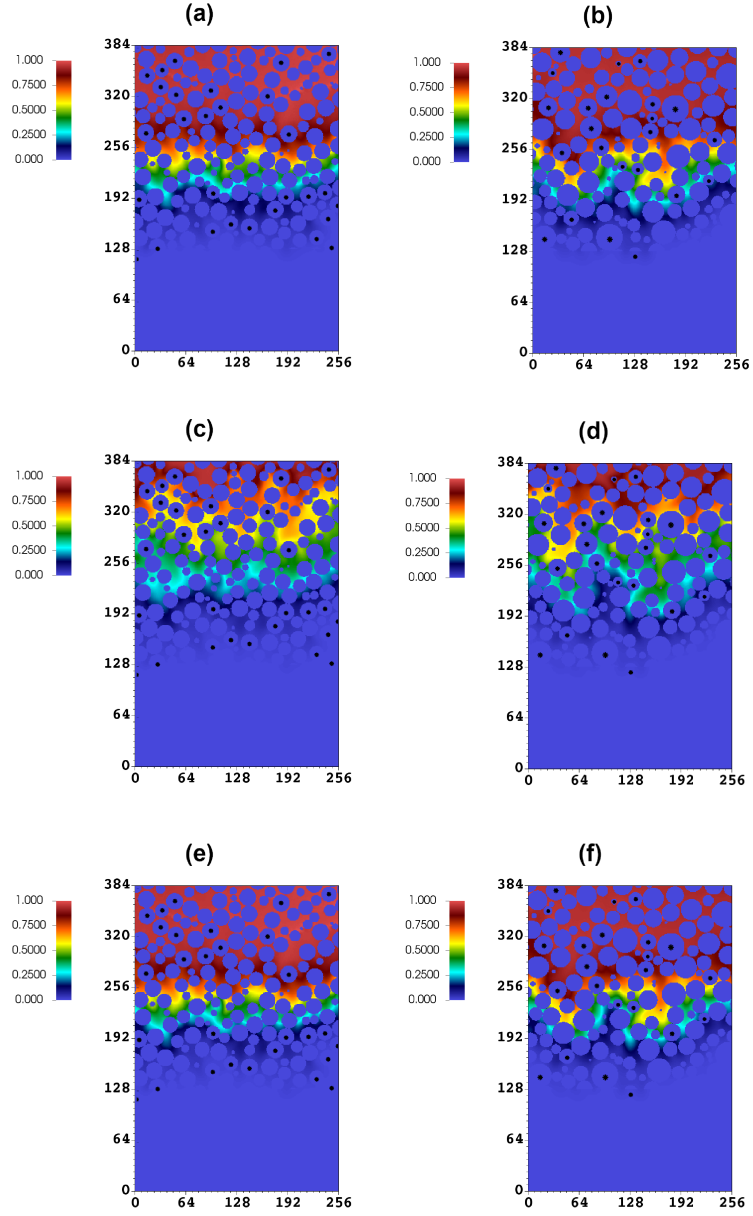


Fig. 6: Concentration profiles cut at $x/l_0 = 140/256$ and $t^* = 0.6 \approx 20$ min. Black stars indicate reactive particles. No capacity: (a) Case 1, (b) Case 2. Unlimited capacity: (c) Case 3, (d) Case 4. Limited capacity: (e) Case 5, (f) Case 6. The polydisperse cases (right panels) appear to generate a less homogeneous concentration front.

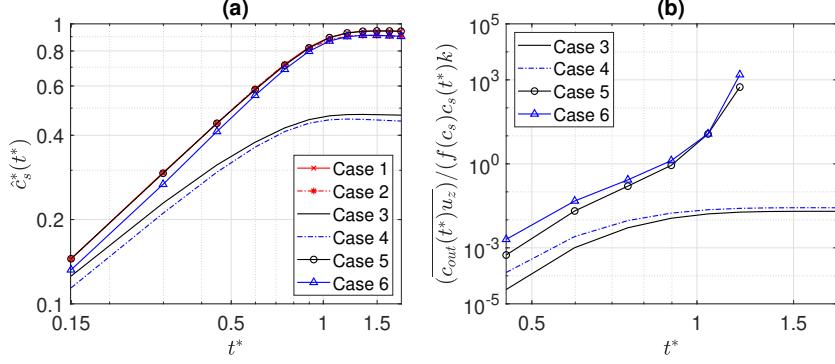


Fig. 7: (a) Average surface concentration and (b) breakthrough flux/adsorption flux ratio as a function of dimensionless time. No capacity: Case 1,2. Unlimited capacity: Case 3,4. Limited capacity: Case 5,6

442 of behavior between the cases with no capacity and those with a limited adsorption
 443 capacity. We see the surface concentrations increase to near unity as the reactive
 444 particles are no longer capable of removing more solute from the liquid. On the other
 445 hand, if one examines the cases with unlimited capacity we see a significantly reduced
 446 surface concentration, around 0.5. This is their effective equilibrium state and further
 447 reduction or buildup will not occur without external stimulus. We also note that there
 448 is little difference between the monodisperse and polydisperse geometries, implying a
 449 similar total reactive surface area despite the difference in individual particle surface
 450 areas, which is the case.

451 In Figure 7(b) the ratio of the breakthrough flux and the adsorption flux is shown.
 452 This quantity can be seen as a measure of the medium leakage reduction as a con-
 453 sequence of biochar adsorption. Note that the cases with the limited capacity model
 454 end prematurely due to the particles ceasing to adsorb after reaching their adsorption
 455 capacity. The ratio in the beginning of the simulations is extremely small, indicating
 456 adsorption is the dominant flux in the system, however this reduces significantly as
 457 the simulations progress. This is expected since the concentration flux at the outlet
 458 will increase over time as the solute travels through the medium. At longer times the

459 ratio for the unlimited capacity cases stabilizes at around 10^{-2} indicating an equi-
 460 librium between the adsorption and the breakthrough flux throughout the simulation
 461 lifetime. This is not true in the cases with limited adsorption capacity, wherein we
 462 see an inflection point at which the particles cease to react and the breakthrough
 463 flux quickly becomes the only contributing factor. This period of approaching particle
 464 inertness is quite similar for both geometries, indicating a negligible effect of the front
 465 homogeneity on this macroscopic quantity.

466 4.3 Breakthrough curves (vs. experiments)

467 Breakthrough curves are calculated for all cases and displayed in Figure 8 where (a)
 468 is the average concentration present in a small outlet volume the thickness of one
 469 particle diameter calculated as

$$\overline{c_{out}(t^*)u_z} = \left(\int_{V_{out}} c_{out}(t^*)u_z dV_{out} \right) / V_{out} \quad (19)$$

470 where $V_{out} = l_0^2 \varepsilon d$ and (b) illustrates the comparison of like cases between the exper-
 imental results and the simulations. In these graphs, a value of 1 represents a full

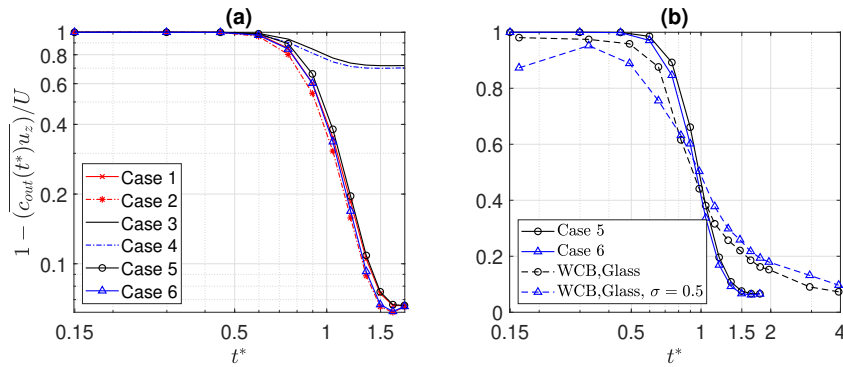


Fig. 8: Breakthrough curves for (a) simulation and (b) between like experimental cases and simulations. 1 - no solute reaches outlet, 0 - no adsorption has occurred, all solute reaches outlet. No capacity: Case 1,2. Unlimited capacity: Case 3,4. Limited capacity: Case 5,6

471 reaction wherein nothing reaches the outlet and 0 represents no change in concentra-
472 tion between inlet and outlet, i.e. nothing has been removed. It is immediately clear
473 in Figure 8(a) that unlimited capacity cases perform significantly better in terms of
474 leakage than those which have a limit or have no reactivity. Interestingly, there is lit-
475 tle difference in performance between the cases with no adsorption capacity and those
476 with limited capacity. This is due to the fact that the limited capacity particles reach
477 capacity very swiftly and thus contribute very little to removing the solute after the
478 earlier stages of the simulation.

479 This hypothesis is given some weight by Figure 8(b) where two experimental cases
480 are directly compared to the simulation cases with limited adsorption capacity. We
481 find a very similar behavior in that both experiments and simulations swiftly reach
482 capacity and subsequently remove little of the solute. Note that there is an initial
483 period of time for the MB solution to reach the porous media through the piping and
484 we do not take wall effects into account in the simulation; both of which are present in
485 the experiment. Consequently, the experimental curves have a lower gradient and take
486 additional time to reach full capacity, however the steady-state behavior is correctly
487 reflected by the simulations.

488 At lower rainfall intensities we expect to see an increased residence time of the
489 adsorbent near the biochar surfaces, however this will not matter if the biochar is
490 already at capacity. In addition to the uncertain reaction kinetics, lower rainfall inten-
491 sities may also result in unsaturated flow conditions, radically altering the system and
492 introducing capillary forces, making any prediction based upon the current work void.
493 Finally, a lower flow velocity may transition from more complex mixing caused by the
494 microstructure to a more simplified laminar flow in larger pore spaces.

495 **4.4 Flow homogeneity and outlet flow profile**

496 We examine the probability distribution for the streamwise and transverse velocity
 497 magnitude as a quantification of the flow homogeneity within each geometry as well
 as compare between the two.

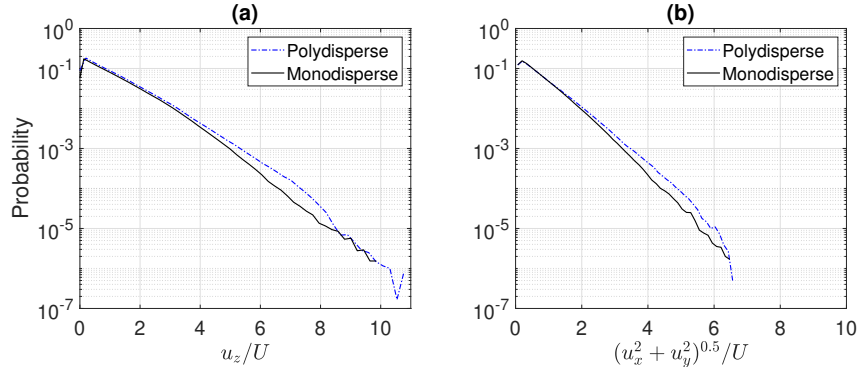


Fig. 9: Probability distribution of the domain velocity with (a) u_z/U where u_z is the streamwise velocity component and (b) $(u_x^2 + u_y^2)^{0.5}/U$ the transverse velocity magnitude

498
 499 Figure 9(a) shows the normalized streamwise velocity and it is clear that the
 500 streamwise velocity is largely similar to that of the mean velocity. However, varia-
 501 tions up to 10 times that value exist within the flow field which is also reflected in the
 502 distribution of the transverse velocity. There is no real discernible difference in the
 503 distributions between the two geometries, thus we can be reasonably confident that
 504 the flow alone is not a primary factor in notable differences observed between cases.
 505 Indeed, we do see increased inhomogeneity induced by increased adsorption in the
 506 front profiles shown in Figure 6.

507 Figure 10 displays the probability distributions for the breakthrough flux, measured
 508 $c(t^*)u_z/U$, as a quantification of the flow homogeneity at the outlet. This gives an
 509 indication of how the flow interacts with the reactive particles, producing tendrils

510 of increased concentration as opposed to a more uniformly distributed concentration
 511 front.

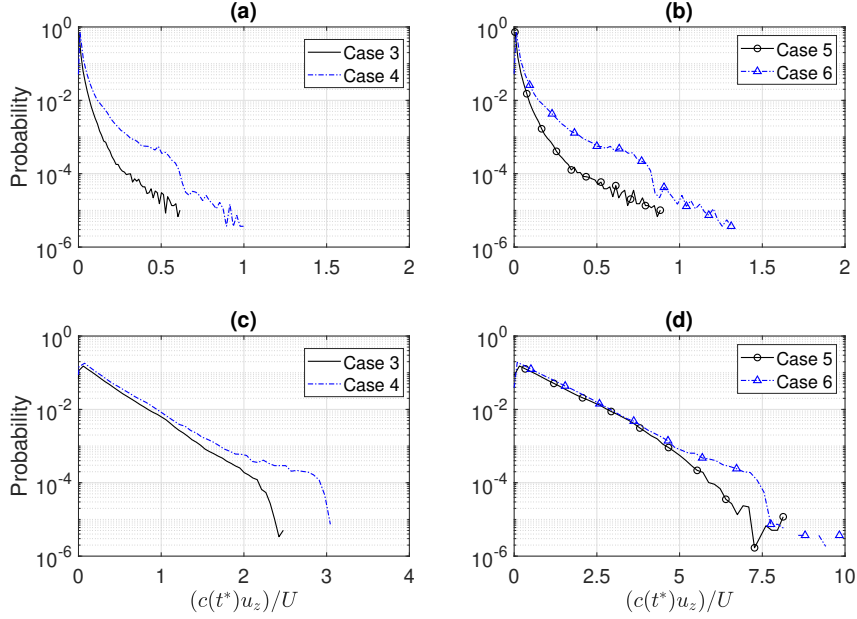


Fig. 10: Breakthrough flux distributions for (a) Unlimited capacity, $t^* = 0.6$ (b) limited capacity, $t^* = 0.6$ (c) Unlimited capacity, $t^* = 1.5$ (d) limited capacity, $t^* = 1.5$

511

512 We compare the distributions during the period where the solute first reaches the
 513 outlet ($t^* = 0.6$), figures 10(a) (unlimited capacity) and 10(b) (limited capacity) and
 514 when the steady state at the outlet is reached ($t^* = 1.5$), figures 10(c) (unlimited)
 515 and 10(d) (limited). A value near 1 indicates tendrils of high concentration trans-
 516 ported at a velocity around that of the streamwise mean velocity. Deviations from
 517 this imply a change to the local concentration or streamwise velocity. In other words,
 518 fluctuations around the mean of the concentration flux. Note a strong similarity in dis-
 519 tribution between 10(a) and 10(b), though the measured concentration flux is slightly
 520 higher in the limited capacity case. In all cases the monodisperse geometry exhibits
 521 a lower and tighter distribution of outflow concentration, indicating higher and more

522 efficient adsorption of the solute. The largest deviation is found in Figure 10(d), which
523 compared to the unlimited capacity case in 10(c), has a higher concentration flux mag-
524 nitude. We know from our analysis of the flow itself there is little influence on the flow
525 induced by each geometry, thus the adsorption rate spatial distribution is the likely
526 cause for this phenomenon.

527 4.5 Particle adsorption capacity

528 Figure 11 displays the PDFs of average particle surface concentration c_s^* during the
529 transition stage $t^* = 0.6$, figures 11(a),(b) wherein particles are reaching their capacity
530 and begin to become non-reactive. The lower figures, (c),(d) show the same cases,
531 however the timestep is altered to reflect the steady-state distribution found at $t^* =$
532 1.5. Figures 11(a),(c) are unlimited capacity and (b),(d) are limited capacity. The
533 order of cases and times is replicated for Figure 12.

534 Figure 12 displays PDFs for the surface concentration flux $c_s^* S_p / S_\mu$, using the
535 prefactor S_p / S_μ , where S_p is individual particle surface area and S_μ is mean particle
536 surface area. This ratio is the measure of the available adsorptive surface area com-
537 pared to that of the ideal surface area of a representative particle. When combined
538 with a particle's surface concentration we can get an idea of which particles are more
539 effective individually in terms of the adsorptive flux.

540 In Figure 11 we show the distribution of each particles' average surface concentra-
541 tion, taken at an intermediate and steady-state time. We observe no notable differences
542 between the monodisperse and polydisperse geometries. At the intermediate time the
543 distribution for the limited capacity cases exhibits the U-shaped distribution typi-
544 cal of diffusion-dominated systems, with two peaks at the extrema. In the cases with
545 unlimited reactivity the peak at higher concentration disappears due to the contin-
546 uous adsorption, figure 11(a). At the steady-state, the cases with limited adsorption

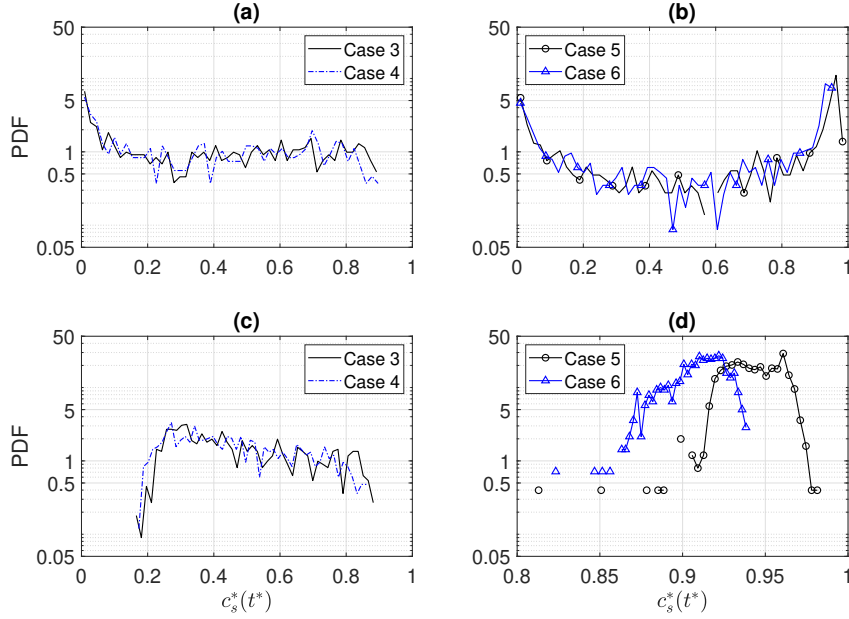


Fig. 11: Particle average surface concentration PDFs for (a),(b) $t^* = 0.6$ and (c),(d) $t^* = 1.5$. Unlimited capacity: Case 3,4. Limited capacity: Case 5,6

547 tend towards concentration of 1 with a very narrow distribution of values whereas the
 548 unlimited are more widely distributed, figures 11(c),(d).

549 When one examines the surface concentration flux $c_s^* S_p / S_\mu$ in the cases with unlim-
 550 ited capacity, figures 12(a),(c), we observe a similar behavior to that of the average
 551 particle surface concentration. As expected, a similar trend is also evident in the
 552 monodisperse case with limited capacity, figures 12(b),(d), when compared to the dis-
 553 tribution evolution in time of figures 11(b),(d). Indeed $S_p / S_\mu \approx 1$ in the monodisperse
 554 case.

555 This is not reflected in the polydisperse case with limited capacity. At longer times
 556 where the concentrations are uniformly $c_s^* \approx 1$, the fluxes will tend to the distribution
 557 of S_p / S_μ , figure 12(d). Due to the fact that the particle radii are normally distributed,
 558 the probability of S_p / S_μ will be χ^2 distributed, exhibiting an exponential decay away
 559 from the mean.

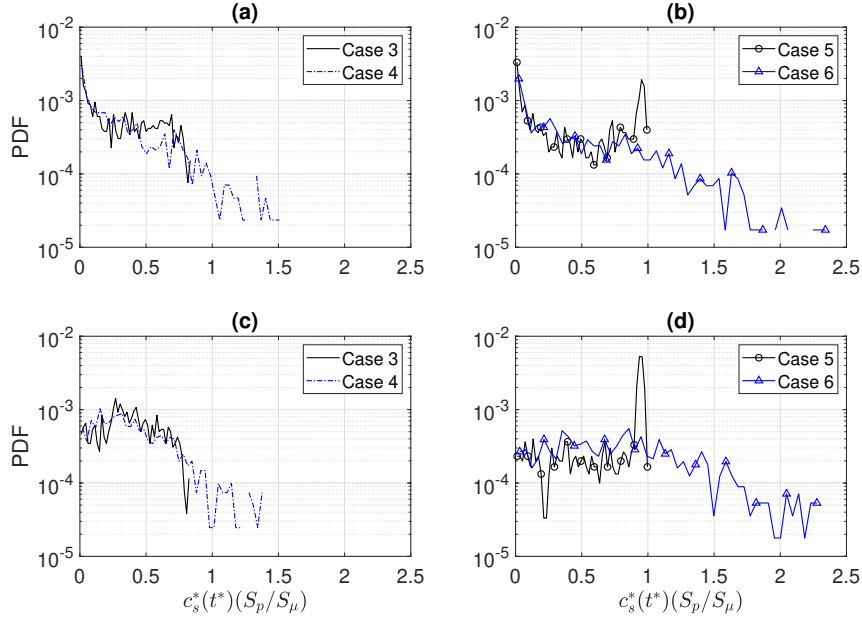


Fig. 12: Surface concentration flux PDFs for (a),(b) $t^* = 0.6$ and (c),(d) $t^* = 1.5$. Unlimited capacity: Case 3,4. Limited capacity: Case 5,6

Table 4: Ratio of mean particle size with concentration higher than concentration threshold vs. mean particle size of the rest at $t^* = 0.6$

Concentration	0.3000	0.5000	0.7000	0.9000
Ratio of means	0.9924	0.9908	0.9515	0.8853

560 Interestingly, at the intermediate time, the distribution of the fluxes preserves the
561 peak at low concentration whereas the peak at higher concentration visible in the
562 monodisperse case here is absent for the polydisperse case. We calculate the ratio of
563 mean particle size with concentration higher than a certain threshold against the mean
564 size of the remainder particles, shown in Table 4. It is noticeable that high surface con-
565 centrations, that is above a specified threshold, are found on smaller particles. In turn
566 the distribution of fluxes ($c_s^* S_p / S_\mu$) decreases uniformly as the flux itself increases,
567 figure 12(b). This may indicate that some particles in the polydisperse geometry are

568 being underutilized. If one examines the cuts shown in Figure 6 where the polydis-
569 perse cases display preferential pathing we see some occurrences of preferential paths
570 probably following high concentrations around smaller particles which have reached
571 capacity.

572 The behavior discussed above regarding the monodisperse geometry is indicative
573 of a more homogeneous front, where the particles are either being approached by the
574 front or are surrounded by it, whereas the front reaches the particles in the polydisperse
575 geometry at different times, leading to a higher distribution of different magnitudes.
576 We note that the monodisperse case exhibits an overall higher surface concentration
577 at the steady-state than that of the polydisperse cases. This is coupled with a simi-
578 larly lower breakthrough flux. One explanation for this is the increased inhomogeneity
579 observed in the concentration profiles for the polydisperse geometry. This preferential
580 pathing by the formation of tendrils of higher concentration removes solute from reach-
581 ing particles that would otherwise aid in the removal of concentration from the flow.
582 This channeling effect reduces the efficiency of the reactive particles as some avail-
583 able surface area is left unused, effectively underutilizing them. A more homogenous
584 front allows for the maximum surface area to be reached at any given time.

585 Figure 13 shows the particle diameter and surface area distributions to aid in the
586 interpretation of the results as discussed above. Figure 13(a) shows the distribution
587 of reactive particles only and all particles for the polydisperse case as well as the
588 resultant normal distribution curve. The distribution of dimensionless surface area is
589 shown in Figure 13(b) for the polydisperse case only. It is compared to the ideal PDF
590 of diameter squared d^2 which follows a χ^2 distribution. The difference observed are
591 due to surface contact or cutting along the domain edges. Despite this fact, we are
592 satisfied that the distributions shown here justify the discussion we have entertained
593 regarding geometry effects and the potential for preferential pathing induced by the
594 polydisperse geometry in particular.

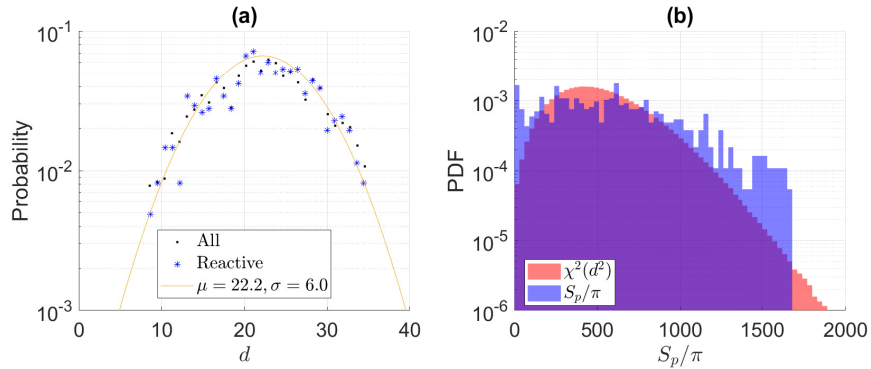


Fig. 13: (a) Particle diameter d distribution in l.u.. Dots indicate all domain particles, stars are just reactive particles. Line is the normal distribution function with $\mu = 22.2, \sigma = 6.0$. (b) PDF of reactive particle surface area S_p/π (blue), $\chi^2(d^2)$ distribution of particle diameter d (red)

595 We can now state with reasonable certainty that reactive particles do influence the
 596 concentration profiles, particularly the available reactive surface area. An advantage
 597 may be achieved by using more monodisperse particles, as they promote a more homo-
 598 geneous front for the advancing solute and reduce the solute leakage, particularly in
 599 the case of particles with limited adsorbing capacity.

600 4.6 Modifying the reaction kinetics

601 We close the paper with a short discussion on the practicalities of accurately modelling
 602 the adsorption dynamics present in reality on the surface of biochar. There are several
 603 different mechanisms by which adsorption occurs; namely pore-filling, hydrophobic
 604 interaction, surface complexation, electrostatic interaction, hydrogen bonding inter-
 605 action, $\pi - \pi$ electron-donor-acceptor (EDA) interaction, and intra-particle diffusion.
 606 In addition it has been shown that thermal conditions as well as the pH of the envi-
 607 ronment play a non-negligible role in the reaction speed [Ji et al. \(2024\)](#); [Gupta et al.](#)
 608 [\(2020\)](#), as does aging or the presence of dissolved organic matter. The sum total of
 609 considering individual biochar characteristics, their intrinsic modes of adsorption, as
 610 well as environmental factors renders the modelling a significant challenge. In general

611 current works have made use of first and second order pseudo-kinetic models along-
612 side Langmuir and Freundlich isotherms. Some forays have been undertaken in the
613 realm of applied artificial neural networks and statistical chemical modelling however
614 this is still in its infancy for such an application. If one wishes to enhance the models
615 governing the reaction kinetics we need more experimental data to determine which of
616 the above modes of adsorption should be considered and how the environmental and
617 aging aspects can be included in the models. While some kind of pre-factors can be
618 easily applied they are not representative of any physical phenomenon and some possi-
619 ble empirical model must be constructed which accurately captures these effects may
620 be a simple and efficient solution. Alternatively the full chemical species and reactions
621 can be included in the modeling but this undertaking may not be compatible with
622 how the lattice Boltzmann method operates but would ensure a more chemically con-
623 sistent interaction. Pore filling and intra-particle diffusion might be handled via some
624 volumetric functions that account for internal pore volume and pore network but this
625 is also impractical to implement. Whichever strategy is used, more experimental data
626 is likely to be required and understanding the fundamental physical interactions in
627 such a system are a good place to aid in determining where to next add the increased
628 realism required for more accurate and applicable predictions.

629 **5 Conclusion**

630 Experiments have been undertaken to determine the adsorption rate and capacity of
631 two different kinds of biochar alongside breakthrough curves for same. The break-
632 through curves are calculated using the absorbance of an MB solution over a period
633 of time. Simulations are run using the experimental data and a comparison is made
634 between the predicted breakthrough curves and the experimental results, with good
635 agreement found.

636 A deeper investigation of the underlying factors determining the concentration field
637 evolution is described. This analysis consists of flow velocity and breakthrough con-
638 centration profiles, average and individual surface concentration distributions, particle
639 capacity distributions, and a flux ratio comparison. The results show that the flow
640 velocity distribution remains the same for both simulated geometries, implying that
641 the differences in concentration distribution may not be a result of the flow velocity
642 profile. Examination of the breakthrough curves and individual particle concentra-
643 tion distributions show that the polydisperse geometry promotes preferential pathing
644 throughout the medium and leads to a more varied distribution of particle states
645 than those found in the monodisperse cases. This preferential pathing is undesirable
646 in the context of removal of contaminants from the flow, as a more homogeneous
647 front ensures the randomly distributed reactive particles will interact with the solute,
648 whereas tendrils may bypass them entirely and flow directly for the outlet.

649 We have chosen to use spherical packed beds over a realistic soil substrate geom-
650 etry due to the intrinsic inhomogeneity found within soil scans taken using x-ray
651 microtomography (XMT) or any similar technique. A chosen domain may contain few
652 very large particles and multitudes of tiny particles or anywhere in between, rendering
653 the porosity of any such domains fluctuating wildly, making comparisons difficult. In
654 future it is worthwhile to determine if the trends observed in this work hold true for
655 the realistic soils as well.

656 If one extends these results to application recommendations, we can state that
657 the observed differences between the mono- and polydisperse cases are larger than
658 those observed when biochar is present or not. This would correspond to cases 1
659 and 2 (no biochar) and 5 and 6 (biochar with a limited capacity). The concept of
660 limited adsorption capacity is analogous to the realistic adsorbance occurring in the
661 experimental biochar, which cannot remove the solute indefinitely. These cases only
662 slightly outperform the cases in which there are no reactive particles present. This

663 is due to the rate at which the limited capacity particles reach capacity and become
664 inert. Cases 3 and 4 have unlimited capacity, which one could say is analogous with
665 roots or some other living biological matter that does not have a capacity in the same
666 manner as biochar.

667 The practical implication here is that monodisperse beds are preferred as they pro-
668 mote more even distribution of the solute within the domain and thus allow the random
669 adsorbers to act with maximum effect, i.e. reaction-limited. Additionally, the presence
670 of adsorbers with an unlimited adsorption capacity must be taken into account as this
671 can dramatically effect the results, particularly in proximity to each other. This effect
672 will obviously increase if the adsorption rate is increased.

673 If one wishes to increase the efficacy of biochar, a high absorptive rate with a
674 similarly high capacity will greatly reduce breakthrough. This can be accomplished
675 by modifying the material itself and/or increasing the total quantity of biochar within
676 the soil, which will consequently increase its capacity. Current practice suggests no
677 more than 15% biochar by volume is beneficial given common rainfall quantities;
678 however our results show that performance can be increased if one takes into account
679 the factors mentioned above, with the additional mention of total reactive surface
680 area and the idea of induced preferential pathing. Lower rainfall intensities will cause
681 higher residence time of the concentration front near the biochar; however once they
682 saturate, which we show can take place quite quickly, breakthrough will still occur.
683 Thus a more accurate method for modeling the capacity of different adsorbers should
684 be investigated to improve the predictive ability of the models. Finally, given that
685 monodisperse particles promote a more homogeneous concentration front and that
686 total reactive area matters more than individual particle size we suggest that more
687 uniform sized substrates are used.

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