Plume mixing determines contaminant leakage from saturated chemically heterogeneous porous subsurfaces

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We show the impact that stretching and mixing has on the fate of plumes of waterborne contaminant solutes transported through a chemically heterogeneous, partially adsorbing porous medium, at a typical Péclet number characterizing saturated flows in subsurfaces, \( Pe = O(1) \). Via pore-scale lattice Boltzmann simulations, we follow the dynamic of a passive scalar injected in a packed bed consisting of a mixture of chemically inert and adsorbing spherical particles. By varying the fraction of the adsorbers, randomly and uniformly distributed in the porous volume, and the adsorption rate, we find that the waterborne solute forms different plumes emerging between pairs of adsorbing particles. The plumes are stretched at a rate linearly increasing with time and inversely proportional to the adsorbers’ interparticle dimensionless distance \( \xi^* = \xi/d \), with \( d \) being the pore size. We provide a relationship between the characteristic small-scale scalar concentration width \( \sigma_B \) and the adsorption-induced stretching rate. The stretching process competes with diffusion broadening to asymptotically determine \( \sigma_B/d \propto (Pe/\xi^*)^{-1/2} \) and sets the characteristic scale of concentration width larger than the characteristic pore size, that is \( \sigma_B > d \). Because of the latter condition, small scalar structures overlap among adjacent pores until mass transport and adsorption are equilibrated at a time \( t_\xi \), when the plume is well-mixed at a larger scale, corresponding to its transverse cross-section dimension. The plume mixing rate related to the average flow velocity \( 1/(Ut_\xi) \) very well approximates a macrohomogenous adsorption coefficient, thus predicting the macroscopic adsorption process and the probability of solute leakage from the porous volume. On the basis of these observations, we also derive the probability of formation of large solute plume volumes, which we find to exponentially decay with large \( \xi^* \) and small fraction of adsorbers.

I. INTRODUCTION

Transport of waterborne solutes in porous media occurs in many natural processes and engineering applications. Of particular interest in the context of environmental pollution is the transport of contaminants in subsurfaces, both in agricultural and urban environments. Such pollutants are indeed carried by moving fluids within soil media in agricultural landscapes as well in the urban substrates devoted to the control of rain events, such as green areas and green roofs. In such subsurface environments, a rain event is the usual triggering mechanism, which induces the movement of fluids through the porous spaces, carrying contaminants gathered from the external environment or internally present in the soil media and mobilized by the flow. A notable example of such contaminant sources are fertilizers, which occur as solid particles that dissolve in water infiltrating the subsurface and cause pollution of aquifers and urban water systems. [1, 2].

A promising solution to prevent such pollution scenarios is the introduction of adsorbers in the soil media, such as biochar, able to adsorb the waterborne pollutants [3,4]. Biochar not only provides a sink for waterborne contaminants, but also supports plant growth [5]. In this scenario, the porous system becomes strongly heterogeneous in its chemical adsorption capacity, being formed of a mix of chemically inert and adsorbing particles. The identification of an effective strategy for the introduction of adsorbers requires not only knowledge of the specific surface chemistry determining the solute contaminant adsorption onto and into biochar particles, but also of the fluid-dynamic mechanisms that govern the mobilization, transport and spatial redistribution of solute molecules transported within such an heterogeneously adsorbing porous medium.

The transport of a solute in a porous medium is a complex mechanism that may exhibit chaotic features also in laminar flows through three-dimensional homogeneous materials. It has been shown how the specific topological traits
that distinguish three-dimensional porous materials, a sequence of pore throats in the proximity of grain contact points and enlargements in the cores of pore spaces, trigger stretching and folding of pockets of solute, leading to anomalous dispersion and chaotic advection [6, 7]. This anomalous behaviors may persist as long as the advective forces are on the same order of magnitude as molecular diffusion, i.e., for a finite value of the Péclet number $Pe \gtrsim 1$ [8]. Such a condition holds for water infiltration into agricultural soil and urban green substrates during moderately intense rainfall events of the order of 10 mm/h, which implies that, in the typical millimeter-size pore space of soil media, the water infiltration rate is of the same order of the molecular diffusive rate of contaminants [9]. With the trend of increasing intensity of stormwater events in Northern latitudes [10], the condition $Pe \gtrsim 1$ is likely to be encountered even more frequently in such urban and agricultural areas.

A pore-scale characterization of the transport is thus necessary to understand the behavior of a waterborne contaminant flowing into a subsurface. Direct visualization of mixing in porous media via high-resolution experimental images at high Péclet numbers has recently confirmed the role of diffusive and advective forces in stretching scalar elements and determining the rate of the chaotic dispersion [11], the mixing of initially separated scalars [12] and, in turn, the intensity of the chemical gradients that control pore-scale reaction and adsorbing mechanisms [8]. Such experiments, complemented with pore-scale numerical studies, have supported the development of mathematical formulations able to predict the stretching and mixing processes of transported scalars in homogeneous and heterogeneous media [13–15] and their impact on reactive processes [16]. Nevertheless, research on the impact of pore-scale heterogeneous adsorption on stretching and mixing is instead scarce. Adsorption in porous media can be regarded as a filtration process which strongly depends on the pore-scale transport mechanisms, and macroscopic models can be formulated in order to take into account the pore-scale geometrical features that affect local fluid velocities [17]. In the presence of chemical heterogeneities of the medium surfaces and of their adsorption processes, predictive macrohomogeneous models for contaminant transport must include the effects of spatial variation of both pore-scale velocities and local adsorption rates [18], which may greatly impact the fate of the transported scalar as local disturbances in hydraulic conductivities [19]. Effective velocity, dispersion, and reaction exhibit a complex dependence on the physical parameters, Péclet and Damköhler numbers, making the prediction of such transport mechanisms challenging from a mathematical point of view [20]. In the present study, we clarify the role that the introduction of chemically adsorbing particles in inert porous media has on the mechanisms of mixing, stretching, and macroscopic transport and adsorption of a waterborne contaminant. We will study such a scenario via pore-scale numerical simulations with varying the volume fraction of adsorbers introduced in a homogenous packed bed for a moderate value of the Péclet number, $Pe \sim O(1)$ and typical adsorption rates of waterborne pollutant into carbonaceous material, such as biochar. We will provide a relationship between fraction of adsorbers and stretching process of the transported scalar, which will allow us to determine the characteristic small-scale sizes and structure of the contaminant concentration. We will show how scalar transverse mixing at the contaminant plume scale determines the macroscopic adsorption rate, and we will propose a model to predict the contaminant leakage from such chemically heterogeneous porous media.

II. NUMERICAL METHOD

A. Pore structure generation and surface adsorption

We generate a packed bed sample by solving the rigid body dynamics of falling spherical particles within a cylindrical container [21, 22]. A cubic domain is then selected within the container and the volumetric space is discretized in equally sized voxels, so that the spherical particle diameter and the domain size are $d = 21.6$ and $\ell_0^3 = 256^3$ computational nodes, respectively. We check planar porosity values along the packing direction $z$ to ensure that the selected volume is sufficiently distant from the container walls and it is homogeneous, see Fig. 1, panels (a) and (b). The volumetric porosity is $\Phi = 0.39$, from which we calculate the effective number of particles contained in the volume space as $n_0 = \ell_0^{-3} \left(1 - \Phi\right)/\pi = 1939$, with $\ell_0^3 = \ell_0/d$ the dimensionless domain size along the three Cartesian directions. We compute the pore size distribution via a watershed algorithm and extract an equivalent average pore diameter $\approx d$. For each simulation case, we select a random fraction $\xi$ of spherical particles (via a random uniform permutation of particles indexes) and along their surface $S_\xi$ we assign a solute adsorbing rate expressed via the following first-order reaction kinetics:

$$Da \frac{\partial c^*}{\partial \eta_s^*} \bigg|_{S_\xi} = -\frac{\partial c^*}{\partial \eta_s^*} \bigg|_{S_\xi},$$

where $Da = k a d^2/D_m$ is the Damköhler number characterising the ratio between adsorption rate $k$ and diffusion rate $D_m/d^2$ (with $D_m$ the molecular diffusion), $c^* = c(x,t)/c_0$ is the dimensionless concentration at position $x = (x,y,z)$ and time $t$ that refers to the injected concentration $c_0$, and $\eta_s^* = \eta_s/d$ is the dimensionless direction pointing inward...
steady-state flow field, whose dimensionless solenoidal injection symmetry is guaranteed with free-slip boundary conditions, while we impose periodic conditions along the streamwise direction. The observed discrepancies between the measured probability and the Poisson distribution effects, induced by the symmetric boundary conditions along the transverse directions, and by the finite particle size that impedes overlapping. (d) Snapshot of solute transport and adsorption, visualized via dimensionless concentration from the top plane at \( z^* = 0 \) with inlet concentration \( c^*_0 = 1 \). Note the concentration sheet \( \Sigma \) at \( c^* = 1/2 \) visible from the sharp change in color of the solute.

to the adsorbing particle surface. The adsorbing spherical particles are randomly and uniformly distributed in the volume space with an average dimensionless interparticle distance \( \ell_x^* = \ell_x/d = \ell_0^*/\sqrt[3]{n_0} \). Thus, the probability of having a certain number of adsorbing particles \( n_\xi \) within an arbitrary spherical domain of radius \( \ell_\xi/2 \) follows a Poisson distribution with average rate \( \langle n_\xi \rangle = 1 \), as confirmed by a spherical-box counting computation performed in the porous domains, shown in Fig. 1 (c).

B. Numerical simulations of pore-scale transport

We investigate solute transport and adsorption into media with variable adsorption capacity, in order to mimic the process of waterborne contaminant treatment by means of the introduction of adsorbers into the subsurface. We consider 11 simulation cases, 6 simulations cases with an increasing fraction of adsorbers \( \xi = 1/160, 1/80, 1/40, 1/20, 1/10, 1/5 \) and \( Da = 1.3 \) and 5 simulation cases with \( \xi = 1/160, 1/80, 1/40, 1/20, 1/10 \) and \( Da = 2.6 \). The values of \( Da = O(1) \) are chosen to represent the balance between adsorption rates typically observed in biochar batch experiments, of the order of 1 mg/L per 100 mg/L of solution over a minute, i.e. \( k = O(10^{-3} \text{ s}^{-1}) \), and the diffusion rate of species in liquids within a typical 1 mm pore space, i.e. \( D_m/d^2 = O(10^{-3} \text{ s}^{-1}) \). For each simulation case, 3 random arrangements of the adsorbing particles are considered, for a total of 33 simulations. The computed data that follows in the manuscript thus refer to the ensemble averaged values among such different realizations. The advection-reaction-dispersion equations (ARDE) for the transport of the scalar concentration \( c^*(x,t) \) is solved for a steady-state flow field, whose dimensionless solenoidal \( j \)-th Euleran velocity component is \( u_j^* = u_j(x)/U \). The ARDE reads as:

\[
\frac{\partial c^*(x,t)}{\partial t^*} + \frac{\partial c^*(x,t)u_j^*(x)}{\partial x_j^*} = \frac{\partial}{\partial x_j^*} \left( \frac{1}{Pe} \frac{\partial c^*(x,t)}{\partial x_j^*} \right),
\]

with \( U \) the intrinsic average flow velocity in the medium, \( x_j^* = x_j/d \) the dimensionless \( j \)-th direction, \( t_a = t/t^* = d/U \) the pore-scale characteristic advective time and \( Pe = Ud/D_m \) the Péclet number. Equation (2) is solved via the lattice-Boltzmann methodology [23]. The steady-state flow solution is achieved by solving a first lattice population within the void space of the porous medium, with no-slip boundary conditions at the fluid-solid interface and a pressure gradient acting to force the flow along \( z \). At the boundaries along the transverse directions \( x \) and \( y \), the symmetry is guaranteed with free-slip boundary conditions, while we impose periodic conditions along the streamwise direction \( z \). A second population is then computed for solving the transport of the passive scalar \( c^* \) with constant injection \( c^*(z = 0) = 1 \) and its adsorption at the boundaries \( S_\xi \), according to Eq. 1 [24]. At the rest of the fluid-solid
boundaries and at the outlet a zero-gradient condition is imposed. The applied pressure gradient that drives the flow is chosen to achieve a Péclet number representative of the balance between the infiltration rate into soil media during an intense rain event and the diffusion rate of solute within the pore space. The intrinsic average flow velocity in a soil medium during an intense event is of the order of 10 mm/h [9]. The infiltration rate in a typical pore space $d \sim 1$ mm thus results $U/d = O(10^{-3} \text{ s}^{-1})$, on the same order of the diffusive rate, and the Péclet number $Pe = 1.72 = O(1)$. The resulting behavior of the constantly injected solute concentration will depend on the transport and adsorption mechanisms occurring within the pore space, as illustrated and intuitively inferable from Fig. 1(d). Further numerical details and a validation of the computational methodology are provided in the Appendix A.

III. RESULTS

A. Plume stretching

We follow the temporal evolution of the concentration of the transported scalar $c^*$. Between the surfaces of the adsorbing particles, placed, on average, at a distance $\ell^*_\xi$, the transported scalar is advected through the pores, forming plumes of solute concentration. We found that such plumes experience a stretching process developing linearly in time. We report the growth of the plume surface $\Sigma$ by computing the extent of the scalar sheet to which corresponds a concentration value $c^* = 1/2$. Thus $\Sigma$ represents the backbone concentration sheet at half-way between maximum concentration and null-concentration areas and with $\Sigma^*_\xi = (\Sigma/d^3)/(\Phi t_0^2)$ we indicate the dimensionless specific surface area of such a sheet per volume of void space. At the initial time $t = 0$, the solute surface corresponds to a sharp front placed at the inlet cross section $\Phi t_0^2$, thus leading to $\Sigma^*_\xi(t = 0) = t_0^2$. In Fig. 2(a) we report the computation of $\Sigma^*_\xi$ showing the evolution of the solute plume surface as a consequence of a linear time-dependent stretching process:

$$\Sigma^*_\xi(t) = \frac{1}{t_0} \left(1 + \gamma^* \frac{t}{t_s}\right),$$

with $t_s = d\ell^*_\xi/U$ the characteristic plume stretching time and $\gamma^* = \gamma t_s$ the dimensionless stretching rate. The stretching rate $\gamma$ results proportional to the average pore-scale mass transport rate $t_0^{-1} = U/d$ and inversely proportional to the characteristic length $\ell^*_\xi$, i.e. $\gamma \propto t_s^{-1} = (\ell^*_\xi)^{-1}$. Thus, the plume stretching per fluid volume occurs faster for adsorbing particles placed at shorter distances. This proportionality is a direct consequence of the linear stretching process. Solute plumes emerge between pairs of adsorbing particles placed, on average, along a perimeter proportional to their average distance, i.e. $\pi \sim \Phi \ell^*_\xi$. The concentration sheet $\Sigma$ grows following the extrusion of such a perimeter line advected at a rate $t_0^{-1}$ along the streamwise direction. The average number of evolving plumes in the two-dimensional transverse plane $(x, y)$ is $n_2 = (\ell^*_0/\ell^*_\xi)^2$ and the concentration sheet stretching rate per unit inlet fluid area can be derived as:

$$\gamma \propto t_s^{-1} n_2 \pi \ell^*_\xi/\Phi t_0^{-2} = (t_s \ell^*_\xi)^{-1} = t_s^{-1}. \quad (4)$$

In particular, we obtain $\gamma = \gamma^* t_s$ and we will discuss later in the manuscript, in Section IIII, the value of the prefactor $\gamma^*$. For now, we limit ourselves to notice that $\gamma^* U$ is the average solute velocity for a plume of concentration $c^* = 1/2$. At a time $t$, such a plume had traveled a distance along $z$ that equals:

$$h^*_\xi(t) \equiv \gamma^* U t/d = (\Sigma^*_\xi(t) \ell^*_0 - 1) \ell^*_\xi, \quad (5)$$

where the right hand side is recovered from Eq. $[\xi]$. We can interpret Eq. (4) as the measure of a kinetic roughening process of a scalar element, whose extent along the longitudinal direction—its roughness height—is induced by the flow velocity $\propto t_0^{-1}$ and whose transversal periodicity—its lateral correlation length—is proportional to the average adsorbers distance $\ell^*$. This stretching behavior resembles a kinetic roughening process statistically constant over a length $\ell^*$. We also note in Fig. 2(a) that for low values of fraction of adsorbers, i.e. $\xi < 0.025$, the computed values of $\Sigma$ exhibit a sharp decay at long times, because the plume sheet $\Sigma$ escapes the porous volume. However, we note that the linear trend holds for all cases, at least as long as the surface $\Sigma$ is contained within such a volume.

The observed linear time-dependent stretching of solute plumes suggests that chaotic advection, which can be observed also at moderate Péclet numbers in three-dimensional porous media [3], if any, is confined within the plume volume and suppressed outside it by adsorption. Within this picture, we are thus allowed to represent the solute plume evolution as a statistical average of independent individual plumes that do not interact with each other but evolve according to their specific pore space volume available between adsorbing particles. The evolving shape of such individual plumes is well captured by snapshots of our simulations depicted in Fig. 2(a). It takes approximately
a time \( t_s \) (i.e. the average time that takes the solute to encounter an adsorbing particle) to observe such a plume formation mechanism, after which the solute concentration is transported along spaces defined by random pairs of adsorbing particles, with clear effects of voiding and clustering of such particles on the solute plume evolution.

### B. Pore-scale diffusion and small-scale scalar structures

A scalar element under spatially varying advective forces is stretched along its length and compressed along its width, while diffusion broadens its width and counteract the latter compression \[13\]. The continuous injection of concentration at the top of domain can be thought as the injection of an infinite number of scalar elements, or scalar sheets, that are subjected to both the latter deforming mechanisms, whose quantification may depend on the reference system, and on the primary directions of deformation taken into account \[25\]. Here, we quantify the stretching and diffusion broadening process by following the dynamic of the concentration sheet \( \Sigma \), as a representative element of the scalar continuous injection at the top boundary. Thus, we compute the average scalar gradient along the concentration sheet \( \Sigma \), (indicated by the averaging operator \( \langle \cdot \rangle_{\Sigma} \)) which, for short times \( t \leq t_s \) rapidly decays as a consequence of the diffusion process that broadens the initially sharp scalar front. For a constant concentration input \( c_0^* = 1 \) the Fick’s law solution at a dimensionless distance from such an input \( \eta^* = \eta/d \) and perpendicular to the concentration sheet \( \Sigma \) leads to:

\[
- \left\langle \frac{\partial c^*}{\partial \eta^*} \right\rangle_\Sigma = \frac{e^{-\eta^*/(4D_m t^*)}}{\sqrt{\pi}} \left( \frac{D_m t^*}{d^2} \right)^{-1/2}.
\]  

\( (6) \)
width of the plume increases as the interparticle distance between adsorbers
and it is deformed and chaotically transported under the effect of stretching and folding events. Such a condition
is such a large fraction of adsorbers to induce a significant plume adsorption, possibly suppressing the small-scale scalar
Batchelor scale is sufficiently small
Equation (8) explicitly quantifies the role of spatial distribution of adsorbers into pore-scale mixing. When the
process as
where we make use of the dimensionless concentration gradient width
and compressive stretching, γ equilibrates at \( t = t_s/\gamma^{*} \), indicating the equilibrium concentration width and Batchelor scale \( \sigma_B^* \), see Eq. (6).

\[
\sigma_B^* \sim \sigma^*(t_s/\gamma^{*}) = (\gamma^{*} Pe/\ell_s^*)^{-1/2}.
\] (8)

Equation (8) explicitly quantifies the role of spatial distribution of adsorbers into pore-scale mixing. When the
Batchelor scale is sufficiently small \( \sigma_B^* < 1 \) the scalar element is smaller than the characteristic pore and grain sizes
and it is deformed and chaotically transported under the effect of stretching and folding events. Such a condition is thus not only met at high Péclet numbers but also at high stretching rates, which are here inversely proportional to the interparticle distance between adsorbers \( \ell_s^* \). In all the here considered cases, we compute \( \sigma_B^* > 1 \), indicating that the scalar field is well-mixed at the pore scale, leading to the compact plume structure observed, see e.g Fig. 3 (a).

The limiting case of \( Da = 1.3 \) and \( \xi = 0.2 \), leads to \( \sigma_B^* \approx 1 \), so that we can predict for a larger fraction of adsorbers, \( \xi > 0.2 \), the possibility of observing scalar elements smaller than the pore size transported under the deformation of chaotic advection. However, for adsorbers uniformly distributed in the three-dimensional space, we also expect such a large fraction of adsorbers to induce a significant plume adsorption, possibly suppressing the small-scale scalar transport. Interestingly, a different picture may arise for non-uniformly distributed adsorbers.

In the condition \( \sigma_B^* > 1 \), diffusion and compression are statistically compensated at the pore scale, the scalar structures have a width larger than the pore size, thus they overlap, contributing to increase the plume concentration. From this moment, at \( t > t_s/\gamma^{*} \), diffusion further smooths the concentration field at a larger scale and stretching continues to shape the plume until an equilibrium between scalar transport and adsorption is achieved, a condition that we here refer as plume mixing.

C. Plume mixing

Because of small scale scalar structure overlapping, diffusion acts perpendicularly to the surface \( \Sigma \) for a longer time \( t > t_s/\gamma^{*} \), contributing to further mix the solute concentration within the advected plume and delivering
the fluid-borne species to the adsorption sites. Here we derive, by heuristic arguments, a formulation for the time taken to achieve full plume mixing and stabilize the plume structure as a consequence of a steady-state equilibrium condition between advection, diffusion and adsorption. A solute molecule travels, driven by diffusion, in the direction perpendicular to the main plume stretching direction, covering a dimensionless distance that on average is \((\ell_\xi^* - 1)\), defined between the surfaces of pairs of adsorbers. The characteristic time for transverse plume mixing is thus \(t_D = d^2(\ell_\xi^* - 1)^2/D_m\). Intuitively, after diffusion has broadened the plume within a distance \((\ell_\xi^* - 1)\), it will take an additional time for molecules to be adsorbed. Such a time is inversely proportional to the concentration gradient determined between pairs of adsorbing particles \(\Sigma_c^*/(\ell_\xi^* - 1)\) and to the adsorption rate \(k\), and we can write it as \(t_k = (\ell_\xi^* - 1)/k\). Following this reasoning, a steady-state equilibrium in the transport and adsorption process is reached at a dimensionless time \(t_\xi^* = t_\xi/t_a = (t_D + t_k)/t_a\) that indicates transverse plume mixing, defined as:

\[
t_\xi^* = Pe (\ell_\xi^* - 1)^2 + \frac{Pe}{Da}(\ell_\xi^* - 1) .
\]

Through Eq. (9), at long times we thus predict \(\Sigma_c^*(t \gg t_s) \approx (1 + \gamma^* t_\xi)/t_0\) or, equivalently:

\[
(\Sigma_c^* t_\xi^* - 1) \xrightarrow{t \gg t_s} \gamma^* \frac{t_\xi^*}{\ell_\xi^*} .
\]

Results of simulations confirm such an analysis as visible from the inset of Fig. 2. Equation (10) well predicts the asymptotic solution of plume stretching, for the simulation cases providing enough adsorbers to contain the concentration sheet \(\Sigma\) within the computational volume. For the other cases, with low values of fraction of adsorbers, it is reasonable to expect a similar behaviour at long times. To confirm such an expectation we perform an additional simulation in a longer computational domain, sizing the double in the streamwise length, at very low value of fraction of adsorbers, i.e. \(\xi = 0.00625\). Results are presented on Fig. 2(b) where we observe the expected linear stretching behavior up to a the time \(t_\xi\). Equation (9) thus predicts the stretching history, from the mixing at the pore-scale reached at a time \(t_s/\gamma^*\), to the plume mixing reached at \(t_\xi\). For the case \(\xi = 0.2\) one can compute \(t_\xi \approx t_s/\gamma^*\), pointing out that plume mixing is achieved almost simultaneously with pore-scale mixing.

It is worth to notice that Eq. (9) predicts an infinite long diffusion and stretching process for \(Da \to 0\), pointing out in the absence of adsorbing sources the scalar quantity \(c^*\) should fill an ideally infinite volume space. Equation (9) also predicts a long stretching process for high values of \(Pe\), when advection-sustained stretching continues for long times before diffusion broadens effectively the plume. Since the stretching history time \(t_\xi\) is the average time taken by diffusion and adsorption to compensate plume stretching and \(t_s = t_\xi t_s^*/\ell_\xi^*\) is the average time taken to stretch the plume between two adsorbing particles, as can be also seen in Fig. 3(a), the ratio \(n_s = t_\xi/t_s = t_\xi^*/\ell_\xi^*\) represents the average number of adsorbers that the plume encounters during its stretching history before reaching a steady state condition that ensures a balance between solute transport and adsorption.

### D. Modelling solute leakage at steady-state

The asymptotic solution of Eq. (2) can be formulated by projecting molecule trajectories along the streamwise direction \(z\) and defining a macroscopic collection or adsorption coefficient [27]. Following this assumptions, one can write an one-dimensional advection-dispersion equation with a term embedding the macroscopic particle deposition kinetics. Here we follow the classic derivation of steady-state concentration profile, which holds for media exhibiting weak heterogeneities [17] and in the assumption of spatially uniform pore-scale velocity \(U\):

\[
\langle c^*(z) \rangle = \exp \left[ - \frac{k^*_c}{U} z \right]
\]

where the operator \(\langle \cdot \rangle\) indicates an ensemble average over different statistical realisation of molecule trajectories. The ratio \(k^*_c/U\), often called filter coefficient, is the inverse of a characteristic length that indicates the distance travelled by molecules, at a velocity \(U\), before being adsorbed at a rate \(k_c\). As we have previously seen, at moderate Péclet and Damkohler numbers, the solute transport can be formulated by averaging different stretching plumes weakly interacting with each others. Thus, the ensemble averaging may be performed over the collection of such plumes. In each of this plume, the average distance traveled by a molecule before diffusing enough transversally to reach an adjacent adsorbers and being collected is statistically constant in space and approximately equals \(t_\xi U\), from which we write:

\[
\langle k^*_c/U \rangle \approx \frac{1}{t_\xi U} = \frac{\gamma^*}{\Sigma_c^*(t_\xi t_0^* - 1) \ell_\xi^*}.
\]
FIG. 4. (a) Spatially averaged concentration $c^*$ at different medium depth from the inlet $z^*$. The exponential decay is visible and well predicted by Eq. 13 (solid, $Da = 1.3$, and dashed, $Da = 2.6$ lines). (b) Upper panel: the data collapse along a single master curve when the depth is non-dimensionalized with the dimensionless adsorption rate $1/t^*_ξ$. Lower panel: it is shown how to use the model defined by Eq. 13, based on plume mixing time $t^*_ξ$, to predict the solute leakage at an arbitrary position, here $\langle c^*(t^*_0) \rangle$.

By reminding that $t^*_ξ = t_ξ/ta$, we insert Eq. 12 in Eq. 11 and determine the concentration profile as:

$$\langle c^*(z) \rangle \approx \exp \left[-\frac{z^*}{t^*_ξ} \right].$$

We calculate the ensemble average of concentration profile $\langle c^*(z) \rangle$ by spatially averaging all the fluid nodes belonging to the cross section at depth $z$ at steady-state and we report the results in Fig. 4. The concentration profiles do indeed follow an exponential decay whose rate is well predicted by Eq. 13. Furthermore, we calculate the dimensionless stretching rate $γ^*$ of the solute sheet $Σ$, computed at $c^* = 1/2$ by imposing in Eq. 13 $\langle c^*(z) \rangle = 1/2$ and solving for $z^* = h^*_ξ(t^*_ξ)$, which is the average distance traveled by a solute plume at long times, see Eq. 5. By combining Eq. 10 and Eq. 13, we obtain $γ^* = \ln(2)$, which very well approximates the linear stretching observed in Fig. 2(a) (black dashed line).

We also show, in Fig. 4 (b) bottom panel, that such a model very well capture the concentration leakage from the adsorbing media, $\langle c^*(t_ξ) \rangle$, therefore establishing a deterministic relationship between plume mixing and steady-state solute leakage, at a variable fraction of particles adsorbed. As a practical example, we can calculate the number of adsorbers per centimeter square $ξn_p/ξ_0$ necessary to limit the solute leakage $\langle c^*(t_0) \rangle < O(10^{-1})$, for a medium of depth $t_0 = 1$ m and particle size $d = 1$ mm. Using Eq. 13 we get $t^*_ξ \sim 430$ and, by applying Eq. 9 with typical values of transport, diffusion and adsorption rates during rainfall infiltration into soils, i.e. $Pe = Da \sim 1$, we obtain the average distance between adsorbers $ξ^*_ξ \sim 21$. From this value it is easy to calculate the necessary number of adsorbers, which results $ξn_p/ξ_0 = t_0/(ξ^*_ξd)^3 \sim 10^{-4} \approx 1/cm^2$.

In light of these results, it is also interesting to further analyze the physical meaning of the collection coefficient formulated in Eq. 12. In the right hand side of Eq. 12 we show that such a coefficient is equivalent to the dimensionless plume stretching rate $γ^*$, distributed over the average plume stretching length along the flow direction, which, at steady-state, is $h^*_ξ(t^*_ξ) = Σξ^*(t^*_ξ)/ξ_0 - 1/ξ^*_ξ$, see Eq. 6. Thus, in the context of moderate Péclet and Damkohler numbers, the collection coefficient measures how fast molecules collection occurs, $γ^*$, over a given distance traveled by the solute plume, $h^*_ξ$. 
FIG. 5. (a) Probability of plume volumes $V_p$, with $V_\xi$ indicating the expected average value of $V_p$ for a certain fraction of adsorbers $\xi$. Small plumes probability, $V_p < V_\xi$, decays following the probability of merging events between adjacent parallel pores transporting the solute, which is $\propto \sqrt{V_\xi/V_p}$, see Eq. (10). The probability of larger plume volumes, $V_p > V_\xi$, instead decays exponentially, following the void probability $F_{V_p}(V_p) \propto \exp[-(\beta^* Pe) V_p/V_\xi \ell^*_\xi]$ as indicated in Eq. (13) and highlighted in the bottom left inset. The dashed line indicate the exponential solution with the constant with $\xi^*$. Small plumes probability, $V_p/V_\xi = h^2/h_\xi^2$ (case $\xi = 0.05$).

E. Plume volumes probability

We are not only interested in the average concentration profile at a certain depth $z$ but also in the probability of plume spatial extension, which varies according to the local spatial arrangement of adsorbers. In particular, if $\ell^*_\xi$ indicates the dimensionless average distance between adsorbers, we have a set $\ell^*_p = \ell_p/d$ of variable adsorbing interparticle distances determined by their random spatial distribution and a set of corresponding plume mixing times $t^*_p(\ell^*_p)$, determined by Eq. (9). A packet of solute may emerge from random pairs of adsorbers, forming a plume whose cross section is $A_p \sim \ell^*_p$ and whose depth at steady state reaches a value $h^*_p(t^*_p)$ defined via eqs. (5) and (9). Since in the herein considered fluid-dynamic conditions $Da \sim 1$, we can roughly assume $t^*_p/Pe \approx \ell^*_p$. Following this assumption, we find that the plume volume is $V_p = h_p A_p \propto \ell^*_p$ and its mean value at a given fraction of adsorber $V_\xi \propto \ell^*_p^4$.

To emerge, a plume must thus find a volumetric space between adsorbing particles $\propto \ell^*_p$. We compute plume volumes from the steady state concentration depth $h(x,y)$ for $c^* = 1/2$, on the plane $(x,y)$. We count the number of nodes $n_h$ for which $h(x,y)$ takes a certain value $h_p$; since we expect $A_p \propto h_p$, we calculate the number of plumes that had traveled $h_p$ with cross section $A_p$ and volume $V_p = h_p A_p$, as $n_p = (n_h/h_p)$, from which we get the corresponding probability of plume volumes $P(V_p)$. In Fig. 5 panel (a), we report such a computation and on panel (b) we visualize an example of plume volume distribution along the plane $(x,y)$. To avoid finite-domain effects, we perform the plume volume calculation only for the cases for which the surface sheet $\Sigma$ is fully contained within the volume domain, i.e. for $\xi > 0.025$.

We find that the probability of small plume, $V_p < V_\xi$, slowly decays while for large plumes, $V_p > V_\xi$, it decays exponentially, with a more rapid decay for smaller volume fraction of adsorbers. Since the adsorbing particles are spatially distributed according to a Poisson point process, see Fig. 2(c), the probability of finding a volume $V = \ell^*_p$ containing no adsorbers, i.e. the void probability $F_V(\ell^*_p)$ decays exponentially as:

$$F_V(\ell^*_p) = e^{-\ell^*_p/\ell^*_\xi}.$$ (14)
We may thus interpret the exponential decay of probability for large plumes as a consequence of the exponentially decreasing probability of volumes without adsorbers, that is:

\[ P(V_p)_{V_p > V_\xi} \sim F_V(V_p) = \exp \left[ -\beta \gamma^* Pe \frac{V_p}{\xi} \right] , \]

which derives from \( V_\xi = h_\xi \beta \ell_2 = \beta \gamma^* Pe \ell_2^* \ell_2 \), with \( \beta \) a geometric constant giving the plume mean area \( \beta \ell_2^2 \). On the inset of Fig. 5, we show that Eq. (15) well predicts the exponential decay of plume volume probabilities, with \( \beta \sim 1/2 \). The formation of small plume volumes \( V_p < V_\xi \) may instead follow a different constraints, following the probability of merging a number \( M \) of small plumes emerging from each individual pore space. Since the number of pore spaces accessible from the inlet are \( M \propto \ell_2^3 / d^2 \propto V_\xi^{3/2} \) and the number of merging events necessary to form a plume of volume \( V_p \) is \( m \propto \ell_2^2 / d^2 \propto V_\xi^{1/2} \), we deduce the probability of small plume volumes:

\[ P(V_p)_{V_p < V_\xi} \sim M/m \propto (V_p/V_\xi)^{-1/2} . \]

It is worth to notice that the derived Eq. (15) highlights the spatial volumetric constraints induced by the presence of randomly placed adsorbing particles, which effectively limit the development of large plume volumes at large Péclet numbers, stretching rates and, maybe more interestingly, at small volume fraction of adsorbers.

IV. CONCLUSIONS

Via pore scale lattice Boltzmann simulations, we have investigated the transport and adsorption of a scalar through a chemically heterogeneous, partially adsorbing, porous medium. We have generated a packed bed microstructure of monodisperse spherical particles, of which a randomly chosen fraction \( \xi \) is capable of adsorption. We have looked at the dynamics of a solute continuously injected into the medium and adsorbed on the fluid-solid surfaces of such adsorbing particles, focusing on the quantification of the deformation of the transported plumes of solute and limiting the analysis to fluid-dynamic conditions characterising the transport of contaminant into subsurfaces, i.e. at \( Pe = O(1) \), and mimicking the adsorption process in a typical carbonaceous particle as biochar, i.e. setting the ratio between adsorbing and diffusive rates as \( Da = O(1) \).

We have measured the dynamical shaping of a scalar element, the solute sheet \( \Sigma \) corresponding to \( c^* = 1/2 \), that is half the inlet concentration value. We have followed such a dynamic process with the intent of performing a quantitative measurement of the deformation that scalar elements, such as a pocket of contaminant molecule, are subjected to when injected into chemically heterogeneous porous subsurfaces. We have found that such elements undergo an advective stretching process linearly dependent on time, whose rate is inversely proportional to the average distance between adsorbers \( \ell_\xi \), resembling a kinetic roughening process statistically constant over a length \( \ell_\xi \). Furthermore, the scalar element is subjected to diffusion broadening and, provided the mathematical formulation of the stretching rate, we have identified its equilibrium width \( \sigma_B \). This width is the small-scale width that an element exhibits when diffusion and stretching equilibrate, thus indicating the characteristic size of the transported pocket of contaminant molecules.

We have derived \( \sigma_B/d \propto (Pe/\ell_\xi^2)^{-1/2} \), which follows from the stretching rate inversely proportional to \( \ell_\xi^2 \) and points out the role of adsorbers interparticle distance on the size of the scalar structure. We have also found that, for \( \xi > 0.2 \) and spatially homogeneous adsorbers, \( \sigma_B > d \) and the solute is well-mixed at the pore-scale. This condition also implies that scalar elements can overlap between adjacent pores and diffusion acts at a larger scale to broaden such overlapping elements contained within a solute plume.

Following these arguments, we have derived the plume mixing time as the time taken to mix a solute plume along its transverse direction. Since we have observed plumes forming between pairs of adsorbers, we formulate the plume mixing time on the basis of the average time taken by a molecule to diffuse among adjacent adsorbing particles and being adsorbed. The so-formulated time, \( t_\xi \), well predicts the moment when an equilibrium between transport and adsorption is found in the porous domain, the stretching of the solute sheet \( \Sigma \) stops, and the plume structure is stabilized. Thus, solute plume equilibrium corresponds to plume transverse mixing. We have also derived the macrohomogenous adsorption coefficient, as the inverse of the distance traveled by a molecule at an average velocity \( U \), before being collected at an adsorbing particle surface with a certain rate. By taking this rate as the rate of plume mixing, we have expressed the macroscopic coefficient as \( 1/(Ut_\xi) \) and shown that it well predicts the exponential decay of contaminant concentration in porous subsurfaces along the main transport direction, as well as the contaminant leakage at a given distance from the inlet, with the here considered fluid-dynamic and surface chemistry conditions.

Finally, we have computed the probability of plume volumes from the statistics of the concentration traveled distances and the expected size of the plume cross-section at equilibrium. We have found that the probability of formation of large plumes follows the void probability between particle adsorbers, decaying exponentially for large plume volumes.
at a rate proportional to the average interparticle distance $\ell^*, \text{ which indicates that large plumes are less probable at low volume fraction of adsorbers.}$

**Appendix A: Lattice-Boltzmann adsorption scheme**

We use the lattice Boltzmann method (LBM) to solve the transport and adsorption equations defined in eqs. [1] and [2]. The LBM is an alternative way to solve Navier-Stokes equations that exhibits sizable computational benefits when dealing with complex geometries such as porous media [23]. The LBM solves the local momentum transport equation by projecting the discretized Boltzmann equation along the discrete lattice directions $r$. It reads as:

$$f_r(x + c_r, t + 1) - f_r(x, t) = -\tau_r^{-1}(f_r(x, t) - f_r^{eq}(x, t)) + F_r,$$

where $f_r(x, t)$ is the distribution function at the position $x = (x, y, z)$ and time $t$ along the $r$-th direction, $c_r$ is the discrete velocity vector along the $r$-th direction, $\tau_r$ is the relaxation time (proportional to fluid viscosity). With $f_r^{eq}$ we indicate the equilibrium distribution function along the $r$-th direction:

$$f_r^{eq}(x, t) = w_r \rho \left(1 + \frac{c_r u_j(x, t)}{c_r^2} + \frac{(c_r u_j(x, t))^2}{c_r^4} - \frac{u_j^2(x, t)}{2c_r^2}\right),$$

where $c_r$ is the speed of sound and $w_r$ the D3Q19 weight parameter of the three-dimensional lattice structure along the $r$-th direction. The solution of the fluid field is deduced in each computational cell by integrating the hydrodynamic moments of the distribution functions. We can thus calculate the steady state velocity vector $u_j(x)$, and density $\rho(x)$ as:

$$\rho(x) = \sum_r f_r(x)$$

$$\rho(x) u_j(x) = \sum_r c_r f_r(x) + \frac{1}{2} \left(\frac{\Delta P}{L}\right) c_r u_j(x)$$

In the case of low Mach numbers, the density can be considered constant and the solution of the momentum transport equation, provided by Eq. [A1] exact with second order accuracy [23, 28].

The first step to solve Eq. [2] consists of computing the steady-state solution for an incompressible fluid flowing through a given porous matrix, that is to calculate $u_j(x)$, via Eq. [A1]. We apply a pressure gradient $\Delta P/L$ that forces the fluid through the porous microstructure, modeling it via an equivalent body force $F_r$ inserted in Eq. [A1] as:

$$F_r(x, t) = \left(1 - \frac{1}{2\tau_r}\right) w_r \left(\frac{c_r u_j(x, t)}{c_r^2} + \frac{(c_r u_j(x, t))^2}{c_r^4} c_r u_j(x, t)\right) \left(\frac{\Delta P}{L}\right) r.$$

Along the streamwise direction $z$, the porous domain is extended, to straighten the flow after it exits the porous medium and avoid nonphysical effects at the $z$ border of the samples. No-slip, free-slip, and periodic boundary conditions are imposed at the fluid-solid interface, at the $x$ an $y$ transverse boundaries, and along the streamwise direction $z$, respectively.

As a second step, we solve a second LBM transport equation, which provide the solution of the scalar concentration field $c(x, t)$ transported by the underlying flow $u_j(x)$, see also [24]. The solute is injected at the inlet face of the samples with a step input change of concentration $c_{in}$. From the first hydrodynamic moment of this second lattice population—which we address as $g_r$—the local concentration is then extracted:

$$c(x, t) = \sum_r g_r(x, t).$$

We impose Neumann boundary condition at the adsorbing particle surfaces for the scalar lattice Boltzmann quantity $g_r$, in order to solve Eq. [1]. The distribution function at a fluid node $x_a$ in the proximity of an adsorbing surface placed at $(x_a - c_r)$ is corrected along the wall-normal direction $r$ as:

$$g_r(x_a, t + 1) = A_1 + A_2 g_r(x_a, t) + \frac{2w_r A_3}{A_1 + A_2},$$

where, for recovering the adsorption Eq. [1], the parameters are set as $A_1 = k$, $A_2 = 1/3$ and $A_3 = 0$ [29]. We validate the algorithm by solving the transport of a scalar quantity $c^*$ between two parallel plates, of which the bottom one adsorbs the solute with a rate $k$. In the upper boundary, zero-flux conditions are instead imposed. We considered two cases, with dimensionless adsorption rates given by $Da = kB^2 / D_m = 1$ and 10. In Fig. 6 we report the results, which shows the excellent agreement between numerical data and the analytical solution reported in Zhang et al. [30].
FIG. 6. The validation tests are set on a rectangular domain of length $L_x = 40$ and height $L_y = 20$ computational nodes. Two parallel plates are placed at $y = 0$ and $y = L$. At the initial time, the concentration field is $c^*(x = 0) = 1$ at the inlet and $c^*(x > 0) = 0$ elsewhere. The lower boundary adsorbs the diffusing scalar $c^*$ according to the scheme provided in Eq. (A7) and the continuum Eq. (1), for $Da = 1$, left panel (a), and $Da = 10$, right panel (b).

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