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The nonlinear adsorptive kinetics of solute transport in soil does not change with pore-water velocity: Demonstration with pore-scale simulations

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SUMMARY

The adsorptive kinetics of reactive solutes in soils is usually measured in batch experiments by keeping the water stagnant. One concern over such measured parameters is their representative of describing the adsorption in field where the water is not stagnant but moves in a spatially variable velocity. Answer to this question appears to be conflict in the literature with some finding a dependence of the adsorptive kinetics on water flow rate and others showing contradiction. Since the adsorption occurring at water–solid interface is inaccessible, affected by various physical and biochemical processes, the existing explanations about an dependence, or independence, of the adsorptive kinetics on water flow rate are not consensus. In this paper a pore-scale model was developed to investigate the adsorptive kinetics of solute in soil. It was assumed that each water–solid interface has a limited number of adsorptive sites to adsorb solute, and that the rate at which the interface adsorbs solute is proportional to the number of the adsorptive sites that still remain unoccupied by solute particles. In the meantime, each adsorbed solute particle can come off the interface at a given probability to become desorbed. Water flow and solute transport through the void space was simulated using a lattice Boltzmann method, and the simulated solute distribution at pore scale was then spatially averaged to yield two profiles: one for solute in fluid and one for solute adsorbed on the fluid–solid interface, in an attempt to test if the spatial average leads to a macroscopic adsorptive kinetics that changes with water flow rate. The results indicated that when the microscopic adsorptive kinetics is homogeneous in that the adsorption and desorption rates operating on the fluid–solid interface are both constants, the associated macroscopic adsorptive rates do not change with water flow rate and their values measured in batch experiments can accurately predict solute displacement under different pore-water velocities. When the microscopic adsorptive kinetics becomes spatially heterogeneous, however, the macroscopic adsorption rates measured in the batch experiments are no longer able to describe solute displacement. The results presented in this paper provide some insight into the adsorptive kinetics of solute in soils, suggesting that the reported dependence of adsorptive rates on water flow rate could be due to an inappropriate use of adsorptive models in describing the heterogeneous adsorption in soil, rather than truly that a change in pore-water velocity indeed results in a change in adsorption rates.

Introduction

Most contaminants and nutrients in soil and groundwater are adsorptive. A sound understanding of the adsorptive kinetics of these chemicals is therefore crucial to predicting their migration and has been studied intensively over the past few decades (Zhang and Selim, 2008). Although recent development in some new approaches such as continuous time random walk intends to model the transport and adsorption as an integrative process by means of a transition function (Deng et al., 2008; Margolin et al., 2003), most models currently in use decouple the adsorption and transport into two separate processes with the parameters associated with each process measured separately. In practice, the adsorptive kinetics of a solute is often measured using batch experiments where the water is kept stagnant, whilst the transport parameters are estimated from displacement experiments by analysing the breakthrough of a nonreactive tracer through the same soil.

The adsorption takes place at the water–solid interface, and is thus controlled by solute concentration in the vicinity of the interface. Whilst in practical modelling, the concentration is a spatial average, measured as the mass of solute in a unit volume of water contained within the soil, including the solute far away from the water–solid interface. As a result, such a spatial average is likely to render the adsorption rates at macroscopic scale different from

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the adsorption rates operating at the water–solid interface. A question raised naturally is therefore if the parameters measured in batch experiments are representative enough to describe the adsorptive kinetics in field where the water is not stagnant but flows in a spatially variable velocity (Pang et al., 2004). Since the adsorption in soil is a complicated process, controlled by many physical and biochemical processes, it is difficult to keep the conditions in batch experiments the same as that in the field. As a result, it is not surprising that the answer to above question appears to be conflict in the literature with some finding that the batch-experiment parameters serve well in predicting solute transport in soil, whilst others showing otherwise (Dousset et al., 2007; Mao and Ren, 2004; Pang et al., 2004; Zhang and Selim, 2006). For those who found the failure of batch-experiment parameters to predict solute migration, the discrepancy is often attributed to pore-water velocity (Darland and Inskeep, 1997). One phenomenon reported by some researchers is that when solute migrates in flowing water, a change in pore-water velocity could result in a change in adsorption rate. However, there is not conclusive view on how the adsorption rate responses to a change in pore velocity, as some showed an increase in reaction rate with pore-water velocity (Akratanakul et al., 1983; Pang et al., 2002), some showed decrease (Brusseau, 1992; Kim et al., 2006; Schulin et al., 1987; Theis et al., 1988), and others showed no change at all (Bajracharya et al., 1996). These conflict results speak for themselves that the relationship between adsorption rate and pore-water velocity is not simply controlled by the contact time between solute and the water–solid interface as some researchers had suggested (Kim et al., 2006), but might depend on other factors (Chen and Wagenet, 1995).

Most transport models for reactive solutes are based on the advection–dispersion equation with a predefined reactive kinetics to describe the reactions. For adsorptive solutes, the commonly used adsorptive model is the linear first-order kinetics (van Genuchten, 1981). Although the adsorptive parameters can be measured independently in batch experiments, in practice, such measured parameters often fail to predict solute migration due to either that the soil structure in the batch experiment cannot be kept the same as that in the column experiment, or that a change in pore-water velocity might indeed result in a change in adsorption rates (Altfelder et al., 2001). As a result, most researchers used inverse methods to calibrate the adsorptive parameters based on the breakthrough curves measured under different water flow rates. It is well known that the inverse methods are problematic because different combinations of the parameters could yield almost the same breakthrough curves. Therefore, depending on the assumptions made in choosing an adsorptive kinetics, the conclusions on the relationship between transport and adsorptive parameters could be very different. For example, some researchers (Pot and Genty, 2007) assumed that the adsorptive kinetics of a solute is the same under different water flow rates, and they then found that the adsorption could enhance the hydrodynamic dispersion. In contract, by assuming that the dispersion of the adsorptive solute is the same as of inert tracer, other researchers founded that a change in pore-water velocity resulted in a change in adsorption rate (Brusseau, 1992; Kim et al., 2006; Pang et al., 2002).

Despite the tremendous efforts made over the past few decades, it is still not conclusive that if the adsorption rate indeed changes with pore-water velocity. This is largely due to the difficulty associated with measuring the spatial distribution of solute adsorbed on water–solid interface. Pore-scale modelling can act as a complement to overcome some limitations of experiments and has been increasingly applied to explore some fundamental processes in porous materials that otherwise remain unknown (Bijeljic and Blunt, 2006; Kang et al., 2006; Li et al., 2007). For example, based on pore-scale simulations, it was shown that when the adsorption operating at the water–solid interface is a homogeneous linear first-order kinetics, the adsorption rates at macroscopic scale do not change with pore-water velocity, and that the adsorptive and transport parameters measured in batch and displacement experiments can accurately predict solute migration under various water flow rates (Zhang et al., 2008). Whilst the linear adsorptive kinetics is a reasonable approximation when solute concentration is relatively low in comparison with the potential adsorptive capacity of a soil, most environmental problems do need to deal with chemicals for which the soil has only a limited capacity to sorb them. In such situations, the rate at which the soil sorbs the solutes is not constant, but depends on the number of free adsorptive sites that are still available to adsorb solute molecules, leading to a nonlinear adsorptive kinetics. As a result, it is useful to study how the nonlinear adsorptive kinetics responds to a change in water flow rate after spatially averaging the adsorption process at the water–solid interface to a macroscopic scale.

The purpose of this paper is to investigate the nonlinear adsorptive kinetics of an idealized porous medium based on pore-scale modelling. The simulations were to mimic the batch and displacement experiments commonly used in laboratory to study reactive solute transport in soils. Water flow was assumed to be in saturated condition and solute transport comprised diffusion, advection and adsorption. The nonlinear adsorption was simulated by assuming that each water–solid interface has a limited number of adsorptive sites to adsorb solute particles, and the probability that the interface sorbs a solute particle at any time is proportional to the number of adsorptive sites that are still free. In the meantime, each adsorbed particle can come off the water–solid interface at a given probability to become desorbed. Both water flow and solute transport were simulated by the lattice Boltzmann equation models. The simulated solute distributions at pore scale were then averaged in cross sections perpendicular to the flow direction to yield two averaged concentration profiles: one for solute in the water and one for solute adsorbed to the water–solid interface. The two concentration profiles were then used to test if the adsorptive and transport parameters obtained from the batch and displacement experiments are able to predict solute migration in soil column. Both homogenous adsorptive kinetics, where the adsorptive parameters operating at water–solid interface are constant everywhere, and heterogeneous adsorptive kinetics, where the adsorptive parameters operating at water–solid interface are spatially heterogeneous, were simulated. The result presented in this paper will provide some insight into the transport of adsorptive solute in soil, offering a guidance to interpreting data measured from both field and soil column experiments.

Description of the models

Fig. 1 shows the idealized reactive porous medium investigated in this paper; it is regularly packed by discs with diameters in the range from 28 to 48 pixels. The length and the width of the column are 6182 and 1095 pixels, respectively, and the number of pore pixels is approximately 4.2 millions, giving a porosity of 63%. Fluid flow was assumed to be laminar and in saturated condition, and solute transport consists of molecular diffusion and advection. The adsorption and desorption take place at the fluid–solid interface, and all above processes were simulated by the lattice Boltzmann equation models.

Model for fluid flow

Fluid flow through the void space of the medium was simulated by the following single-relaxation time LBE model (Qian et al., 1992)