# Coupled effects of hydrodynamic and solution chemistry on long-term nanoparticle transport and deposition in saturated porous media

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## HIGHLIGHTS

- The breakthrough curves of the NPs exhibited a bimodal shape with increasing solution ionic strength.
- Deposition dynamics of the NPs was simulated using a two-site kinetic model.
- NP deposition is controlled by the coupled effects of flow velocity, solution chemistry, and particle size.
- NP interactions with the collector tend to strengthen with increasing contact time.

## GRAPHICAL ABSTRACT
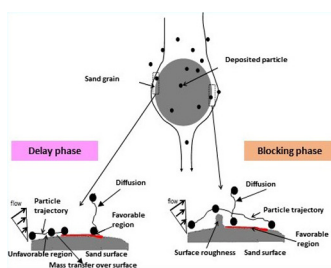
## ABSTRACT

This study aims to systematically explore the coupled effects of hydrodynamic and solution chemistry conditions on the long-term transport and deposition kinetics of nanoparticles (NPs) in saturated porous media. Column transport experiments were carried out at various solution ionic strengths (IS), ionic composition, and flow velocities utilizing negatively charged carboxyl-modified latex NPs of two different sizes (50 and 100 nm). These experiments were designed to obtain the long-term breakthrough curves (BTCs) in order to unambiguously determine the full deposition kinetics and the fraction of the solid surface area ($S_f$) that was available for NP deposition. The BTCs exhibited a bimodal shape with increasing solution IS; i.e., BTCs were initially delayed, next they rapidly increased, and then they slowly approached the influent particle concentration. NP deposition was much more pronounced in the presence of $Ca^{2+}$ than $Na^+$ at any given solution IS. Deposition kinetic of NPs was successfully simulated using a two-site kinetic model that accounted for irreversible deposition and blocking on each site, i.e., a decreasing deposition rate as the site filled. Results showed that $S_f$ values were controlled by the coupled effects of flow velocity, solution chemistry, and particle size. Data analyses further demonstrated that only a small fraction of sand surface area contributed in NP deposition even at the highest IS (60 mM) and lowest flow velocity (1 m/day) tested. Consistent with previous studies, our results imply that NP deposition is controlled by physicochemical interactions between the NPs and nanoscale physical and/or chemical heterogeneities on the sand surfaces that produce localized nanoscale favorable sites for deposition. Furthermore, our results suggest that the NP interactions with the collector surfaces tended to strengthen with increasing contact time.

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## 1. Introduction

An understanding of nanoparticle (NP) transport and deposition in porous media is important in a range of processes in natural and engineered systems. These processes may include the transport and fate of pathogenic viruses and engineered NPs in soils and aquifers [1–4], and deep bed filtration in water and wastewater treatment systems [5,6]. Most experimental studies of NP deposition in porous media have focused on the initial, clean-bed, deposition behavior when the collector surfaces are devoid or only contain small amounts of deposited particles [4,7,8]. In this case, the deposition rate is constant and a first-order kinetic model is commonly employed to describe the deposition behavior [9,10]. However, as NP deposition on collector surfaces proceeds, a decrease in the deposition rate occurs due to blocking (filling) of the available sites [3,11–14]. This blocking phenomenon usually occurs when a considerable net-repulsive energy barrier exists between the NPs and collector surfaces. Therefore, in most natural systems only a small fraction of the solid surface contributes to NP deposition because of the prevalence of net-repulsive electrostatic conditions [3,15–18]. Consequently, it is imperative that theoretical models are able to describe the entire dynamics of deposition from the initial to later stages when a decline in deposition rates occurs. An understanding of the dynamics of NP deposition is especially important because NP deposition is essentially irreversible (insignificant detachment) during steady-state chemical and hydrodynamic conditions [3,19–22].

Two different blocking models have been developed to describe the declining rate of deposition during the filling process, namely: the Langmuirian model [23,24] and the random sequential adsorption (RSA) model [25,26]. The Langmuirian and RSA models assume a linear and a nonlinear decrease in the deposition rate during filling of deposition sites, respectively. The Langmuirian approach is commonly employed in short-term colloid deposition modeling studies [2,22]. However, the RSA model provides a superior description of deposition dynamics when the coverage of collector surfaces approaches the maximum attainable coverage (∼54%), often referred to as the hard sphere jamming limit [24,27–29]. Both Langmuirian and RSA models assume that deposited NPs eventually achieve monolayer coverage on the fraction of the solid surface area that is favorable for deposition ($S_f$).

Previous studies have reported that $S_f$ is influenced by a range of physicochemical factors such as particle size, the amount and size of physical and/or chemical heterogeneities, solution chemistry, and flow rate [11,30–32]. In particular, $S_f$ has been reported to increase with increasing ionic strength (IS) under net-repulsive electrostatic conditions, suggesting that deposition locations on the collector surfaces are largely determined by nano-scale heterogeneities and/or increasing the depth of the secondary energy minimum [33–36]. Furthermore, increasing the flow velocity and/or particle size has been shown to decrease $S_f$, suggesting that hydrodynamic conditions are also important in determining deposition kinetics and blocking [2,37,38]. Several explanations have been proposed in the literature to explain the role of flow velocity or particle size on the deposition behavior. Some researchers have attributed the decrease in $S_f$ at higher velocities to the "shadow effect" [37], e.g., the excluded region created down gradient of micro-scale surface roughness or deposited particles. More recently, the influence of hydrodynamic conditions on $S_f$ has been explained by the balance of applied hydrodynamic and resisting adhesive torques [39–43]. Only limited experimental information is available in the literature on the dependence of $S_f$ on physicochemical and hydrodynamic factors, especially for NPs. In this paper, we will systematically explore the coupled effects of these factors on the value of $S_f$. This information is required to better deduce the underlying mechanisms and theoretical description of NP deposition kinetics under net-unfavorable conditions.

The overall deposition rate of NPs in porous media depends not only on $S_f$, but also on the mass transfer of NPs to favorable sites on the solid surfaces where deposition can occur. Mass transfer of NPs to favorable sites occurs by two means: (1) aqueous phase mass transfer from the bulk aqueous phase to the solid surface [44,45] and (2) solid phase mass transfer on unfavorable regions of the solid surface to favorable sites [30,33,46]. Aqueous phase mass transfer of NPs to the solid surface has been the subject of much research [10] and colloid filtration theory [47] is commonly used to quantify this process. Conversely, the role of solid phase mass transfer has received less research attention [30]. It has been shown that particles colliding with unfavorable regions of the solid surface may become weakly associated with the solid surface via a shallow secondary energy minimum. These particles can be translated along the collector surface by tangential hydrodynamic forces to favorable deposition sites [48]. It is expected that nano- and micro-scale surface roughness and the pore-space topography should influence the solid phase mass transfer of the NPs. Furthermore, the amount of colloid transfer on the solid surface is expected to increase with increasing IS and decreasing flow velocity [33,35]. The solid phase mass transfer rate of NPs is likely to decrease during the filling processes, but little research has been conducted to address this issue.

The objective of this study is to develop a more thorough understanding of the combined effects of hydrodynamics and solution chemistry on the long-term kinetics of NP deposition in saturated porous media. Specifically, a series of laboratory experiments was carried out in saturated sand columns to investigate the coupled effects of solution IS, cation type, particle size, and flow velocity on the deposition rate constants and the fraction of the sold surface area available for NP deposition. A two-site kinetic model was found to satisfactorily simulate and describe the long-term dynamics of the deposition process. Fitted values of $S_f$ and deposition rate constants over a wide range of physicochemical conditions increased our understanding of the dynamics of long-term NP deposition in porous media. This information is needed to improve our theoretical description of these processes and to improve continuum scale models for predicting the long-term fate and mobility of NPs in the subsurface environment.

## 2. Materials and methods

### 2.1. NPs

Carboxylate-modified latex (CML) microspheres have often been used as model NPs in transport studies due to their spherical shape, well-defined size and surface charge, and ease in detection at low concentration [2]. Two sizes (50 and 100 nm) of Fluoresbrite®Yellow-Green CML microspheres (Polysciences, Inc), that have an excitation wavelength at 441 nm and an emission wavelength at 486 nm, were used in this research. Stock solutions of CML NPs were diluted in selected electrolyte solutions to achieve a desired initial concentration ($C_0$). All solutions were prepared using analytical graded reagents and Milli-Q water with its unadjusted pH 5.8. A near neutral pH and negatively charged NPs were chosen in order to understand the NP transport mechanism under most unfavorable condition. The initial concentration for 50 and 100 nm CML NPs was typically $4.55 \times 10^{10}$ mL$^{-1}$. NP aqueous phase concentrations were determined using a fluorescence spectrophotometer (Synergy HT, BioTek Instruments, Inc., Winooski, VT, USA) and a calibration curve. The CML NPs have carboxylate groups on their surfaces that are highly negatively charged. The zeta potential and size uniformity of the CML microspheres in various electrolyte