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Modeling colloid deposition on a protein layer adsorbed to iron-oxide-coated sand

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ABSTRACT

Our recent study reported that conformation change of granule-associated Bovine Serum Albumin (BSA) may influence the role of the protein controlling colloid deposition in porous media (Flynn et al., 2012). The present study conceptualized the observed phenomena with an ellipsoid morphology model, describing BSA as an ellipsoid taking a side-on or end-on conformation on granular surface, and identified the following processes: (1) at low adsorbed concentrations, BSA exhibited a side-on conformation blocking colloid deposition; (2) at high adsorbed concentrations, BSA adapted to an end-on conformation promoted colloid deposition; and (3) colloid deposition on the BSA layer may progressively generate end-on molecules (sites) by conformation change of side-on BSA, resulting in sustained increasing deposition rates. Generally, the protein layer lowered colloid attenuation by the porous medium, suggesting the overall effect of BSA was inhibitory at the experimental time scale. A mathematical model was developed to interpret the ripening curves. Modeling analysis identified the site generation efficiency of colloid as a control on the ripening rate (declining rate in colloid concentrations), and this efficiency was higher for BSA adsorbed from a more dilute BSA solution.

1. Introduction

Colloids are usually defined as entities with at least one dimension between 1 nm and 1 μm (IUPAC: McNaught and Wilkinson, 1997). Groundwater colloids may originate locally by mobilization or precipitation, or enter groundwater from external sources such as septic tank effluent, leaky sewer, river bank infiltration, artificial recharge, and anthropogenic nanomaterials (Kretzschmar et al., 1999; Foppen et al., 2006; Nowack and Bucheli, 2007). The large specific surface areas of colloids make them potentially important sorbents and vehicles of environmental contaminants, which may include heavy metals, radionuclides and hydrophobic organic compounds (Hofmann and Wendelborn, 2007; Bekhit et al., 2009). Meanwhile, certain colloid types such as pathogenic microorganisms and engineered nanoparticles may themselves constitute intrinsic hazard to human health (Levy et al., 2007; Mueller and Nowack, 2008). Thus, understanding the key controls on colloid transport in porous medium is important for better groundwater protection.

Protein is a major organic compound widespread in wastewater-impacted groundwater (Harrison, 2001; Imai et al., 2002; Tchobanoglous et al., 2003). Published studies have reported the contrasting influence protein may have on colloid mobility (Weber-Shirk, 2002; Kuznar and Elimelech, 2005; Kim et al., 2009). Weber-Shirk (2002) found that a low adsorbed protein mass (acid-soluble seston extract, <1.2 g/m^2) may substantially increase colloid attenuation by porous medium.

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Conversely, Kuznar and Elimelech (2005) and Kim et al. (2009) noted that the protein expression in a bacteria surface may inhibit the colloid deposition. Several authors noted that conformation change may cause a redistribution of the surface adsorbing property of a protein and influence its interaction with solid phases (Bhattacharjee et al., 2000; Urano and Fukuzaki, 2000). The outcome of these studies implies that protein adsorption conformation might be controlling the function of protein on colloid deposition. On the other hand, protein conformation was universally recognized to be influenced by its adsorption concentration (density) (Urano and Fukuzaki, 2000; Nakanishi et al., 2001; Stutz, 2009). Our recent study conducted with distinct protein adsorption concentrations showed that a single type of protein, Bovine Serum Albumin (BSA), may act either as colloid deposition site or inhibitor, depending on the adsorbed conformation (Flynn et al., 2012). This reconciles the conflicting responses observed in previous studies. However, lack of a suitable ripening model for describing the influence of a protein adsorption layer restricted our previous study solely to quantifying the site blockage by BSA, while the fundamental processes driving the ripening phenomenon remain unclear.

This study aims to address this research gap by developing a mathematical model and applying the model to further explore the ripening process. As a prerequisite for model development, a conceptualization of the observed processes needs to be established, utilizing a widely accepted ellipsoid morphology BSA model for analyzing the experimental results. This conceptual model permits the mathematical formulation of the ripening process to be achieved based on a modification of existing filter ripening models, developed for organic matter-free pure colloid deposition systems.

2. Double pulse column experiments (DPEs)

2.1. Materials

With the exception of the organic matter (protein), all materials and apparatus employed in column experiments were the same as those employed by Yang et al. (2010). Fluoresbrite® yellow-green fluorescent stained polystyrene latex microspheres (microspheres) with carboxylic functional groups and a nominal diameter of 0.2 μm (Polysciences Inc., Eppelheim, Germany) were used as model colloid. Microsphere suspension was prepared and dispersed ultrasonically in the same way as described in Yang et al. (2010) (see Supplement). Bovine Serum Albumin (BSA) (Acros Organics, Geel, Belgium), a model of wastewater protein (Ang and Elimelech, 2007), was investigated. The molecule is flexible and amorphous, consisted of amino acids and peptide bonds (Nakanishi et al., 2001; Rogalinski et al., 2005) and has an isoelectric point of approximately pH 4.7 (Chiku et al., 2008). There is a consensus that surface properties of BSA vary across the molecule giving rise to charge heterogeneity (Baier et al., 2011), along with hydrophobic and hydrophilic regions (Yoon et al., 1998). Consequently, morphological models of BSA need simplification to certain degrees: it is described either as a globular ellipsoid of about $14\times3.8\times3.8$ nm (Ke et al., 2009; Togashi et al., 2009), a heart-shaped solid with three different domains (Voros, 2004), or a flexible foldable polymer (Chiku et al., 2008). Among them, the ellipsoid model not only provides explicit size and geometry description of the protein molecule, but also offers a realistic means to characterize the adsorbed conformation in end-on (long axis perpendicular to collector surface) or side-on (short axis perpendicular to collector surface) (Yoon et al., 2003; Schrott et al., 2009). This renders the globular ellipsoid model well suited for this study. In this study, BSA levels in column effluent were measured online by HPLC UV–vis spectrophotometer (VWD) (Agilent 1100 Series, Waldbronn, Germany) set at 230 nm.

2.2. Methods

Double pulse column experiments (DPEs: see Table 1) all consisted of a prolonged pulse of multiple pore volumes (PV) of BSA at contrasting concentrations, succeeded by flush with microsphere-free/BSA-free electrolyte solution, and a second 13 PV pulse of microsphere dispersion at 10.4 ppm (2.5×10^{9} colloids mL^{-1}), followed by a final flush with microsphere-free/BSA-free electrolyte solution. The BSA pulse, injected for variable durations, aims to produce a BSA layer of distinct adsorption concentrations and consequently different BSA conformations on the granular surface. Employing a range of injection BSA concentrations permitted the influence of the suspending concentration on the property of the adsorbed protein layer to be evaluated.

Based on the injected BSA masses, the DPEs fall into two groups. The first group consisted of three DPEs, injecting a BSA mass of 1.2×10^{-9} mol (DPE A), 3×10^{-10} mol (DPE B), and 6×10^{-10} mol (DPE C), respectively. The approach permitted characterization of the general trend in microsphere response to different levels of BSA adsorption concentrations where low masses of BSA were adsorbed. In a similar manner, a second group of DPEs consisted of three experiments, injecting 1.2×10^{-7} mol (DPE D), 3×10^{-8} mol (DPE E), and 7.5×10^{-9} mol BSA (DPE F). This series of experiments aimed to characterize the functional relationship between microsphere responses and high BSA adsorption concentrations. In addition to these experiments, a separate series of experiments were conducted, using only a microsphere tracer without any addition of BSA, to directly compare the effects of BSA. All the experiments were carried out in triplicate.

3. Experimental results and discussions

3.1. Double pulse column experiment (DPE) results

Fig. 1 summarizes the results of DPEs (DPE A, DPE B, DPE C) employing low BSA concentrations. Breakthrough curves (BTCs) reveal that no BSA was detected in the column effluent, suggesting nearly complete attenuation of BSA by the column matrix. Table 1 lists the adsorbed BSA concentrations calculated by averaging the total BSA mass adsorbed in the column matrix over the overall surface area of the column sand, assuming sand grain to be spherical with a mean diameter of 125 μm. The adsorbed BSA mass declined in the order of DPE A > DPE C > DPE B. The succeeding microsphere BTCs in DPE A, DPE B, and DPE C display similar shapes: microsphere relative concentrations initially rose rapidly, before reaching a point of inflection, and following that point, concentrations rose at lower rates. By comparison, the height of the inflection point decreases in the order of DPE A (22%) > DPE C (12%) > DPE B