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Sepia ink as a surrogate for colloid transport tests in porous media

Diego Soto-Gómez [a,*], Paula Pérez-Rodríguez [a], J. Eugenio López-Periago [a], Marcos Paradelo [a,b]

[a] Soil Science and Agricultural Chemistry Group, Department of Plant Biology and Soil Science, Faculty of Sciences, University of Vigo, E-32004 Ourense, Spain
[b] Department of Agroecology, Faculty of Sciences and Technology, Aarhus University, Blichers Allé 20, P.O. Box 50, DK-8830 Tjele, Denmark

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ABSTRACT

We examined the suitability of the ink of *Sepia officinalis* as a surrogate for transport studies of microorganisms and microparticles in porous media. Sepia ink is an organic pigment consisted on a suspension of eumelanin, and that has several advantages for its use as a promising material for introducing the frugal-innovation in the fields of public health and environmental research: very low cost, non-toxic, spherical shape, moderate polydispersivity, size near large viruses, non-anomalous electrokinetic behavior, low retention in the soil, and high stability.

Electrokinetic determinations and transport experiments in quartz sand columns and soil columns were done with purified suspensions of sepia ink. Influence of ionic strength on the electrophoretic mobility of ink particles showed the typical behavior of polystyrene latex spheres. Breakthrough curve (BTC) and retention profile (RP) in quartz sand columns showed a depth dependent and blocking adsorption model with an increase in adsorption rates with the ionic strength. Partially saturated transport through undisturbed soil showed less retention than in quartz sand, and matrix exclusion was also observed. Quantification of ink in leachate fractions by light absorbance is direct, but quantification in the soil profile with moderate to high organic matter content was rather cumbersome.

We concluded that sepia ink is a suitable cheap surrogate for exploring transport of pathogenic viruses, bacteria and particulate contaminants in groundwater, and could be used for developing frugal-innovation related with the assessment of soil and aquifer filtration function, and monitoring of water filtration systems in low-income regions.

1. Introduction

There is a great variety of engineered nanoparticles, colloid facilitated chemicals and virus families relevant to human disease that can contaminate the surface water or groundwater. The spread of these substances, especially human viral pathogens and bacteria, in natural waters relies on the effectiveness of soil as a natural filter (Perrier et al., 2010). Soil can reduce the presence of this kind of particles by a factor of 10^{-4}. Knowledge of colloid filtration in porous media has been developed during the past years to estimate the effectiveness of filtration of pathogenic microorganisms from drinking water (Bradford et al., 2014).

Bacteria transport studies time consuming in bacterial quantification (Hornberger et al., 1992), large uncertainties regarding the theory.

Surrogates for viruses and micro or nano-sized contaminants can be used to facilitate the study of transport in porous media (Gitis et al., 2002; Harvey et al., 2011; Knappett et al., 2008; Schijven et al., 2003). Particle surrogates should be easy to obtain and quantify, with constant composition and

* Corresponding author.
E-mail address: disoto@uvigo.es (D. Soto-Gómez).

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properties, and safe for humans and the environment (Cheng et al., 1994a,b). These can be used to study the interactions between colloidal particles and soil, and to test hypotheses about their fate in the environment, including facilitated transport of contaminants and spreading of bacteria and viruses in soil and aquifers (Dongdem et al., 2009).

Reliable surrogates for pathogenic microorganisms can be used in testing and monitoring of water purification systems, especially in developing countries with very limited technical resources (Xagoraraki et al., 2014), or in research of new materials for virus purification (Gutierrez et al., 2009). In addition, surrogates can be used to identify technical and management deficiencies in wastewater treatment systems which may lead to human exposure and disease. Also can be used for potable reuse of reclaimed wastewater via artificial recharge (Verbyla and Mihelcic, 2014), especially to examine removal of bacteria and viruses.

An important number of the studies of colloid transport in porous media use fluorescent or radio-labeled polystyrene latex microspheres (Frimmel et al., 2007) with different functional groups attached to their surface. However, carboxylated latex microspheres (20 and 200 nm) show different responses to changes in solution chemistry compared to viral pathogens and bacteriophages (Mondal and Sleep, 2013). Besides, these materials are costly: 100 mL of this particles cost between 460 and 2000 €. Sharma et al. (2012) proposed the use of DNA-tagged polylactic microspheres for tracking of the paths of colloids in natural media. DNA-labeled, protein-coated silica nanoparticles were used to mimic filtration and transport of rotavirus and adenovirus in sand media (Pang et al., 2014).

Particle deposition in porous media is complex. In the case of saturated water flow three mechanisms have commonly been identified (McDowell-Boyer et al., 1986): attachment, mechanical filtration (i.e. which occurs at the top of the filter), and mechanical retention into the matrix (straining) (Torkzaban et al., 2008). Briefly, attachment is referred to the retention of particles in the matrix by adsorption to the porous matrix (Bradford et al., 2002). Attachment of particles in granular porous media can be described in part by models based on the capture of colloids by spherical collectors, formulated for first time by Yao et al. (Yao et al., 1971). Thus, small spherical particles with large negative charge will have small deposition rates in soil. In addition, adsorption rate can be time dependent, either decreasing rate by progressive occupation of available adsorption sites (blocking) or increasing rate by cooperative adsorption of new arriving particles by the first adsorbed ones (ripening) (Bradford et al., 2003).

Many laboratory experiments have demonstrated that the colloidal filtration is less effective in structured soils. Particles can travel faster through macropores, and several models were developed to differentiate between the transport in macropores and in the matrix (Jarvis et al., 1999). Additionally, in unsaturated porous media, colloids can be deposited through capillary force interactions in soil-water interface (SWI) and air-water interface (AWI) found in pendular rings, triple points and water films (DeNovio et al., 2004).

Sepia ink is considered to be pure eumelanin and is used as a standard for natural eumelanins. A comprehensive description of these compounds can be found in other works (Liu and Simon, 2003a). Sepia ink is formed by an almost pure colloidal suspension of eumelanin. All melanins are generated from the oxidation of molecules of tyrosine, forming DOPA-quinone, which polymerizes to different types of melanins. The first aggregation level cell comprises two or three of these molecules or nanoclusters forming a core (Zajac et al., 1994). These stacks of oligomers are joined by edges and form filaments that aggregate to form spheres with a size ~154 ± 10 nm. Sepia ink has a total metal content of 4.7%, being 2.4% Mg and 1.7% Ca the most abundant and 170 mg kg^{-1} Fe, that contribute to the conformational structure during biosynthesis but are not required to sustain the morphology once the granule is assembled (Liu and Simon, 2005). The spherical shape and size of sepia ink particles can mimic the colloidal properties of some families of viruses such as Adenoviridae and Retroviridae.

Sepia ink eumelanin is insoluble and stable in water, absorbs ultraviolet and visible radiation, and can relax photo-excited states without emitting radiation (Meredith and Sarna, 2006).These properties are optimal for optical shielding in seawater which serves to protect sepias from predators (Derby, 2014).The stability of this substance in saline environments suggests that sepia ink could be a good candidate for colloidal transport studies.

In this work, we examine the colloidal properties of diluted sepia ink suspensions for their potential use as a surrogate to study of the transport of bacteria, viral pathogens and nanoparticles in packed quartz sand and undisturbed soil. Firstly, we determined the electrokinetic properties of sepia ink; then, transport of sepia ink in water-saturated quartz sand column was examined to identify the attachment model, by using steady-state breakthroughs and stopped flow tests; and finally, transport experiments in partially-saturated undisturbed soil cores were done to examine the influence of the soil physical properties in the movement of suspended sepia ink particles.

2. Material and methods

2.1. Materials

2.1.1. Sepia ink

Sepia ink was obtained as frozen ink stabilized with sodium carboxy methyl cellulose (Nortidal Sea Products Ltd., Guipúzcoa, Spain). The price of this material (buying small amounts) is about 0.05–0.08 € g^{-1}, around 700–1000 times cheaper than polystyrene particles of the same size. A stock suspension of purified eumelanins was obtained by washing a suspension of 4 g of commercial ink in 250 mL of deionized water (DW). The washing process was performed as follows: centrifugation at 20,000 *g* for 30 min (Beckmann, using a rotor JA-24.50) and resuspension by vortex-stirring in warm DW and sonication (Bandelin electronic sonoplus HD 2200, Berlin, Germany). This washing was repeated five times. Aliquots of diluted stock suspension were analyzed to determine size and shape by using Scanning Electron Microscopy (SEM). Particle counts in purified suspensions in DW, with a qNano (Izon, Oxfod, UK), were used in conjunction with the particle diameter in order to calculate the concentration of suspended particles. Particle density measured with a He pycnometer on freeze-dried samples was 1.27 g cm^{-3} which is lighter than rotavirus, 1.36–1.4 g cm^{-3} (Vonderfecht et al., 1984) and