Environmental Pollution 159 (2011) 1896–1904

Contents lists available at ScienceDirect

Environmental Pollution

journal homepage: www.elsevier.com/locate/envpol

# Influence of ionic strength and pH on the limitation of latex microsphere deposition sites on iron-oxide coated sand by humic acid

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ARTICLE INFO

*Article history:*
Received 16 November 2010
Received in revised form
17 March 2011
Accepted 18 March 2011

*Keywords:*
Colloidal transport
Natural organic matter
pH-ionic strength effect
Conformation change
Deposition site coverage

ABSTRACT

This study, for the first time, investigates and quantifies the influence of slight changes in solution pH and ionic strength (IS) on colloidal microsphere deposition site coverage by Suwannee River Humic Acid (SRHA) in a column matrix packed with saturated iron-oxide coated sand.

Triple pulse experimental (TPE) results show adsorbed SRHA enhances microsphere mobility more at higher pH and lower IS and covers more sites than at higher IS and lower pH. Random sequential adsorption (RSA) modelling of experimental data suggests 1 μg of adsorbed SRHA occupied $9.28 \pm 0.03 \times 10^9$ sites at pH7.6 and IS of 1.6 mMol but covered $2.75 \pm 0.2 \times 10^9$ sites at pH6.3 and IS of 20 mMol. Experimental responses are suspected to arise from molecular conformation changes whereby SRHA extends more at higher pH and lower ionic strength but is more compact at lower pH and higher IS. Results suggest effects of pH and IS on regulating SRHA conformation were additive.

## 1. Introduction

Colloids are defined as entities with at least one dimension between 1 nm and 1 μm (IUPAC: McNaught and Wilkinson, 1997; Hofmann et al., 2003a). A wide variety of environmental particles fall into this size range including naturally generated inorganic particles (clay, oxides, minerals, and silica, etc.), viruses & bacteria (biocolloids), and anthropogenic colloids (polymeric microspheres, nanoscale zero-valent iron, etc.) (Gustafsson and Gschwend, 1997; Schijven and Hassanizadeh, 2000; Hofmann et al., 2003b; Hofmann and v.d. Kammer, 2009).

Colloids are ubiquitous in the environment and may influence environmental water quality. In a negative sense they may act as contaminants in the own right, such as pathogenic microorganisms (Schijven and Hassanizadeh, 2000; Ranville et al., 2005). Alternatively they may facilitate the transport of otherwise immobile contaminants such as highly hydrophobic substances (Hassellöv and v.d. Kammer, 2008; Mueller and Nowack, 2008; Hochella et al., 2008; Hofmann and Wendelborn, 2007). Conversely, anthropogenic colloids have been successfully employed for groundwater remediation (Kim et al., 2004; Tungittiplakorn et al., 2005; Nowack and Bucheli, 2007). The impact of colloids on water quality strongly depends upon the nature of their interactions with porous media. Consequently, improved knowledge of the physicochemical controls on colloidal mobility assists in better protecting water resources (Lecoanet et al., 2004; Karn et al., 2009; Battin et al. 2009).

Previous studies have highlighted the role of three hydrochemical parameters in affecting colloid fate and transport through porous media: (1) pH (Bunn et al., 2002; Bekhit et al., 2006; Kim et al., 2009); (2) ionic strength (Ko and Elimelech, 2000; Zhuang and Jin, 2003; Franchi and O'Melia, 2003; Tosco et al., 2009); and (3) the occurrence of natural organic matter (NOM) in solution/suspension(Akbour et al., 2002; Foppen et al., 2006, 2008; Pelley and Tufenkji, 2008; Johnson et al., 2009). Since NOM is widespread in the aquatic environment (Thurman, 1985) and pH & IS may vary spatially and temporally (Young, 1988), a quantitative investigation of the influence of their interactions on colloidal mobility has implications for understanding water quality under a wide range of environmental conditions.

Humic acid (HA) constitutes of about 60% of all NOM in the environment (Ochs et al., 1994). Although widely regarded as large complex assemblages of molecules, published work often suggests that dissolved/suspended HA could be viewed in more simple terms as linearly-structured flexible polyelectrolytic macromolecules whose conformation largely depends on pH and IS (e.g., Tiller

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doi:10.1016/j.envpol.2011.03.026

and O'Melia, 1993; Buffle and van Leeuwen, 1993; Stumm and Morgan, 1996; Vermeer et al., 1998; Au et al., 1999).

The adsorbed conformation of HA has been noted to influence colloid transport through porous media (Amirbahman and Olson, 1993, 1995; Franchi and O'Melia, 2003; Pelley and Tufenkji, 2008; Chen and Elimelech, 2008; Kumpulainen et al. 2008), i.e., both the magnitude and type of the HA-colloid interaction forces are controlled by HA conformation. High pH and low ionic strength have been noted to increase lateral repulsions between negatively charged segments of HA with such increased intra-compound forces resulting in a more extended linear structure that enables it to cover a relatively large area of an adsorbing surface (Amirbahman and Olson, 1993, 1995; Franchi and O'Melia, 2003; Pelley and Tufenkji, 2008; Chen and Elimelech, 2008). Conversely, lower pH and higher ionic strength reduce intra-compound electrostatic interactions, resulting in a more compact HA conformation and lower surface coverage (Buffle and van Leeuwen, 1993; Stumm and Morgan, 1996; Vermeer et al., 1998).

This paper aims to investigate and quantify how the conformation of Suwannee River Humic Acid (SRHA) may influence microsphere deposition in saturated porous media as a function of variations in solution pH and ionic strength, employing the method presented in Yang et al. (2010). This was achieved by carrying out triple pulse column experiments, for a range of solution chemical conditions, coupled with Random Sequential Adsorption (RSA) modelling to quantify the effect of both parameters on humic acid surface coverage of colloid deposition sites in the porous medium.

Study findings suggest that a slight change in pH and/or ionic strength may significantly affect the role of the adsorbed SRHA in controlling colloid transport in the porous medium. This is suspected to result from a change in the conformation of the adsorbed SRHA on the porous medium surface in response to the change in pH and IS which consequently changes the number of microsphere sites that organic matter can cover. RSA modelling and statistical analysis have permitted quantification of colloid deposition site coverage by SRHA and characterisation of the relative importance & interactions of pH and IS in controlling the SRHA's behaviour. This study is, to the best knowledge of the authors, the first to systematically address the effects of both pH and IS in assessing HA coverage of colloid deposition sites in porous medium. The pH and IS values employed fall within the range of those encountered in naturally occurring conditions for many groundwaters and surface waters. Study findings have implications for a range of Environmental Science and Environmental Engineering fields, including enhancement of filter bed performance in water and wastewater treatment, and manipulation of humic acid for mobility enhancement of engineered polymeric nanoparticles for aquifer remediation. More generally study findings may have wider implications for environmental protection and environmental remediation, including determination of safe setback distances for groundwater supplies from sources of colloidal contaminants, e.g. septic tanks, and for oil recovery enhancement by polymer flooding.

## 2. Column experiments

Fig. 1 presents a schematic of the apparatus employed in all experiments. The methodology and materials employed have been described in detail in Yang et al. (2010). Table 1 summarises the composition of the liquid phases including microsphere dispersions, SRHA solutions, and flushing solutions. All the liquids had a pH6.3 or pH7.6 and an IS of 1.6 mMol or 20 mMol. This design permits investigation of the influence of both factors (pH and IS) using waters with chemistries comparable to those encountered in the natural environment. Fluoresbrite® yellow–green fluorescent stained polystyrene latex microspheres with carboxylic functional groups and a nominal diameter of 0.2 μm (Polysciences Inc., Eppelheim, Germany) and Suwannee River Humic Acid (SRHA) from International Humic Substance Society (IHSS) were used as model colloids and natural organic matter (NOM), respectively.

Electrophoretic mobility and dynamic light scattering measurements of microspheres were carried out using a Malvern Zetasizer (Model NanoZS: Malvern Instruments Ltd, Worcestershire, UK) for dispersions in liquids, with/without SRHA. Microsphere bearing solutions had the same characteristics of those used in column experiments. Measurement results suggested that microspheres have dense negative surface charge under the experimental conditions employed and were little affected by the presence of SRHA (see Table S1). Moreover, size measurements indicated that particles had sizes consistent with those stated by the manufacturer suggesting that microsphere aggregation due to adsorption of SRHA on microspheres did not occur (See Table S1).

An HPLC UV–Vis (VWD) spectrophotometer (Agilent 1100 Series, Waldbronn, Germany) and an HPLC fluorescence detector (FLD, Agilent 1200 Series, Waldbronn, Germany) were used to continuously monitor SRHA and microsphere concentrations online. Sustained and constant signals generated in bypass injection of microsphere and SRHA were identical to those obtained by direct injection into the FLD and VWD flow cells, indicating that the

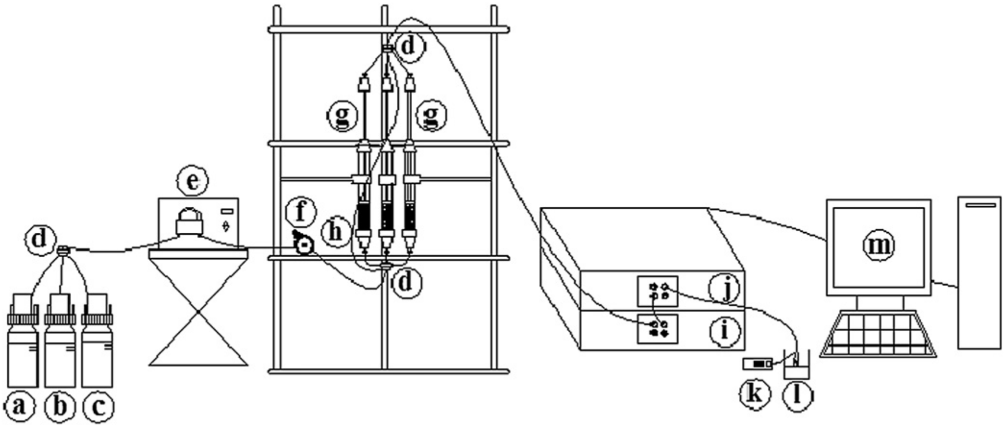

**Fig. 1.** Schematic illustration of the experimental setup. (a) Humic acid reservoir. (b) Flushing solution reservoir. (c) Microsphere suspension reservoir. (d) Switch valve. (e) HPLC pump. (f) Manual sample injector. (g) Sand columns (x 3). (h) Bypass line. (i) UV–Vis Spectrophotometer. (j) HPLC fluorescence detector. (k) pH meter. (l) Effluent collector. (m) Computer/data logger.