Supplementary Information (SI) for RSC Advances.

Supplementary Information

Influence of Solution Chemical Properties and Porous Medium Surface Coatings on the Transport and Retention Behavior of Polystyrene Microplastics

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S1. Preparation of HA

HA was used as model NOM compounds in in soils and groundwater environments. The HA used in this study was extracted from the soil samples (from Dunhua, Jilin Province, China) according to the method recommended by the International Humic Substances Society (IHSS). The HA stock solution was stirred overnight in the dark, and filtered through a 0.22 μm cellulose acetate filter paper (Milli pore Billerica, MA, USA) and stored at 4 °C for future use. The total organic carbon content of the HA stock solution was determined through high-temperature oxidation (TOC-L CPH, SHIMADZU, Japan). And the basic physical and chemical properties of HA can be found in our previous research paper [1].

S2. Electrokinetic Properties of PS – MPs and quartz sand

To better understand the mechanisms governing PS - MPs transport and deposition in saturated sand, PS - MPs was characterized under the same conditions as those employed in the column experiments described below. Electrophoretic mobilities were PS - MPs obtained using microelectrophoresis (Zhongcheng Digital Technology model JS94G, China) at room temperature, as described ealier[2, 3], and converted to zeta potentials using the Smoluchowski equation[4]. Streaming potentials of the iron oxyhydroxide - coated sand grains were measured[5] using a streaming potential analyzer (BI-EKA, Brookhaven Instruments Corp., Holtsville, NY) and converted to zeta potentials using the Helmholtz − Smoluchowski equation[4].

S3. Dynamic Light Scattering (DLS) Measurements.

The particle size distribution and dispersion parameters of PS - MPs in different background solutions were determined by Dynamic Light Scattering (DLS) method. To analyze the influence of background solutions (such as humic acid concentration, ionic strength, pH, etc.) on the agglomeration/ dispersion behavior of PS - MPs, and to provide experimental evidence for understanding the transport and retention behavior of PS - MPs in porous medium environments.

The average PS - MPs aggregate size and the intrinsic size distributions in various suspensions were determined using dynamic light scattering (DLS) (MasterSizer 2000, Malvern Instruments, UK). The DLS measurements were performed with a multi-detector light unit which employs a laser with a wavelength of 640 nm. For each experiment, 3 mL of 40 mg L^{-1} PS-MPs suspension was introduced into a glass vial which had been soaked in cleaning solution, thoroughly rinsed with DI water, and oven-dried under dust-free conditions. The scattered light intensity was detected by a photodetector at a scattering angle of 90°, and each auto - correction function was accumulated for 15 s. The intensity - weighted hydrodynamic particle size distributions were determined from the intensity - autocorrelation functions using the NNLS algorithm assuming the Stokes - Einstein equation for spherical particles. The intensity-weighted particle size distributions were further converted to number-weighted size distributions. The latter number-weighted sizes were used in the DLVO energy calculations. All characterization measurements were conducted in duplicate using freshly prepared suspensions for each condition.

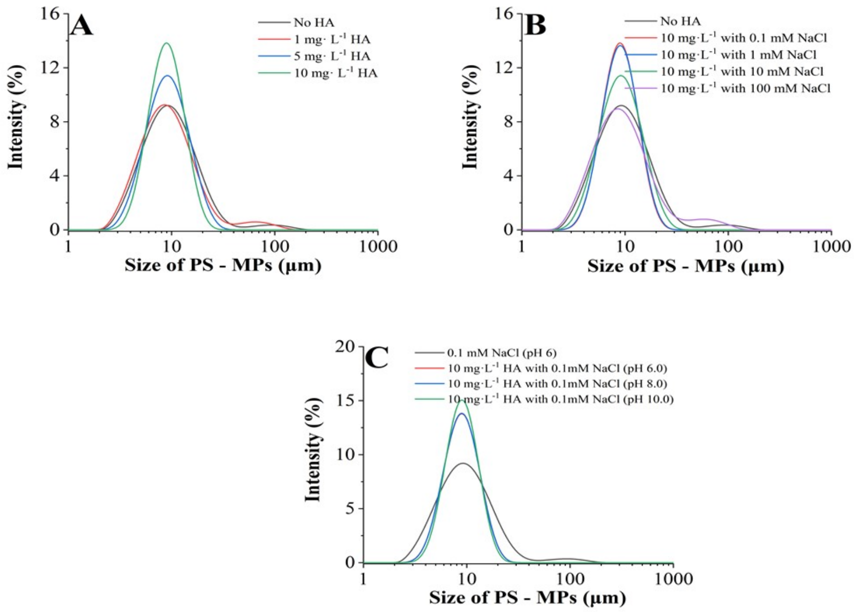

Fig. 1. Hydrodynamic diameter distribution of PS- MPs under different experimental conditions

S4. DLVO Theory

Derjaguin - Landau - Verwey - Overbeek (DLVO) theory was used to evaluate the interaction energy between PS - MPs and quartz sand. The total interaction energy (Φ_{total}) between particles is the sum of van der Waals forces (Φ_{vdw}) and electrostatic interactions (Φ_{elec})[6]. The PS - MPs system is considered as a ball - spherical interaction system, and the PS – MPs - quartz sand system is considered as a ball - plate interaction system to estimate the interaction energy[7].

The electrostatic interactions (Φ_{elec}) and van der Waals (Φ_{vdw}) were calculated for PS – MPs and quartz sand system described below equations, respectively.

$$\Phi_{elec} = \pi\varepsilon_0\varepsilon r_p\left\{2\psi_p\psi_s ln\frac{1 + exp(- kh)}{1 - exp(- kh)} + \left(\psi_p^2 + \psi_S^2\right)ln[1 - exp(- 2kh)]\right\}$$

where ε is the dielectric constant of water (78.5 $C^2 \cdot N^{-1} \cdot m^{-2}$), ε_0 is the vacuum dielectric constant (8.854 × 10^{-12} $C^2 \cdot N^{-1} \cdot m^{-2}$), and r_p is the average radius PS - MPs. Ψ_p and Ψ_s are the surface potentials of PS - MPs and quartz sand, and h is the separation distance [nm] between the interfaces. k is the Debye - Hückel parameter (m^{-1}), the value of which was calculated using the following equation:

$$k = \sqrt{\frac{e^{2\sum_{i} n_{j0} z^2}}{\varepsilon\varepsilon_0 kT}}$$

where e is the electron charge (1.602 × 10^{-19}C), n_{j0} is the number concentration of ions in solution, z is the ion valence, k is Boltzmann's constant (1.38 × 10^{-23}J·K^{-1}), and T is the absolute temperature (298 K).

$$\Phi_{vdw} = - \frac{A_{123}r_p}{6h}\left[1 + \frac{14h}{\lambda}\right]^{-1}$$

where λ is the characteristic wavelength (typically 100 nm), and A_{123} (1.0×10^{-20} J) and A_{121} (1.3×10^{-20} J) are Hamaker constants for PS - MPs - water - PS- MPs. The value of A_{123} was calculated using the following equation:

$$A_{123} = \left(\sqrt{A_{11}} - \sqrt{A_{22}}\right)\left(\sqrt{A_{33}} - \sqrt{A_{22}}\right)$$

where A_{11}, A_{22}, and A_{33} are the Hamaker constants of PS - MPs, water, and quartz sand, respectively, and A_{11} = 7.9 × 10^{-20} J, A_{22} = 4.0 × 10^{-20} J, and A_{33} = 6.0 × 10^{-20} J.

Eventually, equations were used to calculate the electrostatic (Φ_{elec}) and Van der Waals (Φ_{vdw}) interaction energies.

$$\Phi_{elec} = 2\pi\varepsilon_0\varepsilon r_p\psi_p^2 ln[1 + exp(-kh)]$$

$$\Phi_{vdw} = -\frac{A_{121}r_p}{12h}\left[1 + \frac{14h}{\lambda}\right]^{-1}$$

$$A_{121} = \left(\sqrt{A_{11}} - \sqrt{A_{22}}\right)^2$$

S5. Calculation of Single Collector Contact Efficiency (SCCE) η_0

Single Collector Contact Efficiency (SCCE), usually denoted as η_0, is a key parameter in the colloid filtration theory (Colloid Filtration Theory, CFT), and which one is used to describe the efficiency of physical collisions between suspended particles (such as MPs) and individual collector particles (i.e., "collectors") in porous media. The purpose of calculating η_0 is to quantify the collision probability of particles without the influence of surface interaction forces, which is the basis for further calculating the attachment efficiency α[8]. Its calculation formula is as follows:

$$\eta_0 = A_S^{1/3} N_R^{-0.081} N_{Pe}^{-0.715} N_{Vdw}^{0.052} + 0.55N_R^{1.675} N_A^{0.125} + 0.22N_R^{-0.24} N_G^{1.11} + N_{Vdw}^{0.053}$$

Where A_s is the porosity constant; N_R is the aspect ratio; N_{Pe} is the Pickerel constant; N_{vdw} is the van der Waals constant; N_a is the attraction constant; N_G is the gravitational constant. All parameters are dimensionless and calculated using the following series of formulas[9, 10]:

$$A_s = \frac{1 - \varepsilon^5}{1 - 1.5\varepsilon + 1.5\varepsilon^5 - \varepsilon^6}$$

$$\varepsilon = (1 - \theta)^{\frac{1}{3}}$$

$$N_R = \frac{d_p}{d_c}$$

$$N_{pe} = \frac{vd_c}{D_\infty}$$

$$N_{vdW} = \frac{A}{kT}$$

$$N_A = \frac{A}{12\pi a_p^2 v\eta}$$

$$N_G = \frac{2a_p^2(\rho_p - \rho_r)g}{9v\eta}$$

where ε is a parameter related to porosity, d_p is the diameter of PS - MPs (10 μm); v is the pore water flow velocity ($m{\cdot}s^{-1}$); D_∞ is the solution volume coefficient ($m^2{\cdot}s^{-1}$); η is the solution viscosity (8.9×10^{-4} $kg{\cdot}m^{-1}{\cdot}s^{-1}$); ρ_p is the density of PS - MPs (1.05×10^3 $kg{\cdot}m^{-3}$); ρ_r is the solution density (1.0×10^3 $kg{\cdot}m^{-3}$); g is the gravitational acceleration constant (9.8 $m{\cdot}s^{-2}$)[11].

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