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AOPs enhance the migration of polystyrene nanoparticles in saturated quartz sand

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SEM analysis

Briefly, NPs samples were first dispersed in water with sonication for 20 min, and then add dropwise onto an aluminium foil sheet. After desiccation, samples were sprayed with aurum for 240 seconds, and the surface morphologies of all samples were observed using a scanning electron microscope (JSM-7600F, JEOL, Japan).

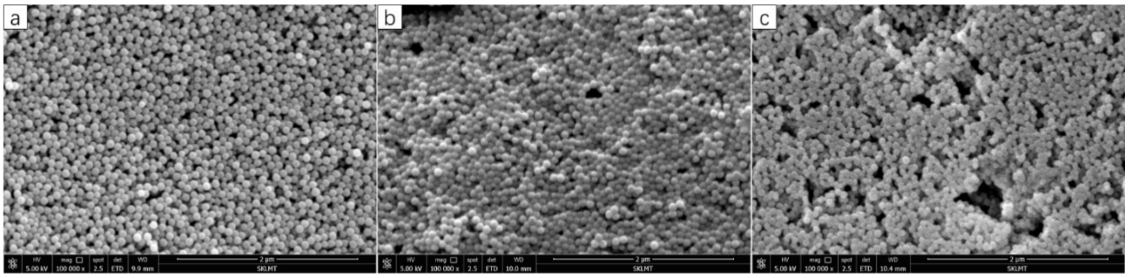

Figure S1 SEM images of NPs: (a) P-PS; (b) F-PS and (c) N-PS

Water contact angles

Contact angle were measured with a optical contact angle goniometer (HARKE - SPCA, China) using a reported method.[1] Briefly, 0.1 g of nanoplastic powder was first flattened on a glass slide. Then, 5.0 μL ultrapure water droplet was deposited onto the flattened nanoplastic, and the digital image of droplet was taken when the droplet reached a steady state on the substrate. All measurement were run at least nine independent times.

Calculation of DLVO and XDLVO interaction energy

The classical Derjaguine-Landaue-Verweye-Overbeek (DLVO) theory was employed to calculate the interaction energies between NPs, and XDLVO theory was used for the interaction between NPs and quartz sand.[2-6]

Total interaction energy (Φ_{TOT}) of DLVO theory includes van der Waals interaction (Φ_{VDW}) and repulsive electrostatic double layer interactions (Φ_{EDL}):[7]

$$\Phi_{TOT} = \Phi_{VDW} + \Phi_{EDL} \tag{S1}$$

The van der Waals interaction between NPs is obtained by the following equation:[7]

$$\Phi_{VDW} = -\frac{Ar_{PS}}{12h} \tag{S2}$$

where r_{PS} is the radius of NPs (m), h is the separation distance of NPs-NPs (m), A is the Hamaker constant of NPs-water system (J), which can be calculated as:[8]

$$A = 24\pi h_0^2 \left(\sqrt{\Upsilon_{PS}^{LW}} - \sqrt{\Upsilon_{W}^{LW}}\right)^2 \tag{S3}$$

where h_0 is the minimum equilibrium distance between NPs (0.157nm), Υ_{PS}^{LW} and Υ_{W}^{LW} represent the Lifshitz–van der Waals interfacial tension values for nanoparticles and water. The value of Υ_{W}^{LW} in this study is 21.8 mJ/m^2. The Υ_{PS}^{LW} of pristine/aged NPs can be calculated by the following equation:[8]

$$\Upsilon_{\mathrm{i}}^{L}(1+\cos\theta) = 2(\sqrt{\Upsilon_{i}^{LW}\Upsilon_{PS}^{LW}} + \sqrt{\Upsilon_{i}^{+}\Upsilon_{PS}^{-}} + \sqrt{\Upsilon_{i}^{-}\Upsilon_{PS}^{+}}) \tag{S4}$$

where the subscripts i represents water (Υ_{W}^{L}=72.8, Υ_{W}^{LW}=21.8, Υ_{W}^{+}= Υ_{W}^{-}=25.5 mJ/m^2), glycerol (Υ_{g}^{L}=64.0, Υ_{g}^{LW}=34.0, Υ_{g}^{+}=3.92, Υ_{g}^{-}=57.4 mJ/m^2), or diiodomethane (Υ_{d}^{L}=72.8, Υ_{d}^{LW}=21.8, Υ_{d}^{+}= Υ_{d}^{-}= 0 mJ/m^2), respectively.[8] The contact angles (θ) of NPs with three probing liquids were shown in Table S1. Using equation S4, we obtain the values of Υ_{P-PS}^{LW}, Υ_{F-PS}^{LW}, Υ_{N-PS}^{LW}, which were 43.72, 45.30 and 46.78 mJ/m^2, respectively. The Hamaker constants for P-PS, F-PS and N-PS in water system were 6.99×10^{-21}, 7.89×10^{-21} and 8.75×10^{-21}J, respectively.

Table S1. The contact angles of NPs with three probing liquids

	θ_w	θ_g	θ_d
P-PS	104.3±1.0°	82.0±0.7°	31.2±0.7 °
F-PS	92.5±0.9 °	73.0±0.8 °	27.3±0.4 °
N-PS	85.4±0.3 °	65.2±0.9 °	23.2±0.7 °

The Φ_{EDL} between NPs can be calculated as:[5]

$$\Phi_{\mathrm{EDL}} = 32\pi\varepsilon_0\varepsilon_r r_{PS}\left(\frac{k_B T}{ze}\right)^2 \tanh^2\left(\frac{ze\varphi}{4k_B T}\right)\exp\left(-\kappa h\right) \tag{S5}$$

where ε_0 is the vacuum permittivity (8.854×10^{-12} C·V^{-1}·m^{-1}), ε_{r} is the relative dielectric permittivity of water at 25 °C (78.4), k_{B} is the Boltzmann constant (1.38×10^{-23} J/K), T is the Kevin temperature (298 K), z is the valence of electrolyte, e is the elementary charge (-1.6×10^{-19} C), and κ is the Debye length (m^{-1}), defined as[5]

$$\kappa = \sqrt{\frac{2000 N_A e^2 I}{\varepsilon_0 \varepsilon_r k_B T}} \tag{S6}$$

N_A is the Avogadro number (6.022×10^{23} mol^{-1}), I is the ionic strength (1.0×10^{-5} mol/L NaCl for deionized water), φ is the surface charge of NPs, taking the zeta-potential (ζ) of NPs here.

The interaction energy of XDLVO theory (Φ'_{TOT}) is defined as the sum of three interactions, Φ'_{VDW}, Φ'_{EDL} and Lewis acid-base interaction (Φ'_{AB}):[7]

$$\Phi'_{TOT} = \Phi'_{VDW} + \Phi'_{EDL} + \Phi'_{AB} \tag{S7}$$

$$\Phi'_{\mathrm{VDW}} = -\frac{A' r_{PS}}{6h\left(1 + 14h/\lambda\right)} \tag{S8}$$

where h is the separation distance of NPs-sand (m), λ is the characteristic wavelength of 100 nm,[6] A' is the Hamaker constant of NPs-sand system, which can be calculated as: [8]

$$A' = 24\pi h_0^2 \left(\sqrt{\Upsilon_{PS}^{LW}} - \sqrt{\Upsilon_W^{LW}}\right)\left(\sqrt{\Upsilon_S^{LW}} - \sqrt{\Upsilon_W^{LW}}\right) \tag{S9}$$

where the Υ_S^{LW} value in this study refers to previous literature (39.2 mJ/m^2), Φ'_{EDL} is calculated by the following equation:[8]

$$\Phi'_{\mathrm{EDL}} = \pi r \varepsilon_0 \varepsilon_r \left\{ 2\varphi_1\varphi_2 \ln\left[\frac{1+\exp(-\kappa h)}{1-\exp(-\kappa h)}\right] + \left(\varphi_1^2 + \varphi_2^2\right)\ln\left[1-\exp(-2\kappa h)\right] \right\} \tag{S10}$$

where φ_1 and φ_2 are the surface zeta-potentials of NPs and sand, respectively.

Φ'_{AB} can be calculated as:[8]

$$\Phi'_{\mathrm{AB}} = 2\pi r_{PS} \lambda_w \Delta G_{h_0}^{AB} \exp\left(\frac{h_0 - h}{\lambda_w}\right) \tag{S11}$$

where λ_w is the characteristic decay length (1.0 nm) of acid-base interactions in water, h_0 is the minimum equilibrium distance between NPs and sand surface (0.157 nm), and $\Delta G_{h_0}^{AB}$ can be calculated as:[8]

$$\Delta G_{h0}^{AB} = 2\left[\sqrt{\gamma_W^+}\left(\sqrt{\gamma_{PS}^-} + \sqrt{\gamma_s^-} - \sqrt{\gamma_W^-}\right) + \sqrt{\gamma_W^-}\left(\sqrt{\gamma_{PS}^+} + \sqrt{\gamma_s^+} - \sqrt{\gamma_W^+}\right) - \sqrt{\gamma_{PS}^- \gamma_s^+} - \sqrt{\gamma_{PS}^+ \gamma_s^-}\right] \tag{S12}$$

where the subscript w, NPs and s represent water, nanoparticles and sand, respectively. The electron-accepting (Υ_{PS}^{+}) and electron-donating (Υ_{PS}^{-}) interfacial tension values of aging nanoplastics can be obtained from equation S6. The interfacial tension values in this study of $\Upsilon_{W}^{+}=\Upsilon_{W}^{-}$=25.5 mJ/m^2, Υ_{s}^{+}=1.4 mJ/m^2, Υ_{s}^{-} =47.8 mJ/m^2, Υ_{PS}^{+}=0.02 mJ/m^2 and Υ_{PS}^{-}=7.6 mJ/m^2 for NPs. [8]

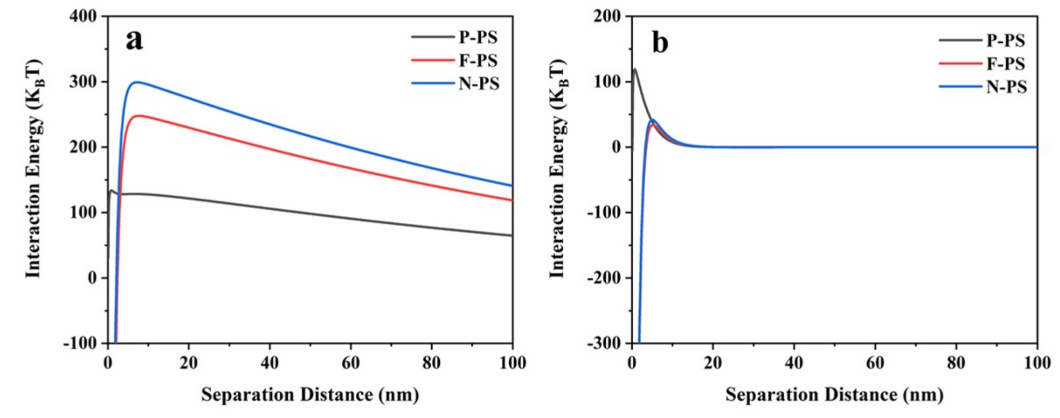

Figure S2 The XDLVO interaction energy profiles between NPs and sand in ultrapure water (a) and 10 mM NaCl solution (b)

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