# Supplementary Material

# Transport Behavior of Polystyrene Nanoplastics in Saturated Quartz Sand: Coupled Experimental and Modeling Approaches

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Equation: 1

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## Equation

Equation S1

$$k^{-1} = \sqrt{\frac{\varepsilon_r \varepsilon_0 k_B T}{2 N_A e^2 I}}$$

The definitions of all symbols used in the equations are provided in Table S3.

## Tables

Table S1 Background solution conditions and influencing factors set for PS NPs transport experiments in saturated quartz sand columns

| Solute Type | Cation Valence State | pH | IS (mmol/L) | $C_0$ (mg/L) | Flow Rate (mL/min) |
|---|---|---|---|---|---|
| | NaCl | 5.5 | 1 | 10 | 1 |
| | NaCl | 5.5 | 10 | 10 | 1 |
| | NaCl | 5.5 | 100 | 10 | 1 |
| | NaCl | 7.5 | 1 | 10 | 1 |
| | NaCl | 7.5 | 10 | 10 | 1 |
| | NaCl | 7.5 | 100 | 10 | 1 |
| | NaCl | 9.5 | 1 | 10 | 1 |
| PS NPs PS | NaCl | 9.5 | 10 | 10 | 1 |
| NPs-8 PS | NaCl | 5.5 | 1 | 10 | 0.5 |
| NPs-24 PS | NaCl | 5.5 | 10 | 10 | 0.5 |
| NPs-800 | NaCl | 5.5 | 1 | 10 | 2 |
| | NaCl | 5.5 | 10 | 10 | 2 |
| | NaCl | 5.5 | 1 | 5 | 1 |
| | NaCl | 5.5 | 10 | 5 | 1 |
| | NaCl | 5.5 | 1 | 20 | 1 |
| | NaCl | 5.5 | 10 | 20 | 1 |
| | $CaCl_2$ | 5.5 | 1 | 10 | 1 |
| | $CaCl_2$ | 5.5 | 10 | 10 | 1 |

35 Table S2 Fitted parameters of BTC for Br.

| Flow Rate (mL/min) | Darcy Velocity (cm/min) | Adsorption Isotherm Coefficient (cm/min) | Dispersion Coefficient ($cm^2$/min) | $R^2$ |
|---|---|---|---|---|
| 1 | 0.566 | 0.785 | 0.0986 | 0.996 |

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37 Table S3 Parameters and significance in the DLVO force calculation equation

| Parameter | Meaning |
|---|---|
| $V_{TOT}$ | Total interaction energy |
| $V_{VDW}$ | Van der Waals potential energy |
| $V_{EDL}$ | Electrostatic repulsion potential energy |
| r | Radius of PS NPs (m) |
| h | Separation distance between PS NPs and porous medium surface (nm) |
| λ | Characteristic wavelength of interaction force (typically 100 nm) |
| $\varepsilon_0$ | Vacuum permittivity ($8.854\times10^{-12}$ F/m) |
| $\varepsilon_r$ | Relative permittivity of water (78.5, dimensionless) |
| $\emptyset_1$ | Zeta potential of PS NPs (mV) |
| $\emptyset_2$ | Zeta potential of quartz sand (mV) |
| k | Reciprocal of Debye length ($m^{-1}$), $k=\sqrt{\frac{2N_A e^2 I}{\varepsilon_r \varepsilon_0 k_B T}}$ |
| I | Ionic strength (mol/L), $I=\frac{1}{2}\sum_{i=1}^{n} c_i z_i^2$ |
| $N_A$ | Avogadro's constant ($6.02\times10^{23}$ $mol^{-1}$) |
| T | Temperature in Kelvin (298 K) |
| e | Elementary charge ($-1.602\times10^{-19}$ C) |
| ci | Concentration of ion i (mol/L) |
| zi | Valence of ion i |
| n | Number of ion species in the system |
| $k_B$ | Boltzmann constant ($1.381\times10^{-23}$ J/K) |
| $A_{11}$ | Hamaker constant of PS NPs ($6.60\times10^{-20}$ J) |

| | |
|---|---|
| $A_{22}$ | Hamaker constant of quartz sand ($8.86\times10^{-20}$ J) |
| $A_{33}$ | Hamaker constant of water ($3.7\times10^{-20}$ J) |
| $A_{132}$ | Combined Hamaker constant for PS NPs–water–quartz sand system |

Table S4 Zeta potential and particle size of PS NPs under different physicochemical conditions

| Solute Type | Cationic valence | pH | IS（mmol/L） | PS NPs Concentration（mg/L） | Zeta Potential（mV） | Particle Size（nm） |
|---|---|---|---|---|---|---|
| PS NPs | NaCl | 5.5 | 1 | 10 | -16.20 | 110.72 |
| | NaCl | 5.5 | 10 | 10 | -10.63 | 103.92 |
| | NaCl | 5.5 | 100 | 10 | -3.36 | 509.45 |
| | NaCl | 7.5 | 1 | 10 | -16.79 | 105.25 |
| | NaCl | 7.5 | 10 | 10 | -11.93 | 102.10 |
| | NaCl | 7.5 | 100 | 10 | -4.35 | 1527.24 |
| | NaCl | 9.5 | 1 | 10 | -19.86 | 103.09 |
| | NaCl | 9.5 | 10 | 10 | -12.34 | 100.74 |
| | NaCl | 5.5 | 1 | 5 | -13.37 | 100.39 |
| | NaCl | 5.5 | 10 | 5 | -8.98 | 104.33 |
| | NaCl | 5.5 | 1 | 20 | -20.89 | 105.97 |
| | NaCl | 5.5 | 10 | 20 | -15.33 | 106.26 |
| | $CaCl_2$ | 5.5 | 1 | 10 | -11.33 | 108.60 |
| | $CaCl_2$ | 5.5 | 10 | 10 | -9.33 | 829.85 |

Table S5 Zeta potential and particle size of PS NPs-8 under different physicochemical conditions

| Solute Type | Cationic valence | pH | IS（mmol/L） | PS NPs Concentration（mg/L） | Zeta Potential（mV） | Particle Size（nm） |
|---|---|---|---|---|---|---|
| PS NPs-8 | NaCl | 5.5 | 1 | 10 | -18.74 | 99.75 |
| | NaCl | 5.5 | 10 | 10 | -14.77 | 99.47 |
| | NaCl | 7.5 | 1 | 10 | -19.60 | 99.63 |
| | NaCl | 7.5 | 10 | 10 | -16.83 | 98.76 |
| | NaCl | 9.5 | 1 | 10 | -20.00 | 101.27 |
| | NaCl | 9.5 | 10 | 10 | -17.20 | 97.29 |
| | NaCl | 5.5 | 1 | 5 | -17.93 | 100.72 |
| | NaCl | 5.5 | 10 | 5 | -11.78 | 99.61 |
| | NaCl | 5.5 | 1 | 20 | -21.45 | 100.21 |
| | NaCl | 5.5 | 10 | 20 | -16.24 | 98.71 |
| | $CaCl_2$ | 5.5 | 1 | 10 | -14.50 | 97.71 |
| | $CaCl_2$ | 5.5 | 10 | 10 | -9.56 | 219.42 |

Table S6 Zeta potential and particle size of PS NPs-24 under different physicochemical conditions

| Solute Type | Cationic valence | pH | IS（mmol/L） | PS NPs Concentration（mg/L） | Zeta Potential（mV） | Particle Size（nm） |
|---|---|---|---|---|---|---|
| PS NPs-24 | NaCl | 5.5 | 1 | 10 | -20.34 | 97.37 |
| | NaCl | 5.5 | 10 | 10 | -17.13 | 94.47 |
| | NaCl | 7.5 | 1 | 10 | -20.98 | 96.15 |
| | NaCl | 7.5 | 10 | 10 | -17.95 | 95.19 |
| | NaCl | 9.5 | 1 | 10 | -22.61 | 98.23 |
| | NaCl | 9.5 | 10 | 10 | -18.90 | 94.40 |
| | NaCl | 5.5 | 1 | 5 | -19.19 | 97.44 |
| | NaCl | 5.5 | 10 | 5 | -15.13 | 95.73 |
| | NaCl | 5.5 | 1 | 20 | -22.14 | 96.21 |
| | NaCl | 5.5 | 10 | 20 | -18.99 | 95.66 |
| | $CaCl_2$ | 5.5 | 1 | 10 | -15.20 | 94.28 |
| | $CaCl_2$ | 5.5 | 10 | 10 | -10.61 | 195.41 |

Table S7 Zeta potential and particle size of PS NPs-800 under different physicochemical conditions

| Solute Type | Cationic valence | pH | IS（mmol/L） | PS NPs Concentration（mg/L） | Zeta Potential（mV） | Particle Size（nm） |
|---|---|---|---|---|---|---|
| PS NPs-800 | NaCl | 5.5 | 1 | 10 | -36.75 | 956.00 |
| | NaCl | 5.5 | 10 | 10 | -16.23 | 1028.58 |
| | NaCl | 7.5 | 1 | 10 | -49.46 | 924.95 |
| | NaCl | 7.5 | 10 | 10 | -31.59 | 925.68 |
| | NaCl | 9.5 | 1 | 10 | -54.52 | 935.86 |
| | NaCl | 9.5 | 10 | 10 | -45.50 | 921.29 |
| | NaCl | 5.5 | 1 | 5 | -24.38 | 804.82 |
| | NaCl | 5.5 | 10 | 5 | -6.75 | 1204.64 |
| | NaCl | 5.5 | 1 | 20 | -44.72 | 908.59 |
| | NaCl | 5.5 | 10 | 20 | -27.49 | 1196.42 |
| | $CaCl_2$ | 5.5 | 1 | 10 | -16.63 | 1117.01 |
| | $CaCl_2$ | 5.5 | 10 | 10 | -8.87 | 1622.52 |

55 Table S8 Zeta potential of quartz sand under different physicochemical conditions

| Media Type | Cationic valence | pH | IS（mmol/L） | Zeta Potential（mV） |
|---|---|---|---|---|
| Quartz sand | NaCl | 5.5 | 1 | -21.78 |
| | NaCl | 5.5 | 10 | -16.84 |
| | NaCl | 5.5 | 100 | -9.72 |
| | NaCl | 7.5 | 1 | -22.74 |
| | NaCl | 7.5 | 10 | -17.18 |
| | NaCl | 7.5 | 100 | -10.80 |
| | NaCl | 9.5 | 1 | -24.04 |
| | NaCl | 9.5 | 10 | -20.46 |
| | $CaCl_2$ | 5.5 | 1 | -12.31 |
| | $CaCl_2$ | 5.5 | 10 | -8.35 |

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57 Table S9 Fitted parameters of PS NPs transport in the quartz sand columns obtained by Hydrus-1D

| Number | Solute Type | Cationic valence | pH | IS（mmol/L） | $C_0$（mg/L） | Flow rate（mL/min） | $k_{1a}$[1]（$min^{-1}$） | $k_{1d}$[2]（$min^{-1}$） | $k_{2a}$[3]（$min^{-1}$） | $S_{max2}$[4]（mg/kg） | Penetration（%） | $R^2$ |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | | NaCl | 5.5 | 1 | 10 | 1 | 9.292 | 3.487 | 0.0524 | 0.405 | 84.483 | 0.9912 |
| 2 | | NaCl | 5.5 | 10 | 10 | 1 | 3.167 | 1.418 | 0.1428 | 0.901 | 64.784 | 0.9846 |
| 3 | | NaCl | 5.5 | 100 | 10 | 1 | NA | NA | NA | NA | 11.697 | 0.9641* |
| 4 | | NaCl | 7.5 | 1 | 10 | 1 | 6.481 | 2.532 | 0.0500 | 0.357 | 85.965 | 0.9936 |
| 5 | | NaCl | 7.5 | 10 | 10 | 1 | 4.216 | 1.882 | 0.1514 | 0.840 | 66.046 | 0.9902 |
| 6 | | NaCl | 7.5 | 100 | 10 | 1 | NA | NA | NA | NA | 14.913 | 0.9125* |
| 7 | | NaCl | 9.5 | 1 | 10 | 1 | 9.774 | 4.317 | 0.0377 | 0.323 | 87.946 | 0.9983 |
| 8 | | NaCl | 9.5 | 10 | 10 | 1 | 6.489 | 2.937 | 0.1100 | 0.773 | 70.359 | 0.9919 |
| 9 | PS NPs | NaCl | 5.5 | 1 | 10 | 0.5 | 5.207 | 2.369 | 0.1447 | 0.488 | 78.768 | 0.9852 |
| 10 | | NaCl | 5.5 | 10 | 10 | 0.5 | 6.540 | 2.924 | 0.1464 | 0.934 | 63.695 | 0.9970 |
| 11 | | NaCl | 5.5 | 1 | 10 | 2 | 8.731 | 3.777 | 0.0341 | 0.323 | 88.358 | 0.9980 |
| 12 | | NaCl | 5.5 | 10 | 10 | 2 | 4.287 | 1.881 | 0.1321 | 0.698 | 71.282 | 0.9932 |
| 13 | | NaCl | 5.5 | 1 | 5 | 1 | 4.701 | 2.048 | 0.0983 | 0.485 | 79.604 | 0.9931 |
| 14 | | NaCl | 5.5 | 10 | 5 | 1 | 4.761 | 2.184 | 0.1771 | 1.024 | 59.526 | 0.9949 |
| 15 | | NaCl | 5.5 | 1 | 20 | 1 | 8.720 | 3.876 | 0.0309 | 0.311 | 89.046 | 0.9975 |
| 16 | | NaCl | 5.5 | 10 | 20 | 1 | 6.845 | 3.047 | 0.0757 | 0.496 | 80.255 | 0.9936 |
| 17 | | $CaCl_2$ | 5.5 | 1 | 10 | 1 | 5.323 | 2.434 | 0.2629 | 1.354 | 46.569 | 0.9949 |

| | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 18 | | $CaCl_2$ | 5.5 | 10 | 10 | 1 | NA | NA | NA | NA | 6.790 | 0.9908* |

Note: [1] represents the first-order attachment coefficient at site 1, [2] represents the first-order desorption coefficient at site 1, [3] represents the first-order attachment coefficient at site 2, and [4] represents the maximum solid-phase retention concentration of the colloid at site 2. NA indicates that valid data could not be fitted using the two-site kinetic retention model (the two-site model is no longer applicable under these experimental conditions). * indicates that the breakthrough curve for this set of experimental data was fitted using the single-site adsorption model.

63 Table 10 Fitted parameters of PS NPs-800 transport in the quartz sand columns obtained by Hydrus-1D

| Number | Solute Type | Cationic valence | pH | IS（mmol/L） | $C_0$（mg/L） | Flow rate（mL/min） | $k_{1a}$[1]（$min^{-1}$） | $k_{1d}$[2]（$min^{-1}$） | $k_{2a}$[3]（$min^{-1}$） | $S_{max2}$[4]（mg/kg） | Penetration（%） | $R^2$ |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | PS NPs-800 | NaCl | 5.5 | 1 | 10 | 1 | 10.000 | 4.468 | 0.0431 | 2.298 | 75.286 | 0.9991 |
| 2 | | NaCl | 5.5 | 10 | 10 | 1 | 4.258 | 1.747 | 0.0711 | 6.390 | 60.829 | 0.9945 |
| 3 | | NaCl | 7.5 | 1 | 10 | 1 | 9.948 | 4.385 | 0.0380 | 2.836 | 77.143 | 0.9991 |
| 4 | | NaCl | 7.5 | 10 | 10 | 1 | 4.529 | 2.049 | 0.0644 | 3.966 | 64.782 | 0.9958 |
| 5 | | NaCl | 9.5 | 1 | 10 | 1 | 8.450 | 3.791 | 0.0400 | 1.847 | 77.299 | 0.9992 |
| 6 | | NaCl | 9.5 | 10 | 10 | 1 | 7.288 | 3.200 | 0.0587 | 3.664 | 67.314 | 0.9978 |
| 7 | | NaCl | 5.5 | 1 | 10 | 0.5 | 6.241 | 2.828 | 0.0455 | 2.123 | 74.516 | 0.9965 |
| 8 | | NaCl | 5.5 | 10 | 10 | 0.5 | 3.751 | 1.642 | 0.0756 | 10.000 | 58.205 | 0.9954 |
| 9 | | NaCl | 5.5 | 1 | 10 | 2 | 10.000 | 4.305 | 0.0390 | 1.337 | 78.855 | 0.9984 |
| 10 | | NaCl | 5.5 | 10 | 10 | 2 | 9.774 | 4.299 | 0.0500 | 9.021 | 69.596 | 0.9988 |
| 11 | | NaCl | 5.5 | 1 | 5 | 1 | NA | NA | NA | NA | 38.203 | 0.9946* |
| 12 | | NaCl | 5.5 | 10 | 5 | 1 | NA | NA | NA | NA | 32.521 | 0.9829* |
| 13 | | NaCl | 5.5 | 1 | 20 | 1 | 10.000 | 4.510 | 0.0439 | 1.516 | 76.440 | 0.9988 |
| 14 | | NaCl | 5.5 | 10 | 20 | 1 | 9.708 | 4.699 | 0.0704 | 3.847 | 62.577 | 0.9986 |
| 15 | | $CaCl_2$ | 5.5 | 1 | 10 | 1 | NA | NA | NA | NA | 47.054 | 0.9954* |
| 16 | | $CaCl_2$ | 5.5 | 10 | 10 | 1 | NA | NA | NA | NA | 38.023 | 0.9951* |

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66 Table 11 Fitted parameters of PS NPs-8 transport in the quartz sand columns obtained by Hydrus-1D

| Number | Solute Type | Cationic valence | pH | IS（mmol/L） | $C_0$（mg/L） | Flow rate（mL/min） | $k_{1a}$[1]（$min^{-1}$） | $k_{1d}$[2]（$min^{-1}$） | $k_{2a}$[3]（$min^{-1}$） | $S_{max2}$[4]（mg/kg） | Penetration（%） | $R^2$ |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | | NaCl | 5.5 | 1 | 10 | 1 | 8.558 | 3.787 | 0.0336 | 0.388 | 87.185 | 0.9973 |
| 2 | | NaCl | 5.5 | 10 | 10 | 1 | 9.860 | 4.228 | 0.0784 | 0.724 | 74.534 | 0.9988 |
| 3 | | NaCl | 7.5 | 1 | 10 | 1 | 9.927 | 4.134 | 0.0294 | 0.348 | 88.577 | 0.9985 |
| 4 | | NaCl | 7.5 | 10 | 10 | 1 | 9.933 | 4.264 | 0.0480 | 0.531 | 82.337 | 0.9983 |
| 5 | | NaCl | 9.5 | 1 | 10 | 1 | 9.759 | 4.059 | 0.0281 | 0.340 | 88.950 | 0.9988 |
| 6 | | NaCl | 9.5 | 10 | 10 | 1 | 5.087 | 2.178 | 0.0405 | 0.478 | 84.475 | 0.9967 |
| 7 | | NaCl | 5.5 | 1 | 10 | 0.5 | 9.933 | 4.498 | 0.0268 | 0.564 | 86.768 | 0.9985 |
| 8 | PS | NaCl | 5.5 | 10 | 10 | 0.5 | 4.292 | 1.942 | 0.1464 | 0.822 | 66.809 | 0.9918 |
| 9 | NPs-8 | NaCl | 5.5 | 1 | 10 | 2 | 10.000 | 4.216 | 0.0190 | 0.300 | 91.464 | 0.9983 |
| 10 | | NaCl | 5.5 | 10 | 10 | 2 | 9.903 | 4.264 | 0.0340 | 0.336 | 88.094 | 0.9988 |
| 11 | | NaCl | 5.5 | 1 | 5 | 1 | 9.716 | 4.220 | 0.0288 | 0.439 | 87.407 | 0.9990 |
| 12 | | NaCl | 5.5 | 10 | 5 | 1 | 6.430 | 2.873 | 0.1219 | 0.950 | 65.248 | 0.9951 |
| 13 | | NaCl | 5.5 | 1 | 20 | 1 | 9.572 | 4.292 | 0.0266 | 0.289 | 90.103 | 0.9980 |
| 14 | | NaCl | 5.5 | 10 | 20 | 1 | 10.000 | 4.445 | 0.0722 | 0.451 | 81.798 | 0.9957 |
| 15 | | $CaCl_2$ | 5.5 | 1 | 10 | 1 | 8.575 | 3.642 | 0.0957 | 0.747 | 72.186 | 0.9884 |
| 16 | | $CaCl_2$ | 5.5 | 10 | 10 | 1 | NA | NA | NA | NA | 12.617 | 0.9858* |

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68 Table 12 Fitted parameters of PS NPs-24 transport in the quartz sand columns obtained by Hydrus-1D

| Number | Solute Type | Cationic valence | pH | IS（mmol/L） | $C_0$（mg/L） | Flow rate（mL/min） | $k_{1a}$[1]（$min^{-1}$） | $k_{1d}$[2]（$min^{-1}$） | $k_{2a}$[3]（$min^{-1}$） | $S_{max2}$[4]（mg/kg） | Penetration（%） | $R^2$ |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | PS NPs-24 | NaCl | 5.5 | 1 | 10 | 1 | 8.293 | 3.564 | 0.0258 | 0.350 | 89.242 | 0.9986 |
| 2 | | NaCl | 5.5 | 10 | 10 | 1 | 9.703 | 4.453 | 0.0292 | 0.488 | 86.754 | 0.9984 |
| 3 | | NaCl | 7.5 | 1 | 10 | 1 | 9.210 | 4.060 | 0.0227 | 0.403 | 89.367 | 0.9981 |
| 4 | | NaCl | 7.5 | 10 | 10 | 1 | 9.906 | 4.614 | 0.0278 | 0.527 | 86.765 | 0.9985 |
| 5 | | NaCl | 9.5 | 1 | 10 | 1 | 10.000 | 4.512 | 0.0212 | 0.246 | 91.784 | 0.9979 |
| 6 | | NaCl | 9.5 | 10 | 10 | 1 | 10.000 | 4.441 | 0.0284 | 0.443 | 87.454 | 0.9987 |
| 7 | | NaCl | 5.5 | 1 | 10 | 0.5 | 8.382 | 3.765 | 0.0282 | 0.470 | 87.195 | 0.9988 |
| 8 | | NaCl | 5.5 | 10 | 10 | 0.5 | 5.236 | 2.262 | 0.0702 | 0.660 | 76.816 | 0.9970 |
| 9 | | NaCl | 5.5 | 1 | 10 | 2 | 9.882 | 4.343 | 0.0191 | 0.283 | 91.625 | 0.9984 |
| 10 | | NaCl | 5.5 | 10 | 10 | 2 | 9.941 | 4.422 | 0.0234 | 0.308 | 90.361 | 0.9988 |
| 11 | | NaCl | 5.5 | 1 | 5 | 1 | 9.998 | 4.366 | 0.0229 | 0.452 | 88.870 | 0.9983 |
| 12 | | NaCl | 5.5 | 10 | 5 | 1 | 7.817 | 3.248 | 0.0375 | 0.625 | 83.235 | 0.9985 |
| 13 | | NaCl | 5.5 | 1 | 20 | 1 | 9.117 | 4.093 | 0.0199 | 0.318 | 91.012 | 0.9980 |
| 14 | | NaCl | 5.5 | 10 | 20 | 1 | 9.793 | 4.185 | 0.0307 | 0.354 | 88.256 | 0.9979 |
| 15 | | $CaCl_2$ | 5.5 | 1 | 10 | 1 | 10.000 | 4.361 | 0.0394 | 0.892 | 80.595 | 0.9961 |
| 16 | | $CaCl_2$ | 5.5 | 10 | 10 | 1 | NA | NA | NA | NA | 22.702 | 0.9907* |

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# Figures

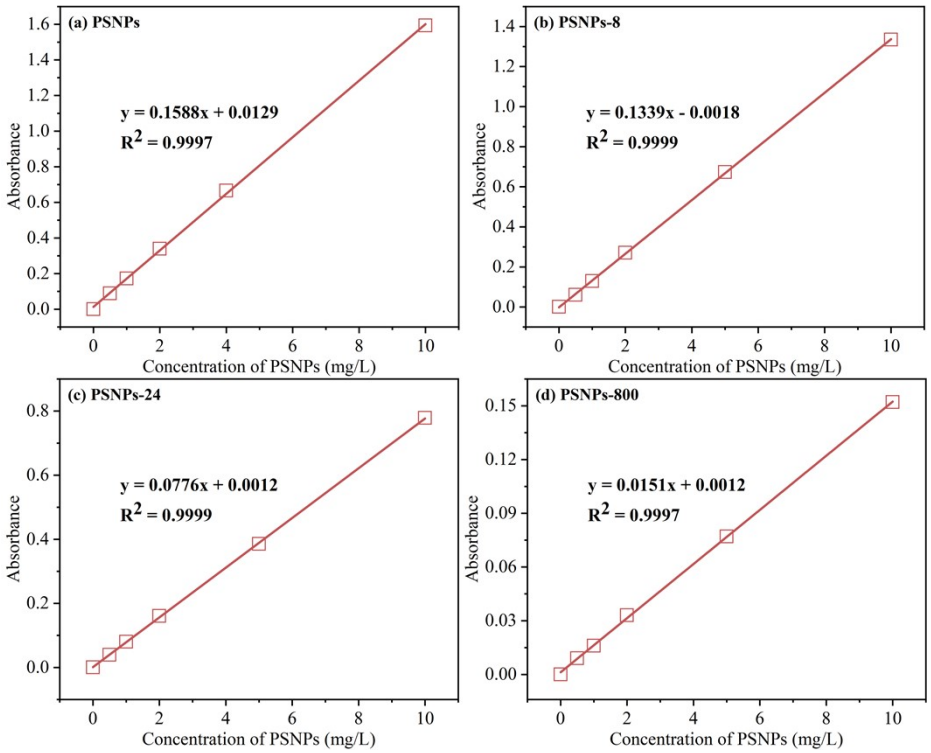
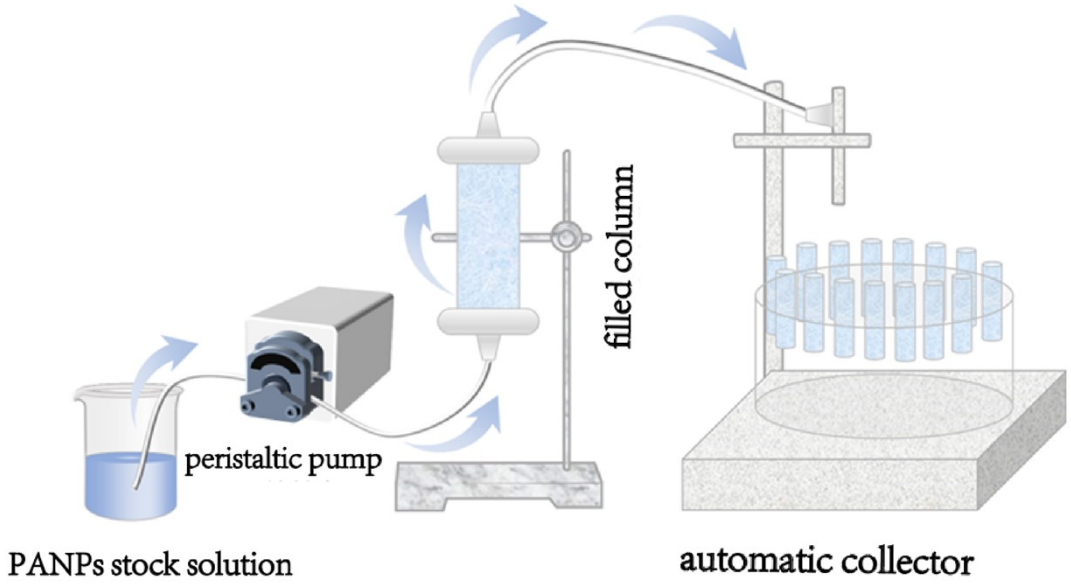



Fig. S1. Standard curves for PS NPs (a), PS NPs-8 (b), PS NPs-24 (c) and PS NPs-800 (d)

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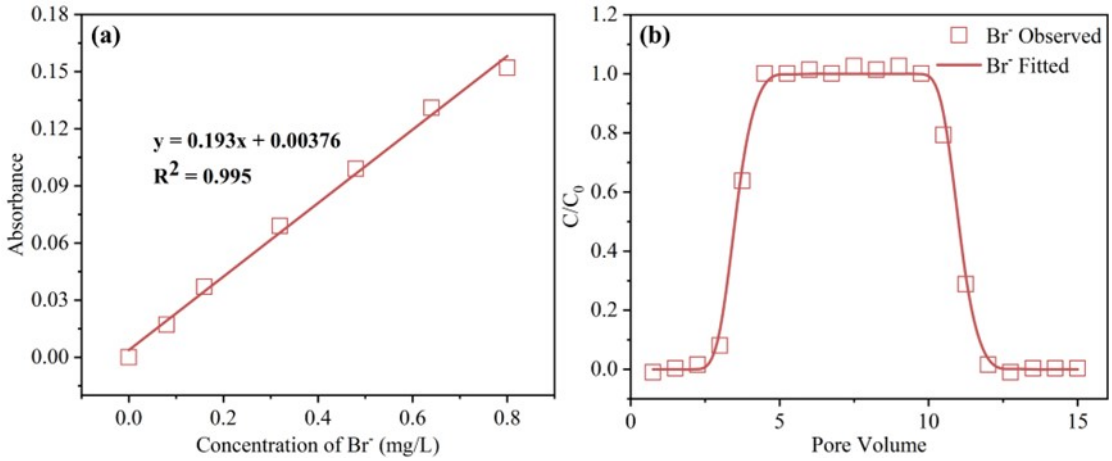
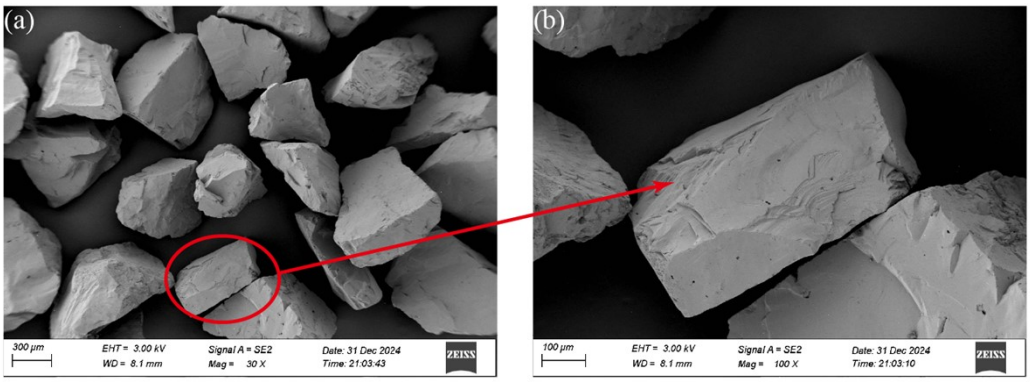
76 Fig. S2. Schematic diagram of the column transport experiments.




77

78 Fig. S3. Standard curve (a) and breakthrough curve (b) for Br in saturated quartz sand

79 columns

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81 Fig. S4. SEM images of quartz sand (a-b)