Supplementary Information for

2 Integrated Multimethod Approach for Size-Specific

3 Assessment of Potentially Toxic Element Adsorption onto

4 Micro- and Nanoplastics: Implications for Environmental Risk

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13 Equations Used:

14 •	Adsorption Efficiency (RE)(%) = $\frac{C_0 - C_e}{C_0} \times 100$	Eq. S1
15 •	Adsorption capacity $(q_e) = \frac{C_0 - C_e}{m}V$	Eq. S2
16 •	Distribution Coefficient $(K_d) = \frac{C_0 - C_e}{C_e} \times \frac{V}{m}$	Eq. S 3
17 •	Separation factor (SF)= $\frac{K_d(metal - 1)}{K_d(metal - 2)}$	Eq. S4

18 Where, C_0 and C_e (mg/L) represents initial and equilibrium concentration of the Cr, As, Se ion in 19 supernatant respectively. m (g) is adsorbent mass, V (mL) is solution volume, K_d (mL/g).

20 S1.2. Kinetics studies

- 21 <u>Pseudo first-order kinetics:</u> 22 $\ln (Q_e - Q_t) = \ln Q_e - k_1 t$ Eq. S5
- 23 Pseudo second-order kinetics:

$$\frac{t}{24} = \frac{1}{k_2 Q_e^2} + \frac{t}{Q_e}$$
Eq. S6

25 Where, q_e and q_t represents the adsorption capacity at equilibrium and time t (mg/g), respectively. 26 k_1 (min⁻¹) and k_2 (g mmol⁻¹ min⁻¹) represents parameters for kinetic rate constants for pseudo-first 27 order and pseudo-second-order model, respectively.

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29 S1.3. Adsorption isotherm studies

30 Langmuir adsorption isotherm:

$$\frac{C_e}{21} = \frac{C_e}{Q_{max}} + \frac{1}{k_L Q_{max}}$$
Eq. S7

32 Freundlich adsorption isotherm:

$$\log Q_e = \log K_f + \frac{1}{n} \log C_e$$
 Eq.S8

Separation factor
$$(R_L) = \frac{1}{1 + K_L C_o}$$
 Eq.S9

35 Where, Q_{max} and Q_e represents the maximum (theoretical) and equilibrium adsorption capacity 36 (mg/g) respectively, C_e is adsorbate concentration at equilibrium (mg/L), k_L (L/mg) and K_F (L/mg).

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39 Multi-angle light scattering

40 The scattered light intensity was detected under 19 active angles ranging from 12° to 156° with 41 an on-line coupled MALS detector. The MALS detector operated at 35 °C and was equipped with 42 a laser with a wavelength of 532 nm. The angular-dependent scattering intensity function $P(\Theta)$ 43 (form factor) for a solid sphere is given by:

$$P_{sphere}(\theta) = \left[\frac{3(\sin(u) - u\cos(u))}{u^3}\right]^2$$

$$u = a \cdot q = a \cdot 4\pi \frac{n_0}{\lambda_0} \sin^2\left(\frac{\theta}{2}\right)$$

46 with u including the particle radius a, refractive index of the eluent n_0 , the squared sin of half of 47 the scattering angle Θ and the incidental wavelength λ .

- 48 U is the product of the radius and the scattering vector, therefore u= a 4 pi n_0 sin^2(theta/2) /
- 49 lambda
- 50 For a solid sphere the relationship between radius of gyration (Rg) and spherical radius (R) can 51 be expressed by the following equation:

$$R = \sqrt{\frac{5}{3}} R_g$$

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53 The particle number per unit volume, N, is related to the angular dependent scattering intensity 54 $I(\Theta)$ by the following equation, taking the particle volume, V_p, the relative refractive index, m, and 55 k, the wave vector of the incident light = 2 π n₀ / λ , where λ is the laser wavelength, into account:

$$I(\theta) = N \frac{k^4 V_p^2 (m-1)^2}{4\pi^2} P(\theta)$$

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The particle volume was calculated after fitting the Rg distribution and converting Rg into a spherical equivalent using the relationship mentioned above. This spherical size was used to calculate the volume of a single sphere, V_p . Here, the described calculations were performed on the 90° scattering signal. After the determination of the number of particles per unit volume, the surface area per particle was calculated based on the spherical radius distribution across the complete size distribution. Finally, the surface area was multiplied by the number of particles to get a total accessible surface area for each size fraction per unit volume.

64 The integrated metal content was then divided by the integral of the total accessible surface area65 per size fraction.

The quantitative amount of heavy metal per COOH-PSNP particle mass was determined by the simple relationship of a calibration line that was constructed from three different injection amounts of native COOH-PSNPs to derive the COOH-PSNP amount and to compensate for recoveries smaller 100%.





71 **Reference:**

72 van de Hulst HC (1958) Light scattering by small particles. Q J R Meteorol Soc 84(360):198-

73 199. <u>https://doi.org/10.1002/qj.49708436025</u>





76 phases of focussing, elution and rinsing.



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78 Figure S2: Analysis of COOH-PSNPs and heavy metal adsorption after incubation in DI

water using AF4-MALS. Fractograms showing the MALS 90° signal for a mixture of COOH-PSNP sizes (100 nm, 500 nm, and 1000 nm) in DI water, demonstrating distinct elution profiles corresponding to each particle size. The radius of gyration (Rg) for each size fraction is plotted on the right axis, indicating significant agglomeration, especially of the 100 nm COOH-PSNP where the spectrum revealed strong agglomeration with a bimodal peak pattern.

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85 86 Figure S3: Analysis of COOH-PSNPs using AF4-MALS. Reference fractograms showing the 87 MALS 90° signal for native individual COOH-PSNP sizes (100 nm, 500 nm, and 1000 nm), 88 demonstrating distinct elution profiles corresponding to each particle size. The radius of gyration 89 (Rg) for each size fraction is plotted alongside, indicating stable particle sizes. The Rg 90 distributions are in good agreement with the size distributions obtained after incubation with metal 91 ions.



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94 Figure S4: Analysis of COOH-PSNPs using AF4-MALS. Reference fractograms showing the

95 MALS 90° signal for native individual COOH-PSNP sizes (100 nm, 500 nm, and 1000 nm),

96 demonstrating distinct elution profiles corresponding to each particle size



97 98 Figure S5: Adsorption kinetic analysis of Cr, As, and Se onto COOH-PSNPs. The figure 99 shows the pseudo-first order (PFO) kinetic fitting for the adsorption of Cr, As, and Se on the 100

100 nm (A), 500 nm (B), 1000 nm (C), and mixed-size systems (D), respectively.

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