Supplementary Information (SI) for Environmental Science: Nano.

Supplementary Document for Impact of Size and UV-ageing of Polystyrene Nanoparticles on Copper(II) Adsorption: Kinetics and Isotherms in Aquatic Environments

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Table S1 Concentrations of chemical components of artificial seawater.

Components	**Conc. (g/L)**
NaCl	24.54
$MgCl_2{\cdot}6H_2O$	11.11
Na_2SO_4	4.09
$CaCl_2$	1.53
KCl	0.69
$NaHCO_3$	0.20
KBr	0.10
$SrCl_2$	0.04
H_3BO_3	0.027
NaF	0.003

Table S2 Molarity of each ions for components of artificial seawater.

Components	**Molarity (M)**
Na^+	0.4799
Cl^-	0.6908
Mg^{2+}	0.1167
SO_4^{2-}	0.0288
Ca^{2+}	0.0138
K^+	0.0101
HCO_3^-	0.00238
BO_3^{3-}	0.00043
Br^-	0.00084
Sr^{2+}	0.000252
F^-	0.000071

Equations used for Calculation of Conversion Rate for Synthesized PS-NPs:

$$Conversion\,rate(\%) = (\frac{Measured\,solid\,content\,(\%)}{Theoritical\,solid\,content\,(\%)}) \times 100 \tag{S1}$$

where theoretical solid content can be expressed as below:

$$Theoretical\,solid\,(\%)\,at\,100\%\,monomer\,conversion = (\frac{Total\,mass\,of\,reagents(g)}{Total\,mass\,of\,reagents\,and\,solvent\,(g)}) \times 100 \tag{S2}$$

Linear forms of Adsorption Isotherm Models: Linear from of Langmuir model can be expressed as:

$$\frac{C_e}{q_e} = \frac{C_e}{q_m} + \frac{1}{K_l q_m} \tag{S3}$$

where q_m and K_l can be calculated from the slope, $1/q_m$, and the intercept, $1/K_l q_m$, of the fitted line.

Linear from of Freundlich model can be written as below:

$$logq_e = logK_f + \frac{1}{n} logC_e \tag{S4}$$

where n and K_f can be determined from the slop, $1/n$, and the intercept, $logK_f$.

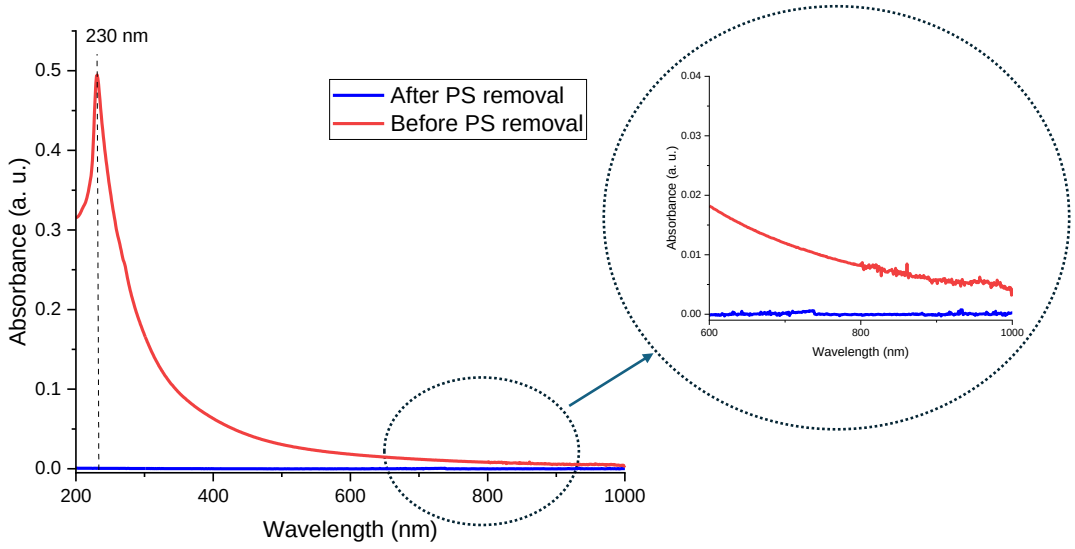

Fig. S1 UV-Vis spectra before and after removal of PS-NPs from the suspension using centrifugation.

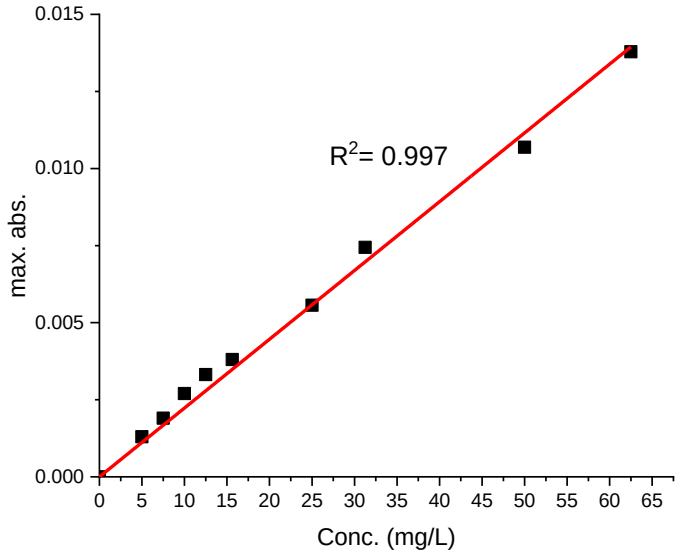

Fig. S2 UV-Vis calibration curve for known concentrations of Cu^{2+} ions with maximum absorbance at λ=800nm.

Calculation of the adsorbed mass of Cu^{2+} ions, q_t (mg/g), by PS-NPs:

$$q_t = \frac{C_0 - C_t}{m} \times V \tag{S5}$$

where C_0 and C_t are initial and time t metal ion concentrations (mg/L), respectively. V is the volume of the solution in litre (L) and m is the mass of the adsorbent, PS-NPs, in grams (g).

Table S3 The value of reactants in synthesizing different PS particle sizes.

Entry No.	Methanol (g)	Water(g)	Styrene(g)	KPS(g)	Average diameter(nm)	Polydispersity Index	Conversion Rate(%)
1	28	2	1	0.0075	760	0.122	96
2	28	2	1	0.007	520	0.044	96
3	27	3	1	0.0075	597	0.134	90
4	21	9	1	0.007	360	0.002	95
5	20	10	1	0.007	320	0.006	94
6	16	14	1	0.007	260	0.009	96
7	10	20	1	0.0074	370	0.004	95
8	10	20	1	0.002	267	0.002	96
9	10	20.5	0.5	0.002	130	0.003	94
10	4	26.5	0.5	0.002	120	0.157	74

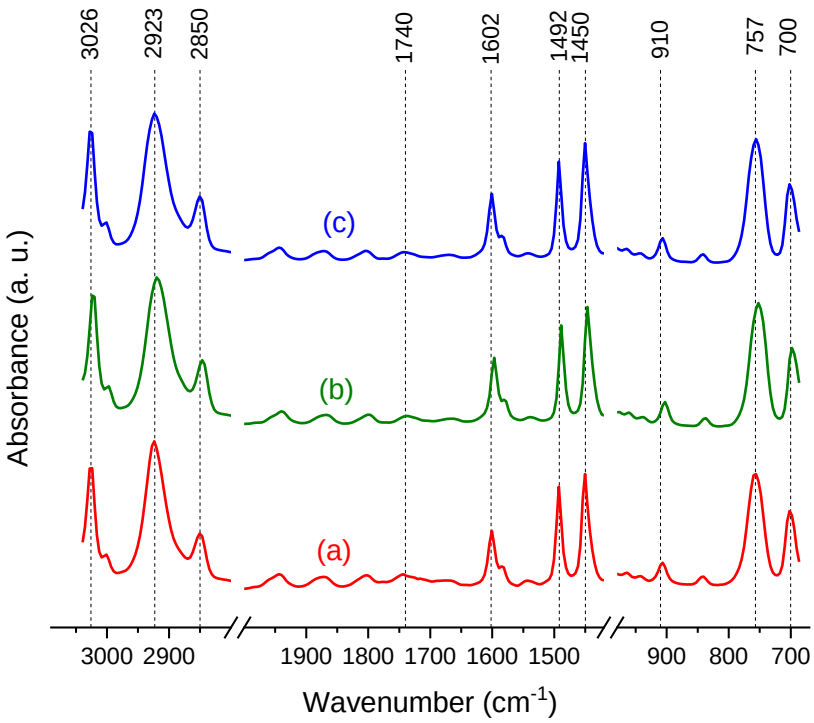

Fig. S3 FTIR spectra of **(a)** PS-130, **(b)** PS-260 and **(c)** PS-520.

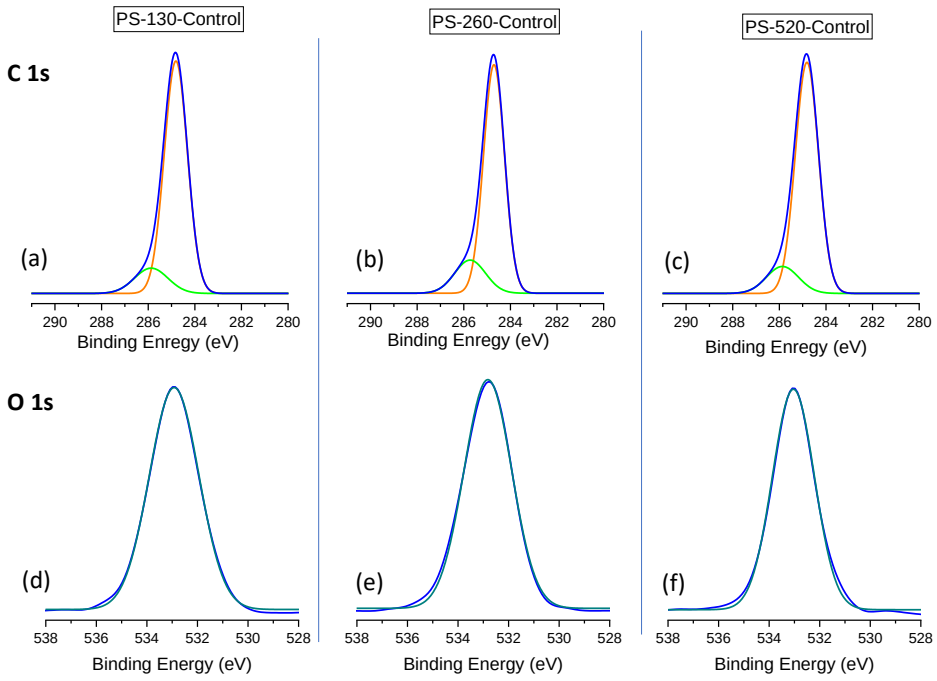

Fig. S4 (a-c) C 1s and **(d-f)** O 1s XPS spectra of PS control samples.

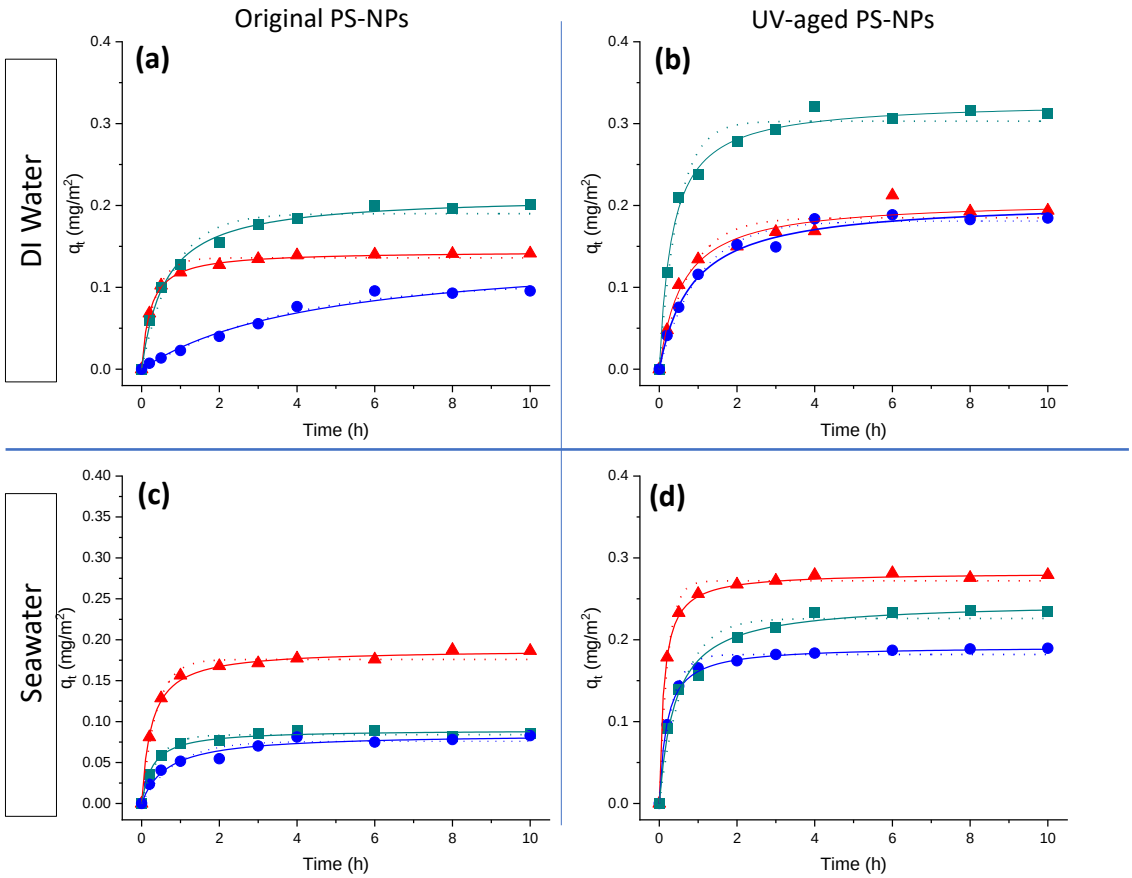

Fig. S5 Adsorption kinetics of Cu^{2+}, where q_t was calculated based on specific surface area of PS-130 (▲), PS-260 (■), and PS-520 (●) in **(a,b)** DI water and **(c,d)** seawater, with PFO (dotted line) and PSO (solid line) model fittings.

Table S4 Fitting parameters of adsorption kinetics of Cu^{2+}, where q_t normalised by the corresponding surface area of the PS-NPs in each condition.

	Medium	Size (nm)	$q_{e,exp_{SSA}}$ (mg/m^2)	PFO $q_{e1,Cal_{SSA}}$ (mg/m^2)	PFO K_1	PFO $R_1{}^2$	PSO $q_{e2,Cal_{SSA}}$ (mg/m^2)	PSO K_2	PSO $R_2{}^2$
Original PS	DI water	130	0.141	0.136	2.947	0.982	0.144	31.526	0.999
		260	0.199	0.190	1.232	0.971	0.212	7.858	0.995
		520	0.095	0.106	0.273	0.985	0.148	1.465	0.979
	Seawater	130	0.186	0.176	2.674	0.986	0.188	21.391	0.997
		260	0.087	0.084	2.401	0.984	0.090	40.362	0.985
		520	0.080	0.076	1.156	0.938	0.085	18.332	0.970
UV-aged PS	DI water	130	0.195	0.185	1.302	0.952	0.207	8.187	0.977
		260	0.314	0.303	2.097	0.978	0.327	9.261	0.994
		520	0.184	0.181	0.974	0.982	0.206	5.823	0.988
	Seawater	130	0.280	0.272	4.800	0.990	0.283	30.725	0.999
		260	0.234	0.226	3.300	0.960	0.246	27.463	0.989
		520	0.190	0.182	1.672	0.989	0.192	9.956	0.999

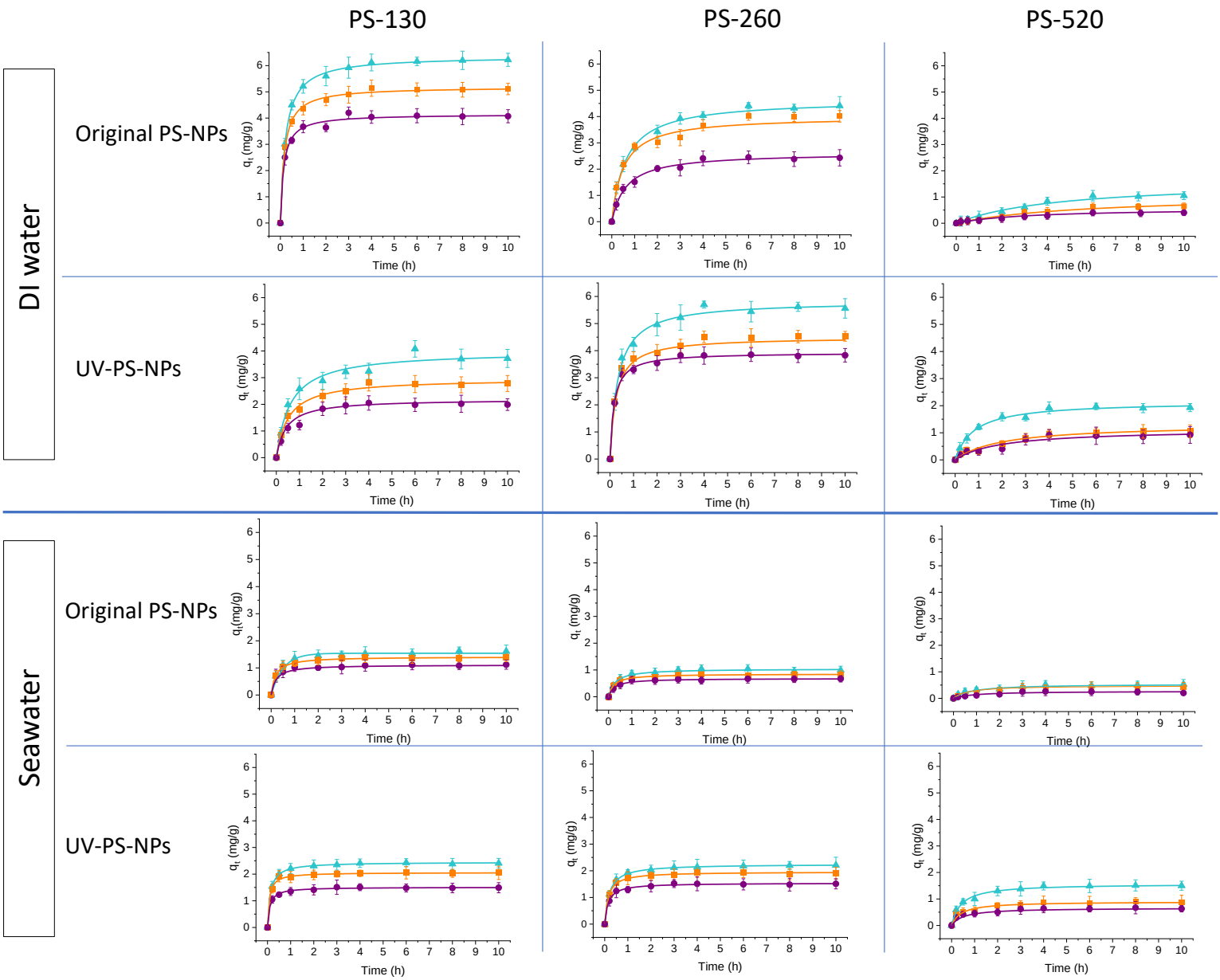

Fig. S6 The kinetics of Cu^{2+} adsorption by original and UV-aged PS-NPs in DI water and seawater at different temperatures (290 K ▲ , 300 K ■ , 310 K ●) including their PSO model fittings.

Table S5 Pseudo-second order (PSO) fitting parameters of adsorption kinetics of Cu^{2+} ions at different temperatures.

	Medium	Particle size(nm)	290 K $q_{e,exp}$	290 K $q_{e2,Cal}$	290 K K_2	290 K $R_2{}^2$	300 K $q_{e,exp}$	300 K $q_{e2,Cal}$	300 K K_2	300 K $R_2{}^2$	310 K $q_{e,exp}$	310 K $q_{e2,Cal}$	310 K K_2	310 K $R_2{}^2$
Original PS	DI water	130	6.20	6.36	0.717	0.999	5.12	5.19	1.154	0.998	4.07	4.15	1.702	0.991
		260	4.41	4.67	0.357	0.995	4.01	4.11	0.499	0.982	2.44	2.62	0.639	0.990
		520	1.05	1.63	0.133	0.979	0.70	1.10	0.154	0.977	0.44	0.58	0.231	0.973
	Seawater	130	1.54	1.63	2.474	0.996	1.37	1.41	3.745	0.997	1.10	1.11	4.403	0.993
		260	1.02	1.05	3.458	0.986	0.82	0.85	4.298	0.989	0.66	0.68	5.002	0.984
		520	0.50	0.54	2.312	0.972	0.41	0.48	3.312	0.971	0.25	0.27	3.938	0.910
UV-aged PS	DI water	130	3.83	3.99	0.418	0.977	2.76	2.96	0.661	0.990	2.01	2.19	1.104	0.981
		260	5.58	5.83	0.522	0.994	4.52	4.50	0.877	0.940	3.84	3.93	1.541	0.995
		520	1.93	2.15	0.279	0.991	1.05	1.31	0.387	0.966	0.90	1.13	0.452	0.925
	Seawater	130	2.42	2.45	3.542	0.999	2.05	2.06	6.471	0.995	1.49	1.51	6.951	0.996
		260	2.19	2.25	2.347	0.999	1.93	1.96	3.504	0.997	1.51	1.54	4.447	0.995
		520	1.49	1.57	1.560	0.989	0.88	0.90	2.393	0.966	0.64	0.66	2.646	0.969

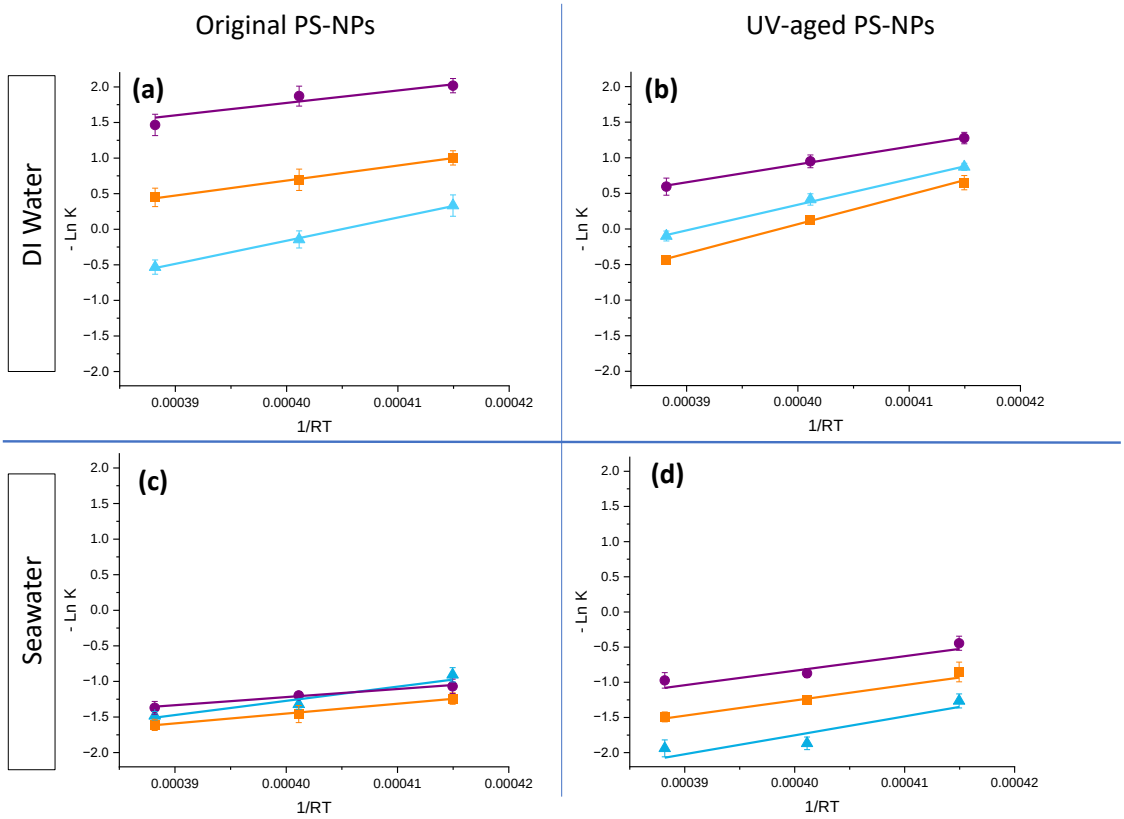

Fig. S7 Arrhenius plots of Cu^{2+} adsorption for original and UV-aged PS-130 (▲), PS-260 (■) and PS-520 (●) in DI water and seawater.

Table S6 Activation energy (E_a) of Cu^{2+} adsorption and corresponding R^2 values.

			PS-130	PS-260	PS-520
Original PS	DI water	E_a(kJ/mol)	32.530	21.090	20.959
		R^2	0.998	0.996	0.959
	Seawater	E_a(kJ/mol)	19.950	13.801	11.368
		R^2	0.931	0.996	0.979
UV-aged PS	DI water	E_a(kJ/mol)	36.018	41.212	25.089
		R^2	0.998	0.997	0.998
	Seawater	E_a(kJ/mol)	26.917	21.690	20.631
		R^2	0.910	0.968	0.917