SUPPLEMENTARY MATERIAL

Label-free Impedimetric analysis of microplastics dispersed in aqueous media polluted by Pb^{2+} ions

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Table S1. q_m values of different types of MPs towards Pb^{2+} ions.

MPs	⌀ (mm) [a]	pH	q_m [b]	Refs
PE [c]	0.29	N.R.	2010	1
PE [d]	<5	5	13600	1
PE [c]	~4	5	0.191	1
PE [c]	N.R.	6.3	2360	1
PE [c]	0.074	5	600	1
PE [c]	0.2867	5	2230	2
PE[e]	2-6	6.5	2.74	1
LDPE [f]	3	7.5	1038	1
LDPE [g]	<0.28	6.5	590	1
LDPE [h]	<0.28	6.5	283	1
CPE [c]	<0.28	6.5	1110	1
PLA [b]	0.6 – 0.8	5	94	3
PLA [f]	0.6 – 0.8	5	1060	3
PMMA [c]	0.0063	5	4790	2
PMMA [c]	0.006	N.R.	4210	1
PS [c]	N.R.	N.R.	2940	1
PS [i]	10^{-4}	N.R.	160	1
PS [l]	10^{-4}	N.R.	200	1
PS [m]	0.074	N.R.	190	1
PS [n]	10^{-4}	N.R.	140	1
PP[c]	3	N.R.	1570	1
PP[c]	0.007-0.15	5	1990	2
PP[c]	0.85	5	1720	2
PP[c]	N.R.	6.3	5550	1
PP[c]	0.085	N.R.	1570	4
PP[c]	<0.28	6.5	1250	1
PP[c]	<0.28	6.3	1900	4
PP[c]	0.074	6.5	800	1
PP[c]	N.R.	6.3	4930	1
CPE [c]	<0.28	6.5	1110	1
PLA [b]	0.6 – 0.8	5	94	3

[a] particle diameter of MPs; [b] expressed in µg g^{-1}; [c] MPs who did not undergo any treatment; [d] naturally aged MPs; [e] MPs sonicated before performing the experiments; [f] MPs treated with oxidizing agents; [g] MPs with low crystallinity index; [h] MPs with high crystallinity index; [i] MPs washed and frozen before performing the experiments; (PE = PolyEthylene, LDPE = Low-Density PolyEthylene, CPE = Chlorinated PolyEthylene, PLA = PolyLactic Acid, PMMA = PolyMethyl MethAcrylate, PP = PolyPropylene)

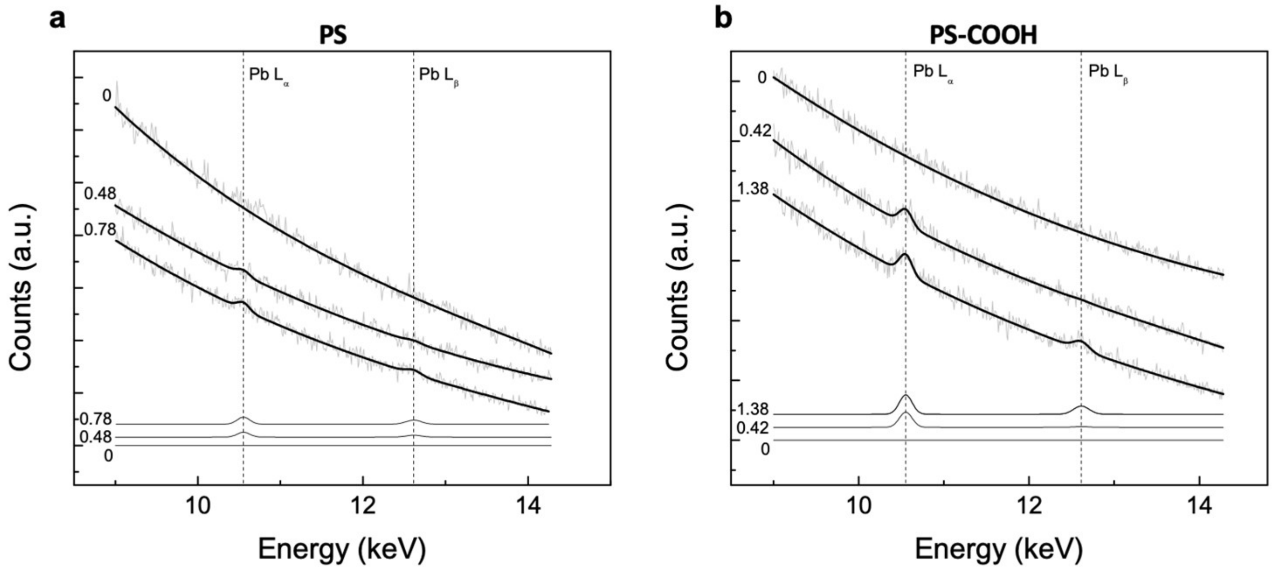

Figure S1. EDS spectra (before and after baseline correction) in the spectral region relative to the transitions towards the L shell (Lα and Lβ) specific to **(a)** Pb^{2+} adsorbed on PS MPs and **(b)** Pb^{2+} adsorbed PS-COOH MPs. The numbers reported for each spectrum are the q_e values.

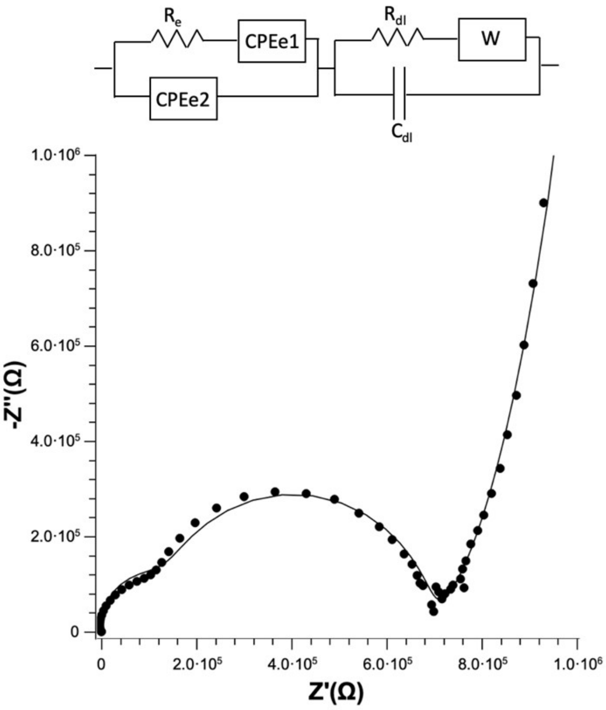

Figure S2. Nyquist spectrum showing the real (Z') and imaginary (-Z'') impedance components as a function of the frequency for a bare graphite screen-printed electrode in DI water. The line represents fits to the experimental data using the circuit schematized in the inset.

Table S2. Tentative fitting parameters obtained for EIS of blank (DI water).

R_e (KOhm)	CPEe1 (μOhm)	CPEe2 (pOhm)	R_{dl} (KOhm)	C_{dl} (pF)	W (μOhm)
127 ± 25	0.8 ± 0.2 (N = 1.0 ± 0.2)	60 ± 30 (N = 1.10 ± 0.06)	555 ± 45	550 ± 100	2 ± 1

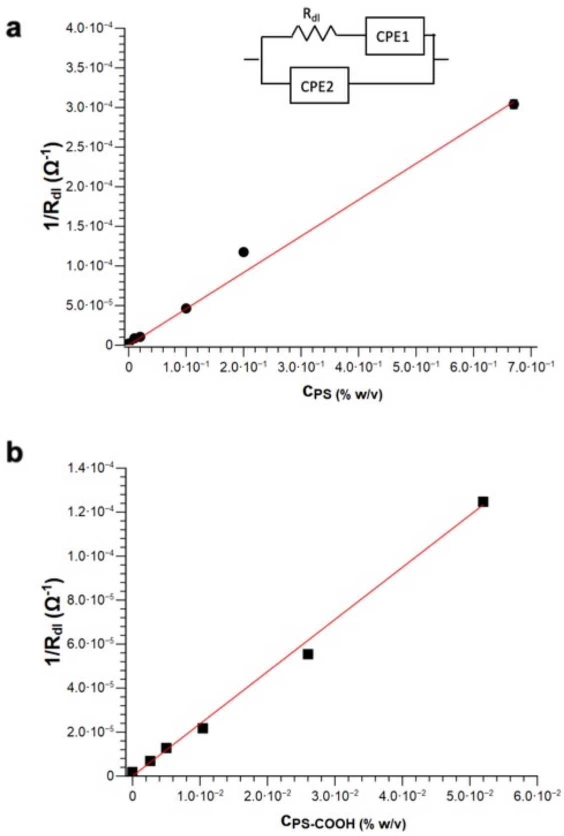

Figure S3. Calibration curve reporting ($1/R_{dl}$) vs. PS or PS-COOH concentration using circuit 2 (reported in the inset) for **(a)** PS and **(b)** PS-COOH suspensions.

Table S3. Fitting parameters obtained for PS and PS-COOH MPs using circuit 1.

PS concentration (% w/v)	CPE1 (µOhm)	R_{dl} (KOhm)	C_{dl} (pF)	W (µOhm)
0.01 % w/v	0.33 ± 0.03 (N = 0.813 ± 0.003)	109 ± 6	210 ± 13	2 ± 0.2
0.02 % w/v	0.24 ± 0.02 (N = 0.798 ± 0.003)	93 ± 4	210 ± 13	10 ± 1
0.1 % w/v	0.30 ± 0.01 (N = 0.944 ± 0.009)	21 ± 4	266 ± 16	76 ± 8
0.2 % w/v	0.52 ± 0.01 (N = 0.892 ± 0.009)	8.8 ± 0.2	336 ± 10	30 ± 2
0.67 % w/v	0.59 ± 0.02 (N = 0.898 ± 0.009)	3.36 ± 0.08	386 ± 19	71 ± 7
PS-COOH concentration (% w/v)	**CPE1 (µOhm)**	**R_{dl} (KOhm)**	**C_{dl} (pF)**	**W (µOhm)**
0.0026 % w/v	0.77 ± 0.09 (N = 0.94 ± 0.06)	150 ± 9	552 ± 40	6.2 ± 0.5
0.005 % w/v	0.72 ± 0.05 (N = 0.92 ± 0.03)	80 ± 3	405 ± 20	12 ± 1
0.0104 % w/v	0.70 ± 0.05 (N = 0.92 ± 0.03)	47± 2	413 ± 21	21 ± 2
0.026 % w/v	0.69 ± 0.04 (N = 0.92 ± 0.04)	18.5 ± 0.5	459 ± 23	63 ± 6
0.052 % w/v	0.55 ± 0.02 (N = 0.89 ± 0.01)	8.3 ± 0.4	340 ± 10	290 ± 30

Table S4. Fitting parameters obtained for PS and PS-COOH MP_S pre- and post- Pb^{2+} ions adsorption using circuit 1**.**

MP sample	CPE1 (µOhm)	R_{dl} (KOhm)	C_{dl} (pF)	W (µOhm)
PS (q_e = 0)[a]	0.26 ± 0.05 (N = 0.90 ± 0.06)	73 ± 5	566 ± 45	130 ± 13
PS (q_e = 480)	0.26 ± 0.16 (N = 0.94 ± 0.07)	105 ± 9	557 ± 45	7 ± 1
PS (q_e = 780)	0.24 ± 0.15 (N = 0.94 ± 0.07)	130 ± 10	567 ± 40	7 ± 1
PS-COOH (q_e = 0)	0.43 ± 0.14 (N = 0.94 ± 0.13)	214 ± 16	480 ± 33	4.4 ± 0.5
PS-COOH (q_e = 420)	0.40 ± 0.16 (N = 0.93 ± 0.13)	235 ± 19	462 ± 32	4 ± 0.5
PS-COOH (q_e = 1380)	0.42 ± 0.16 (N = 0.95 ± 0.16)	307 ± 21	470 ± 33	3.1 ± 0.4

[a] in µg g^{-1}.

Table S5. Langmuir and Freundlich isotherm parameters for the Pb^{2+} ions adsorption onto PS* MPs from aqueous solutions containing $NaNO_3$ 0.1 mol L^{-1}, at pH = 5.0 and at T = 298.15 K.

MPs	**Langmuir model**		
	q_m[b]	K_L[c]	R^2
PS	2100 ± 600	0.05 ± 0.02	0.9680
PS*	198 ± 11	0.7 ± 0.1	0.9783
PS*[a]	535 ± 68	0.12 ± 0.03	0.9703
	Freundlich model		
	K_F[d]	n	R^2
PS	121 ± 23	1.4 ± 0.2	0.9637
PS*	99 ± 11	4 ± 1	0.9367
PS*[a]	76 ± 9	1.8 ± 0.2	0.9771

[a] with Pb^{2+} solution containing SDS 0.1 mmol L^{-1}; [b] µg g^{-1}; [c] L mg^{-1}; [c] $L^{1/n}$ g^{-1} µg $mg^{-1/n}$

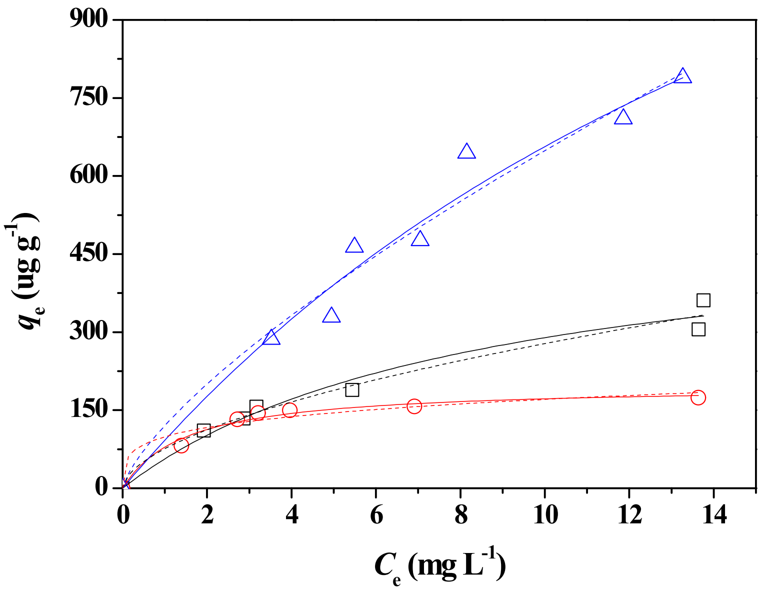

Figure S4. Adsorption isotherms of Pb^{2+} ions onto PS (blue triangles) and PS* (red circles) MPs from aqueous solutions containing $NaNO_3$ 0.1 mol L^{-1}, at pH = 5.0 and T = 298.15 K, and onto PS* MPs (black squares) from aqueous solutions containing $NaNO_3$ 0.1 mol L^{-1}, SDS 0.1 mmol L^{-1}, at pH = 5.0 and T = 298.15 K. The experimental data were fitted with Langmuir (continuous line) and Freundlich (dotted line) isotherm models.

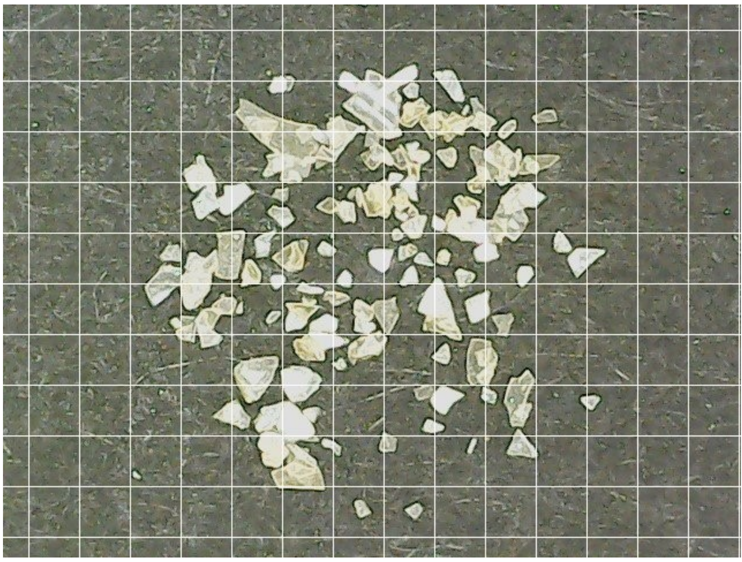

Figure S5. Micrograph of PS* MPs (grid scale div. 1 mm)

References

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