Supplementary Information

Adsorption properties of Merrifield-*bCCA* chelating resins: a new alternative for Pb^{2+} removal from water

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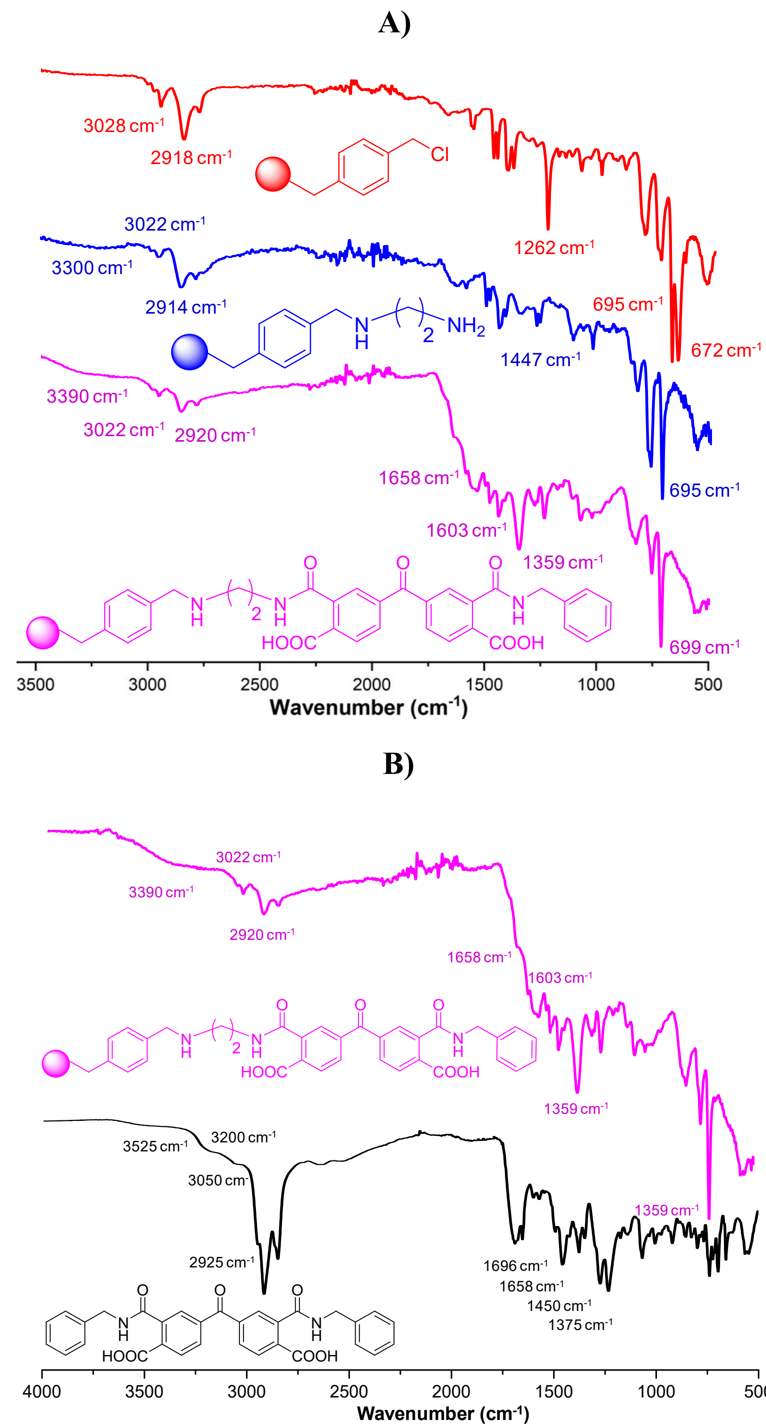


Figure S1. A) FTIR spectra for Merrifield´s resin (red), **MR$_2$** resin (blue) and **MR$_2$Bz** (magenta). B) FTIR spectra of **MR$_2$Bz** (magenta) and **BzCCA** (black).

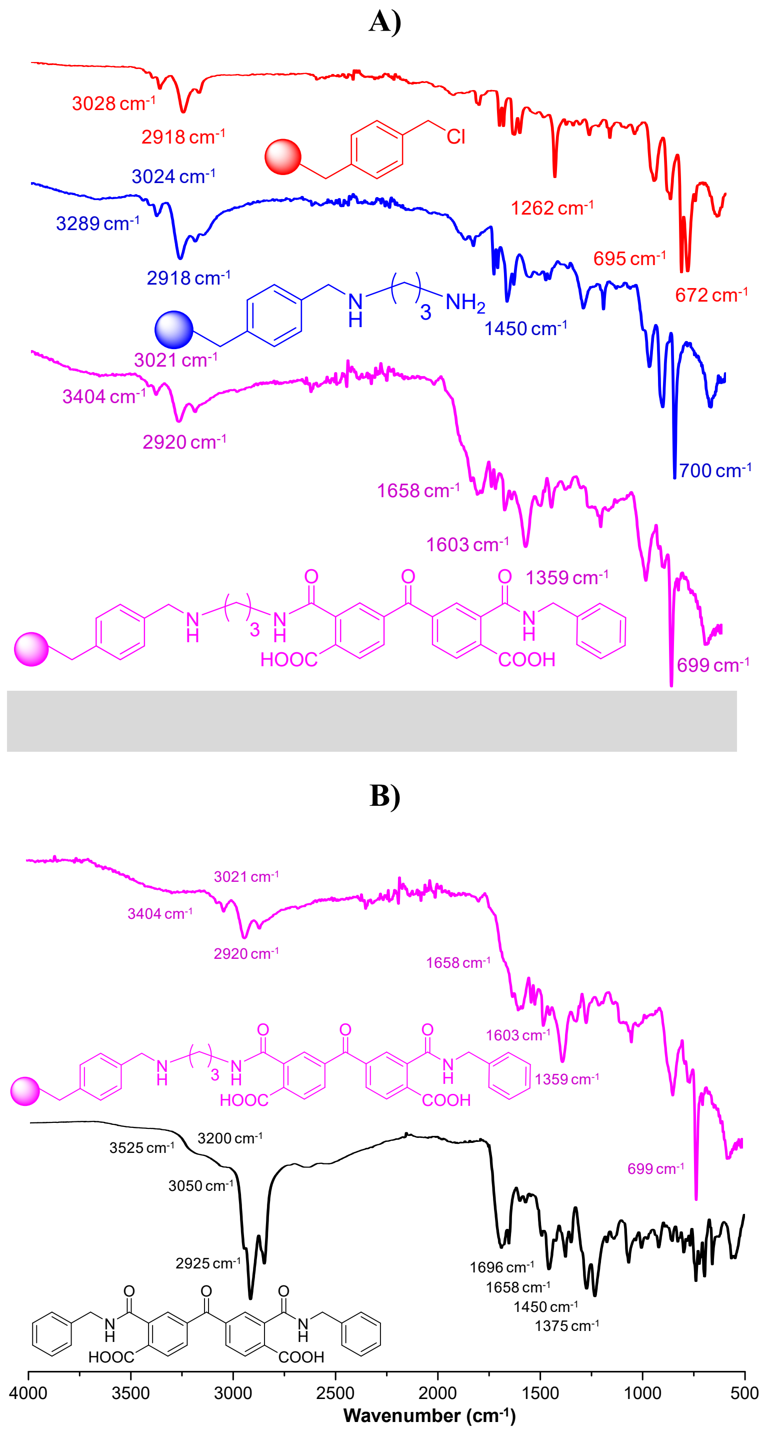
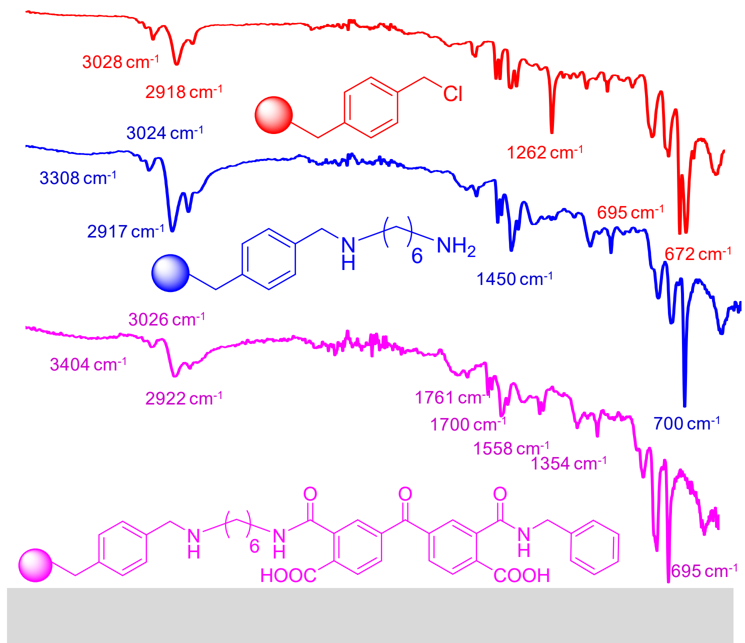


Figure S2. A) FTIR spectra for Merrifield´s resin (red), **MR$_3$** resin (blue) and **MR$_3$Bz** (magenta). B) FTIR spectra of **MR$_3$Bz** (magenta) and **BzCCA** (black).

A)



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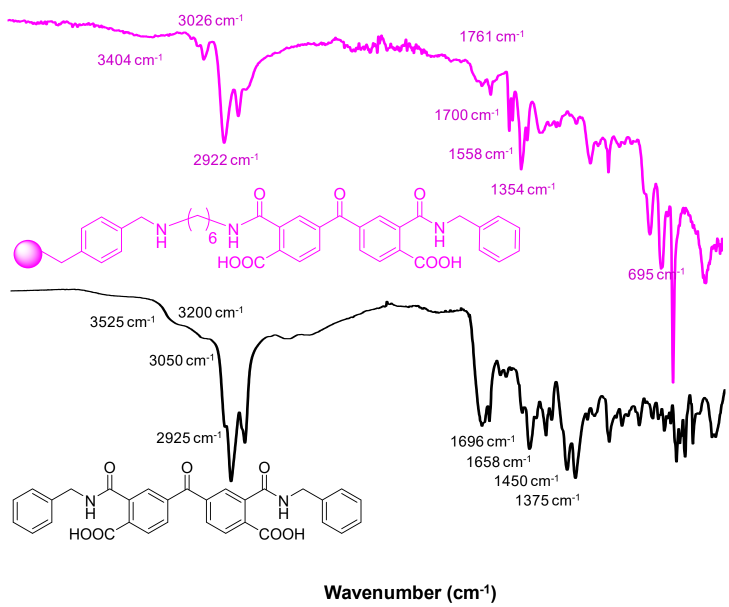


Figure S3. A) FTIR spectra for Merrifield´s resin (red), $\mathbf{MR_6}$ resin (blue) and $\mathbf{MR_6Bz}$ (magenta). B) FTIR spectra of $\mathbf{MR_6Bz}$ (magenta) and **BzCCA** (black).

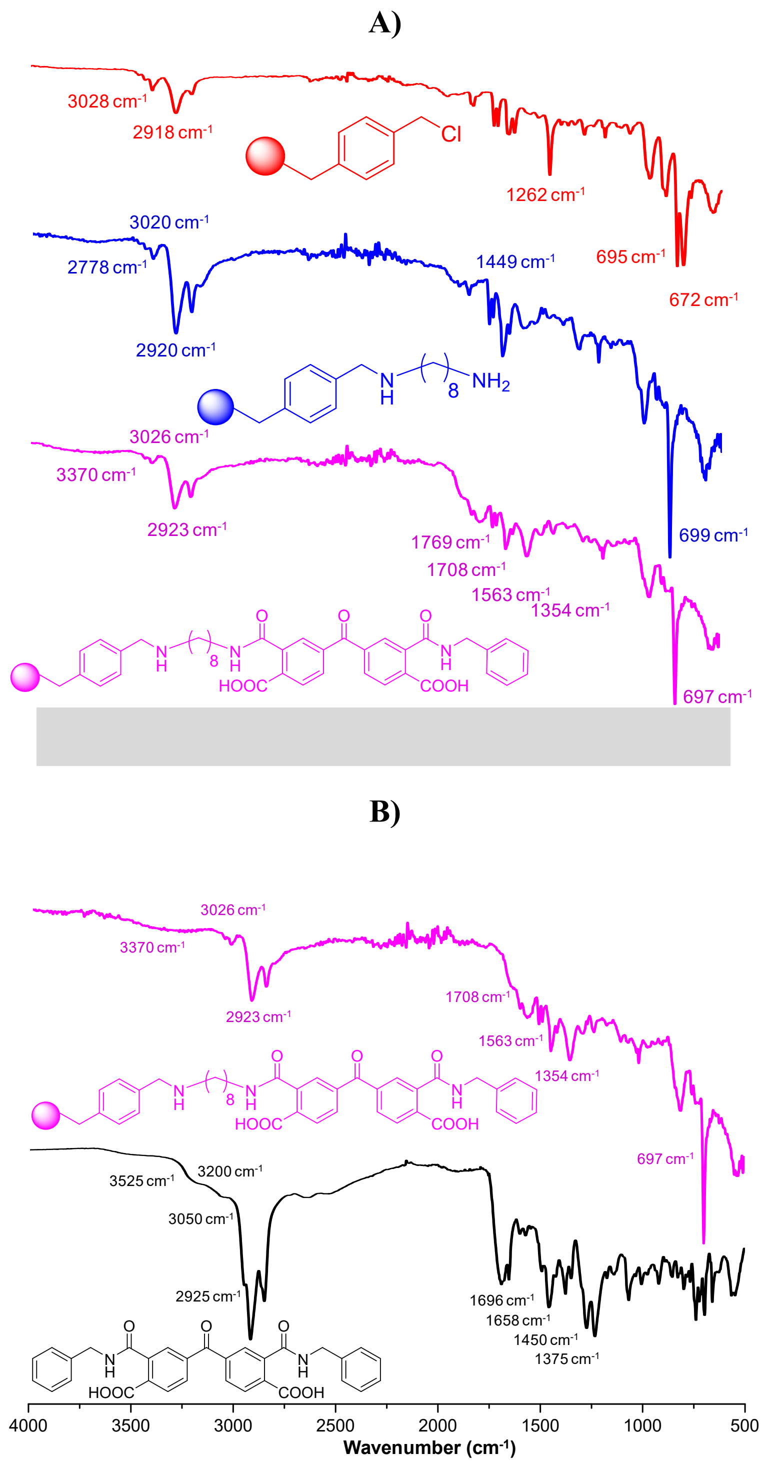


Figure S4. A) FTIR spectra for Merrifield´s resin (red), **MR_8** resin (blue) and **MR_8Bz** (magenta). B) FTIR spectra of **MR_8Bz** (magenta) and **BzCCA** (black).

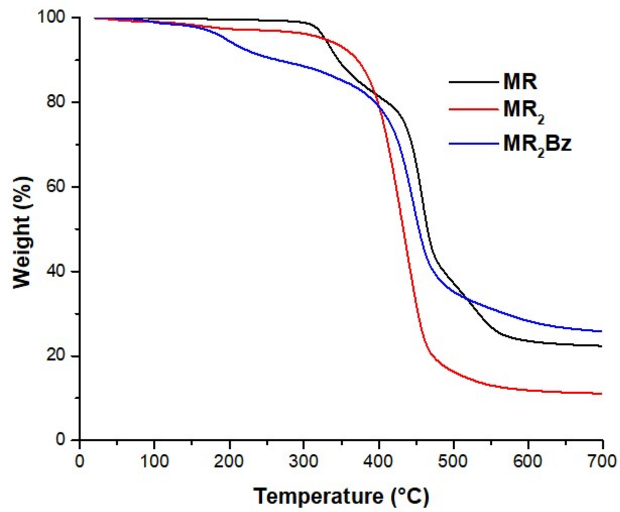


Figure S5. Thermograms of Merrifield´s resin (red), **MR_2** resin (blue) and **MR_2Bz** resin (black) obtained under N_2 atmosphere.

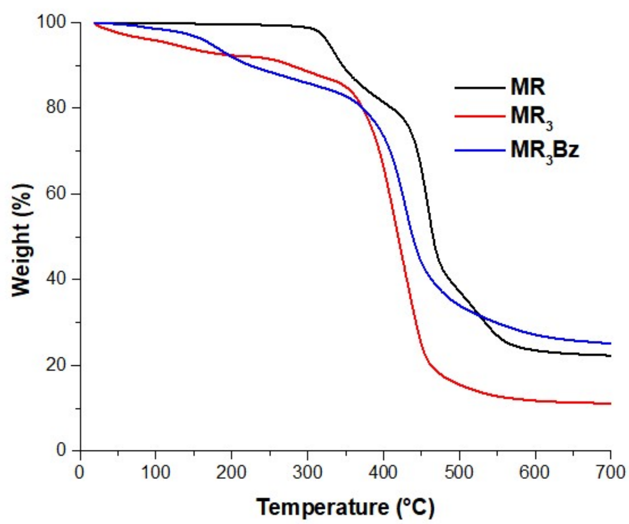


Figure S6. Thermograms of Merrifield´s resin (red), **MR_3** resin (blue) and **MR_3Bz** resin (black) obtained under N_2 atmosphere.

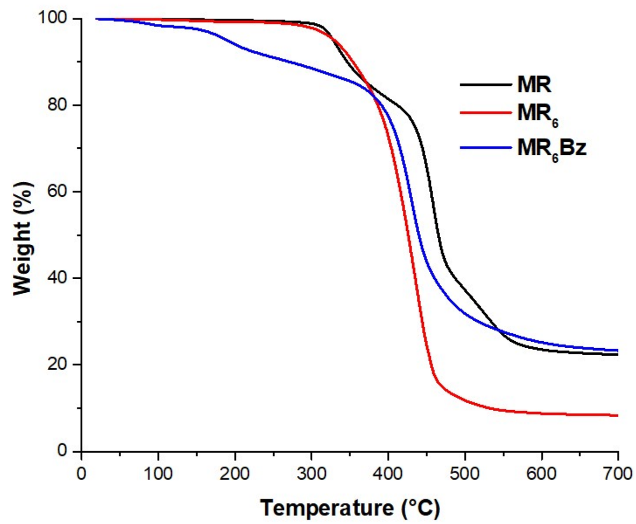


Figure S7. Thermograms of Merrifield´s resin (red), **MR_6** resin (blue) and **MR_6Bz** resin (black) obtained under N_2 atmosphere.

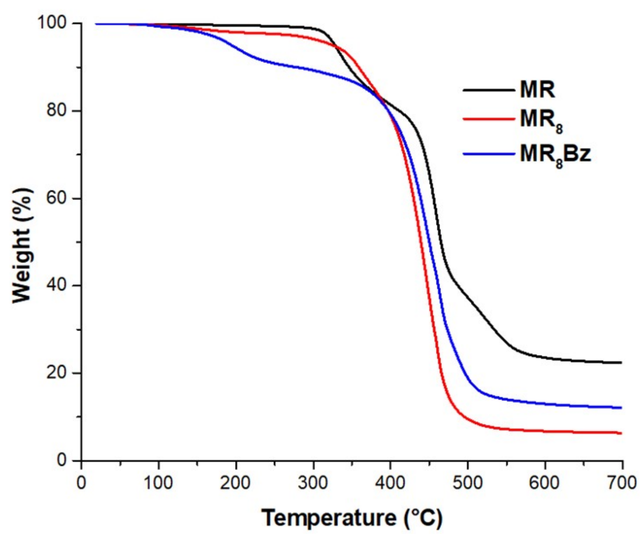


Figure S8. Thermograms of Merrifield´s resin (red), **MR_8** resin (blue) and **MR_8Bz** resin (black) obtained under N_2 atmosphere.

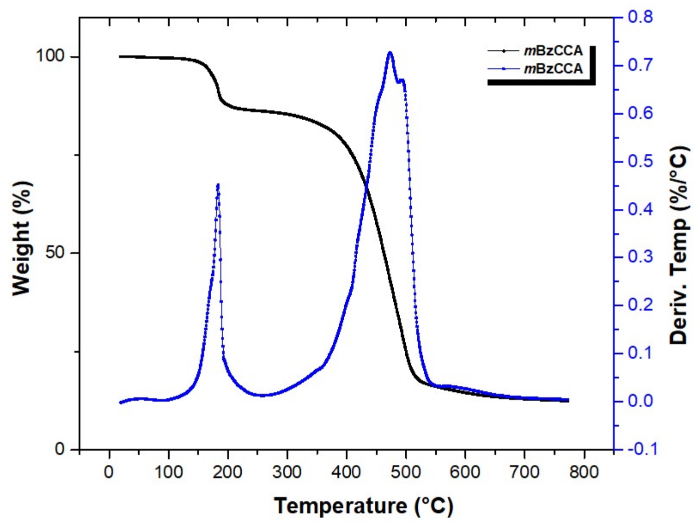


Figure S9. Thermogram of ***m*BzCCA** obtained under N_2 atmosphere.

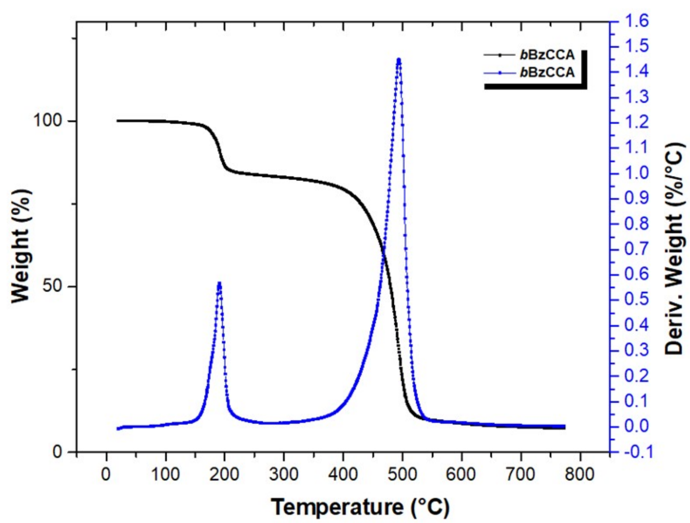


Figure S10. Thermogram of ***b*BzCCA** (blue) obtained under N_2 atmosphere.

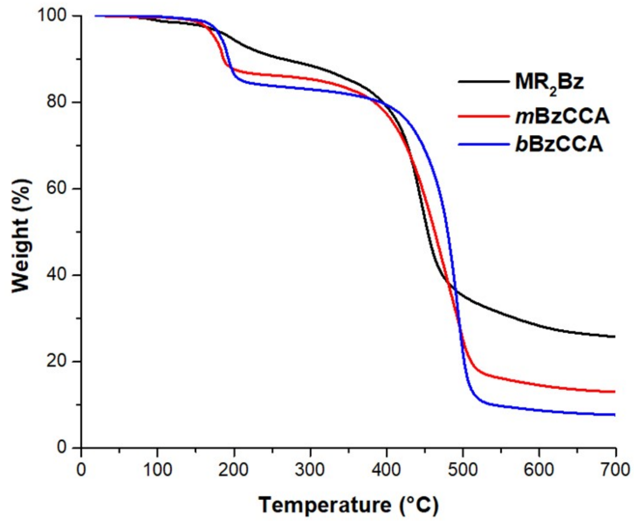


Figure S11. Thermograms of **MR_2Bz** resin (black), ***m*BzCCA** (red) and ***b*BzCCA** (blue) obtained under N_2 atmosphere.

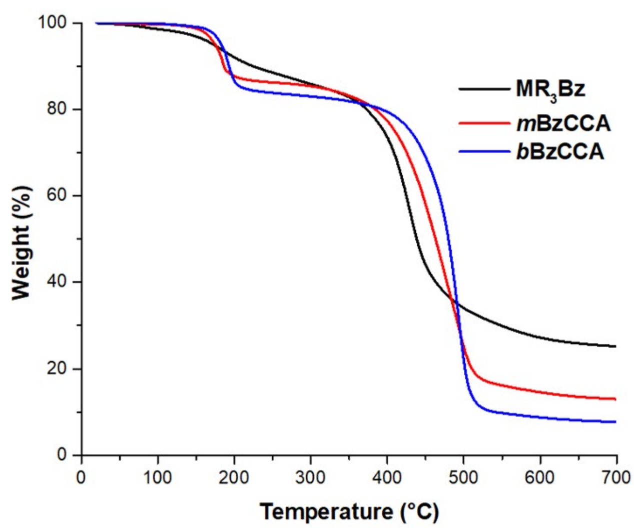


Figure S12. Thermograms of **MR_3Bz** resin (black), ***m*BzCCA** (red) and ***b*BzCCA** (blue) obtained under N_2 atmosphere.

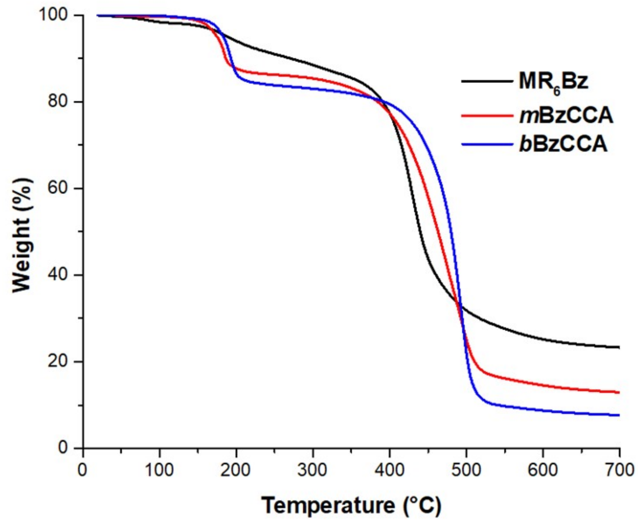


Figure S13. Thermograms of **MR$_6$Bz** resin (black), ***m*BzCCA** (red) and ***b*BzCCA** (blue) obtained under N_2 atmosphere.

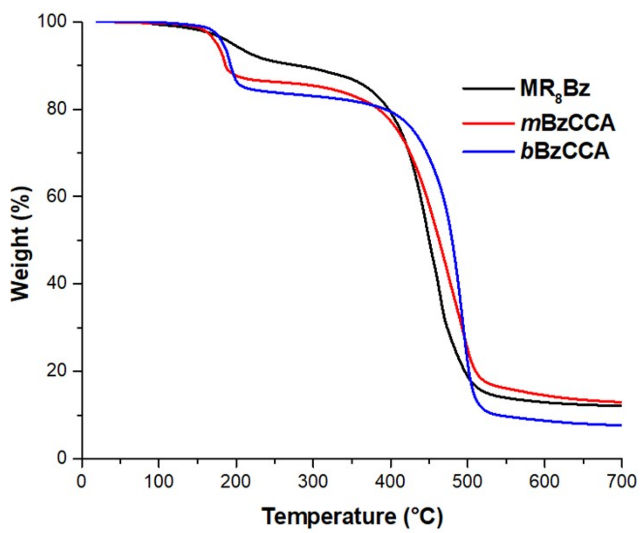
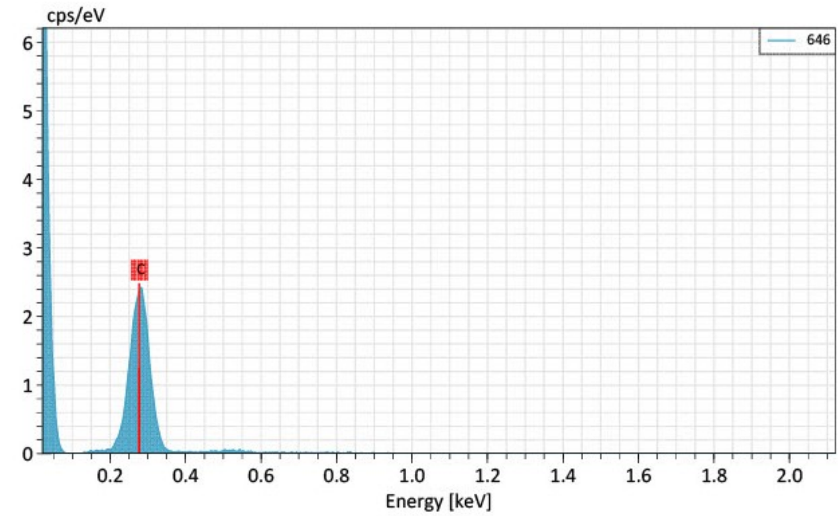


Figure S14. Thermograms of **MR$_8$Bz** resin (black), ***m*BzCCA** (red) and ***b*BzCCA** (blue) obtained under N_2 atmosphere.



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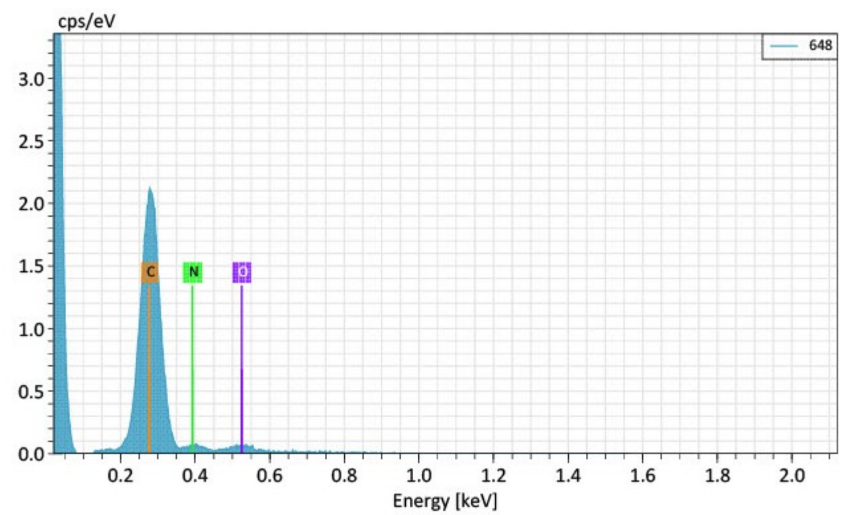
Element	At. No.	Netto	Mass [%]	Mass Norm. [%]	Atom [%]	abs. error [%] (1 sigma)	rel. error [%] (1 sigma)
Carbon	6	12022	100.00	100.00	100.00	13.67	13.67
		Sum	**100.00**	**100.00**	**100.00**		

Figure S15. EDS elemental analysis of Merrifield´s resin (**MR**).



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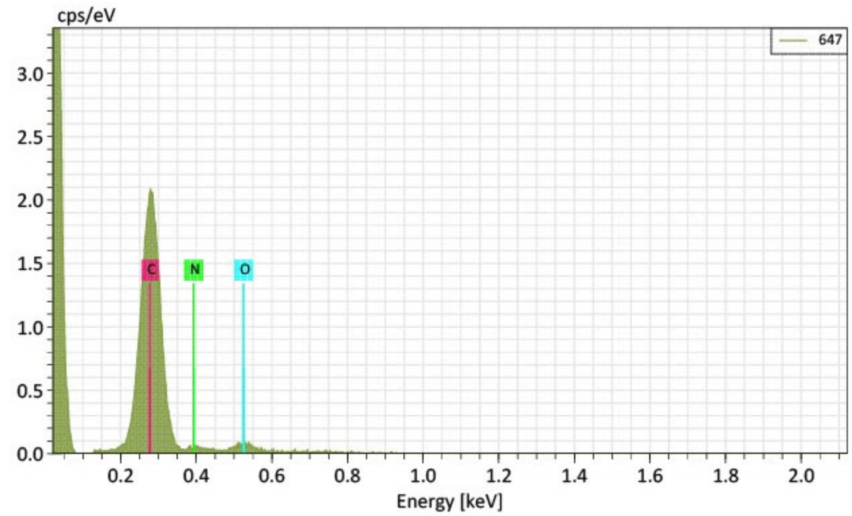
Element	At. No.	Netto	Mass [%]	Mass Norm. [%]	Atom [%]	abs. error [%] (1 sigma)	rel. error [%] (1 sigma)
Carbon	6	27488	87.60	87.60	89.50	10.90	12.44
Nitrogen	7	1122	9.02	9.02	7.90	2.00	22.22
Oxygen	8	613	3.38	3.38	2.59	0.91	26.89
		Sum	**100.00**	**100.00**	**100.00**		

Figure S16. EDS elemental analysis of **MR$_3$Bz** resin.



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Element	At. No.	Netto	Mass [%]	Mass Norm. [%]	Atom [%]	abs. error [%] (1 sigma)	rel. error [%] (1 sigma)
Carbon	6	17223	88.05	88.05	90.01	11.51	13.08
Nitrogen	7	581	7.50	7.50	6.58	2.02	26.93
Oxygen	8	504	4.44	4.44	3.41	1.26	28.37
		Sum	**100.00**	**100.00**	**100.00**		

Figure S17. EDS elemental analysis of **MR_3Bz** resin.

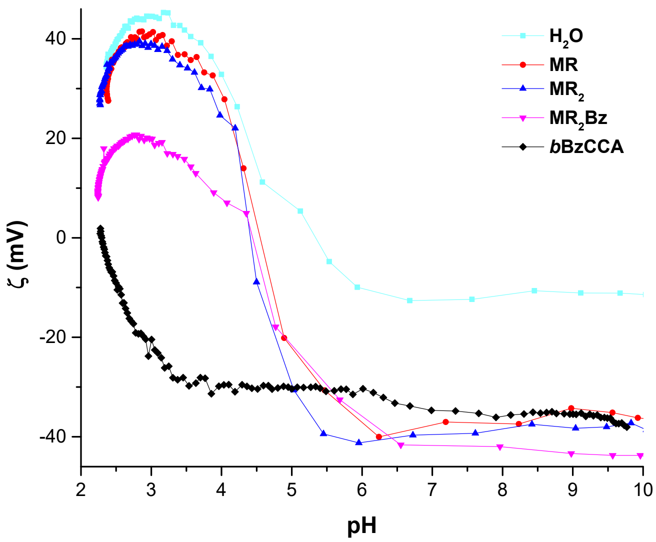


Figure S18. ζ= f[pH] profiles for ***b*BzCCA**, **MR**, **MR_2** and **MR_2Bz**.

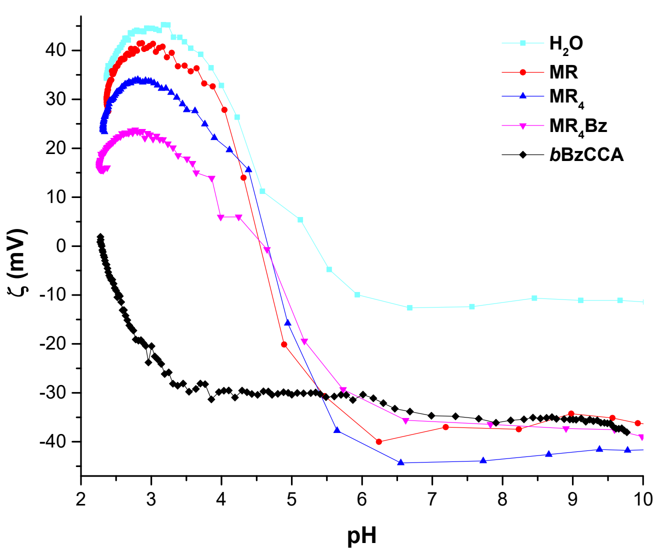


Figure S19. ζ= f[pH] profiles for ***b*BzCCA**, **MR**, **MR_4** and **MR_4Bz**.

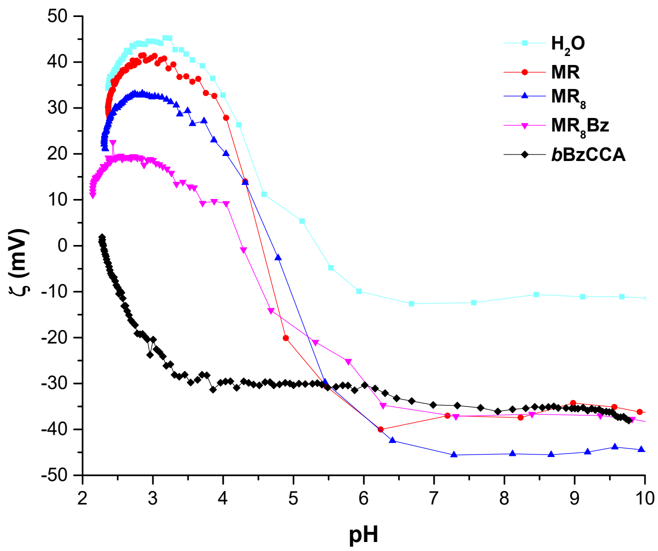


Figure S20. ζ= f[pH] profiles for ***b*BzCCA**, **MR**, **MR_8** and **MR_8Bz**.

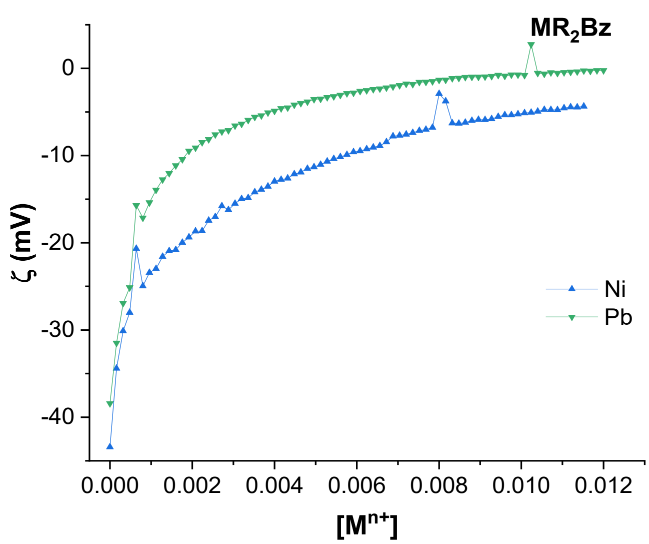


Figure S21. ζ= f[M^{n+}] profiles of **MR_2Bz** with different metal ions.

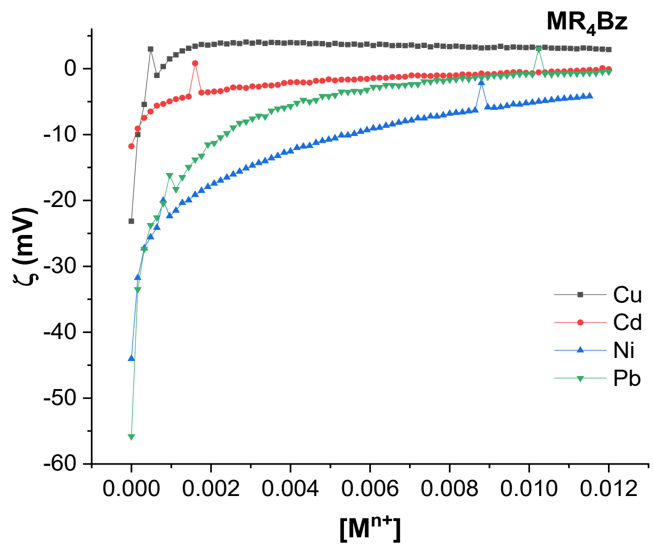


Figure S22. ζ= f[M^{n+}] profiles of **MR$_4$Bz** with different metal ions.

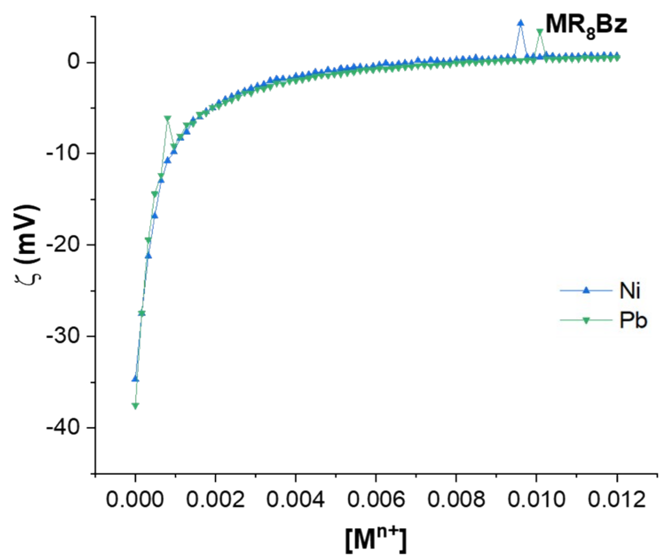


Figure S23. ζ= f[M^{n+}] profiles of **MR$_8$Bz** with different metal ions.

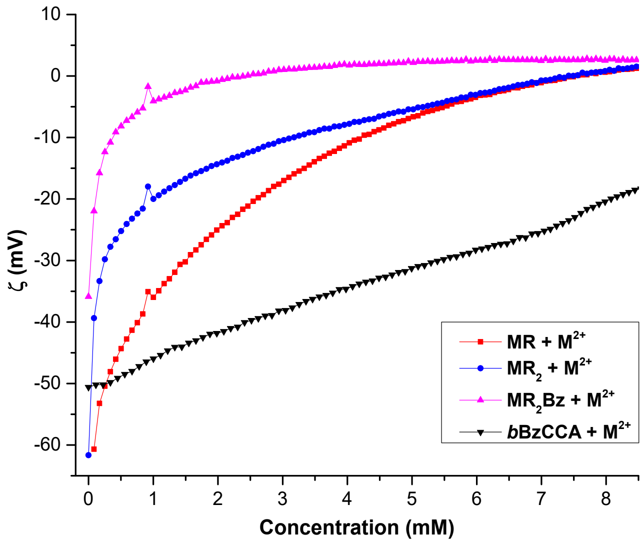


Figure S24. ζ= f[M^{n+}] profiles of ***b*BzCCA**, **MR**, **MR_2** and **MR_2Bz** obtained by titration with a mixture of metal ions.

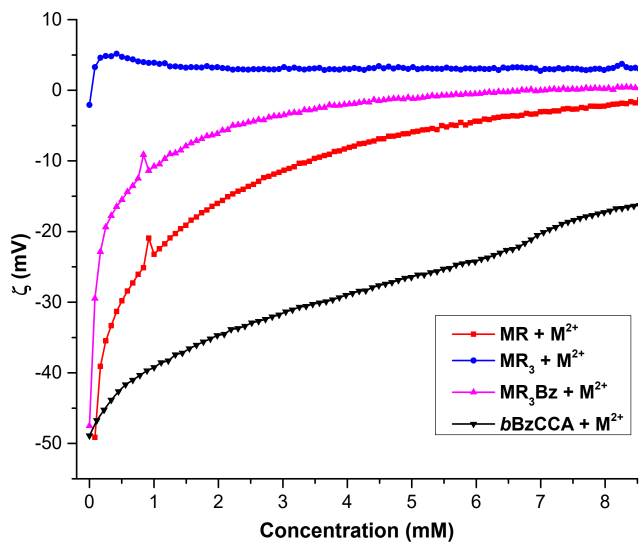


Figure S25. ζ= f[M^{n+}] profiles of ***b*BzCCA**, **MR**, **MR_3** and **MR_3Bz** obtained by titration with a mixture of metal ions.

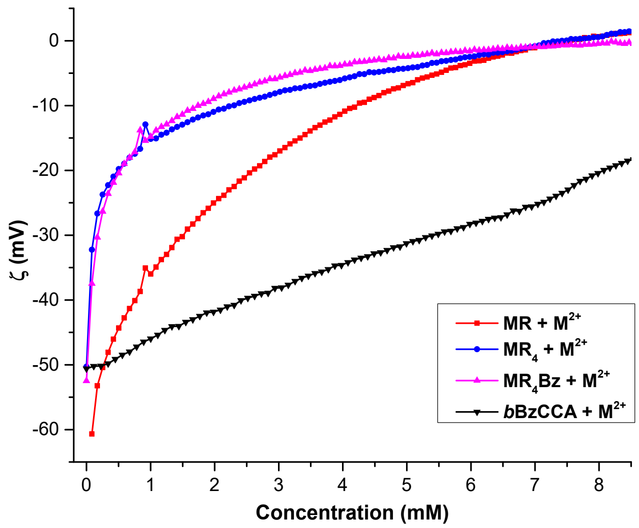


Figure S26. ζ= f[M^{n+}] profiles of ***b*BzCCA**, **MR**, **MR_4** and **MR_4Bz** obtained by titration with a mixture of metal ions.

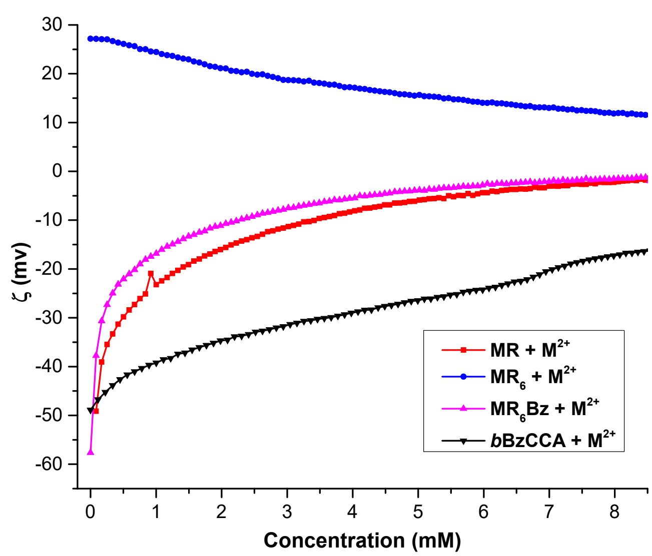


Figure S27. ζ= f[M^{n+}] profiles of ***b*BzCCA**, **MR**, **MR_6** and **MR_6Bz** obtained by titration with a mixture of metal ions.

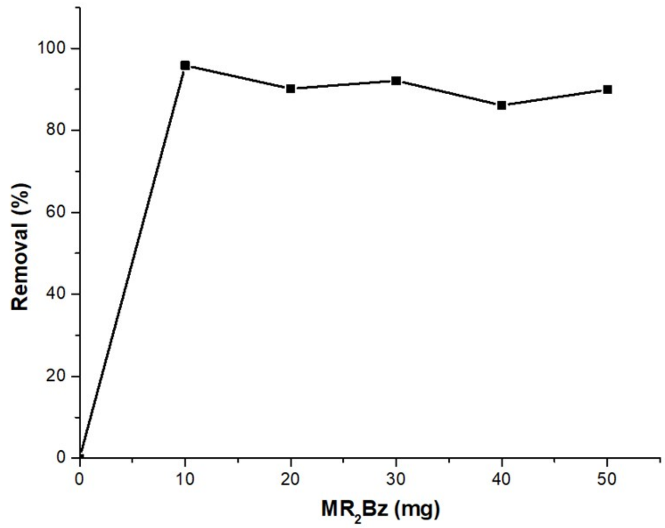


Figure S28. Removal % of Pb^{2+} obtained at different doses of **MR_2Bz** resin. $[Pb^{2+}]_o$ = 28.2 ppm, V= 0.01 L.

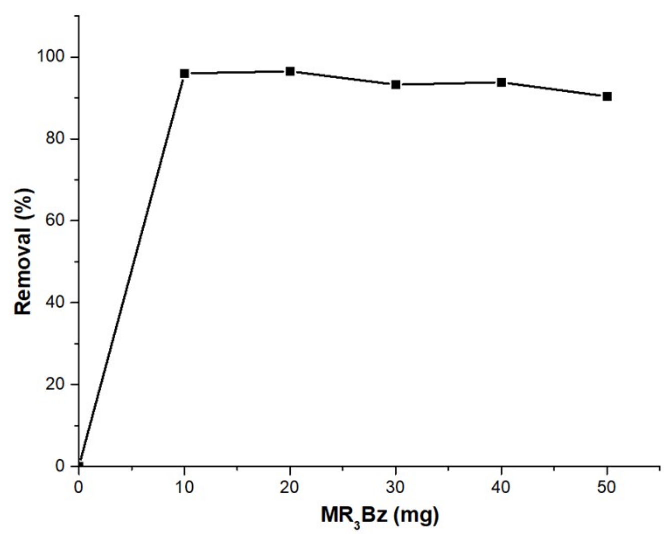


Figure S29. Removal % of Pb^{2+} obtained at different doses of **MR_3Bz** resin$[Pb^{2+}]_o$ = 28.2 ppm, V= 0.01 L.

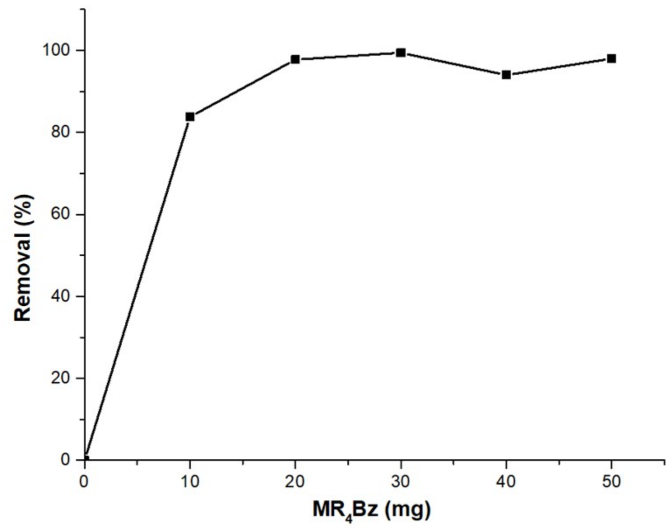


Figure S30. Removal % of Pb^{2+} obtained at different doses of **MR_4Bz** resin. $[Pb^{2+}]_o$ = 28.2 ppm, V= 0.01 L.

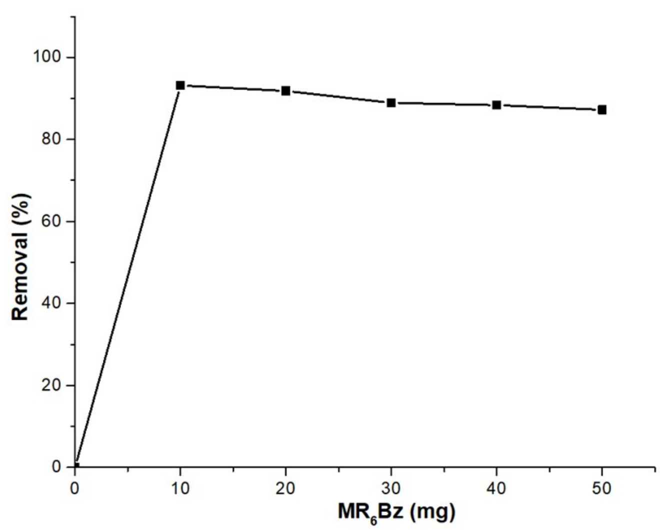


Figure S31. Removal % of Pb^{2+} obtained at different doses of **MR_6Bz** resin. $[Pb^{2+}]_o$ = 28.2 ppm, V= 0.01 L.

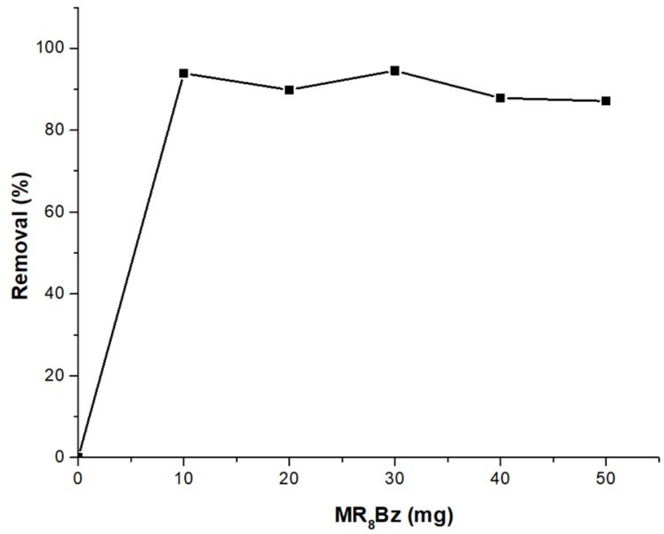


Figure S32. Removal % of Pb^{2+} obtained at different doses of **MR_8Bz** resin. $[Pb^{2+}]_o$= 28.2 ppm, V= 0.01 L.

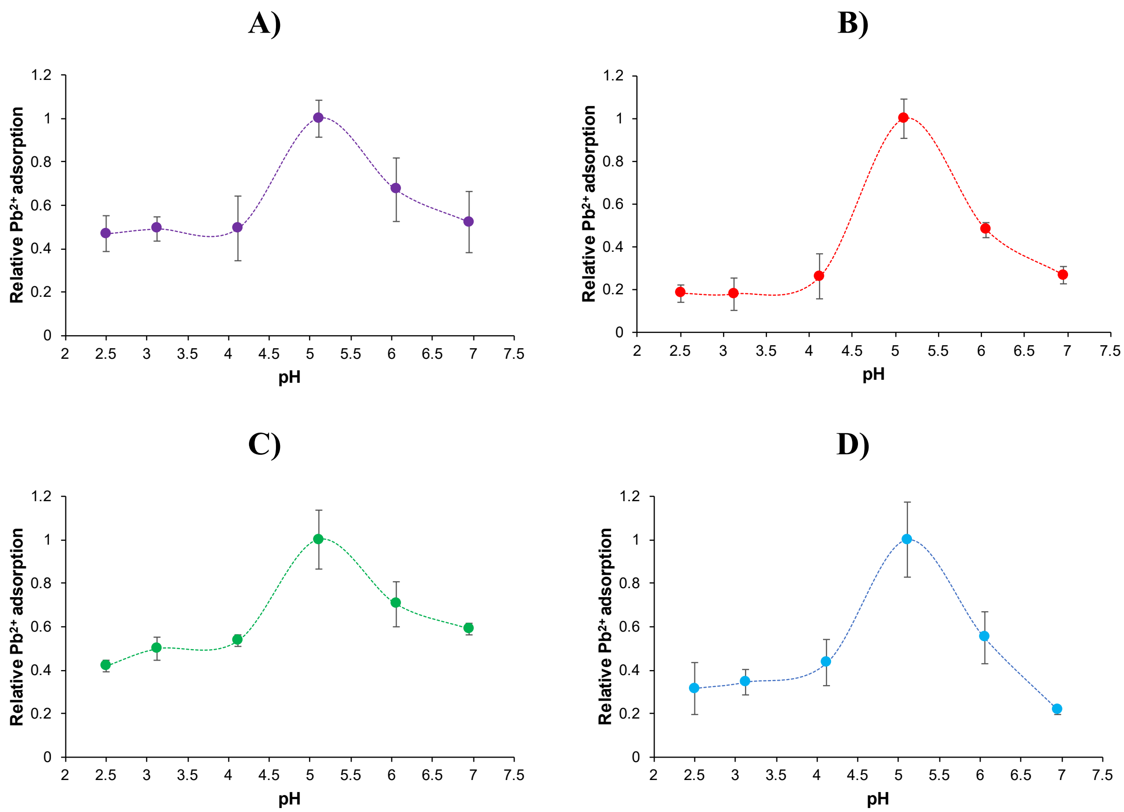


Figure S33. Relative Pb^{2+} adsorption on a)**MR_2Bz**, b) **MR_3Bz**, c) **MR_4Bz** and d) **MR_6Bz** resins as function of pH. Resin mass: 10 mg.

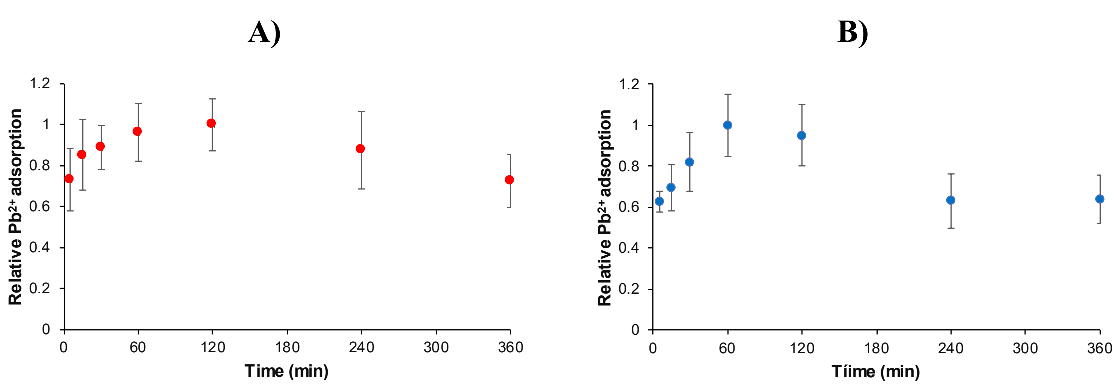


Figure S34. Relative Pb^{2+} adsorption on a) **MR_3Bz** and b) **MR_6Bz** resins as function of time. Resin mass: 10 mg, pH= 5.0.

Table S1. Adsorption of Pb^{2+} on **MR_3Bz** resin as function the concentration at pH=5 and contact time of 60 min.

$[Pb^{2+}]_o$ (mg/L)	$[Pb^{2+}]_f$ (mg/L)	Removal %	Q_e (mg Pb^{2+}/g)	Q_e (mmol Pb^{2+}/g)
3.5	1.7	51.4	1.2±0.43	0.006±0.002
7.7	0.8	89.7	4.6±0.12	0.022±0.0005
14.0	2.2	84.3	7.8±0.41	0.038±0.002
16.9	1.6	90.7	10.1±0.63	0.049±0.003
20.5	0.6	97.0	12.6±1.10	0.061±0.005
32.0	1.2	96.2	20.2±1.42	0.097±0.007
74.0	4.1	94.4	44.8±3.34	0.216±0.016
164.2	65.4	60.2	64.7±2.20	0.312±0.011
238.9	137.5	42.4	67.1±5.20	0.324±0.025
334.8	231.2	30.9	67.0±7.30	0.323±0.035
422.6	321.5	23.9	65.7±9.10	0.317±0.044

Table S2. Adsorption capacity of **MR_4Bz** resin as function of Pb^{2+} concentration at pH=5 and contact time of 60 min.

$[Pb^{2+}]_o$ (mg/L)	$[Pb^{2+}]_f$ (mg/L)	Removal %	Q_e (mg Pb^{2+}/g)	Q_e (mmol Pb^{2+}/g)
3.5	0.9	73.6	1.7±0.34	0.008±0.002
7.7	2.3	69.5	3.5±0.75	0.017±0.004
14.0	6.6	52.8	4.8±0.56	0.023±0.003
16.9	7.2	57.2	6.5±0.95	0.031±0.004
20.5	8.5	58.6	7.9±3.19	0.038±0.015
32.0	14.1	56.0	11.8±3.56	0.057±0.017
74.0	34.5	53.4	26.4±6.2	0.127±0.030
164.2	110.2	32.9	35.8±6.0	0.173±0.029
238.9	178.0	25.5	39.9±3.48	0.193±0.017
334.8	267.3	20.2	44.6±3.11	0.215±0.015
422.6	355.7	15.8	43.4±5.16	0.210±0.025

Table S3. Adsorption capacity of **MR_6Bz** resin as function of Pb^{2+} concentration at pH=5 and contact time of 60 min.

$[Pb^{2+}]_o$ (mg/L)	$[Pb^{2+}]_f$ (mg/L)	Removal %	Q_e (mg Pb^{2+}/g)	Q_e (mmol Pb^{2+}/g)
3.5	0.3	91.0	2.1±0.28	0.010±0.001
7.7	0.7	91.3	4.6±0.24	0.022±0.001
14.0	0.8	94.4	8.7±0.07	0.042±0.0003
16.9	0.3	98.0	10.9±0.29	0.053±0.001
20.5	2.1	90.4	12.3±2.11	0.039±0.010
32.0	7.7	75.8	16.0±2.14	0.078±0.010
74.0	6.9	90.7	44.3±4.34	0.214±0.021
164.2	56.2	65.7	70.9±4.30	0.342±0.021
238.9	141.4	44.8	74.8±6.70	0.361±0.032
334.8	225.1	32.8	72.7±6.40	0.351±0.031
422.6	310.3	26.6	72.3±5.06	0.349±0.024

Table S4. Linearized isotherm models used to analyze the **MR_nBz** resin adsorption properties.

Isotherm model	Equations
Langmuir	$\frac{C_e}{Qe} = \frac{C_e}{Q_{max}} + \frac{1}{K_L Q_{max}}$ (Equation S1)
Freundlich	$LnQ_e = LnK_F + \frac{1}{n} LnC_e$ (Equation S2)
Temkin	$Q_e = \frac{RT}{b_T} LnK_T + \frac{RT}{b_T} LnC_e$ (Equation S3)
Dubinin-Radushkevich (D-R)	$LnQ_e = LnQ_{max} - \beta\varepsilon$ (Equation S4) $\varepsilon = RTLn\left(1 + \frac{1}{C_e}\right)$ (Equation S5) $E_a = \frac{1}{\sqrt{2\beta}}$ (Equation S6)

Table S5. Parameters of $\mathbf{MR_3Bz}$ resin adsorption isotherm models for Pb^{2+}.

Isotherm model	**Parameters**	
Langmuir	Q_{max}	66.667
	K_L	0.570
	R^2	0.999
Freundlich	1/n	0.240
	K_F	19.967
	R^2	0.853
Temkin	K_T	1.471
	b_T	9.043
	R^2	0.928
Dubinin-Radushkevich (D-R)	β	0.712
	Q_{max}	66.188
	E_a	0.838
	R^2	0.993
	$\mathbf{Q_{max(exp)}}$	**67.130**

Table S6. Parameters of $\mathbf{MR_4Bz}$ resin adsorption isotherm models for Pb^{2+}.

Isotherm model	**Parameters**	
Langmuir	Q_{max}	49.260
	K_L	0.025
	R^2	0.997
Freundlich	1/n	0.448
	K_F	3.782
	R^2	0.917
Temkin	K_T	0.452
	b_T	-5.085
	R^2	0.978
Dubinin-Radushkevich (D-R)	β	6.586
	Q_{max}	43.150
	E_a	0.275
	R^2	0.980
	$\mathbf{Q_{max(exp)}}$	**44.635**

Table S7. Parameters of $\mathbf{MR_6Bz}$ resin adsorption isotherm models for Pb^{2+}.

Isotherm model	Parameters	
Langmuir	Q_{max}	81.301
	K_L	0.035
	R^2	0.964
Freundlich	1/n	0.350
	K_F	12.21
	R^2	0.772
Temkin	K_T	10.970
	b_T	2.208
	R^2	0.847
Dubinin-Radushkevich (D-R)	β	1.951
	Q_{max}	67.660
	E_a	0.506
	R^2	0.757
	$\mathbf{Q_{max(exp)}}$	**74.504**

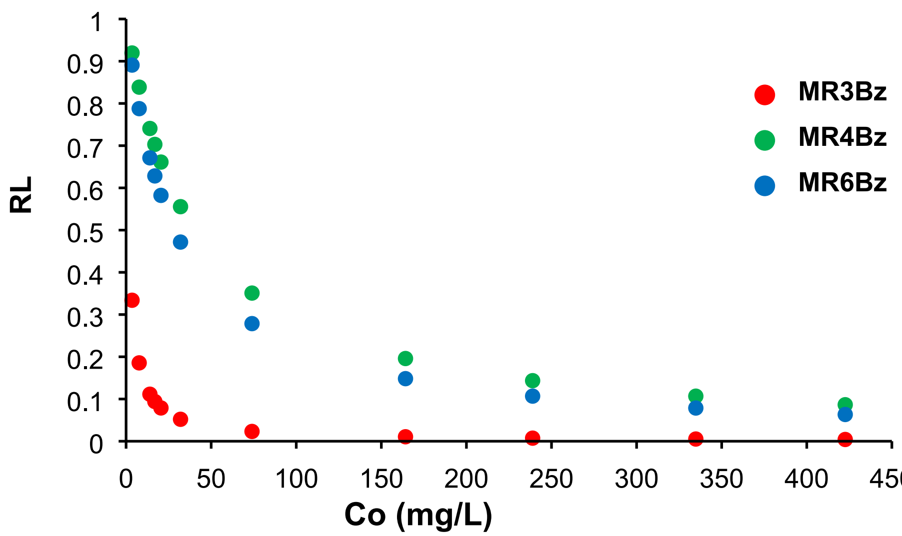


Figure S35. Changes in separation factor (R_L) in $\mathbf{MR_nBz}$ resins as function of initial concentration of Pb^{2+} at 25 °C and pH= 5. Contact time: 1 h, mass of resin: 10 mg.

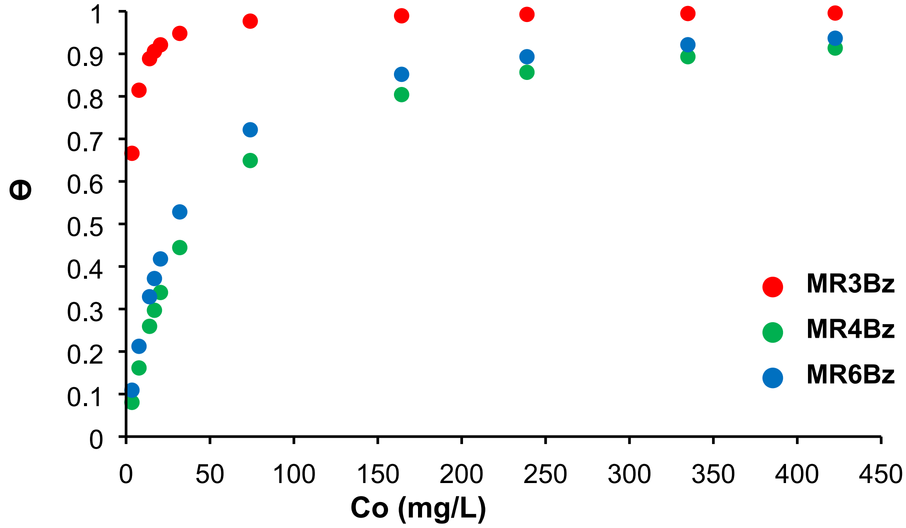


Figure S36. Changes in surface (Θ) of **MR$_n$Bz** resins as function of initial concentration of Pb^{2+} at 25 °C and pH= 5. Contact time: 1 h, mass of resin: 10 mg.

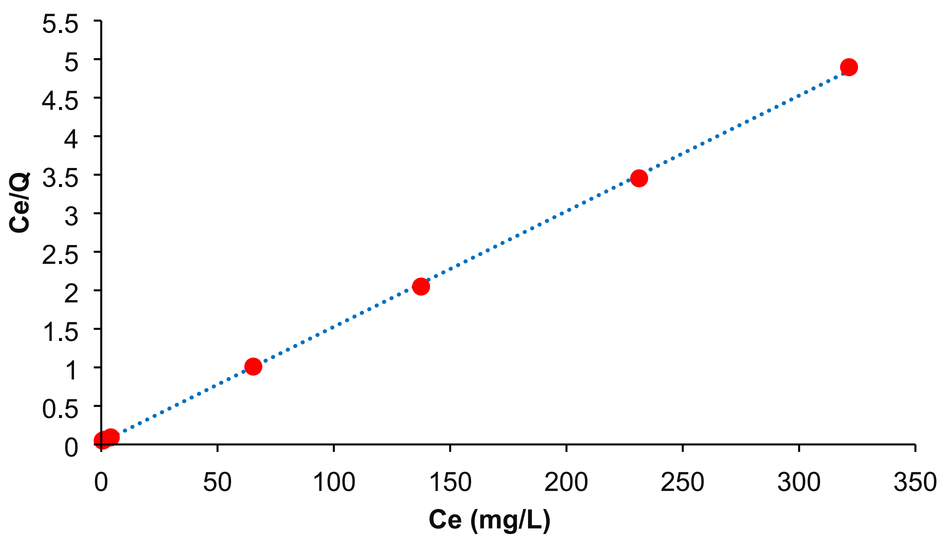


Figure S37. Linearized form of the Langmuir isotherm model for the data with **MR$_3$Bz** and Pb^{2+} solutions.

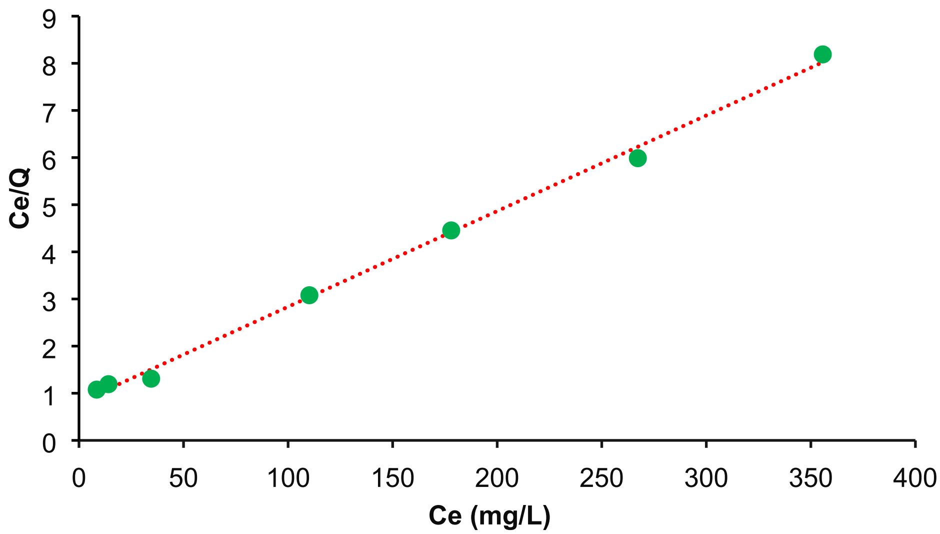


Figure S38. Linearized form of the Langmuir isotherm model for the data with **MR_4Bz** and Pb^{2+} solutions.

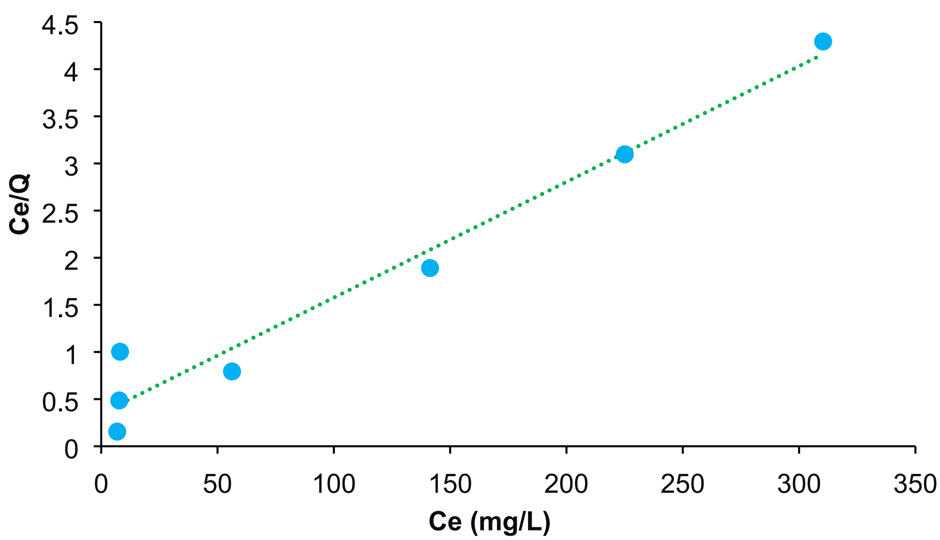


Figure S39. Linearized form of the Langmuir isotherm model for the data with **MR_6Bz** and Pb^{2+} solutions.

Table S8. ΔG values for the Pb^{2+} absorption on **MR_3Bz** resin as function the concentration at pH=5 and contact time of 60 min.

$[Pb^{2+}]_o$ (mg/L)	$[Pb^{2+}]_f$ (mg/L)	Adsorption (mg Pb^{2+}/g)	K_c	ΔG (kJ/mol)
3.5	1.7	1.2	0.693	0.9082
7.7	0.8	4.6	5.689	-4.308
14.0	2.2	7.8	3.556	-3.143
16.9	1.6	10.1	6.307	-4.563
20.5	0.6	12.6	20.993	-7.542
32.0	1.2	20.2	16.808	-6.991
74.0	4.1	44.8	10.936	-5.927
164.2	65.4	64.7	0.989	0.025
238.9	137.5	67.1	0.488	1.776
334.8	231.2	67.0	0.289	3.067
422.6	321.5	65.7	0.204	3.935

Table S9. ΔG values for the Pb^{2+} absorption on **MR_4Bz** resin as function of Pb^{2+} concentration at pH=5 and contact time of 60 min.

$[Pb^{2+}]_o$ (mg/L)	$[Pb^{2+}]_f$ (mg/L)	Adsorption (mg Pb^{2+}/g)	K_c	ΔG (kJ/mol)
3.5	0.9	1.7	1.865	-1.544
7.7	2.3	3.5	1.545	-1.078
14.0	6.6	4.8	0.734	0.764
16.9	7.2	6.5	0.898	0.266
20.5	8.5	7.9	0.923	0.197
32.0	14.1	11.8	0.842	0.423
74.0	34.5	26.4	0.764	0.666
164.2	110.2	35.8	0.324	2.785
238.9	178.0	39.9	0.216	3.791
334.8	267.3	44.6	0.167	4.434
422.6	355.7	43.4	0.122	5.212

Table S10. ΔG values for the Pb^{2+} absorption on **MR_6Bz** resin as function of Pb^{2+} concentration at pH=5 and contact time of 60 min.

$[Pb^{2+}]_o$ (mg/L)	$[Pb^{2+}]_f$ (mg/L)	Adsorption (mg Pb^{2+}/g)	Kc	ΔG (kJ/mol)
3.5	0.3	2.1	6.913	-4.790
7.7	0.7	4.6	6.574	-4.666
14.0	0.8	8.7	10.923	-5.923
16.9	0.3	10.9	36.463	-8.910
20.5	2.1	12.3	5.878	-4.388
32.0	7.7	16.0	2.039	-1.765
74.0	6.9	44.3	6.407	-4.602
164.2	56.2	70.9	1.269	-0.589
238.9	141.4	74.8	0.527	1.587
334.8	225.1	72.7	0.325	2.784
422.6	310.3	72.3	0.235	3.588

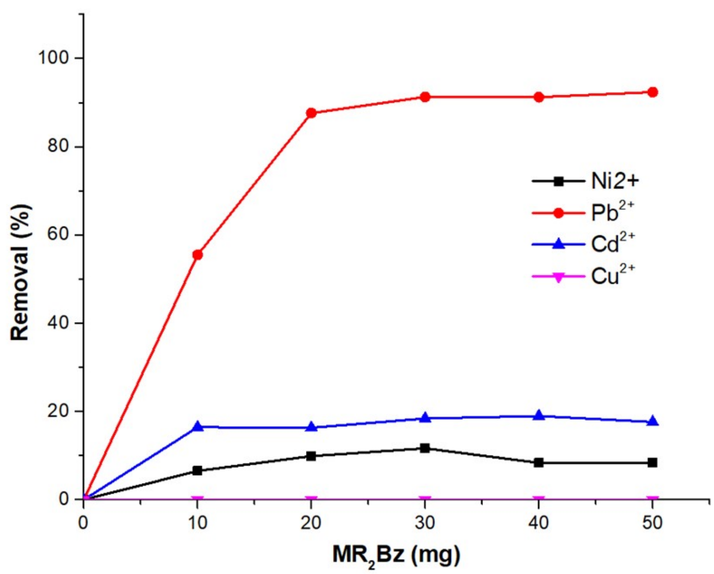


Figure S40. Removal % of metal ions obtained at different doses of **MR_2Bz** resin. $[Pb^{2+}]$= 33.5 ppm, $[Cu^{2+}]$= 27.5 ppm, $[Cd^{2+}]$= 21.5 ppm, $[Ni^{2+}]$= 23.7 ppm, V= 0.01 L.

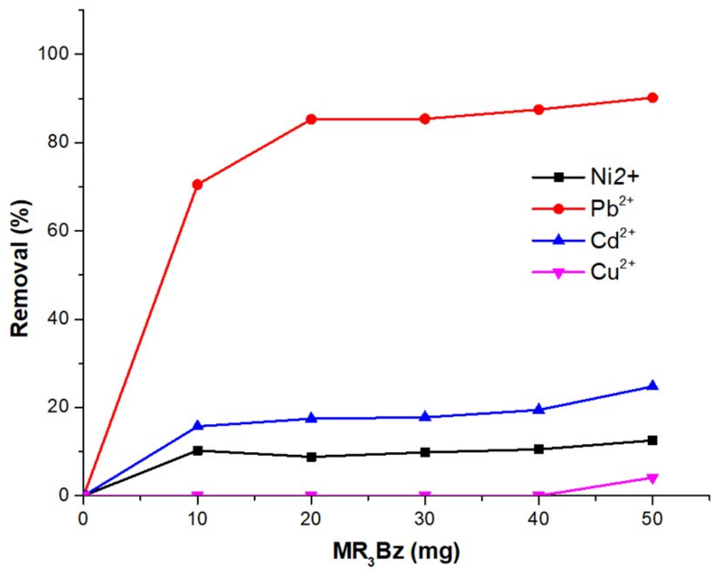


Figure S41. Removal % of metal ions obtained at different doses of **MR$_3$Bz** resin. [Pb^{2+}]= 33.5 ppm, [Cu^{2+}]= 27.5 ppm, [Cd^{2+}]= 21.5 ppm, [Ni^{2+}]= 23.7 ppm, V= 0.01 L.

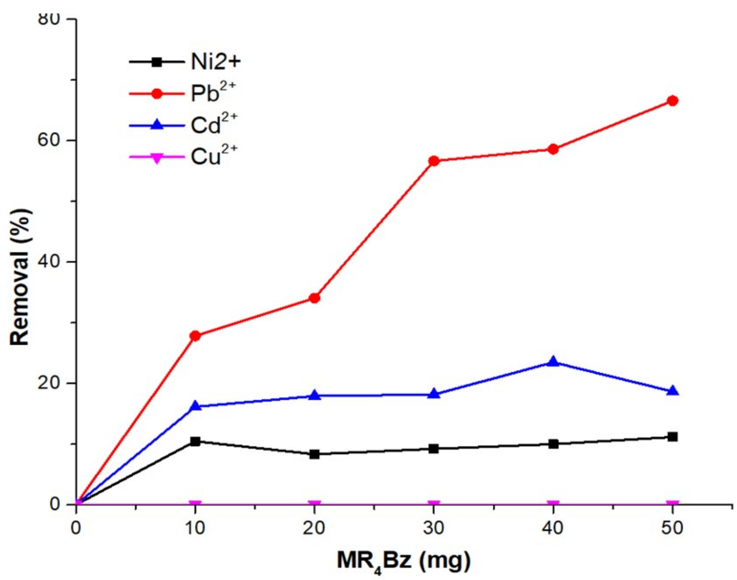


Figure S42. Removal % of metal ions obtained at different doses of **MR$_4$Bz** resin. [Pb^{2+}]= 33.5 ppm, [Cu^{2+}]= 27.5 ppm, [Cd^{2+}]= 21.5 ppm, [Ni^{2+}]= 23.7 ppm, V= 0.01 L.

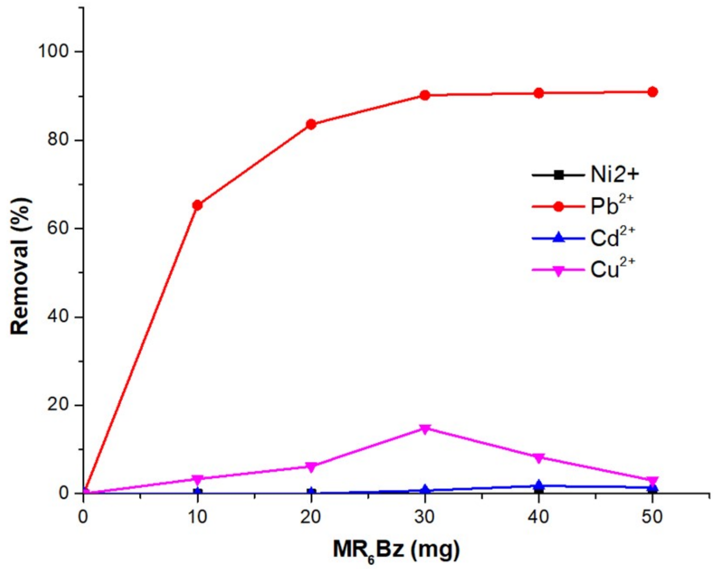


Figure S43. Removal % of metal ions obtained at different doses of **MR_6Bz** resin. [Pb^{2+}]= 33.5 ppm, [Cu^{2+}]= 27.5 ppm, [Cd^{2+}]= 21.5 ppm, [Ni^{2+}]= 23.7 ppm, V= 0.01 L.

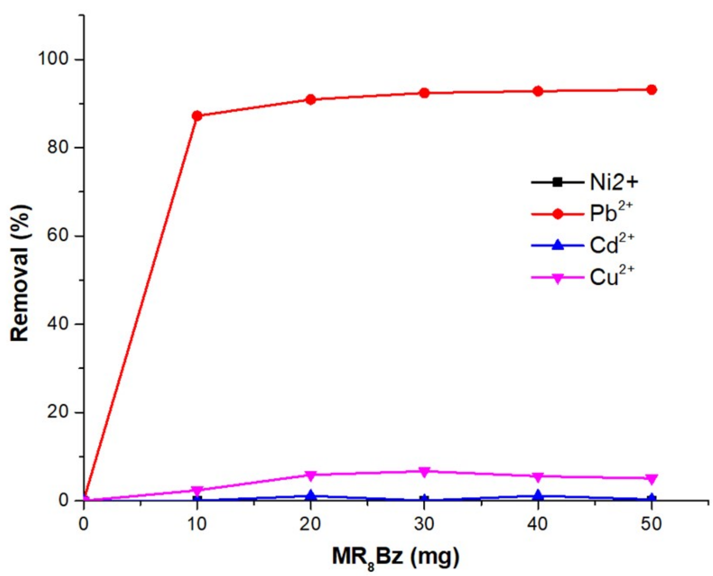


Figure S44. Removal % of metal ions obtained at different doses of **MR_8Bz** resin. [Pb^{2+}]= 33.5 ppm, [Cu^{2+}]= 27.5 ppm, [Cd^{2+}]= 21.5 ppm, [Ni^{2+}]= 23.7 ppm, V= 0.01 L.

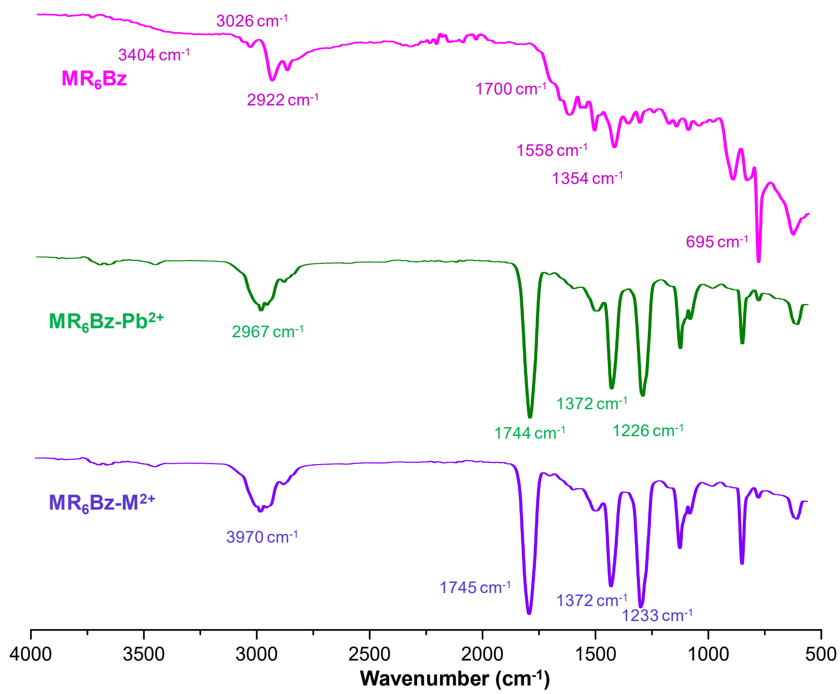


Figure S45. FTIR spectra of pristine **MR_6Bz** (magenta), Pb^{2+}-loaded **MR_6Bz** (green) and M^{2+}-loaded **MR_6Bz** (purple) resins obtained under N_2 atmosphere.

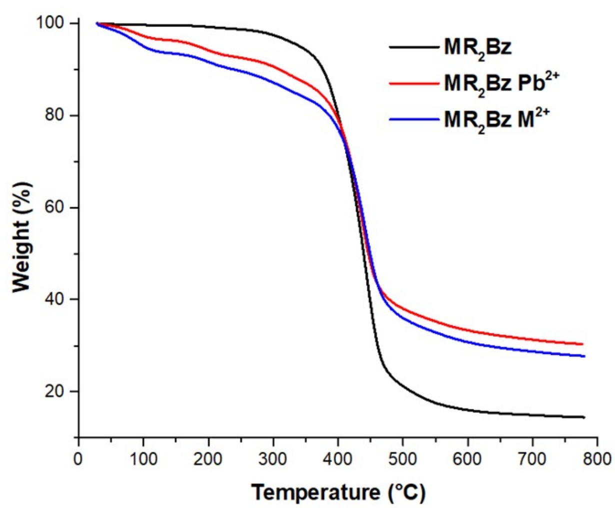


Figure S46. Thermograms of pristine **MR_2Bz** resin (black), Pb^{2+}-loaded **MR_2Bz** (red) and metal-loaded **MR_2Bz** (blue) obtained under N_2 atmosphere.

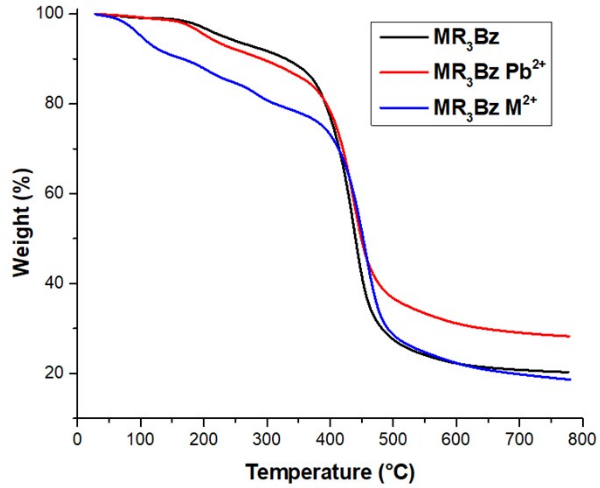


Figure S47. Thermograms of pristine **MR$_3$Bz** resin (black), Pb^{2+}-loaded **MR$_3$Bz** (red) and metal-loaded **MR$_3$Bz** (blue) obtained under N_2 atmosphere.

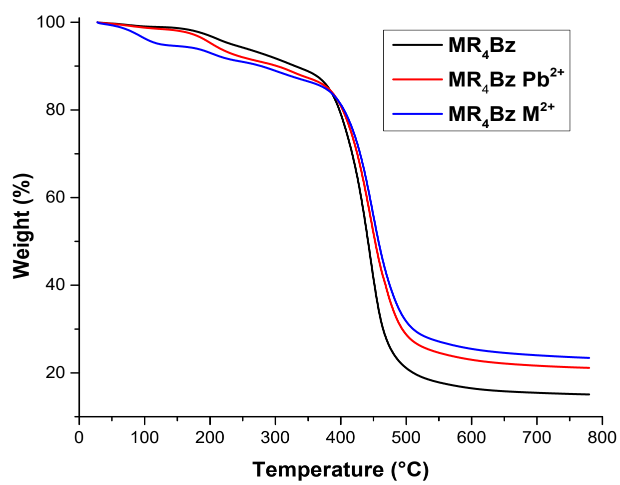


Figure S48. Thermograms of pristine **MR$_4$Bz** resin (black), Pb^{2+}-loaded **MR$_4$Bz** (red) and metal ions-loaded **MR$_4$Bz** (blue) obtained under N_2 atmosphere.

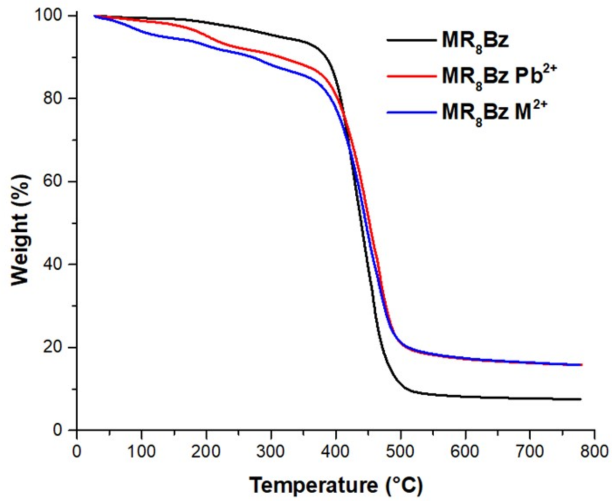
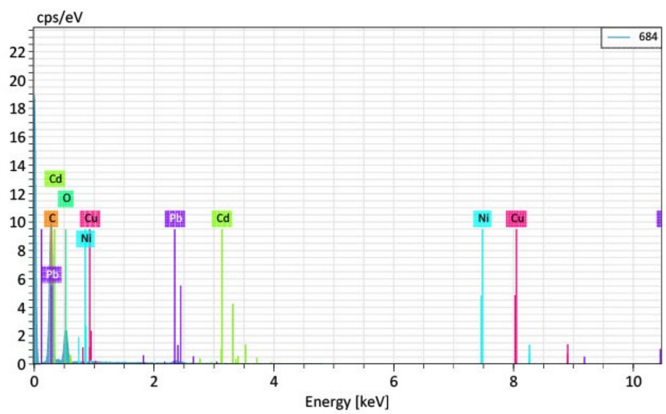


Figure S49. Thermograms of pristine **MR$_8$Bz** resin (black), Pb^{2+}-loaded **MR$_8$Bz** (red) and metal ions-loaded **MR$_8$Bz** (blue) obtained under N_2 atmosphere.



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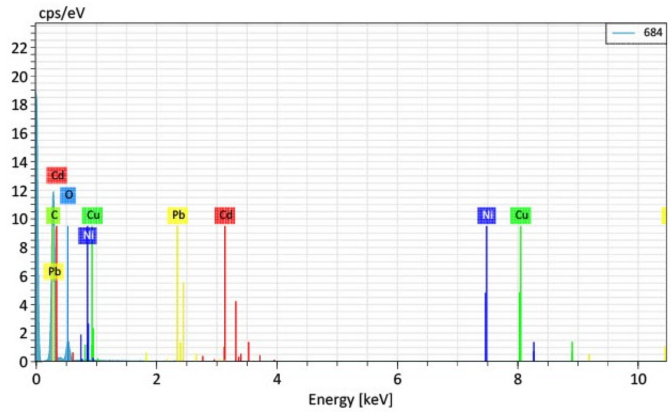
Element	At. No.	Netto	Mass [%]	Mass Norm. [%]	Atom [%]	abs. error [%] (1 sigma)	rel. error [%] (1 sigma)
Carbon	6	44976	17.47	46.40	66.98	2.10	12.03
Oxygen	8	18543	10.38	27.58	29.89	1.37	13.18
Lead	82	2717	6.95	18.46	1.54	0.42	5.98
Cadmium	48	213	1.58	4.19	0.65	0.21	13.34
Copper	29	1041	0.80	2.14	0.58	0.21	25.51
Nickel	28	802	0.46	1.23	0.36	0.14	29.53
		Sum	37.65	100.00	100.00		

Figure S50. EDS elemental analysis of metal ions-loaded **MR$_3$Bz** resin after the treatment of a mixture of metal ions solution.



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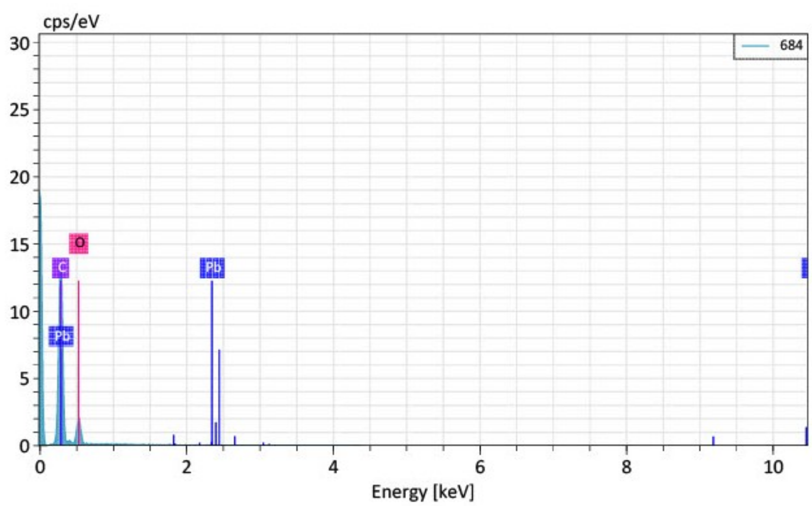
Element	At. No.	Netto	Mass [%]	Mass Norm. [%]	Atom [%]	abs. error [%] (1 sigma)	rel. error [%] (1 sigma)
Carbon	6	84363	72.71	72.71	79.38	8.30	11.41
Oxygen	8	17631	24.70	24.70	20.25	3.24	13.11
Cadmium	48	51	1.02	1.02	0.12	0.22	21.20
Copper	29	349	0.63	0.63	0.13	0.22	35.39
Lead	82	71	0.51	0.51	0.03	0.10	19.78
Nickel	28	318	0.43	0.43	0.10	0.16	38.23
		Sum	100.00	100.00	100.00		

Figure S51. EDS elemental analysis of metal ions-loaded $\mathbf{MR_6Bz}$ resin after the treatment of a mixture of metal ions solution.



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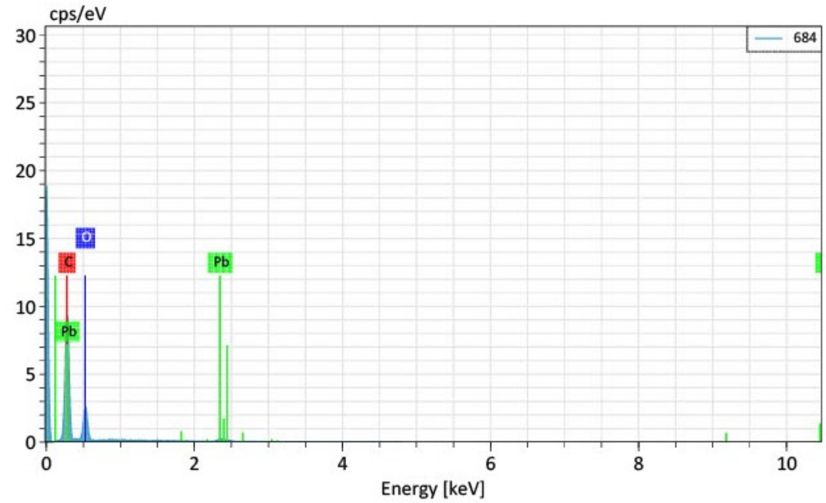
Element	At. No.	Netto	Mass [%]	Mass Norm. [%]	Atom [%]	abs. error [%] (1 sigma)	rel. error [%] (1 sigma)
Carbon	6	19366	68.20	68.20	75.46	8.80	12.91
Oxygen	8	5287	29.36	29.36	24.38	4.58	15.59
Lead	82	102	2.45	2.45	0.16	0.34	13.98
		Sum	100.00	100.00	100.00		

Figure S52. EDS elemental analysis of Pb^{2+}-loaded $\mathbf{MR_3Bz}$ resin after the treatment of Pb^{2+} solution at 28.2 mg/L.



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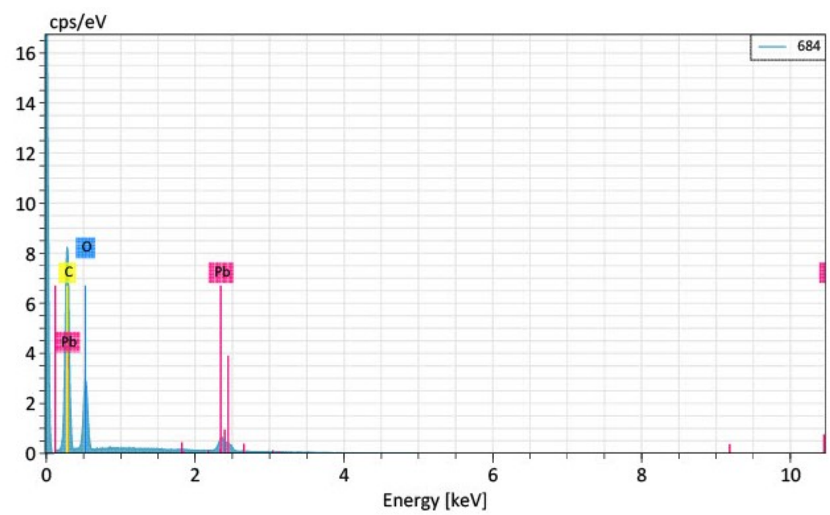
Element	At. No.	Netto	Mass [%]	Mass Norm. [%]	Atom [%]	abs. error [%] (1 sigma)	rel. error [%] (1 sigma)
Carbon	6	26561	15.04	46.04	64.25	1.90	12.62
Oxygen	8	13225	10.61	32.46	34.01	1.45	13.71
Lead	82	1970	7.02	21.50	1.74	0.44	6.22
		Sum	32.68	100.00	100.00		

Figure S53. EDS elemental analysis of Pb^{2+}-loaded $\mathbf{MR_6Bz}$ resin after the treatment of Pb^{2+} solution at 28.2 mg/L.



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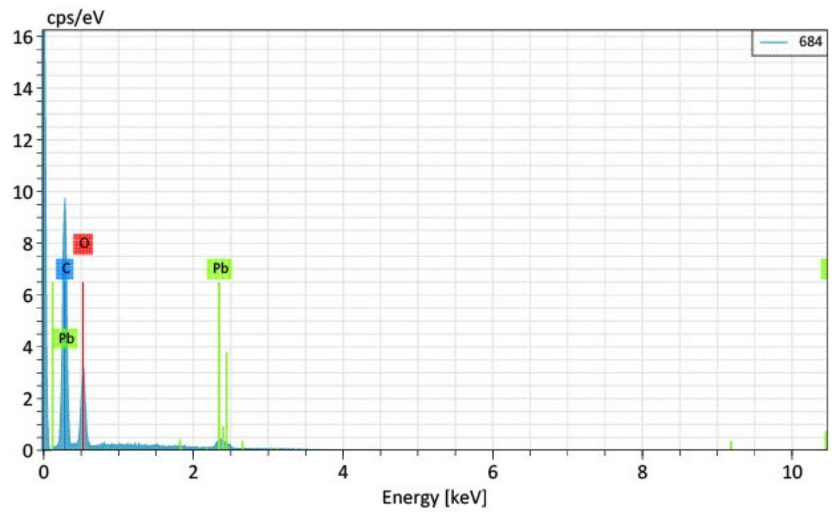
Element	At. No.	Netto	Mass [%]	Mass Norm. [%]	Atom [%]	abs. error [%] (1 sigma)	rel. error [%] (1 sigma)
Lead	82	16243	118.63	87.22	30.96	18.00	15.17
Carbon	6	65985	9.14	6.72	41.17	1.08	11.83
Oxygen	8	40174	8.24	6.06	27.86	1.01	12.30
		Sum	136.02	100.00	100.00		

Figure S54. EDS elemental analysis of Pb^{2+}-loaded $\mathbf{MR_3Bz}$ resin after the treatment of Pb^{2+} solution at 340 mg/L.



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Element	At. No.	Netto	Mass [%]	Mass Norm. [%]	Atom [%]	abs. error [%] (1 sigma)	rel. error [%] (1 sigma)
Lead	82	3193	98.31	80.74	21.48	15.43	15.70
Carbon	6	22915	12.93	10.62	48.74	1.66	12.84
Oxygen	8	12553	10.52	8.64	29.77	1.45	13.81
		Sum	**121.76**	**100.00**	**100.00**		

Figure S55. EDS elemental analysis of Pb^{2+}-loaded $\mathbf{MR_6Bz}$ resin after the treatment of Pb^{2+} solution at 340 mg/L.