Supporting Information for

Evaluation of the colloidal stability and adsorption performance of reduced graphene oxide–elemental silver/magnetite nanohybrids for selected toxic heavy metals in aqueous solutions

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S1. Adsorption of heavy metal ions by rGO and NHs in single metal system

For single metal system, the adsorption capacities for Cd(II), Ni(II), Zn(II), Co(II), Pb(II), and Cu(II) on rGO, rGO/magnetite, rGO/silver, and rGO/magnetite/silver were compared (Fig. S1). Heavy metal ions were more easily adsorbed on rGO at pH 4 than that of iron- and elemental silver-deposited rGOs (*i.e.,* rGO/magnetite, rGO/silver, and rGO/magnetite/silver), according to following order: Cu(II) > Zn(II) > Ni(II) > Co(II) > Cd(II), Pb(II). The maximum pH at which metallic ions began to hydrolyze was calculated using the solubility product constant (K_{sp}, summarized in Table S1) and metallic ion concentrations to ensure that only dissociated ions would be adsorbed. The K_{sp} value reflects the dissolvability of $Me(OH)_2$ in water [1], as follows:

$$Me(OH)_2 \leftrightarrow Me^{2+} + 2OH^- \quad \text{(S1)}$$

$$K_{sp} = [Me^{2+}][OH^-]^2. \quad \text{(S2)}$$

The calculated maximum pH values for Cd(II), Ni(II), Zn(II), Co(II), Pb(II), and Cu(II) were 6.78, 6.87, 6.04, 7.39, 4.58, and 5.10, respectively. At pH levels below these maxima, the adsorption process can be achieved by complex formations with deprotonated sites of the rGO and NHs (Eq. (S3)), exchange with Na^+/H^+ ions (Eqs. (S4) and (S5)), and hydrolysis of metal ions (Me^{2+}) in solution ($n > m$) (Eqs. (S6) and (S7)) [2].

$$\equiv SO^- + Me^{2+} \leftrightarrow \equiv SOMe^+ \quad \text{(S3)}$$

$$\equiv SONa/H + Me^{2+} \leftrightarrow \equiv SOMe^+ + Na^+/H^+ \quad \text{(S4)}$$

$$2(\equiv \mathrm{SONa/H}) + \mathrm{Me^{2+}} \leftrightarrow (\equiv \mathrm{SO})_2\,\mathrm{Me^0} + 2\mathrm{Na^+/H^+} \quad \text{(S5)}$$

$$\mathrm{Me}^{n+} + n\mathrm{H_2O} \leftrightarrow \mathrm{Me(OH)}m(\mathrm{H_2O})_{n-1}^{2-m} + m\mathrm{H^+} \quad \text{(S6)}$$

$$\equiv \mathrm{SO^-} + \mathrm{Me(OH)}m(\mathrm{H_2O})_{n-1}^{2-m} \leftrightarrow \equiv \mathrm{SOMe(OH)}_m^{1-m} + (n-1)\mathrm{H_2O} \quad \text{(S7)}$$

The physicochemical properties of metallic ions, such as electronegativity, ionic radius, K_{sp}, and hydrolysis constant (pK_h), are responsible for the adsorption selectivity [3, 4]. The highest adsorption capacity of Cu(II) on rGO, rGO/magnetite, rGO/silver, and rGO/magnetite/silver (4.998, 4.203, 4.996, and 4.997 mmol/g, respectively) can be explained by a smallest ionic radius (0.73 Å) readily occupying the pores of the rGO and NHs despite the low solubility product of Cu(II) ion (1.6×10^{-19}).

Table S1. Hydrolysis constants (pK_h), ionic radii, and solubility products (K_{sp}) of the heavy metal ions investigated in this study [3, 5, 6].

Heavy metal ions	Cd(II)	Ni(II)	Zn(II)	Co(II)	Pb(II)	Cu(II)
pK_h	10.80	9.40	8.96	9.60	7.71	8.00
Ionic radius (Å)	0.95	0.74	0.75	0.78	1.21	0.73
K_{sp} of $Me(OH)_x$	7.2×10^{-15}	5.5×10^{-16}	1.2×10^{-17}	5.9×10^{-15}	1.4×10^{-20}	1.6×10^{-19}

Table S2. Parameters of the pseudo first-order and second-order kinetic models for Cd(II) adsorption on rGO, rGO/magnetite, rGO/silver, and rGO/magnetite/silver NHs.

Adsorbent	Exp.	Pseudo-first-order kinetic model			Pseudo-second-order kinetic model		
	$q_{e,exp}$ (mmol/g)	k_1 (1/min)	$q_{e,cal1}$ (mmol/g)	r^2	k_2 (1/min)	$q_{e,cal2}$ (mmol/g)	r^2
rGO	3.769	0.125	3.835	0.866	0.221	3.811	0.984
rGO/magnetite	2.477	0.070	2.569	0.945	0.171	2.615	0.982
rGO/silver	3.208	0.075	3.322	0.973	0.089	3.427	0.992
rGO/magnetite/silver	3.354	0.101	3.404	0.864	0.209	3.444	0.973

Table S3. Parameters of Langmuir and Freundlich isotherms for Cd(II) adsorption on rGO, rGO/magnetite, rGO/silver, and rGO/magnetite/silver NHs.

Adsorbent	Langmuir isotherm model				Freundlich isotherm model			
	$q_e = \frac{q_m b C_e}{1 + b C_e}$				$q_e = k_F C_e^n$			
	q_m (mmol/g)	K_L (L/mmol)	r^2	χ^2	k_F	n	r^2	χ^2
rGO	3.854	51.90	0.999	1.29×10^{-2}	3.778	12.45	0.910	1.16×10^{-0}
rGO/magnetite	2.605	83.46	0.985	1.14×10^{-1}	2.709	8.850	0.776	4.78×10^{-1}
rGO/silver	3.317	50.25	0.995	8.52×10^{-2}	3.396	7.680	0.854	7.20×10^{-1}
rGO/magnetite/silver	3.441	56.98	0.996	6.10×10^{-2}	3.477	8.718	0.774	7.96×10^{-1}

Table S4. Elemental content (%) of the rGO, rGO/magnetite, rGO/silver, and rGO/magnetite/silver NHs before and after Cd(II) adsorption based on the XPS analyses.

Element	Before Cd(II) adsorption				After Cd(II) adsorption			
	rGO	rGO/ magnetite	rGO/ silver	rGO/ magnetite/ silver	rGO	rGO/ magnetite	rGO/ silver	rGO/ magnetite/ silver
C1s	80.56	42.06	58.42	53.10	77.83	49.74	82.05	30.18
O1s	19.44	52.55	14.91	40.10	20.08	41.17	9.06	54.42
Fe2p3	-	5.38	-	5.23	-	9.03	-	14.44
Ag3d	-	-	26.67	1.56	-	-	8.62	0.59
Cd3d5	-	-	-	-	2.09	0.05	0.27	0.38

77 **Table S5.** Influence of natural organic matters (Suwannee River humic and fulvic acids) on heavy
78 metal ion adsorption by rGO, rGO/magnetite, rGO/silver, and rGO/magnetite/silver NHs.

Heavy metals	Adsorbent	Adsorption capacity (mmol/g)			Percentage increase (%)	
		No NOM	Suwannee River humic acid	Suwannee River fulvic acid	Suwannee River humic acid	Suwannee River fulvic acid
Cd(II)	rGO	2.55	3.16	3.03	23.79	18.84
	rGO/magnetite	1.91	2.85	2.85	48.89	48.76
	rGO/silver	2.26	2.86	2.93	26.91	29.93
	rGO/magnetite/silver	2.52	2.85	2.91	13.32	15.38
Ni(II)	rGO	3.81	3.95	3.74	3.54	-1.94
	rGO/magnetite	2.32	3.05	3.16	31.58	36.33
	rGO/silver	3.18	3.48	3.55	9.45	11.62
	rGO/magnetite/silver	3.80	3.84	3.95	1.20	4.09
Zn(II)	rGO	5.0	5.0	5.0	0.0	0.0
	rGO/magnetite	3.11	3.37	3.48	8.36	11.90
	rGO/silver	3.25	3.76	3.74	15.69	15.08
	rGO/magnetite/silver	4.15	4.46	4.33	7.47	4.34
Co(II)	rGO	2.96	3.86	3.16	30.21	6.76
	rGO/magnetite	2.16	2.99	3.08	38.69	42.74
	rGO/silver	2.92	2.97	3.21	1.83	9.95
	rGO/magnetite/silver	2.95	3.11	3.14	5.47	6.56
Pb(II)	rGO	2.76	2.86	3.15	3.81	14.20
	rGO/magnetite	1.91	2.88	2.85	51.09	49.51
	rGO/silver	2.50	2.19	2.97	-12.29	18.85
	rGO/magnetite/silver	2.56	2.66	2.90	3.98	13.39
Cu(II)	rGO	5.0	5.0	5.0	0.0	0.0
	rGO/magnetite	3.98	4.12	4.18	3.52	5.03
	rGO/silver	5.0	5.0	5.0	0.0	0.0
	rGO/magnetite/silver	5.0	5.0	5.0	0.0	0.0

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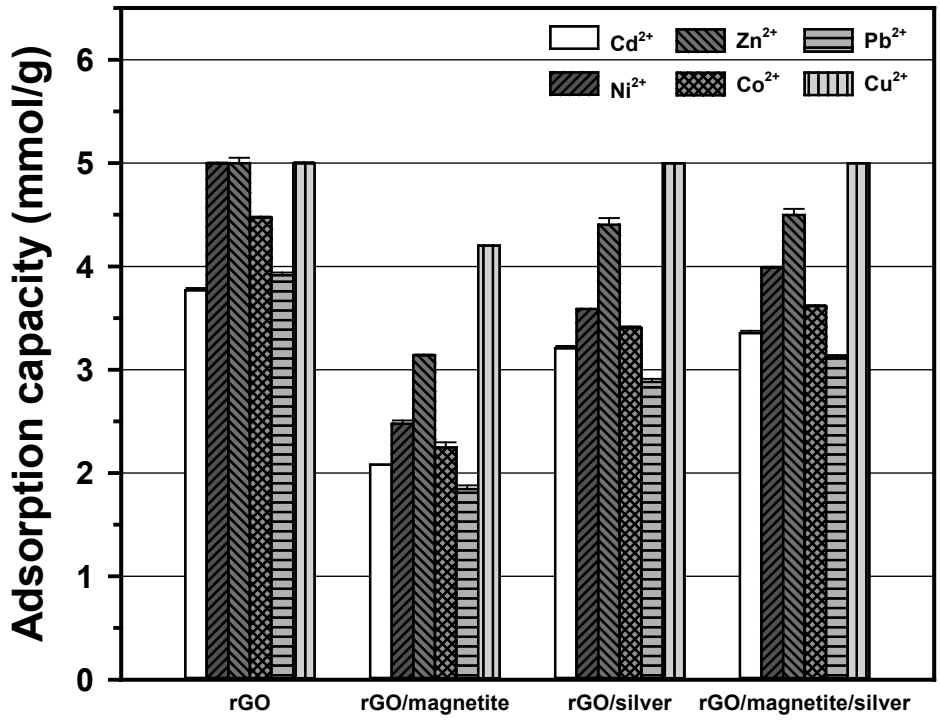

Fig. S1. Comparison of the adsorption capacity of Cd(II), Ni(II), Zn(II), Co(II), Pb(II), and Cu(II) by rGO, rGO/magnetite, rGO/silver, and rGO/magnetite/silver nanohybrids. Experimental conditions: m/V = 0.2 g/L; initial pH = 4.0 ± 0.1; $[Cd(II)]_0 = [Ni(II)]_0 = [Zn(II)]_0 = [Co(II)]_0 = [Pb(II)]_0 = [Cu(II)]_0$ = 1 mM; I = 0.01 mol/L $NaNO_3$; and T = 298 K.

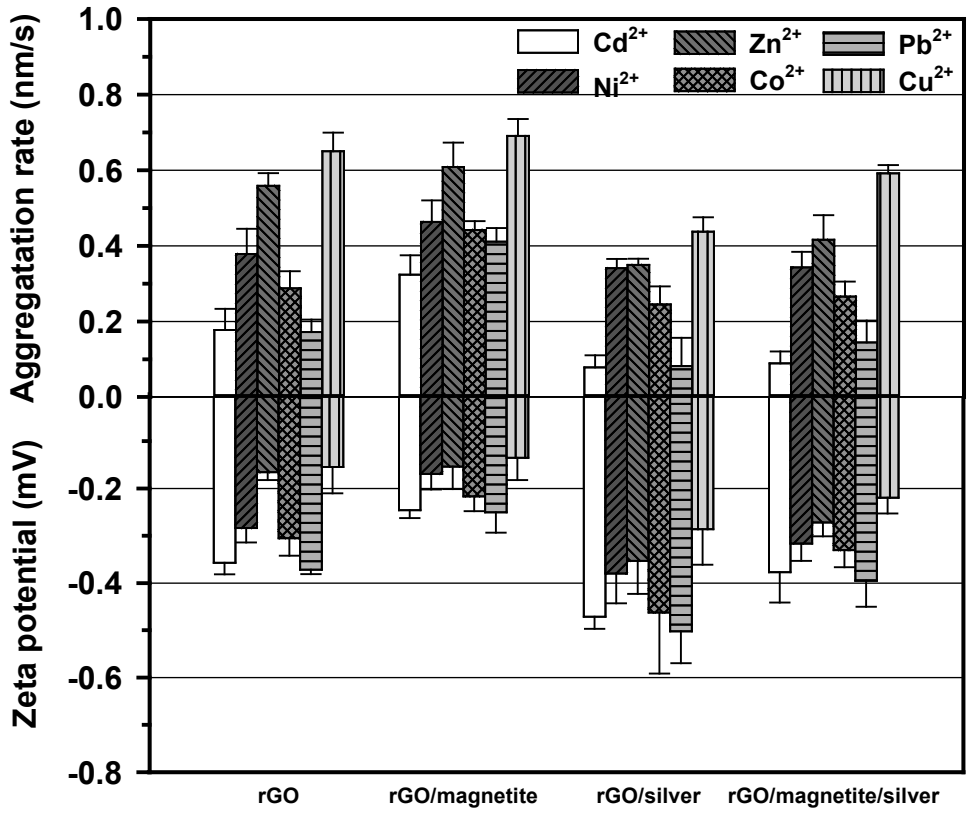

Fig. S2. Aggregation rate plots and zeta potentials of rGO, rGO/magnetite, rGO/silver, and rGO/magnetite/silver nanohybrids with heavy metal ions. Experimental conditions: $m/V = 0.2$ g/L; $[Cd(II)]_0 = [Ni(II)]_0 = [Zn(II)]_0 = [Co(II)]_0 = [Pb(II)]_0 = [Cu(II)]_0 = 1$ mM; and $T = 298$ K.

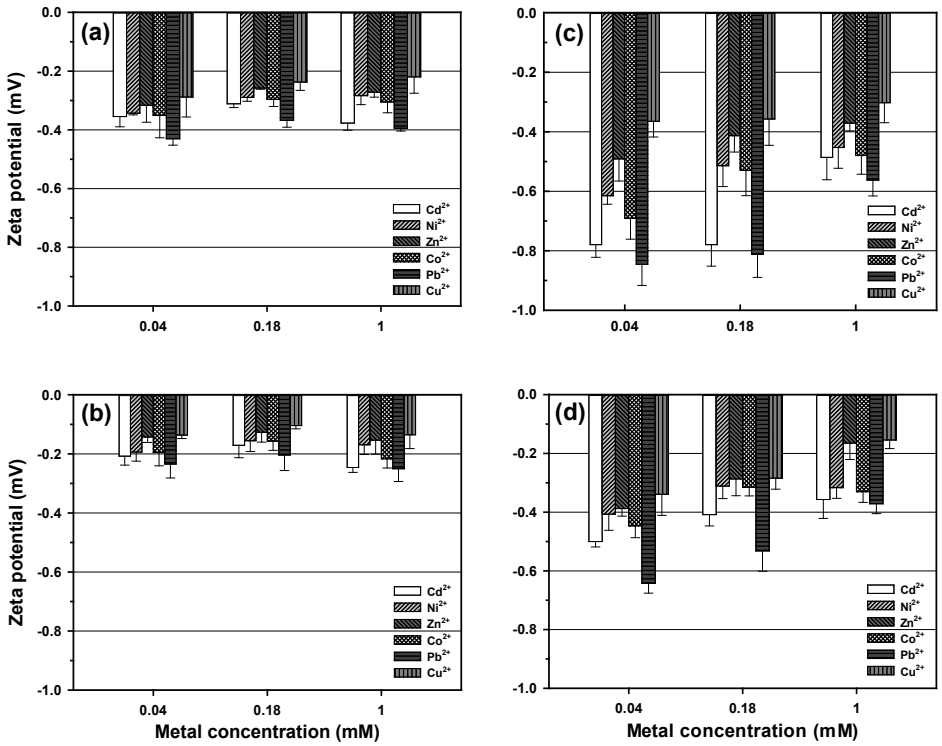

Fig. S3. Comparison of the zeta potential of (a) rGO, (b) rGO/magnetite, (c) rGO/silver, and (d) rGO/magnetite/silver nanohybrids with heavy metal ions. Experimental conditions: $m/V = 0.2$ g/L; $[Cd(II)]_0 = [Ni(II)]_0 = [Zn(II)]_0 = [Co(II)]_0 = [Pb(II)]_0 = [Cu(II)]_0 = 0.04$, 0.18, and 1 mM; and $T =$ 298 K.

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