

Supplementary information

A biocompatible nanodendrimer for efficient adsorption and reduction of Hg(II)

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EXPERIMENTAL SECTION

Synthesis of Bis(phthaloyl)diethylenetriamine (BPA)

A mixture of 33.2 g (0.20 mol) of phthalic anhydride and DETA (10.3 g, 0.10 mol) was refluxed about 2 h by adding 160 g glacial acetic acid. Then a rotary evaporator used to evaporate solvent and was changed with 95% hot ethanol (160 g) with stirring up to the precipitation formation. The sample was recovered and treated by using the cold ethanol: yield of the product 151 g (83%); m.p. 182–183 °C. ¹H-NMR in DMSO-*d*₆: δ 2.76 and 3.59 (CH₂, ³J_{HH} = 6.3 Hz, 2 × 4H, t), 7.80 (arom, 8H, m). ¹³C-NMR in DMSO-*d*₆: NCH₂CH₂N: δ 37.14, 46.10, aromatic: δ 122.70, 131.59 and 134.07, CO: δ 167.81.

Synthesis of L-cysteine methyl ester (LCME)

In order to preserve and convert the L-cysteine -COOH group to the ester one, 5.0 g of L-cysteine was mixed with SOCl₂ (30 ml) and stirred for 2.5 h in the presence of methanol. Then it was treated and washed with dry chloroform and dimethyl formamide (DMF), as shown in Scheme 1. The thionyl chloride method in the cold temperature (0 °C) was used for the esterification of the optically pure amino acid or of its hydrochloride that leads to ester hydrochloride, and the melting point changes from 143 °C to 125–136 °C. The purification of this unpurified sample (crude LCME) simply accomplished as follows: 30 ml of hot methanol was used to dissolve LCME (5 g) of m.p. ~130 °C at ~40 °C. Most of the methanol was eliminated by vacuum distillation (30 °C) after adding isopropyl alcohol (75 mL). Pure ester hydrochloride can be separated during distillation process, and particularly through cooling in ice bath. It was then recovered and treated by cold isopropyl alcohol. The collected amounts of purified LCME was ~4.4 g (88%) with m.p. of 144 °C and [α]³²_D -3°. ¹H-NMR in DMSO-*d*₆: δ 1.37 (1H, t), δ 2.93-2.97 (2H, m), 3.15 (1H, d), 3.18 (1H, d), 3.75 (3H, s), δ 4.48 (1H, t); ¹³C-NMR in DMSO-*d*₆: δ 169.58, 55.31, 54.7, 24.59; ESI-MS found (M+H)/z: 136.1, calcd. (M+H)/z 136.0.

Synthesis of SiO₂-Al₂O₃ nanoparticles

SiO₂-Al₂O₃ NPs were prepared using a sol-gel method to stabilize the studied dendrimers, where 50 ml of n-butanol were used to dissolve 13.0 mmol of tetraethyl orthosilicate and aluminum tri-sec-butylate. The obtained solution was then heated and stirred to 60 °C, and then cooled down to 25 °C before gently adding 5 ml acetylacetone. The transparent solution was then hydrolyzed using DI-H₂O (11.0 mol H₂O/mol alkoxide) and left overnight, producing a clear gel. Next, the gel was dried (110 °C) to eliminate the solvents. At the end, to eliminate the organic materials, the sample was calcined (500 °C) (5 h). The material was pretreated at 550 °C for ~6 h under air prior to subsequent dendrimer functionalization.

Artificial neural network simulation

The quantity of input and output neurons in network was determined based on the quantity of effective parameters in the process and the quantity of the expected output. However, the quantity of hidden layer neurons can be variable depending on system performance. In addition, a linear transfer function (purelin) at output layer and a three layered back propagation algorithm with tangent sigmoid transfer function (tansig) at hidden layer were employed. All simulation calculation were performed by using 2016a version of MATLAB software.

Table S1. Normalized adsorption data, adsorption isotherm, kinetics equations, separation factor and ANN simulation.

Formula	Equation*
Normalized adsorption data	$q_e = V \cdot (C_0 - C_e) / m$
Langmuir	$q_e = \frac{q_m K_L C_e}{1 + K_L C_e}$
Freundlich	$q_e = K_F C_e^{1/n}$
Sips	$q_e = \frac{q_m K_L C_e^{1/n}}{1 + K_L C_e^{1/n}}$
Pseudo-first-order	$q_t = q_e [1 - \exp(-k_1 t)]$
Pseudo-second-order	$q_t = k_2 q_e^2 t / 1 + k_2 q_e t$
Weber-Morris	$q_t = k_{int} t^{1/2}$
Initial adsorption rate	$h = k_2 q_e^2$
Distribution coefficient	$K_d = \left(\frac{V}{m} \right) \cdot (C_0 - C_e) / C_e$
Separation factor	$\alpha_M^{Hg} = \frac{K_d^{Hg}}{K_d^M}$
ANN simulation	$I_j = \frac{\sum_{m=1}^{m=N_h} \left(\left(\frac{ \mathbf{W}_{jm}^{ih} }{\sum_{k=1}^{N_i} \mathbf{W}_{km}^{ih} } \right) \times \mathbf{W}_{mn}^{ho} \right)}{\sum_{k=1}^{k=N_i} \left\{ \sum_{m=1}^{m=N_h} \left(\left(\frac{ \mathbf{W}_{km}^{ih} }{\sum_{k=1}^{N_i} \mathbf{W}_{km}^{ih} } \right) \times \mathbf{W}_{mn}^{ho} \right) \right\}}$

* q_e (mg g⁻¹) is the specific equilibrium amount of adsorbate, C_e (mg L⁻¹) is the equilibrium concentration of adsorbate, C_0 (mg L⁻¹) is the anion concentration, C_t (mg L⁻¹) is the outlet concentration at time t , V is the volume of the solution (L); m is the amount of adsorbent (g); q_m is the maximum adsorption capacity; and K (K_L and K_{LF}) (L mol⁻¹) and n are empirical constants that indicate the extent of adsorption and the adsorption effectiveness, respectively. The constant n gives an idea of the grade of heterogeneity in the energetic centers distribution of the adsorbent's active sites and is related to the magnitude of the adsorption driving force. Therefore, high n values indicate a relatively uniform adsorbent surface, while low value one mean high adsorption at low solution concentrations. Furthermore, low n values indicate the existence of a high proportion of high-energy active sites.

k_1 , k_2 , and k_{int} are the adsorption rate constants of first and second order kinetic and intra-particle diffusion models, in min⁻¹, (g (mg min)⁻¹) and mg g⁻¹ min^{-1/2}, respectively; q_e and q_t in mg g⁻¹, are equilibrium adsorption uptake (at time $t = \infty$) and adsorption uptake (at time t), respectively.

I_j is the relative significance of the j^{th} input on the output variables, N_h and N_i are the number of hidden neurons and inputs, respectively; W 's are connection weights, subscripts 'k', 'm' and 'n', respectively, attribute to input, hidden, and output neurons, and the superscripts 'i', 'h' and 'o', respectively, attribute to input, hidden, and output layers.

Table S2. Chemical composition and physicochemical properties of the nanodendrimer at different stages of synthesis.

Nanomaterial	Elemental analyses (wt%) ^a		Organic functional group (mmol g ⁻¹ mixed oxide) ^b	Structural parameters ^c		
	N	S		Surface area (m ² g ⁻¹)	Pore volume (cm ³ g ⁻¹)	Pore diameter (Å)
SiO ₂ /Al ₂ O ₃	-	-	-	243	0.028	20
SiO ₂ /Al ₂ O ₃ -G0	3.6	-	2.57	87	0.014	19
SiO ₂ /Al ₂ O ₃ -G0.5	2.9	-	2.07	84	0.0134	18
SiO ₂ /Al ₂ O ₃ -G1.0	5.6	-	3.71	79	0.012	17
SiO ₂ /Al ₂ O ₃ -G1.5	8.1	-	4.57	74	0.0105	16.8
SiO ₂ /Al ₂ O ₃ -G2.0	8.8	7.92	2.47	71	0.010	16

^a Nitrogen and sulfur was estimated from the CHNS elemental analyses.

^b Determined from the N and S-contents.

^c pore size calculated using the BJH method.

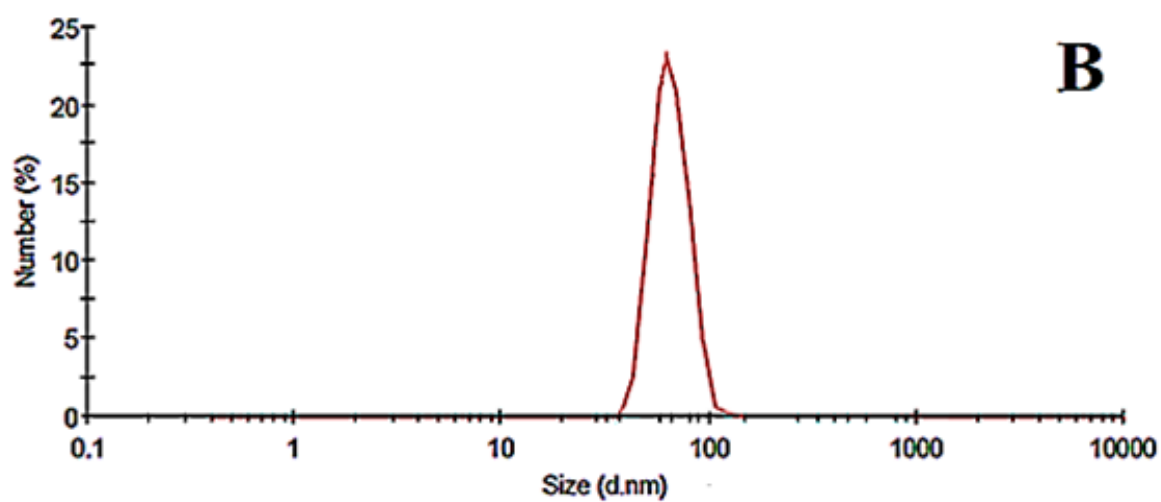
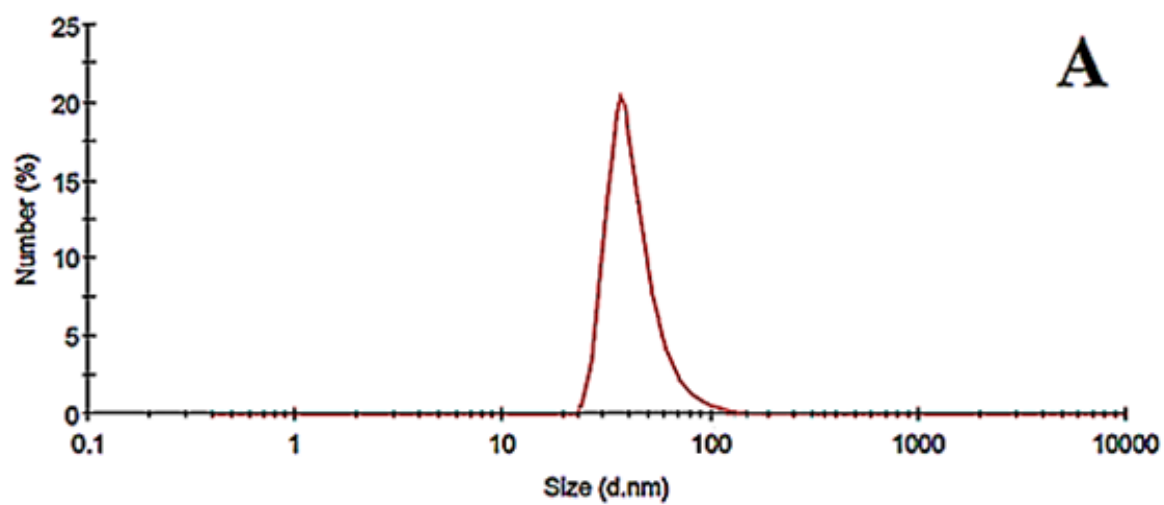


Fig. S1. Particle size distribution of the unmodified A) $\text{SiO}_2\text{-Al}_2\text{O}_3$ nanoparticles and B) $\text{SiO}_2/\text{Al}_2\text{O}_3\text{-G2.0}$ nanodendrimer.

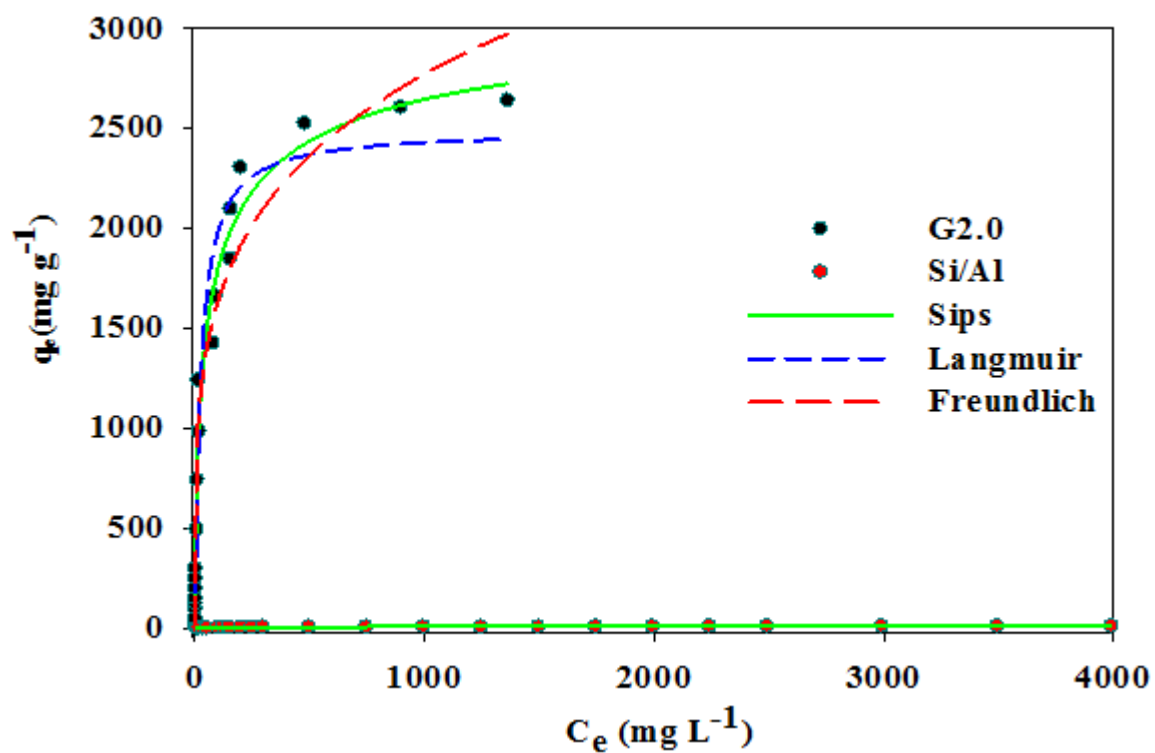


Fig. S2. Equilibrium absorption of Hg(II) on $\text{SiO}_2/\text{Al}_2\text{O}_3$ and $\text{SiO}_2/\text{Al}_2\text{O}_3$ -G2.0, at 25 °C and pH = 6.0.

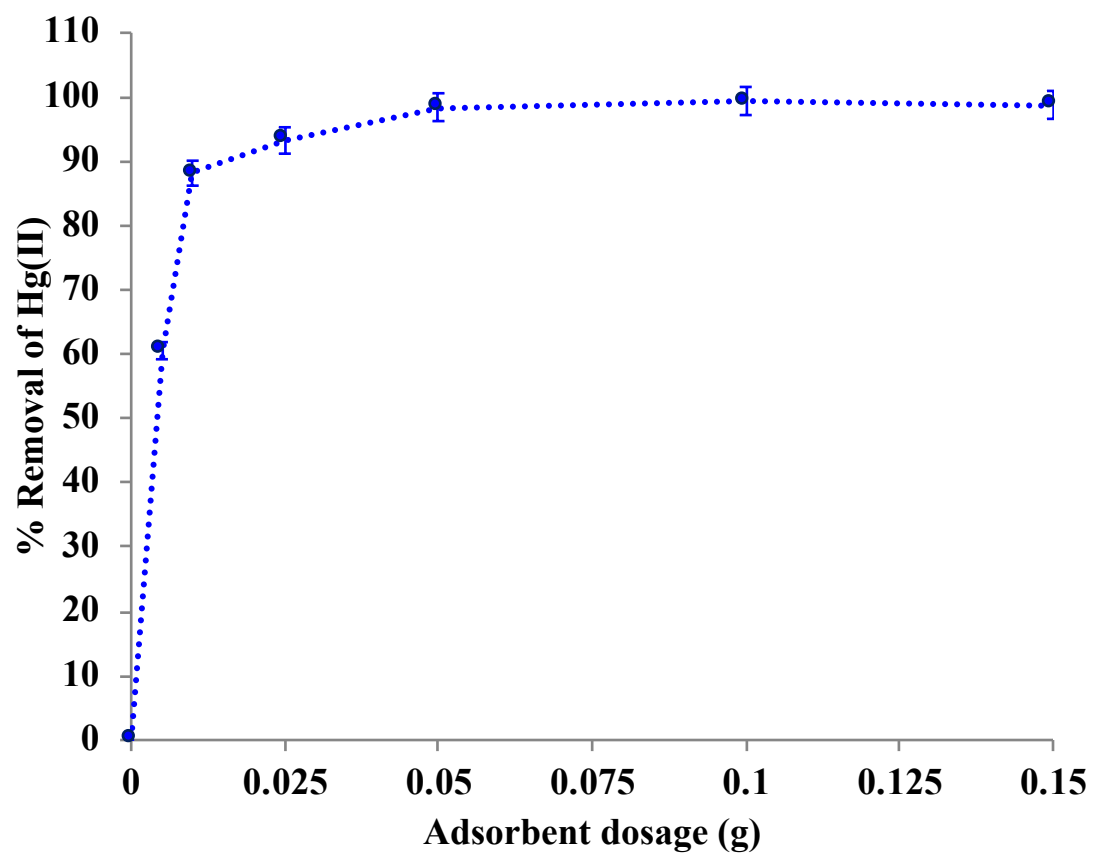


Fig. S3. Effect of $\text{SiO}_2/\text{Al}_2\text{O}_3\text{-G2.0}$ dosage on the adsorption of Hg(II) ions.

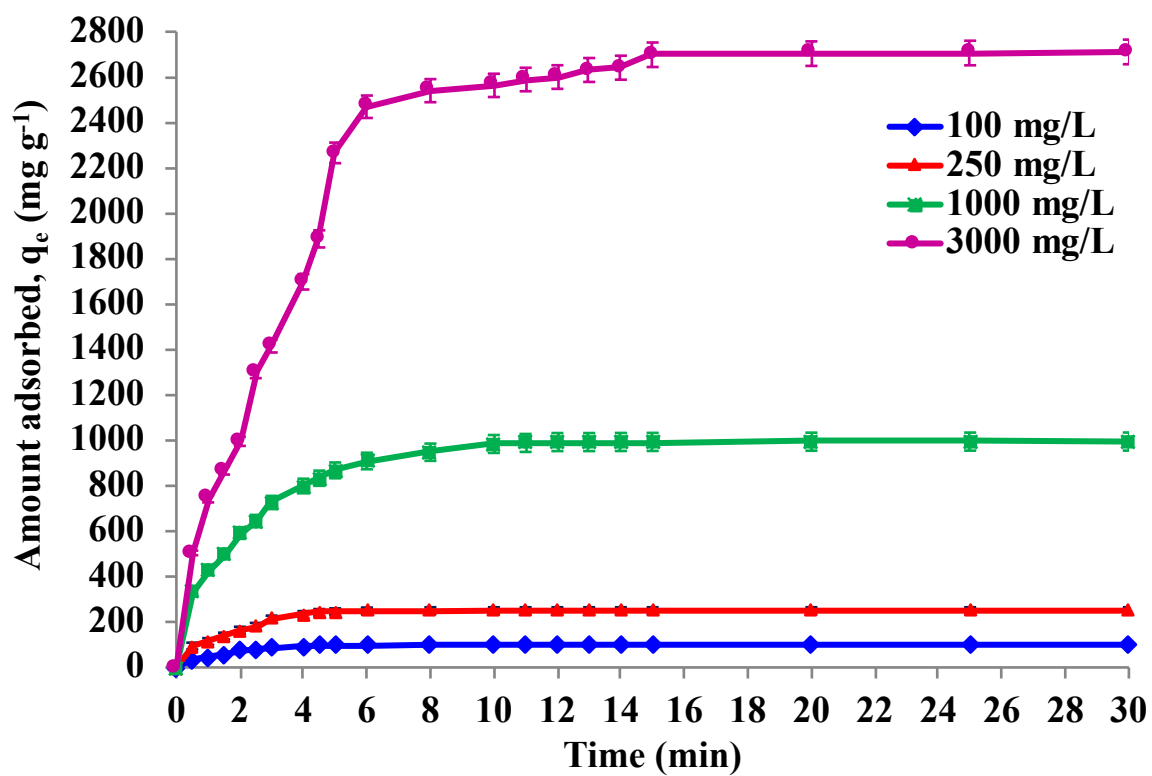


Fig. S4. The adsorption kinetics of $\text{SiO}_2/\text{Al}_2\text{O}_3\text{-G2.0}$ for the adsorption of Hg(II) ions at different concentrations

Table S3. Kinetic parameters for the removal of Hg(II) ions onto SiO₂/Al₂O₃-G2.0 at various initial concentrations*.

C _o (mg L ⁻¹)	q _{e,exp} (mg g ⁻¹)	Pseudo first order constants			Pseudo second order constants				Intra-particle diffusion constants	
		k ₁ (min ⁻¹)	q ₁ (mg g ⁻¹)	R ²	k ₂ (g (mg min) ⁻¹)	q ₂ (mg g ⁻¹)	h (mg (g min) ⁻¹)	R ²	K _{int} (mg (g min ^{1/2}) ⁻¹)	R ²
100	99.8	1.568	78.7	0.8862	16.8 × 10 ⁻³	103.1	179.5	0.9980	14.89	0.5939
250	237.9	1.171	243.9	0.810	5.9 × 10 ⁻³	259.0	396.8	0.9976	37.57	0.6206
1000	894.5	1.355	819.6	0.8479	97.1 × 10 ⁻²	1041	1011	0.9975	165.1	0.7427
3000	1697	2.906	1075	0.9305	41.7 × 10 ⁻²	3030	1265	0.9867	546.1	0.8122

* Each experiment was repeated three times and the relative standard deviation was lower than 3.6%.

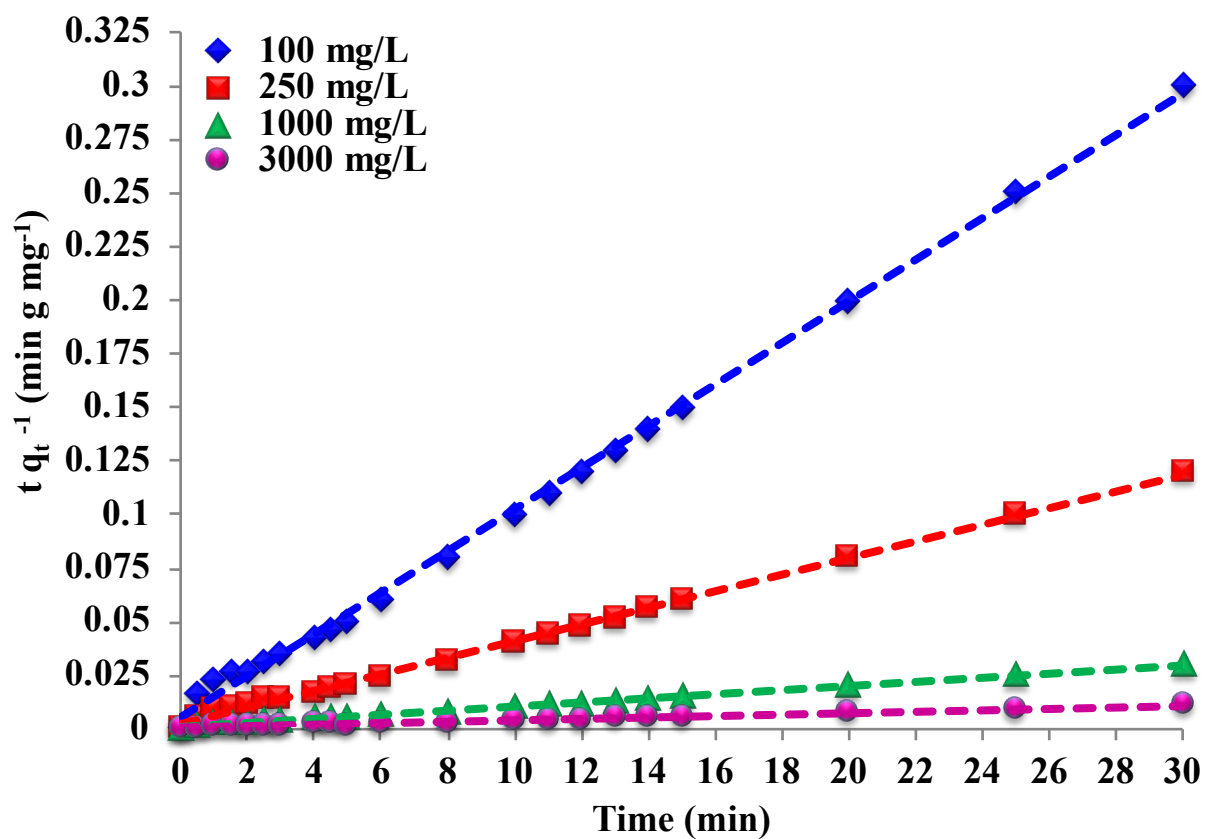


Fig. S5. Pseudo-second order plots of SiO₂/Al₂O₃-G2.0 for the adsorption of Hg(II) ions at different concentrations.

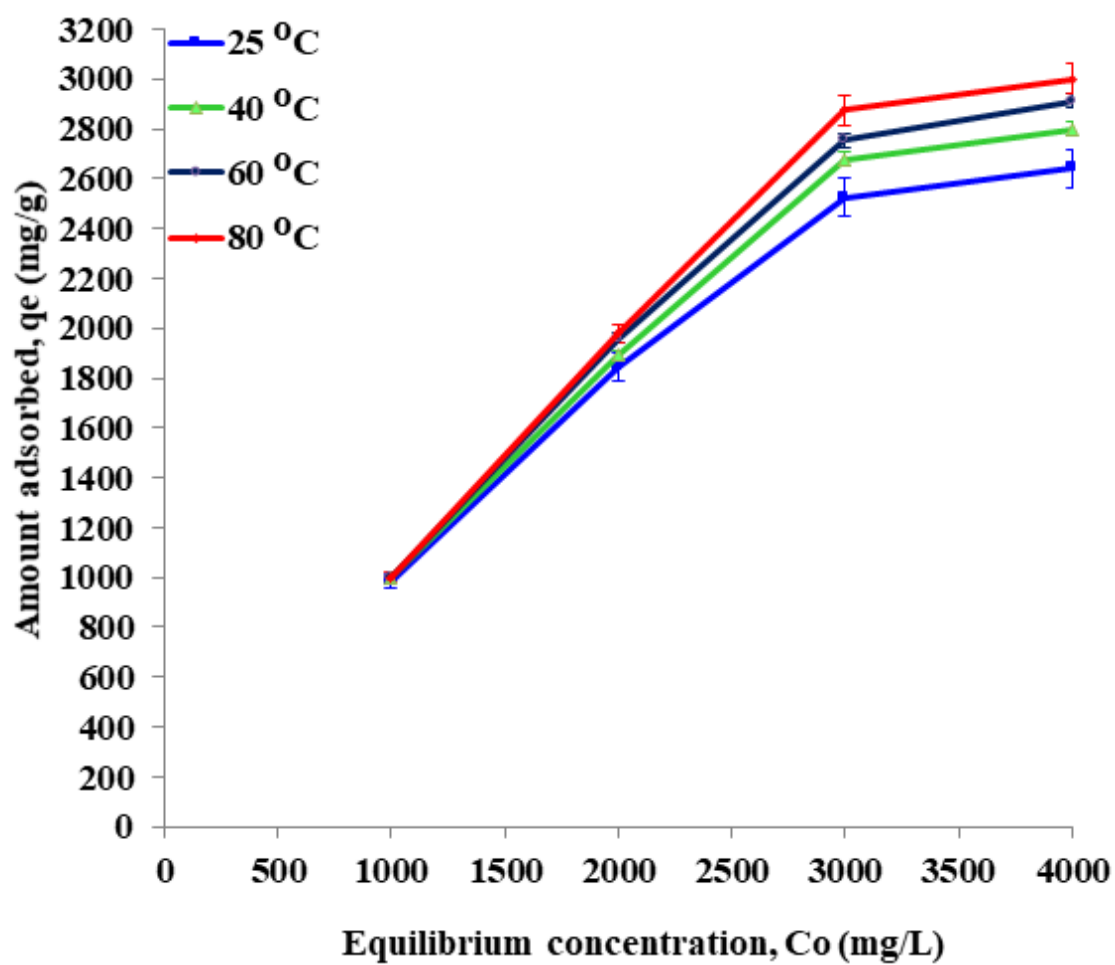


Fig. S6. The effect of initial concentration of Hg(II) ions and solution temperature on the adsorption capacity of SiO₂/Al₂O₃-G2.0.

The thermodynamic parameters for the mercury removal system were measured using the following equations:

$$\Delta G = -RT \ln K \quad (1)$$

in which R ($8.314 \text{ J}/(\text{mol} \cdot \text{K})$) is the ideal gas constant, K is the thermodynamic equilibrium constant. The values of K can be calculated by plotting $\ln(q_e C_e^{-1})$ against q_e and extrapolating to zero, where q_e is the adsorbed Hg(II) ion concentration at equilibrium and C_e is the equilibrium concentration of Hg(II) ions in bulk solution.

The ΔH° and ΔS° values were determined from the slope and intercept of the linear plot of $\ln K$ vs T^{-1} as indicated in Fig. S7.

$$\ln K = \Delta S^\circ/R - \Delta H^\circ/RT \quad (2)$$

The Gibbs free energy is given by Eq. (3), where ΔG° is the free energy change (kJ/mol); R and T are the universal constant and the absolute temperature (K), respectively.

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \quad (3)$$

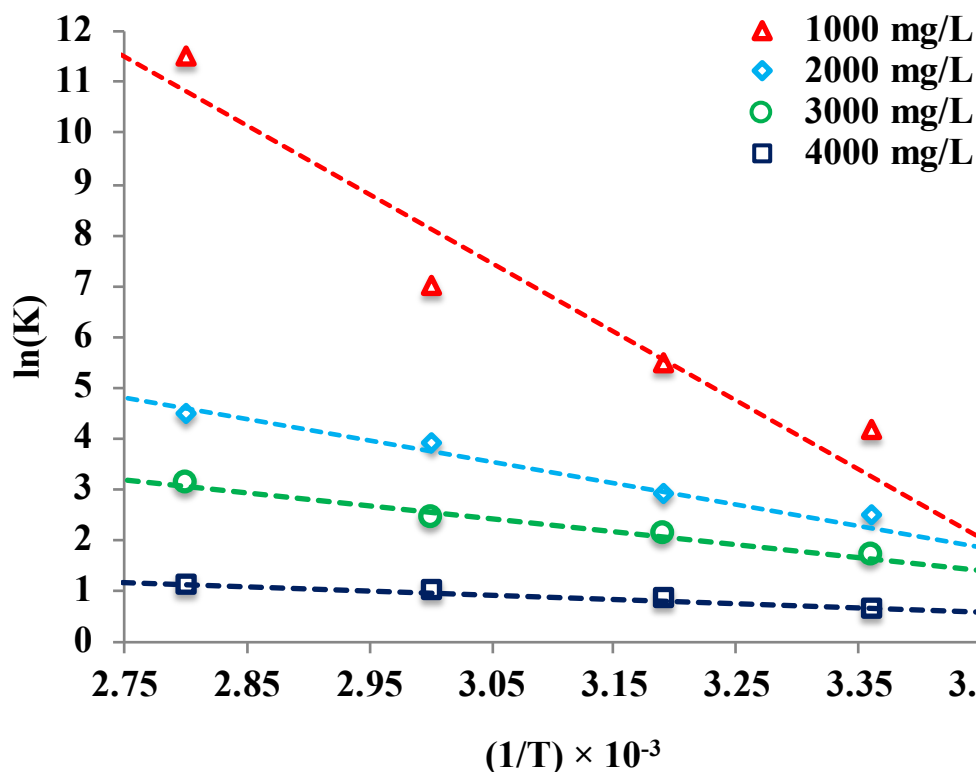


Fig. S7. The plot of $\ln K$ vs. $1/T$ of the adsorption of Hg(II) ions by $\text{SiO}_2/\text{Al}_2\text{O}_3\text{-G2.0}$ at different initial concentrations of mercury.

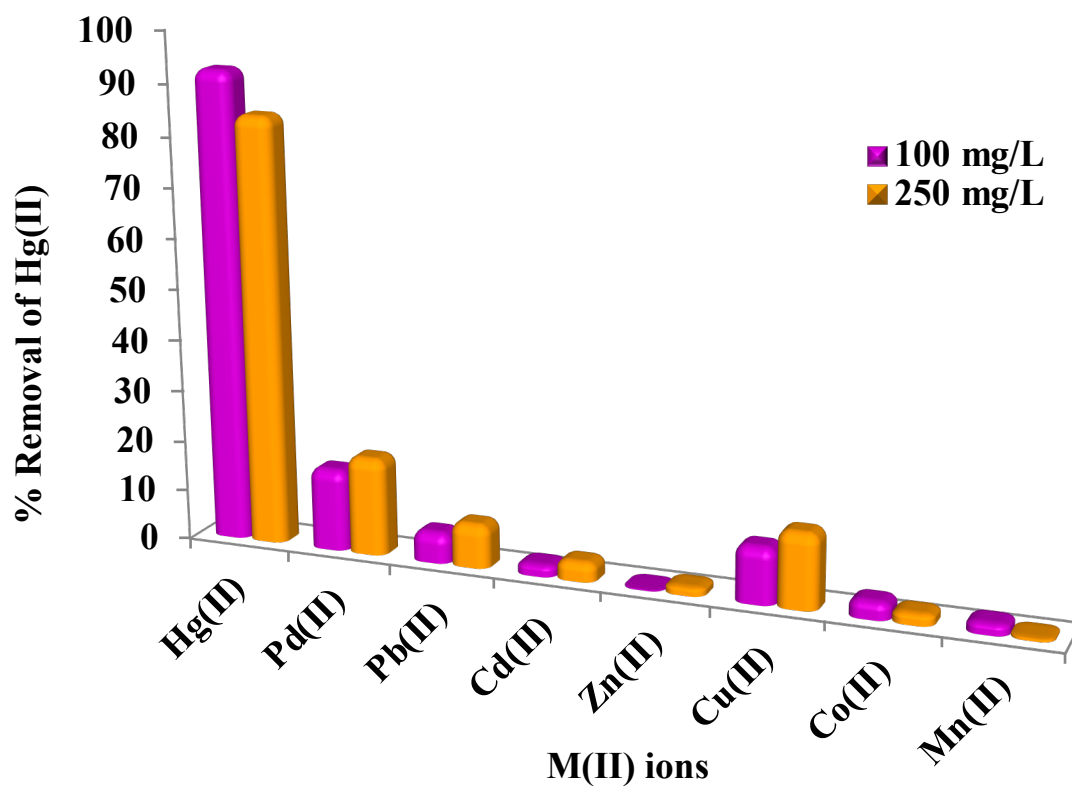


Fig. S8. Effect of some coexisting heavy metals on Hg(II) adsorption capacity of the SiO₂/Al₂O₃-G2.0.

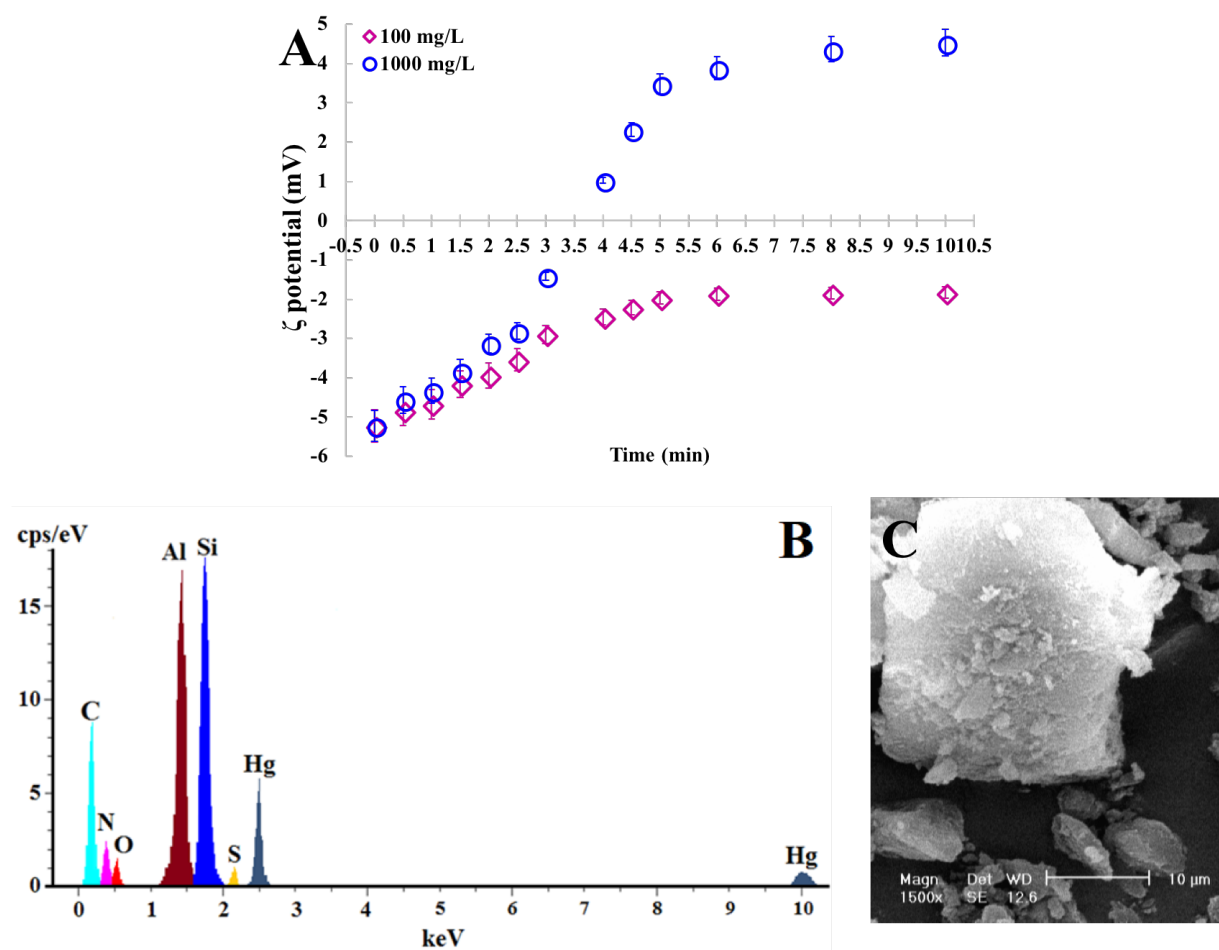


Fig. S9. (A) The zeta potential , (B) EDS spectrum, and (C) an SEM micrograph of $\text{SiO}_2/\text{Al}_2\text{O}_3\text{-G2.0}$ after the adsorption of Hg(II) ions from aqueous solution.

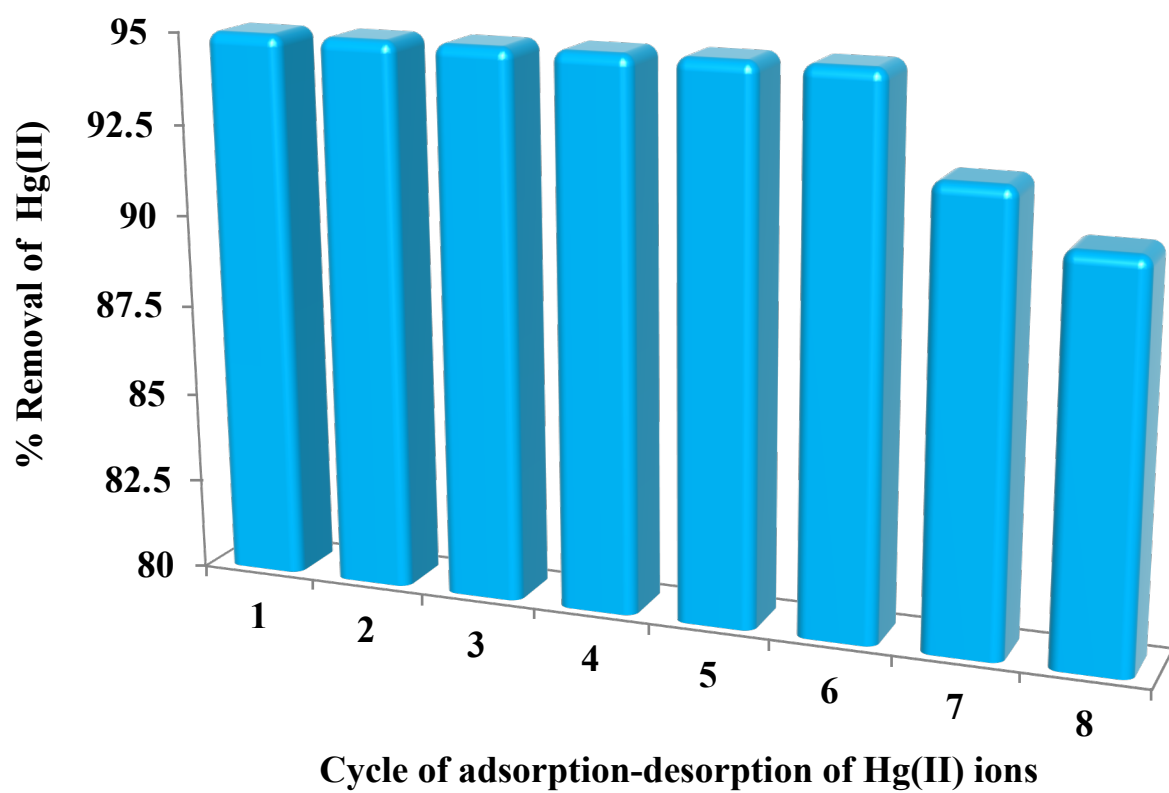


Fig. S10. adsorption capacity of the $\text{SiO}_2/\text{Al}_2\text{O}_3\text{-G2.0}$ after repeated regeneration.

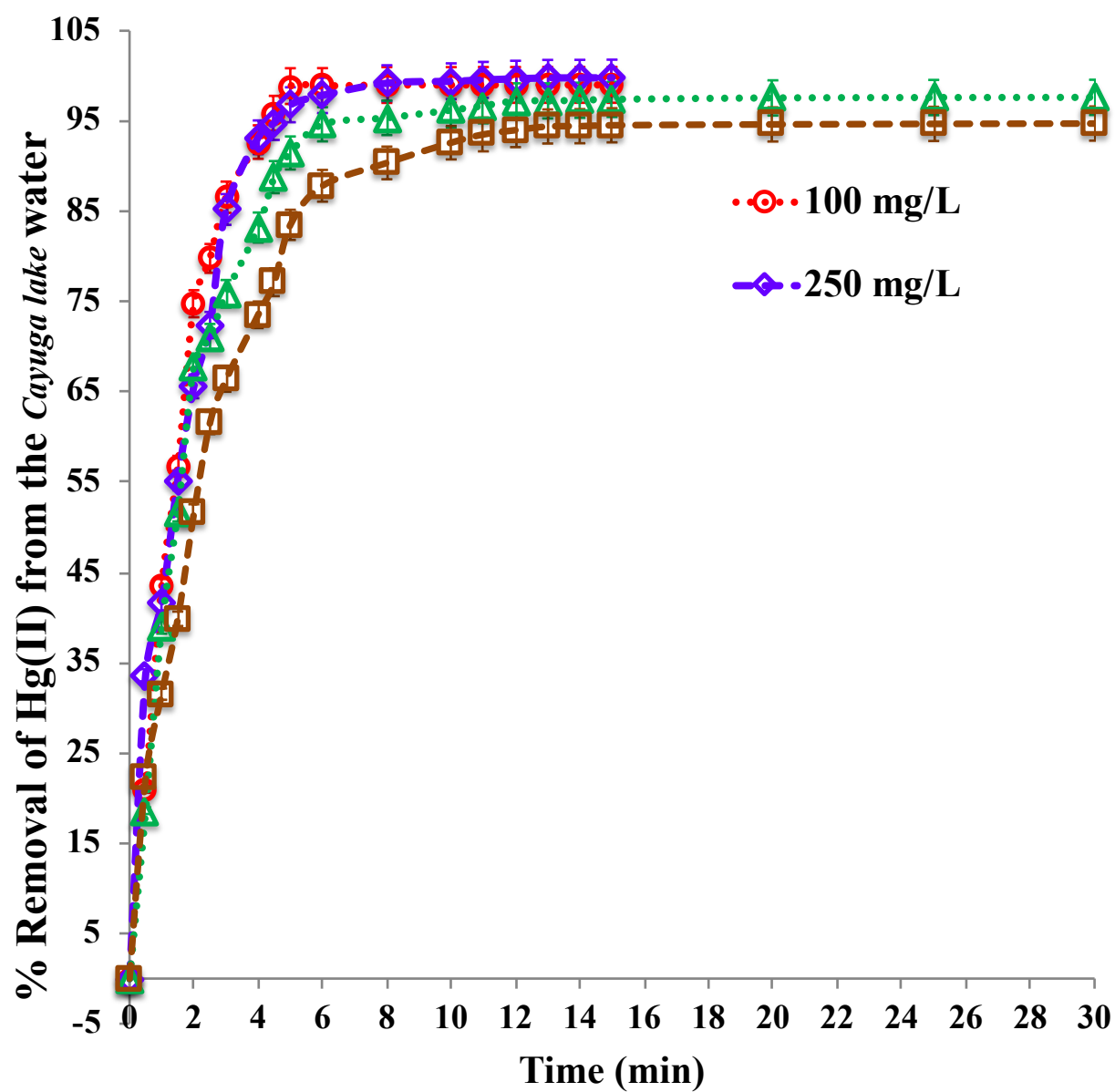


Fig. S11. Hg(II) ion removal from *Cayuga Lake* water after exposure to SiO₂/Al₂O₃-G2.0 at various concentration of mercury.

Table S4. Comparison of Hg(II) ion adsorption capacities for different adsorbents.

Adsorbent	$q_{\max}$ (mg g ⁻¹)	Ref.
Graphene oxide/2-pyridinecarboxaldehyde thiosemicarbazone	555	1
Si/Al@cyanuric@L-cysteine methyl ester	2293	2
Silica-Vinyl imidazole	355.9	3
SiO ₂ -G2.0-SA	356	4
Chitosan-poly(vinyl alcohol)	585	5
Chitosan-thiourea	625.2	6
Activated carbon	724.0	7
Commercial chitosan	1127	8
Chitosan immobilized in polyvinyl alcohol	1896	9
Propylthiol	560	10
Mesoporous organosilicas with sulfide bridges	437	11
Hyperbranched nanodendrimer	2825	12
SiO ₂ /Al ₂ O ₃ -G2.0	2639	This work

Table S5. The ranges of input and output parameters.

Parameter	Range of the parameter value
Input layer	
Initial Hg(II) concentration (mg/L)	5–4000
Solution pH	1–12
Temperature (°C)	15–80
Adsorbent dosage (g)	0.005–0.15
Output layer	
q_e (mg/g)	5–2999

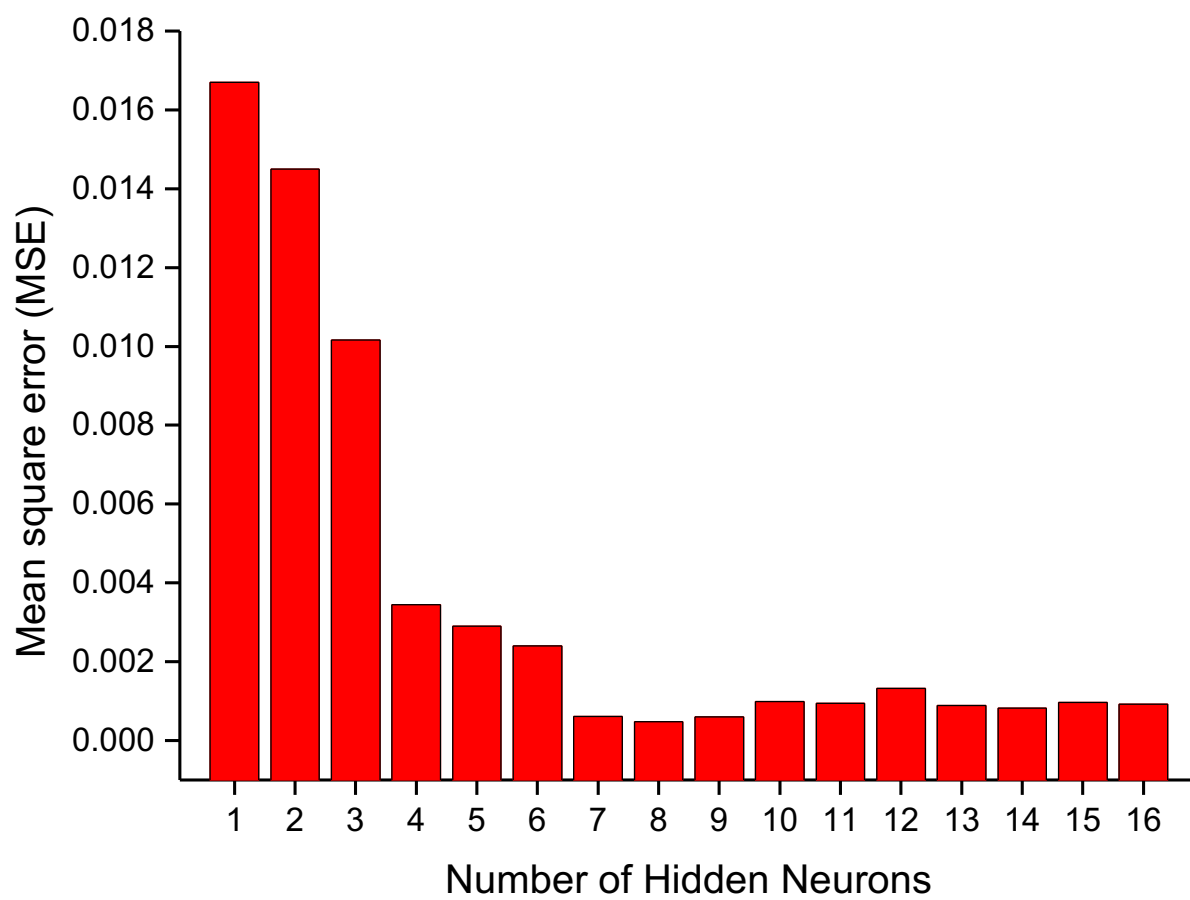


Figure S12. Influence of the neurons number in the hidden layer on the efficiency of the designed ANN-model.

Table S6. Weight matrix for input parameters: weight between input and hidden layers (W_1) and weights between hidden and output layers (W_2).

W_1						W_2	
Neuron	Input parameter				Bias	Neuron	Output
	Initial Hg(II) concentration	Solution pH	Temperature	Adsorbent dosage			qe (mg/g)
1	0.6974	1.6746	1.0854	1.1097	-2.4048	1	-0.6277
2	1.5655	-0.386	1.256	-1.1238	1.685	2	-0.3974
3	-1.5084	-1.4576	0.8527	-0.7527	0.954	3	0.3735
4	-1.5702	-0.9968	-0.5011	1.3335	0.3532	4	-0.1103
5	1.2076	-1.6936	0.1053	1.1171	-0.4168	5	0.1545
6	-2.0623	-1.1341	1.1646	-1.4189	— 0.89668	6	0.6651
7	-0.293	1.3559	0.6244	1.1742	1.7559	7	-0.0955
8	-1.2566	0.8815	-1.7671	1.0638	2.1931	8	1.4474
						Bias	-0.1563

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