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Supporting Information for

β -cyclodextrin modified graphitic carbon nitride for the removal of pollutants from aqueous solution: combined experiments and theoretical calculation study

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29 **The SI contains 11 pages with 6 Figures and 10 Tables.**

30 **1. Preparation of graphitic carbon nitride (g-C₃N₄).**

31 All chemicals used in the experiments were purchased in analytic purity and used
32 without any further purification. g-C₃N₄ was prepared by the pyrolysis of urea in a
33 semiclosed system according to a reported procedure¹. Typically, 25 g of urea crystals
34 was dried at 70 °C for 24 h, and then put into an alumina crucible with a cover and heated
35 at 500 °C in a muffle furnace for 3.5 h with a ramp rate of 4.0 °C min⁻¹ under ambient
36 pressure in air. The resultant yellow powder was collected by centrifugation and rinsed
37 with Milli-Q water (18.2 MΩ·cm⁻¹) and 0.1 M HNO₃ several times, and then dried under
38 vacuum at 60 °C for 24 h prior to further use.

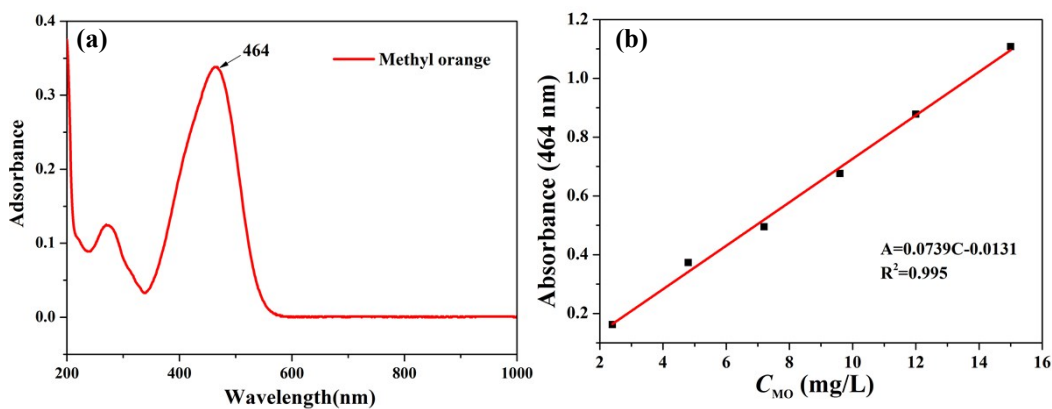
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40 **2. Preparation of β-cyclodextrin modified graphitic carbon nitride (g-C₃N₄/β-CD).**

41 g-C₃N₄/β-CD was synthesized by the facial solvothermal method with the as-
42 prepared g-C₃N₄ as a soft template. Briefly, aqueous suspension of as-prepared g-C₃N₄
43 (5.0 g) in 30 mL of distilled water was added to the solution of 2.0 g β-cyclodextrin (β-
44 CD) in 20 mL of distilled water at room temperature, and followed by the addition of 0.5
45 mL 1 M NaOH solution and 0.02 g potassium persulfate (K₂S₂O₈) as an initiator. The
46 mixture was stirred until the solution became transparent, sealed in an autoclave, heated
47 to 180 °C and maintained at 180 °C for 12 h. The resulted products were washed with
48 Milli-Q water and ethanol several times, and dried in vacuum at 60 °C. Milli-Q water
49 (18.2 MΩ·cm⁻¹) was used in all the experiments.

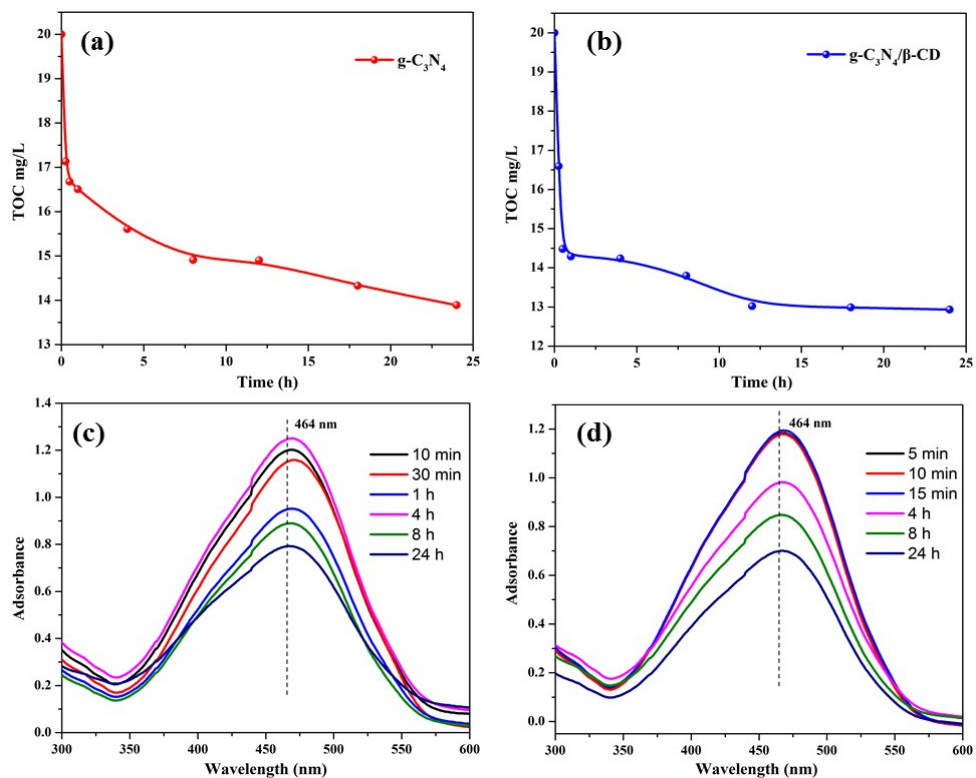
50 **3. UV-vis absorption spectroscopy of MO.**

51 In order to search the optimize peak for the measurement of MO concentrations, the
52 absorbance of MO was determined at various concentrations by UV-vis
53 spectrophotometry (Shimadzu UV-2550). The UV-vis absorption spectroscopy results for
54 MO are presented in **Figure S1**. The optimum wavelength of MO was determined to be
55 464 nm (**Figure S1(a)**), and an $R^2 > 0.99$ for the calibration curve of MO at 464 nm
56 suggested that the MO absorbance results can be directly correlated to their
57 concentrations (**Figure S1(b)**).



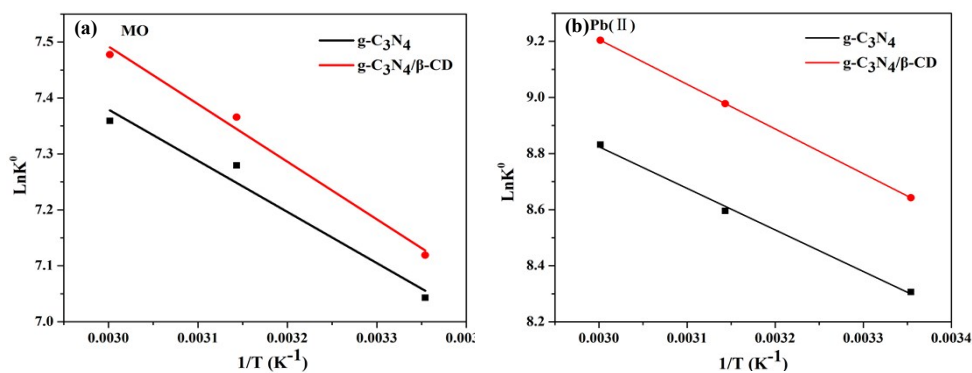
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59 **Figure S1.** UV-vis absorption spectroscopy of MO as a function of MO concentrations. (A)
60 Wavelength scan of MO, (B) Absorbance as a function of MO concentration at the wavelength of
61 464 nm.



62

63 **Figure S2.** The TOC removal curve of MO on g-C₃N₄ (a) and on g-C₃N₄/β-CD (b), and the UV-
 64 vis spectra of MO in a g-C₃N₄ (c) or g-C₃N₄/β-CD (d) aqueous solutions as a function of reaction
 65 time.



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67 **Figure S3.** Linear plots of $\ln K^0$ versus $1/T$ for the adsorption of MO (a) and Pb(II) (b) on g-C₃N₄
 68 and g-C₃N₄/β-CD.

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71 **Table S1** Relative Contents of Different Groups of g-C₃N₄ and g-C₃N₄/β-CD Charactrized from
 72 XPS Analysis (N 1s Spectrum)

Samples	C=N-C	N-(C) ₃ or H-N-(C) ₂	Heterocycles rings
g-C ₃ N ₄	50.76 %	40.08 %	9.16 %
g-C ₃ N ₄ /β-CD	8.44 %	91.56 %	0.00 %

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74 **Table S2** Relative Contents of Different Groups of g-C₃N₄ and g-C₃N₄/β-CD Charactrized from
 75 XPS Analysis (C 1s Spectrum)

Samples	non-oxygenated ring	graphitic carbon	N-C=N	O-C=O
g-C ₃ N ₄	29.57 %	5.18 %	65.25 %	0.00 %
g-C ₃ N ₄ /β-CD	39.84 %	8.02 %	20.37 %	31.77 %

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77 **Table S3** Kinetic parameters for MO and Pb(II) adsorption on g-C₃N₄ and g-C₃N₄/β-CD

Adsorbents	Adsorbates	Pseudo-first-order			Pseudo-second-order		
		$q_{1,cal}$ (mg·g ⁻¹)	k_1 (min ⁻¹)	R^2	$q_{2,cal}$ (mg·g ⁻¹)	k_2 (g·mg ⁻¹ ·min ⁻¹)	R^2
g-C ₃ N ₄	Pb(II)	6.87	2.0×10 ⁻³	0.408	16.11	1.5×10 ⁻⁴	0.988
g-C ₃ N ₄ /β-CD	Pb(II)	9.89	1.8×10 ⁻³	0.775	19.05	2.2×10 ⁻⁴	0.989
g-C ₃ N ₄	MO	14.20	3.3×10 ⁻³	0.828	24.93	1.7×10 ⁻⁴	0.989
g-C ₃ N ₄ /β-CD	MO	23.44	2.0×10 ⁻³	0.825	31.85	1.2×10 ⁻⁴	0.99

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80 **Table S4.** Parameters of various adsorption isotherms of Pb(II) adsorption on g-C₃N₄ and g-C₃N₄/β-
 81 CD at three temperatures (298.15 K, 318.15 K, and 338.15 K).

Adsorbents	Parameters	g-C ₃ N ₄ [Pb(II)]			g-C ₃ N ₄ /β-CD [Pb(II)]		
		298.15 K	318.15 K	333.15 K	298.15 K	318.15 K	333.15 K
Langmuir model	K_L (L·mg ⁻¹)	0.051	0.043	0.049	0.040	0.051	0.068
	q_m (mg·g ⁻¹)	71.1	104.1	118.3	100.5	118.9	128.5
	R^2	0.931	0.934	0.918	0.945	0.943	0.952
Freundlich model	K_F (mg ¹⁻ⁿ ·L ⁿ ·g ⁻¹)	6.3	7.5	9.2	6.5	9.8	13.6
	$1/n_F$	0.558	0.606	0.604	0.625	0.593	0.554
	R^2	0.863	0.868	0.851	0.893	0.875	0.873
Sips model	K_S (L·g ⁻¹)	2.112	2.034	2.028	1.874	1.905	1.838
	a_s (L·mg ⁻¹)	0.008	0.009	0.011	0.011	0.015	0.025
	n_s	0.408	0.581	0.842	0.719	1.129	2.199
	R^2	0.988	0.986	0.964	0.982	0.984	0.993

82

83 **Table S5.** Parameters of various adsorption isotherms of MO adsorption on g-C₃N₄ and g-C₃N₄/β-CD
 84 at three temperatures (298.15 K, 318.15 K, and 338.15 K).

Adsorbents	Parameters	g-C ₃ N ₄ [MO]			g-C ₃ N ₄ /β-CD [MO]		
		298.15 K	318.15 K	333.15 K	298.15 K	318.15 K	333.15 K
Langmuir model	K_L (L·mg ⁻¹)	0.111	0.086	0.098	0.099	0.086	0.114
	q_m (mg·g ⁻¹)	59.1	77.2	82.2	67.9	85.1	87.6
	R^2	0.861	0.934	0.955	0.890	0.924	0.952
Freundlich model	K_F (mg ¹⁻ⁿ ·L ⁿ ·g ⁻¹)	14.084	13.764	16.115	15.830	16.999	20.434
	$1/n_F$	0.339	0.406	0.390	0.339	0.374	0.351
	R^2	0.929	0.972	0.973	0.953	0.974	0.974
Sips model	K_S (L·g ⁻¹)	13.295	13.681	14.852	15.867	16.986	19.948
	a_s (L·mg ⁻¹)	0.011	0.020	0.097	0.009	0.036	0.117
	n_s	0.265	0.433	0.564	0.347	0.364	0.506
	R^2	0.921	0.968	0.975	0.947	0.970	0.976

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92 **Table S6** Comparison of the thermodynamic parameters and adsorption capacities of MO and
 93 Pb(II) with previous related studies at 298.15 K.

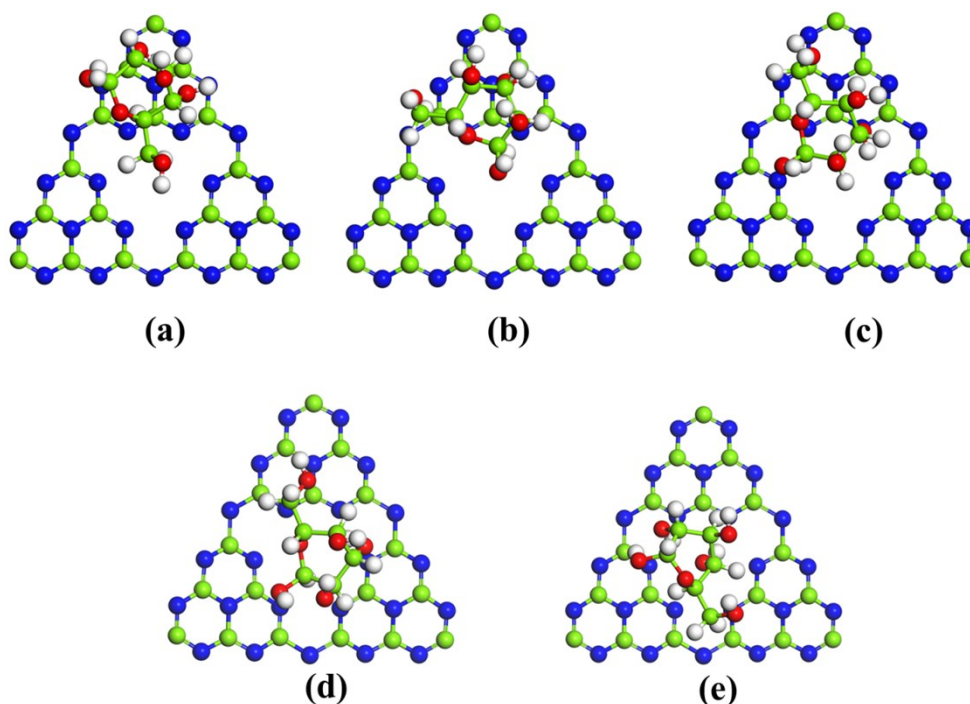
Adsorbents	Thermodynamic parameters			Sorption	Ref.
	ΔH^0	ΔS^0	ΔG^0	Capacity	
	(kJ·mol ⁻¹)	(J·mol ⁻¹ ·K ⁻¹)	(kJ·mol ⁻¹)	(mg·g ⁻¹)	
Pb(II)					
Kaolinite	-46.50	-166.40	-50.40	11.5	[2]
Na-bentonite	27.64	162.24	-20.73	47.8	[3]
Sporopollenin	31.97	150.98	-13.78	8.5	[4]
Iron oxide	8.10	87.10	-17.90	36.0	[5]
Siderite	49.73	261.00	-28.18	10.3	[6]
Coconut-shell	93.42	312.27	-2.79	26.5	[7]
Kaolinite clay	-47.21	-93.61	-19.82	31.75	[8]
g-C ₃ N ₄	12.32	110.33	-30.12	71.1	This work
g-C ₃ N ₄ /β-CD	13.24	116.26	-31.74	100.5	This work
MO					
Carbon nanotubes	19.39	101.50	-27.62	35.4	[9]
CMK-3	-23.14	-9.10	-25.85	294.1	[10]
Modified silkworm exuviae	2.54	19.55	-3.37	87.0	[11]
γ-Fe ₂ O ₃ /SiO ₂ / chitosan	-17.51	-48.89	-2.25	34.29	[12]
m-CS/γ-Fe ₂ O ₃ / MWCNTs	-9.94	-20.65	-3.78	66.09	[13]
g-C ₃ N ₄	7.61	84.17	-17.49	59.1	This work
g-C ₃ N ₄ /β-CD	8.56	87.98	-17.67	67.9	This work

94

95 **4. DFT Theoretical Calculations.**

96 Our calculations on the g-C₃N₄ complex were performed using the plane-wave basis
 97 Vienna Ab-initio Simulation Package (VASP) code.^{14, 15} The projector augmented wave
 98 (PAW) method was used to describe the electron-ion interaction.¹⁶⁻¹⁸ The exchange-
 99 correlation functional of generalized gradient approximation GGA-PBE^{19, 20} was used for

100 all calculations. The vacuum space was 15 Å, which was enough to separate the
 101 interaction between periodic images. For geometry optimizations, the Brillouin zone was
 102 sampled with a Monkhorst-Pack mesh ²¹ of 1 × 1 × 1 k-points. The cutoff energies for
 103 plane waves were chosen to be 500 eV, and the convergence tolerance of force on each
 104 atom during structure relaxation was set at 0.05 eV/Å. The self-consistent field iterations
 105 were considered converged when the change of total energy was smaller than 10⁻⁵ eV.
 106 The g-C₃N₄ layer model was constructed based on the structure of graphite and the
 107 optimized unit cell parameters were $a = b = 7.159$ Å, $c = 15$ Å, $\alpha = \beta = 90^\circ$, $\gamma = 120^\circ$.



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109 **Figure S4.** Optimized complexes for g-C₃N₄ monolayer with β -CD.

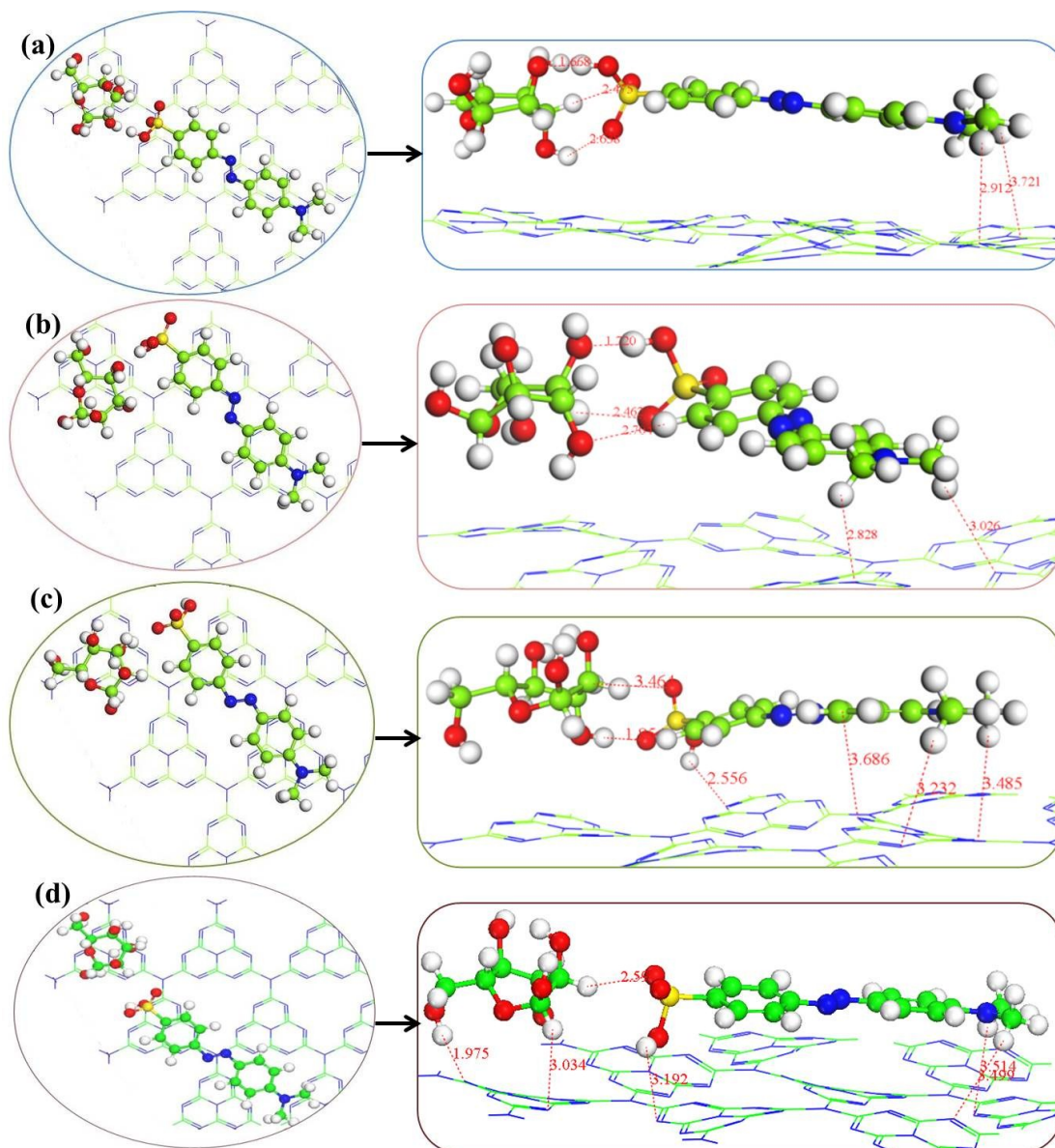
110 **Table S7.** The calculated adsorption energies of different structures in Figure S3.

Types	E_{ad} (eV)
a	1.07098855
b	1.21632674
c	1.44367080
d	1.43488009
e	1.40151666

111

112 **Table S8.** The calculated adsorption energies for the adsorption of Pb(II) and MO on g-C₃N₄ or g-
 113 C₃N₄/β-CD monolayer.

E_{ad} (eV)	g-C ₃ N ₄	g-C ₃ N ₄ /β-CD
Pb	3.56	3.74
MO	1.14	2.11



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115 **Figure S5.** Optimized complexes for g-C₃N₄/β-CD monolayer with MO.

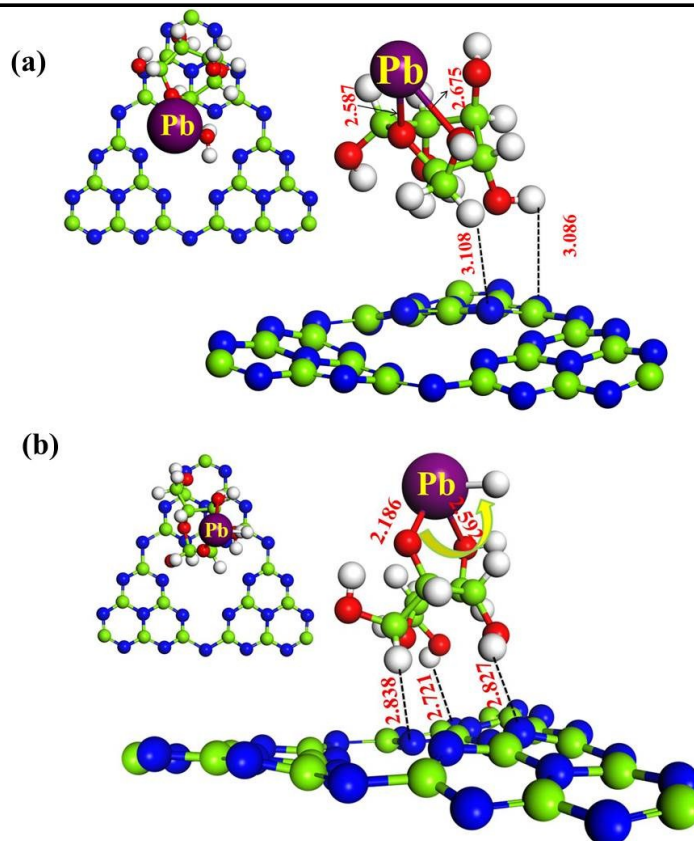
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119 **Table S9.** The calculated adsorption energies of different structures in Figure S4.

Types	E_{ad} (eV)
a	1.91297100
b	1.62540239
c	1.92972305
d	1.67835323



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121 **Figure S6.** Optimized complexes for g-C₃N₄/β-CD monolayer with Pb(II).

122

123 **Table S10.** The calculated adsorption energies of different structures in Figure S5.

Types	E_{ad} (eV)
a	1.71547307
b	2.76911938

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