Supplementary materials

Phosphorous modified porous graphitic carbon nitride activated by phytic acid for efficient selective extraction and photoreduction of uranium from aqueous solutions

Yanni He,[a] Junjun Li,[b,c,*] Jiang Cheng,[c] Tatyana Grigorievna Cherkasova,[b] Lu Li[c]

[a]Chongqing Water Resources and Electric Engineering College, Chongqing 402160, China
[b]Institute of Chemical and Gas and Oil Technologies, T.F. Gorbachev Kuzbass State Technical University, Kemerovo 650000, Russia
[c]School of Materials Science and Engineering, Chongqing University of Arts and Sciences, Chongqing 402160, China

[*]Corresponding author. *Email address*: lijunjun19861211@163.com

1. Data analysis

1.1. Kinetic data analysis

Pseudo-first order model ($\ln(q_e - q_t) = \ln q_e - k_1 t$) and pseudo-second order model ($t/q_t = 1/k_2 q_e^2 + t/q_e$) were applied to fit kinetic data, where q_e (mg/g) is the sorption capacity of U(VI) at the equilibrium, k_1 (1/min) and k_2 (g/mg·min) are the rate constants of pseudo-first order model and pseudo-second order model, respectively.

1.2. Sorption isotherm analysis

Langmuir model (($q_e = q_{max} K_L C_e / (1 + K_L C_e$, where K_L (L/mg) is the indicator of sorption enthalpy relied on temperatures, q_{max} is the maximum sorption capacity) and Freundlich model ($q_e = K_F C e^{1/n}$, where K_F ($mg^{1-n}L^n/g$) and $1/n$ are the parameters relied on q_e and sorption intensity respectively)) were applied to fit temperature-related sorption isotherms.

1.3. Thermodynamic data analysis

Standard free energy change (ΔG^o), the standard enthalpy change (ΔH^o) and the standard entropy change (ΔS^o)) were calculated as $K_d = (C_0 - C_e)V/C_e m$, $\Delta G° = -RT \ln K°$, $\ln K^o = \Delta S^o/R - \Delta H^o/RT$ and $\Delta G^o = \Delta H^o - T\Delta S^o$, where K_d is the equilibrium constant, T is the absolute temperature (K), and R is the universal gas constant 8.314 J/(mol K), $K°$ is the temperature-dependent equilibrium constant of sorption and can be obtained from the intercept of $\ln K_d$ as a function of C_e.

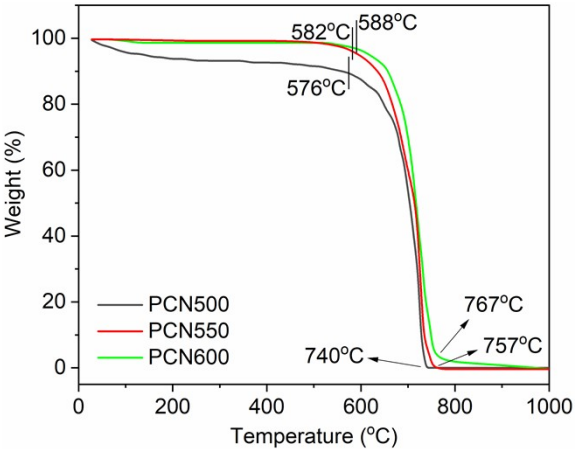

Figure S1. TGA curves of PCNs.

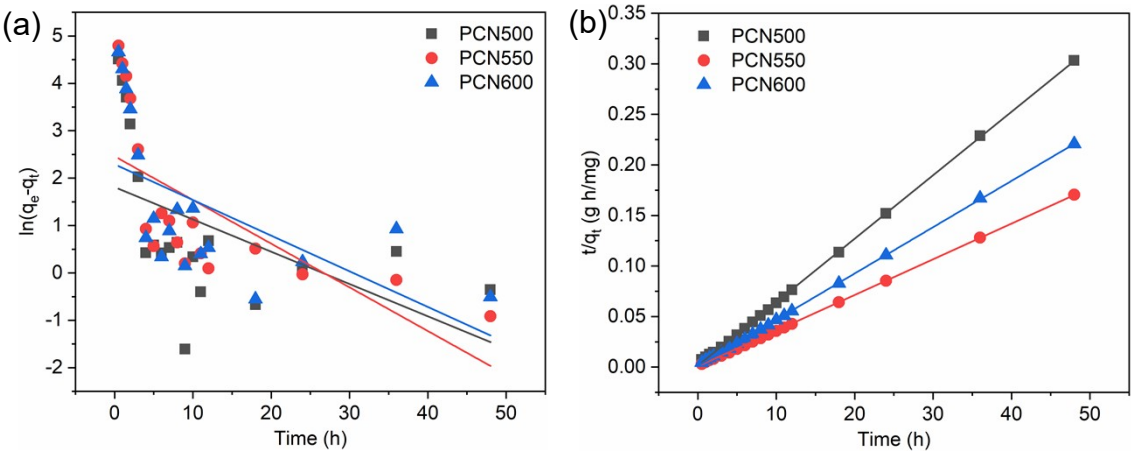

Figure S2. Pseudo-first-order (a) and pseudo-second-order (b) fittings for the sorption of U(VI) on PCNs. $C_{[U(VI)]initial}$=48.0 mg/L, pH=5.0, T=298 K, m/V=0.1 g/L and I=0.01 mol/L $NaNO_3$.

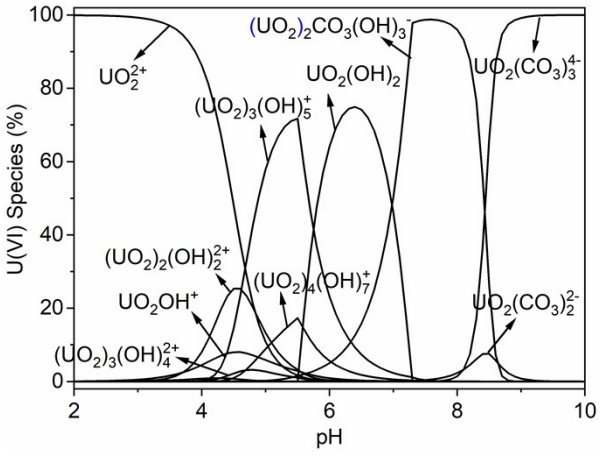

Figure S3. Distribution of uranium species states as a function of pH.

Table S1. Kinetic parameters of the sorption of U(VI) on PCNs (T = 298 K, pH = 5.0 ± 0.1, and I = 0.01 mol/L $NaNO_3$).

Sorbents	$q_{e,exp}$[a)] (mg/g)	Pseudo-first-order			Pseudo-second-order		
		k_1 (/min)	$q_{e,cal}$[b)] (mg/g)	R^2	k_2 (g/min/mg)	$q_{e,cal}$ (mg/g)	R^2
PCN500	158.3	0.068	6.1	0.255	0.027579	159.2	0.999
PCN550	281.6	0.092	11.7	0.463	0.018191	283.3	0.999
PCN600	217.4	0.075	9.9	0.312	0.021873	218.3	0.999

[a)]Experimental uptake capacity.

[b)]Calculated uptake capacity of pseudo first or second order models.

48 Table S2. Langmuir and Freundlich fitting parameters for the sorption of U(VI) on PCNs.

Sorbents	Tem.	Langmuir parameters			Freundlich parameters		
		q_{max} (mg/g)	K_L (L/mg)	R^2	K_F ($mg^{1-n}L^n/g$)	$1/n$	R^2
PCN500	298	220.3	0.0115	0.983	17.36	0.6155	0.885
	318	255.2	0.0139	0.987	19.93	0.6189	0.897
	338	308.4	0.0165	0.989	21.78	0.6432	0.921
PCN550	298	368.1	0.0353	0.983	56.67	0.5097	0.875
	318	425.2	0.0264	0.971	55.58	0.5727	0.859
	338	507.6	0.0271	0.985	55.31	0.6521	0.887
PCN600	298	304.8	0.0127	0.976	23.13	0.6628	0.889
	318	345.9	0.0111	0.984	24.64	0.6942	0.899
	338	410.2	0.0131	0.985	24.96	0.7408	0.914

49

50 Table S3. Comparison of q_{max} values for the sorption of U(VI) on PCNs with other sorbents.

Sorbents	Experimental conditions	q_{max} (mg/g)	References
Wood pin chip biochar	pH 5.0, T 298 K	35.0	1
Oxidized cow manure biochar	pH 4.5, T 298 K	73.3	2
Switchgrass biochar	pH 3.9, T 298 K	2.12	3
Amidoxime graphene oxide	pH 4.5, T 298 K	502.2	4
Activated carbon	pH 3.0, T 293 K	28.3	5
Amino modified graphene oxide	pH 6.0, T 298 K	80.2	6
Magnetic biochar	pH 3.0, T 293 K	54.4	7
Eucalyptus biochar	pH 5.5, T 293 K	27.2	8
Oxidized MWCNTs	pH 5.0, T 298 K	37.8	9
Phosphate graphitic carbon nitride	pH 5.0, T 298 K	333.5	10
g-C_3N_4@Ni-Mg-Al-LDH	pH 5.0, T 298 K	99.7	11
U(VI)-imprinted g-C_3N_4	pH 5.0, T 298 K	859.7	12
PCN500	T 298 K, pH 5.0	158.3	This study
PCN550	T 298 K, pH 5.0	281.6	This study
PCN600	T 298 K, pH 5.0	217.4	This study

51

52 Table S4. Thermodynamic parameters for the sorption of U(VI) on PCNs.

Sorbents	T (K)	$\Delta H°$ (kJ/mol)	$\Delta S°$ (J/mol K)	$\Delta G°$ (kJ/mol)
PCN500	298	6.59	97.78	-22.54
	318	6.62		-24.47
	338	6.59		-26.45
PCN550	298	6.07	105.74	-25.44
	318	6.08		-27.55
	338	6.07		-29.68
PCN600	298	5.23	97.03	-23.69
	318	5.24		-25.62
	338	5.23		-27.57

53

54 Table S5. Components of the simulated wastewater.

Coexist components	Formula weight	Concentration (mg/L)
$CaCl_2 \cdot 2H_2O$	147.0	4.0
NaCl	58.4	7.0
NH_4NO_3	80.0	176.1
$K_2HPO_4 \cdot 3H_2O$	228.2	36.7
CH_3COONa	82.0	204.9
$MgCl_2 \cdot 6H_2O$	203.3	3.4
C_6H_5COONa	144.1	107.1
total-P	—	5.0
total-N	—	61.6
total organic carbon	—	122.3
biochemical oxygen demand	—	222.0
total organic carbon	—	326.0

Table S6. Comparison of photoreduction rate of U(VI) on PCNs with other catalysts.

Catalyst	Conditions	Electron sacrifice	k (min^{-1})*	Ref.
$ZnFe_2O_4$	0.21 mM U(VI), m/V 0.2 g/L, pH 5.0	24.0 mM CH_3OH	0.067	[13]
$Ti_3C_2/SrTiO_3$	0.21 mM U(VI), m/V 0.33 g/L, pH 4.0	None	0.008	[14]
Nb/Titanate	0.084 mM U(VI), m/V 0.2 g/L, pH 5.0	None	0.009	[15]
TiO_2	0.42 mM U(VI), m/V 0.4 g/L, pH 5.5	200 mg/L HCOONa	0.015	[16]
Sn-In_2S_3	0.06 mM, m/V 0.15 g/L, pH 6.0	None	0.078	[17]
g-C_3N_4	0.084 mM U(VI), m/V 1.0 g/L, pH 4.0	20 ppm bisphenol A	0.098	[18]
PCB/CN	0.42 mM U(VI), m/V 0.5 g/L, pH 4.0	None	0.049	[19]
TiO_2	0.168 mM U(VI), pH 2.0	Methanol	0.016	[20]
P-g-C_3N_4	0.12 mM U(VI), m/V 0.5 g/L, pH 7.0	2.5 vol% Methanol	0.110	[21]
ZnO/rectorite	0.021 mM U(VI), m/V 1.5 g/L	1.0 M Methanol	0.014	[22]
TiO_2	0.21 mM U(VI), m/V 1g/L, pH 2.7	1.68 mM EDTA	0.002	[23]
$CaTiO_3$	0.084 mM U(VI), m/V 0.2 g/L, pH 7.5	None	0.011	[24]
PCN500	48 mg/L U(VI), m/V 0.1 g/L, pH 7.0	Methanol	0.034	This work
PCN550	48 mg/L U(VI), m/V 0.1 g/L, pH 7.0	Methanol	0.057	This work
PCN600	48 mg/L U(VI), m/V 0.1 g/L, pH 7.0	Methanol	0.049	This work

*The reaction rates were calculated using the pseudo-first-order kinetics model.

References

1 M.S. Alam, D. Gorman-Lewis, N. Chen, S. Safari, K. Baek, K.O. Konhauser, D.S. Alessi, *Environ. Sci. Technol.* 2018, **52**, 13057–13067.

2 J. Jin, S. Li, X. Peng, W. Liu, C. Zhang, Y. Yang, L. Han, Z. Du, K. Sun, X. Wang, *Bioresource Technol.* 2018, **256**, 247–253.

3 S. Kumar, V.A. Loganathan, R.B. Gupta, M.O. Barnett, *J. Environ. Manage*. 2011, **92**, 2504–2512.

4 Y. Wang, Z. Wang, R. Rang, J. Yang, N. Liu, J. Liao, Y. Yang, J. Tang, *RSC Adv.* 2015, **5**, 89309–89318.

5 A. Mellah, S. Chegrouche, M. Barkat, *J. Colloid Interface Sci.* 2006, **296**, 434–441.

6 S. Verma, R.K. Dutta, *RSC Adv.* 2015, **5**, 77192–771203.

7 Q. Hu, Y. Zhu, B. Hu, S. Lu, G. Sheng, *J. Environ. Sci.* 2018, **70**, 217–225.

8 W. Mishra, M.K. Sureshkumar, N. Gupta, C.P. Kaushik, *Water Air Soil Poll.* 2017, **228**, 309.

9 Y. Sun, S. Yang, G. Sheng, Z. Guo, X. Wang, *J. Environ. Radioact.* 2012, **105**, 40–47.

10 Z. Yang, C. Qi, P. Yuan, R. Hu, X. Du, M. Xiang, *J. Environ. Chem. Eng.* 2023, **11**, 110272.

11 Y. Zou, P. Wang, W. Yao, X. Wang, Y. Liu, D. Yang, L. Wang, J. Hou, A. Alsaedi, T. Hayat, X. Wang, *Chem. Eng. J.* 2017, **330**, 573-584.

12 X. Hao, R. Chen, Q. Liu, J. Liu, H. Zhang, J. Yu, Z. Lia, J. Wang, *Inorg. Chem. Front.*, 2018, **5**, 2218.

13 P.L. Liang, L.Y. Yuan, H. Deng, X.C. Wang, L. Wang, Z.J. Li, S.Z. Luo, W.Q. Shi, *Appl. Catal. B: Environ.* 2020, **267**, 118688.

14 H. Deng, Z. Li, L. Wang, L.Y. Yuan, J. Lan, Z.Y. Chang, Z.F. Chai, W.Q. Shi, *ACS Appl. Nano Mater.* 2019, **2**, 2283–2294.

15 X. Liu, P. Du, W. Pan, C. Dang, T. Qian, H. Liu, W. Liu, D. Zhao, *Appl. Catal. B: Environ.* 2018, **231**, 11–22.

16 G. Wang, J. Zhen, L. Zhou, F. Wu, N. Deng, *J. Radioanal. Nucl. Chem.* 2015, **304**, 579–585.

17 J. Feng, Z. Yang, S. He, X. Niu, T. Zhang, A. Ding, H. Liang, X. Feng, *Chemosphere* 2018, **212**, 114–123.

18 H. Wang, H. Guo, N. Zhang, Z. Chen, B. Hu, X. Wang, *Environ. Sci. Technol.* 2019, **53**, 6454–6461.

19 F. Yu, Z. Yu, Z. Xu, J. Xiong, Q. Fan, X. Feng, Y. Tao, J. Hua, F. Luo, *Mol. Syst. Des. Eng.* 2020, **5**, 882–889.

20 C.J. Evans, G.P. Nicholson, D.A. Faith, M.J. Kan, *Green Chem.* 2004, **6**, 196–197.

21 X. Wu, S. Jiang, S. Song, C. Sun, *Appl. Surf. Sci.* 2018, **430**, 371–379.

22 Y. Guo, L. Li, Y. Li, Z. Li, X. Wang, G. Wang, *J. Radioanal. Nucl. Chem.* 2016, **310**, 883-890.

23 J. Chen, D.F. Ollis, W.H. Rulkens, H. Bruning, *Colloid. Surface. A* 1999, **151**, 339–349.

24 S. Lu, K. Zhu, T. Hayat, N.S. Alharbi, C. Chen, G. Song, D. Chen, Y. Sun, *J. Hazard. Mater.* 2019, **364**, 100-107.