Amidoxime-functionalized hydrothermal carbon material for uranium removal from aqueous solution

Zhibin Zhang[1, 2, 3], Zhimin Dong[1], Ying Dai[1], Saijin Xiao[1], Xiaohong Cao[1], Yunhai Liu [1, 3*],

Weihua Guo[1], Mingbiao Luo[1], Zhanggao Le[1]

[1] Fundamental Science on Radioactive Geology and Exploration Technology Laboratory, East China University of Technology, Nanchang, Jiangxi, 330013, China

[2] Engineering Research Center of Nuclear Technology Application (East China University of Technology), Ministry of Education, Nanchang, Jiangxi, 330013, China

[3] State Key Laboratory Breeding Base of Nuclear Resources and Environment, East China University of Technology, Nanchang, Jiangxi, 330013, China

S1 Reagents

The chemicals and reagents, including soluble starch, ceric ammonium nitrate (CAN), acrylonitrile (ACN), hydroxylamine hydrochloride, dimethylfomamide (DMF) and metal nitrates, were purchased from Aladdin Chemistry Co., Ltd., China. All reagents were of AR grade and were used without further purification.

S2 Characterization

The morphology of the materials was observed via scanning electron microscopy (SEM, NNS-450, FEI, USA). The elemental chemical states on the surface of the produced materials were measured via X-ray photoelectron spectroscopy (XPS, Escalab 250Xi, Thermo Fisher, USA). Fourier transform infrared spectra (FT-IR) were obtained using a Nicolet 380 spectrometer (USA). Contents of carbon, hydrogen, and nitrogen elements in samples were determined by using an elemental-analysis device (Vario EL cube, German). The N_2 adsorption and desorption isotherms at -196 °C were measured using a TriStar 3000 volumetric adsorption analyzer (Micromeritics Instrument Corp, Norcross, GA) after the samples were pretreated at 200 °C overnight under a vacuum. The Zeta potential was measured using a Particle Metrix flowing current potential analyzer (Stabino, German). All concentrations of metal ions in the solution were analyzed via inductively coupled plasma optical emission spectrometry (ICP-OES, Thermo Elemental, USA).

*Corresponding author. Tel.: +86 791 83897791; +86 791 83897791.
E-mail address:walton_liu@163.com (Yunhai Liu).

S3 Batch experiments of uranium(VI) sorption

The sorption behavior of AO-HTC for U(VI) was carried out using the batch technique. 10.0 mg of adsorbent was added to 250 mL Erlenmeyer flasks, along with 100 mL of either pure U(VI) solution or a multi-ion solution (simulated nuclear industrial effluent sample) containing 12 co-existing cations with designed metal ion concentration and pH value (solution pH was adjusted using 0.1 M or 0.01 M HNO_3 and NaOH solution). After being shaken for a certain time (t, min) at specified temperatures (T, K), the solutions were centrifuged at 10000 rpm for 10 min. The initial and residual concentration of uranium was analyzed via the arsenazo III method using a visible spectrophotometer at 650 nm. The concentrations of multi-ions in the selective sorption were determined via inductively coupled plasma optical emission spectrometry. The sorption capacity (q_e ($mg \cdot g^{-1}$)) and distribution coefficient (K_d ($mL \cdot g^{-1}$)) were calculated using Eqs. (1)-(2).

$$q_e = \frac{(C_0 - C_e) \times V}{m} \tag{1}$$

$$K_d = \frac{(C_0 - C_e) \times V}{C_e \times m} \tag{2}$$

where C_0 and C_e are the initial and equilibrium concentrations of the metal ion ($mg \cdot g^{-1}$), respectively. V is the volume of the solution (L) and m is the amount of the sorbent (g).

Uranium selectivity (S_U) describes the potency and degree of the selectivity of the sorbents to uranium and was calculated using Eq. (3).

$$S_U = \frac{q_{e(U)}}{q_{e(Total)}} \times 100\% \tag{3}$$

where $q_{e(U)}$ ($mmol \cdot g^{-1}$) is the amount of uranium and $q_{e(Total)}$ ($mmol \cdot g^{-1}$) is the total amount of all of the multi-ions adsorbed by AO-HTC.
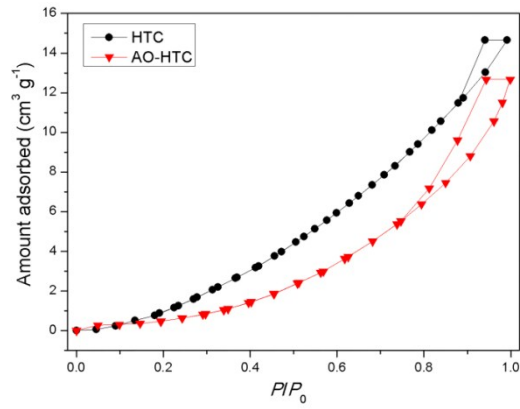
Fig. S1. N_2 adsorption–desorption isotherm at 77 K for HTC and AO-HTC.
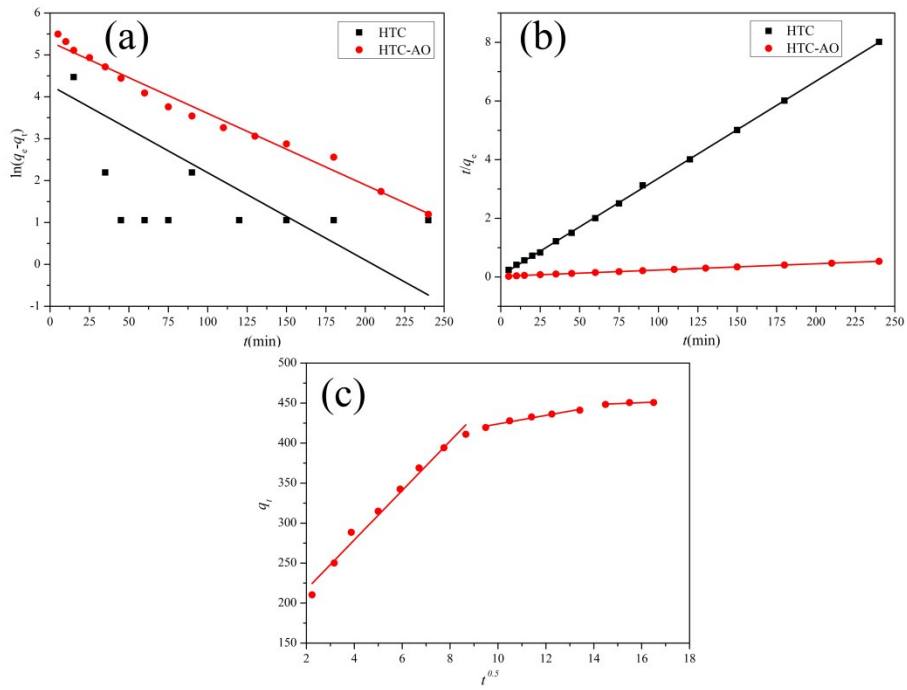

Fig. S2. (a) Pseudo-first-order, (b) pseudo-second-order and (c) intraparticle diffusion model plots for the adsorption of U(VI) onto HTC and AO-HTC.
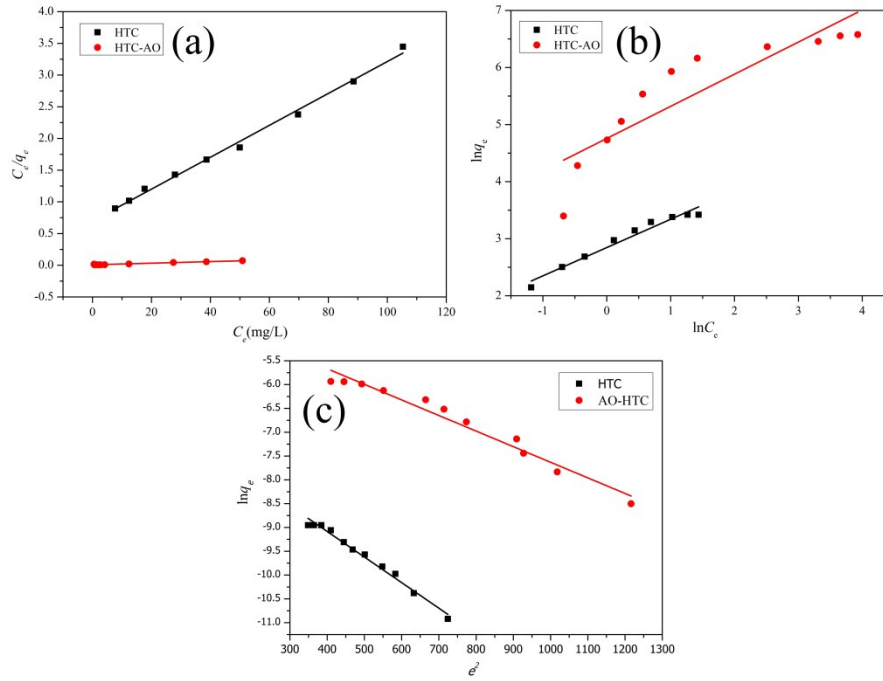
Fig. S3. (a) Langmuir, (b) Freundlich and (c) D-R isotherms of U(VI) adsorbed on HTC and HTC-AO.
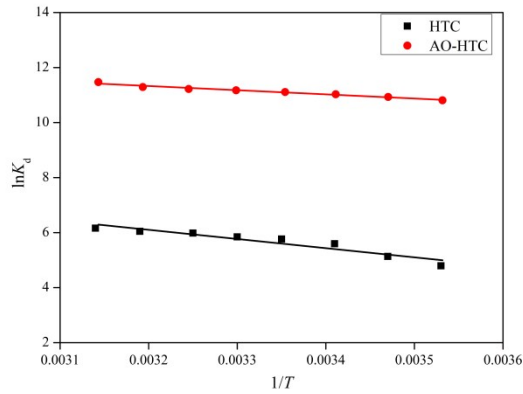

Fig. S4. The plots of ln K_d *vs.* 1/T for the U(VI) sorption onto HTC and AO-HTC.

Table S1. Kinetic parameters of U(VI) sorption for different models.

Sorbents	$q_{e,exp}$ (mg·g⁻¹)	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
HTC	29.9	68.1	$1.9×10^{-2}$	0.19	29.8	$2.1×10^{-2}$	0.99
AO-HTC	455.6	202.4	$1.7×10^{-2}$	0.98	467.3	$2.1×10^{-4}$	0.99

Table S2. Isotherm parameters for U(VI) adsorption on HTC and AO-HTC.

Sorbents	Langmuir isotherm			Freundlich isotherm			D-R isotherm			
	K_L	q_m(mg·g⁻¹)	R^2	K_F	n	R^2	q_{DR}	β	E_{DR}	R^2

HTC	0.09	39.8	0.99	17.2	2.0	0.96	0.001	0.0053	9.71	0.98
AO-HTC	0.20	724.6	0.98	117.5	1.89	0.75	0.013	0.0032	12.5	0.96

Table S3. Langmuir separation factor R_L

U (VI) initial concentration (mg·L^{-1})	10	15	20	30	40	50	70	90	110
HTC	0.52	0.43	0.36	0.27	0.22	0.18	0.14	0.11	0.09
AO-HTC	0.33	0.25	0.20	0.14	0.11	0.09	0.07	0.05	0.04

Table S4. Thermodynamic parameters for the U(VI) adsorption on HTC and AO-HTC.

Sorbents	ΔH (kJ·mol^{-1})	ΔS (J·mol^{-1}·K^{-1})	ΔG (kJ·mol^{-1})				
			283.15 K	288.15 K	293.15 K	298.15 K	303.15 K
HTC	27.73	139.46	-11.76	-12.46	-13.15	-13.85	-14.55
HTC-AO	12.60	134.50	-25.48	-26.16	-26.83	-27.50	-28.17

Table S5. Distribution ratios and selectivity coefficients of HTC and AO-HTC.

Ions	K_d (mL·g^{-1})		$S_{U(VI)/M(x)}$		S_r
	HTC	AO-HTC	HTC	AO-HTC	
U(VI)	154.17	1926.07	-	-	-
La(III)	29.11	77.85	5.30	24.74	4.67
Ce(III)	29.60	94.89	5.21	20.30	3.90
Sm(III)	17.14	156.96	15.20	10.88	1.36
Gd(III)	25.77	142.55	6.49	11.85	2.26
Co(II)	52.15	102.82	2.96	18.73	6.34
Sr(II)	33.56	33.64	4.59	57.26	12.46
Mn(II)	45.76	27.66	3.37	69.63	20.67
Ni(II)	14.00	81.87	11.01	23.53	2.14
Cs(I)	137.02	158.96	1.13	12.12	10.77
Zn(II)	76.75	129.54	2.01	14.87	7.40
Cu(II)	82.32	134.92	1.87	14.27	7.63
V(IV)	34.87	29.48	4.42	65.33	14.78