

## Supporting Information

# Guanidine and Amidoxime Co-Functionalized Polypropylene Nonwoven Fabric for Potential Uranium Seawater Extraction with Antifouling Property

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## 1. Characterization methods.

Field-emitting scanning electron microscopy (FE-SEM) images were carried out by a HITACHI S-570 microscope with an accelerating voltage of 15 kV, and energy-dispersive X-ray (EDX) analysis was performed with an EDAX-PV 9100 energy dispersion X-ray fluorescence analyzer. Fourier transform infrared (FT-IR) spectra were recorded on a Varian-1000 spectrometer. The concentration of uranyl ion was determined by thermo high resolution inductively coupled plasma mass spectrometer (ICP-MS, Element II, Varian 810/820-MS). The analyzer works with 8 kV accelerating voltage, the flow rate of the water circulation should be 7.5 L/min @ 6 bar, and the inlet temperature should be in the range of 15 °C and 17 °C. X-ray photoelectron spectroscopy (XPS) was performed on ESCALAB 250 microprobe system with monochromatization of an exciting X-ray radiation. The contact angle was determined with a Contact Angle Meter Alpha-SE (J. A. Woollam Corporation).

## 2. Synthesis of PP-g-PGMA.

PGMA was grafted onto polypropylene nonwoven fabric through radiation-induced graft polymerization<sup>1</sup>. Typically, PP nonwoven fabric (2.0 g, 0.025 g/mL) was immersed in 80.0 mL of acetone with GMA (8.0 g, 0.1 g/mL) in a 100 mL round-bottomed flask. The contents were then purged with argon for about 30 min to eliminate oxygen. Then the flask was placed in an insulated room with a <sup>60</sup>Co source at a dose rate of 15 Gy/min, which was determined precisely by Fricke dosimeter. After the graft polymerization, the fabric was washed three times with acetone (500 mL) to remove the homopolymer and residual monomer. Finally, the nonwoven fabric was dried at 40 °C in vacuum oven to a constant weight.

The degree of grafting (*Dg*) of PGMA was calculated according to the increase of the weight of fabric after graft polymerization, as described in Equation (1):

$$Dg (\%) = (W_g - W_0) / W_0 \times 100 \quad (1)$$

where  $W_0$  and  $W_g$  (g) represent the weights of nonwoven fabric before and after the graft polymerization, respectively.

Meanwhile, the effects of radiation dose and monomer concentration on the graft degree were investigated (Table S1): *Dg* increases with monomer concentration, and reaches the maximum value when radiation dose is 40 KGy.

### 3. Sorption kinetics.

Pseudo-first-order equation represents the relationship between sorption amount  $q_t$  and time  $t$ <sup>2</sup>:

$$\log(q_e - q_t) = \log q_e - \left(\frac{k_1}{2.303}\right) \times t \quad (2)$$

where  $q_e$  and  $q_t$  (mg/g) are the sorption capacity of uranium at equilibrium time and time  $t$  (h), respectively, and  $k_1$  (h<sup>-1</sup>) represents the pseudo first order kinetic constant.  $k_1$  and  $q_e$  can be calculated from the slope and intercept of the plot of  $\log(q_e - q_t)$  versus  $t$ , respectively (Figure S2A, Supporting Information).

Pseudo-second-order model<sup>3,4</sup> is expressed as the following Equation (3):

$$\frac{t}{q_t} = \frac{1}{k_2 \times q_e^2} + \frac{t}{q_e} \quad (3)$$

where  $k_2$  (g/mg/h) represents the rate constant of the pseudo-second order model, and can be determined from the plot of  $t/q_t$  against  $t$  (Figure S2B, Supporting Information).

Elovich kinetic model can be expressed as (4):

$$q_t = \frac{1}{\beta} \ln(\alpha\beta) + \frac{1}{\beta} \ln t \quad (4)$$

where  $\alpha$  is the initial adsorption rate in mg/(g min), and  $\beta$  (g/mg) is the desorption constant related to the extent of the surface coverage and activation energy for chemisorptions. Both kinetic constants ( $\alpha$  and  $\beta$ ) can be estimated from the slope and intercept from the plot of  $q_t$  versus  $\ln t$ <sup>7</sup> (Figure S3A, Supporting Information).

The intra-particle diffusion model<sup>8</sup> is used to acquire information needed to assess the suitability, effectiveness of the adsorption process and identify the possible rate controlling step. The intra-particle diffusion model can be described the following Equation (5):

$$q_t = K_{id} t^{\frac{1}{2}} + C \quad (5)$$

where  $C$  is the intercept related to the thickness of the boundary layer and  $K_{id}$  is the rate constant of intra-particle diffusion (mg/g/ min<sup>1/2</sup>), which can be fitted with the experimental data presented in the plot of  $q_t$  versus  $t^{1/2}$  (Figure S3B, Supporting Information).

### 4. Sorption isotherms.

Langmuir model represents monolayer sorption based on the hypothesis that all the sorption sites

have equal affinity and that desorption at one site doesn't influence an adjacent site <sup>5</sup>, which can be described as Equation (6):

$$\frac{C_e}{q_e} = \frac{1}{q_{\max} b} + \frac{C_e}{q_{\max}} \quad (6)$$

where  $b$  (L/mg) is the Langmuir constant, which is related to the affinity of binding sites, and  $q_{\max}$  (mg/g) is the maximum sorption capacity. They can be calculated from the linear plot of  $C_e/q_e$  against  $C_e$  (Figure S4A, Supporting Information).

The Freundlich model can be applied for multilayer sorption and the sorption on heterogeneous surfaces <sup>6</sup>, which can be described as Equation (7):

$$\log q_e = \log K_F + \frac{1}{n} \log C_e \quad (7)$$

where  $K_F$  ( $\text{mol}^{1-n}\text{L}^n/\text{g}$ ) and  $n$  are the Freundlich constants related to sorption capacity and sorption intensity, respectively, which can be calculated from the linear plot of  $\log q_e$  versus  $\log C_e$  (Figure S4B, Supporting Information).

The Temkin isotherm model<sup>7</sup> contains a factor that explicitly takes into account adsorbing species-adsorbate interactions. This model assumes the following facts: (i) the heat of adsorption of all the molecules in the layer decreases linearly with coverage due to adsorbent–adsorbate interactions, and then (ii) the adsorption is characterized by a uniform distribution of binding energies, up to a maximum binding energy. The derivation of the Temkin isotherm assumes that the fall in the heat of sorption is linear rather than logarithmic, as implied in the Freundlich equation. The Temkin isotherm has commonly been applied in the following form (8):

$$q_e = B \ln (AC_e) \quad (8)$$

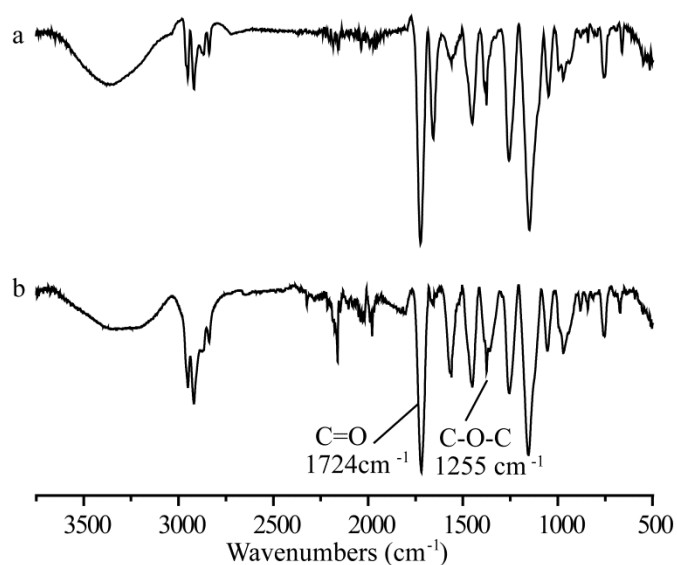
where  $A$  and  $B$  are Temkin isotherm constants, which can be fitted with the experimental data presented in the plot of  $q_e$  versus  $\ln C_e$  (Figure S5, Supporting Information).

**Table S1.** The influences of radiation dose and monomer concentration on graft degree.

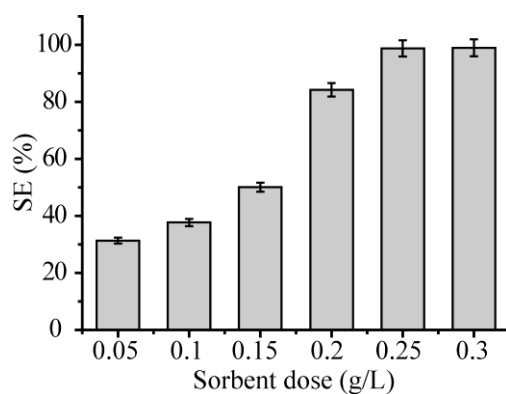
| Entry | Irradiation dose (kGy) | PP fiber (g) | GMA (g) | Acetone (mL) | <i>Dg</i> (%) |
|-------|------------------------|--------------|---------|--------------|---------------|
| 1     | 20                     | 2.00         | 8.00    | 80.0         | 210           |
| 2     | 40                     | 2.00         | 8.00    | 80.0         | 257           |
| 3     | 60                     | 2.00         | 8.00    | 80.0         | 239           |
| 4     | 80                     | 2.00         | 8.00    | 80.0         | 208           |
| 5     | 40                     | 2.00         | 2.00    | 80.0         | 51.0          |
| 6     | 40                     | 2.00         | 4.00    | 80.0         | 117           |
| 7     | 40                     | 2.00         | 6.00    | 80.0         | 182           |

**Table S2.** Kinetic parameters for uranium sorption by PP-g-AO1, PP-g-AO2, and PP-g-AO3. (Experimental condition: 0.25 g/L sorbent dose, 100 mL solution,  $2 \times 10^{-5}$  mol/L uranium, pH 8.0, and 298.15 K)

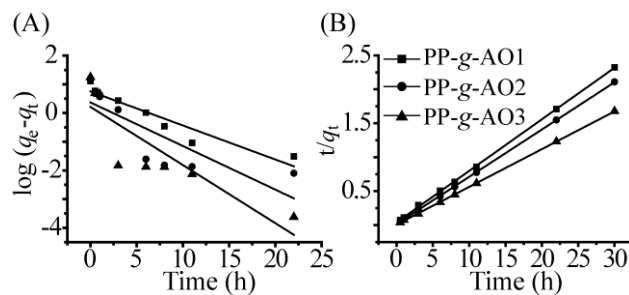
| Sorbent  | Elovich  |         |       | Intra-particle diffusion plot |       |       |
|----------|----------|---------|-------|-------------------------------|-------|-------|
|          | $\alpha$ | $\beta$ | $R^2$ | $K_{id} (mg/g/h^{1/2})$       | $C$   | $R^2$ |
| PP-g-AO1 | 0.086    | 1.59    | 0.91  | 1.86                          | 5.322 | 0.58  |
| PP-g-AO2 | 0.0072   | 1.47    | 0.83  | 1.86                          | 6.927 | 0.46  |
| PP-g-AO3 | 0.00092  | 1.78    | 0.69  | 2.23                          | 9.326 | 0.39  |



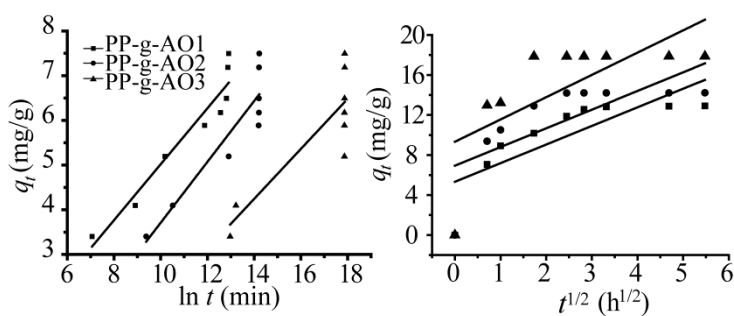
**Figure S1.** FT-IR spectra of PP-g-AO3 (a) before, and (b) after treated with 0.44 mol/L KOH, respectively. (The stretching vibrations of C-O-C ( $1255\text{ cm}^{-1}$ ) and C=O ( $1724\text{ cm}^{-1}$ ) indicate that the ester groups in PP-g-AO could remain stable after the treatment with 0.44 mol/L KOH for 1 h at room temperature.)



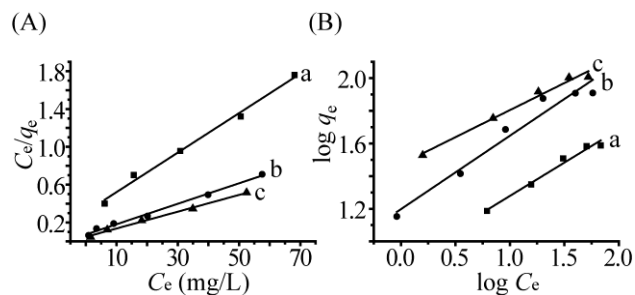
**Figure S2.** Effects of sorbent dose on the sorption of uranium by PP-g-AO3. (Experimental condition: 100 mL solution,  $2 \times 10^{-5}$  mol/L uranium, pH 8.0, and 298.15 K; 0.25 g/L of sorbent dose was selected as the optimum value from the economical point of view.)



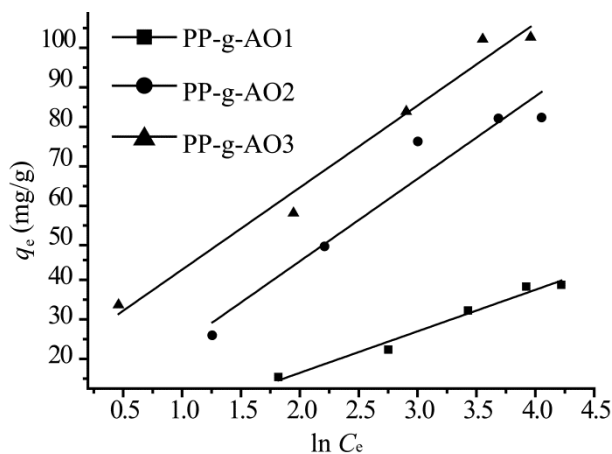
**Figure S3.** (A) Pseudo-first order kinetics and (B) Pseudo-second order kinetics of uranium by PP-g-AO1, PP-g-AO2, PP-g-AO3, respectively. (Experimental condition: 0.25 g/L sorbent dose, 100 mL solution,  $2 \times 10^{-5}$  mol/L uranium, pH 8.0, and 298.15 K.)



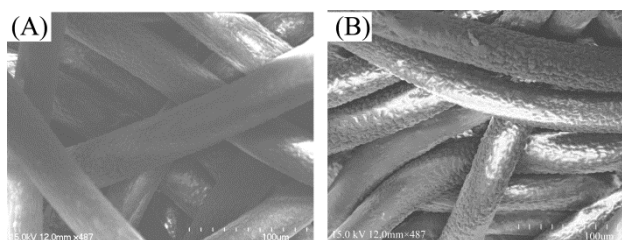
**Figure S4.** (A) Elovich order kinetics and (B) Intra-particle order kinetics of uranium by PP-g-AO1, PP-g-AO2, and PP-g-AO3, respectively. (Experimental condition: 0.25 g/L sorbent dose, 100 mL solution,  $2 \times 10^{-5}$  mol/L uranium, pH 8.0, and 298.15 K.)



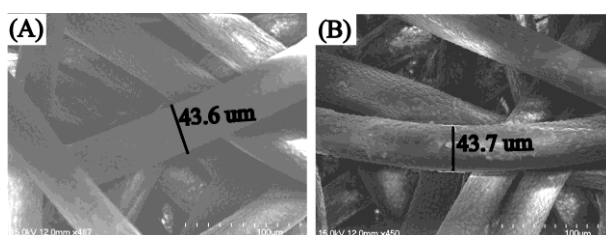
**Figure S5.** (A) Langmuir sorption isotherm plots and (B) Freundlich sorption isotherm plots for the sorption of uranium onto (a) PP-*g*-AO1, (b) PP-*g*-AO2, and (c) PP-*g*-AO3, respectively. (Experimental condition: 0.25 g/L sorbent dose, 100 mL solution, pH 8.0, and 298.15 K)



**Figure S6.** Temkin sorption isotherm plots for the sorption of uranium onto (a) PP-*g*-AO1, (b) PP-*g*-AO2, and (c) PP-*g*-AO3, respectively. (Experimental condition: 0.25 g/L sorbent dose, 100 mL solution, pH 8.0, and 298.15 K)



**Figure S7.** FE-SEM images of PP-*g*-AO3 (A) before (B) after extraction in simulated seawater. Scale bar: 100.0  $\mu\text{m}$ .



**Figure S8.** FE-SEM images of PP-*g*-AO3 (A) before and (B) after antibacterial experiments. Scale bar: 100.0  $\mu\text{m}$ .

## Reference

1. Kavakli, P.; Kavakli, C.; Guven, O. Preparation and characterization of Fe(III)-loaded iminodiacetic acid modified GMA grafted nonwoven fabric adsorbent for anion adsorption. *Radiat. Phys. Chem.* **2014**, *94*, 105-110.
2. Saito, K.; Uezu, K.; Hori, T.; Furusaki, S.; Sugo, T.; Okamoto, J. Recovery of uranium from seawater using amidoxime hollow fibers. *AIChE J.* **1988**, *34*, 411-416.
3. Ho, Y.; McKay, G. Sorption of dye from aqueous solution by peat. *Chem. Eng. J.* **1998**, *70*, 115-124.
4. Ho, Y. Review of second-order models for adsorption systems. *J. Hazard. Mater.* **2006**, *136*,

681-689.

5. Sadeghi, S.; Aboobakri, E. Magnetic nanoparticles with an imprinted polymer coating for the selective extraction of uranyl ions. *Microchim. Acta* **2012**, *178*, 89–97.
6. Freundlich, H. Concerning adsorption in solutions. *Z. Phys. Chem.* **1906**, *57*, 385–470.
7. Kumar, P. S.; Ramalingam, S.; Kirupha, S. D.; Murugesan, A.; Vidhyadevi, T.; Sivanesan, S., Adsorption behavior of nickel(II) onto cashew nut shell: Equilibrium, thermodynamics, kinetics, mechanism and process design. *Chem. Eng. J.* **2011**, *167*, 122-131.
8. Mohamed, A.; Nasser, W. S.; Osman, T. A.; Toprak, M. S.; Muhammed, M.; Uheida, A., Removal of chromium (VI) from aqueous solutions using surface modified composite nanofibers. *J. Colloid Interf. Sci.* **2017**, *505*, 682-691.