Supporting Information

PEI−modified CMKGM/GO Porous Biocomposite for Superior Removal of Pb(II)

Fang Cao[1], Juan Shen[1, 2]*

[1] School of Materials Science and Engineering, Southwest University of Science and Technology, Mianyang 621010, PR China

[2] State Key Laboratory Cultivation Base for Nonmetal Composites and Functional Materials, Southwest University of Science and Technology, Mianyang 621010, PR China

Corresponding Author: Juan Shen (E−mail: sj−shenjuan@163.com)

2.3 Characterization of PCGt

Take appropriate amount of dried PCGt and stick it on the conductive tape for gold spraying treatment. The surface morphology of the PCGt was observed by a scanning electron microscope (SEM, TM–4000, Hitachi, Japan) under a voltage of 15 KV. 1 mg PCGt was compressed into pellets using 100 mg KBr and investigated by Fourier transform infrared spectroscopy (FT–IR, Nicolet–6700, PerkinElmer, America) in transmittance mode within the wavenumber range of 400 to 4000 cm^{-1} to identify the

functional groups. Thermal stability of the PCGt was analyzed by thermal gravimetric analysis (TG, SDT–Q600, TA Instruments, America) at a heating rate of 10 ^{o}C min^{-1} from room temperature to 600 °C and the flow rate of N_2 was 100 mL min^{-1}, the purity of $N_2 \geq 99.99\%$. The nitrogen content of the PCGt was analyzed by an elemental analyzer (EA, Vario ELCUBE, Elementar, Germany) and 2 mg sulfanilic acid as a reference. The surface of the adsorbent before and after Pb(II) adsorption was analyzed by multifunctional X–ray photoelectron spectroscopy (XPS, XSAM800, Kratos, England) to obtain the elements binding energies with the source of Al K alph, the testing energy of 1486.8 eV and the test tube power of 15 kV×15mA. The heavy metal ion concentration before and after adsorption were measured by atomic absorption spectrometer with flame system (AAS, AA700, Perkin Elmer, America) in all batch adsorption experiments. The detection wavelength of Pb(II) is 283.3 nm.

2.4 Batch Adsorption

Accordingly, batch adsorption experiments were designed systematically to detect the Pb(II) removal effect of PCGt containing different initial pH values, adsorbent dose, contact time, initial Pb(II) concentration and temperature. PCGt was added into 50 mL Pb(II) solution in a conical flask with varying pH values, and all conical flasks were put into a water–bathing constant temperature vibrator and shaken at 120 rpm for 12 h. During the adsorption process, pH values were adjusted to the desired range by 0.1 mol L^{-1} HCl and 0.1 mol L^{-1} NaOH solutions. The effect of pH was studied in the range 2 to 7. The pH 5.0 was chose in the further experiments due to closing to the pH of initial Pb(II) solution. The adsorbent dosage effect was tested in the 0.3 to 1.5 g L^{-1} range and

the weight of PCGt was chosen as 0.5 g L^{-1} in the following experiment according to the experimental data. The effect of the contact time was determined from 6 to 4320 min. The fitting kinetic models containing pseudo–first–order kinetic model, pseudo–second–order kinetic model, Elovich kinetic model and intraparticle diffusion kinetic model were performed. The adsorption equilibrium isotherms containing Langmuir and Freundlich models were determined with an initial concentration range of 20 to 1400mg L^{-1} using linear and non–linear methods under the certain temperature; the adsorption thermodynamics were revealed at temperature ranging from 288.15 K to 308.15 K.

After the shaking, the ion concentration before and after adsorption were measured by atomic absorption spectrometer. The adsorption capacity (q_t) and removal efficiency (*RE*) was calculated by Eq S1 and Eq S2, respectively:

$$q_t = (c_0 - c_t)V / m \tag{S1}$$

$$RE = (c_0 - c_t) / c_0 \times 100\% \tag{S2}$$

Where q_t (mg g^{-1}) represents the adsorption capacity of PCGt; c_0 and c_t (mg L^{-1}) are the initial and final ion concentration, respectively; m (g) refers to the mass of the absorbent and V (L) is the solution volume; RE (%) is the adsorption removal efficiency.

In the leaching experiment, we choose 1 mol L^{-1} NaOH solution as desorbing agent to study the reuse ability of PCGt. The desorption capacity (q_{des}) and desorption efficiency (*DE*) was calculated by Eq S3 and Eq S4, respectively:

$$q_{des} = c_{des} V / m \tag{S3}$$

$$DE = q_{des} / q_t \times 100\% \tag{S4}$$

Where q_{des} (mg g^{-1}) represents the desorption capacity of PCGt; c_{des} (mg L^{-1}) is the ion concentration of desorption equilibrium; m (g) refers to the mass of the absorbent and V (L) is the solution volume; DE (%) is the desorption efficiency.

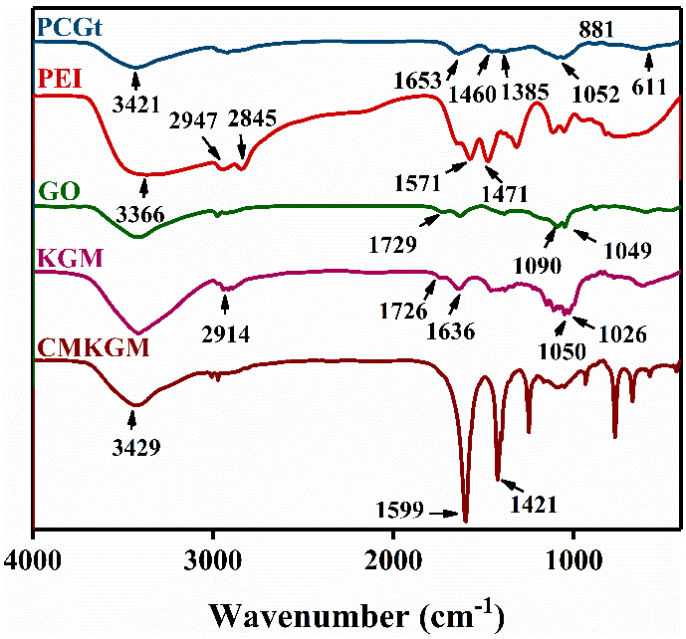

Figure S1. FT–IR spectrum of KGM, CMKGM, GO, PEI and PCGt.

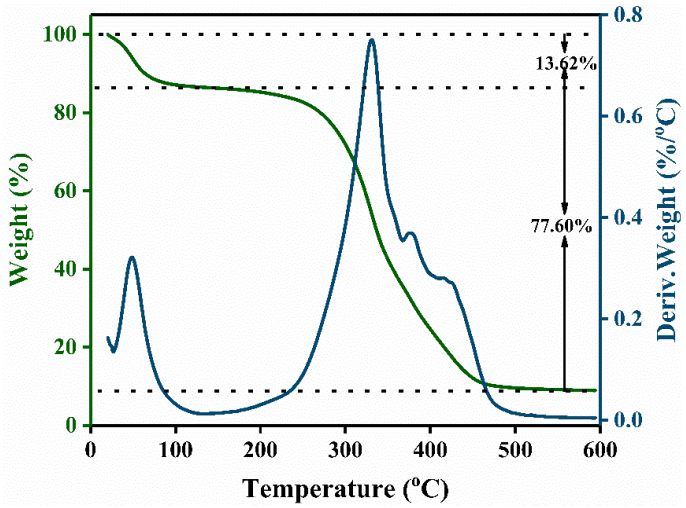

Figure S2. TG and DTG curves of PCGt biocomposite under nitrogen atmosphere.

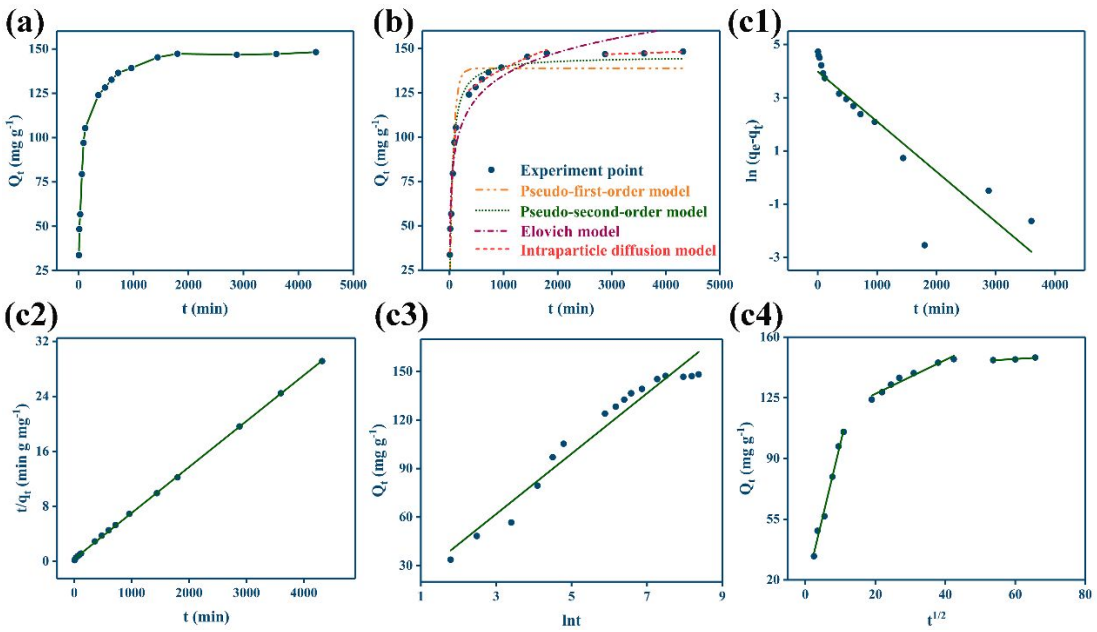

Figure S3. (a) Effect of contact time on the Pb(II) adsorption capacity of PCGt. (b) Nonlinear curves of four adsorption kinetic models. (c1) linear curve of pseudo−first−order kinetic model. (c2) linear curve of pseudo−second−order kinetic model. (c3) linear curve of Elovich model. (c4) linear curve of intraparticle diffusion model. (pH=5, dose: 0.5g L^{-1}, initial Pb(II) concentration: 100 mg L^{-1}, temperature: 298.15 K)

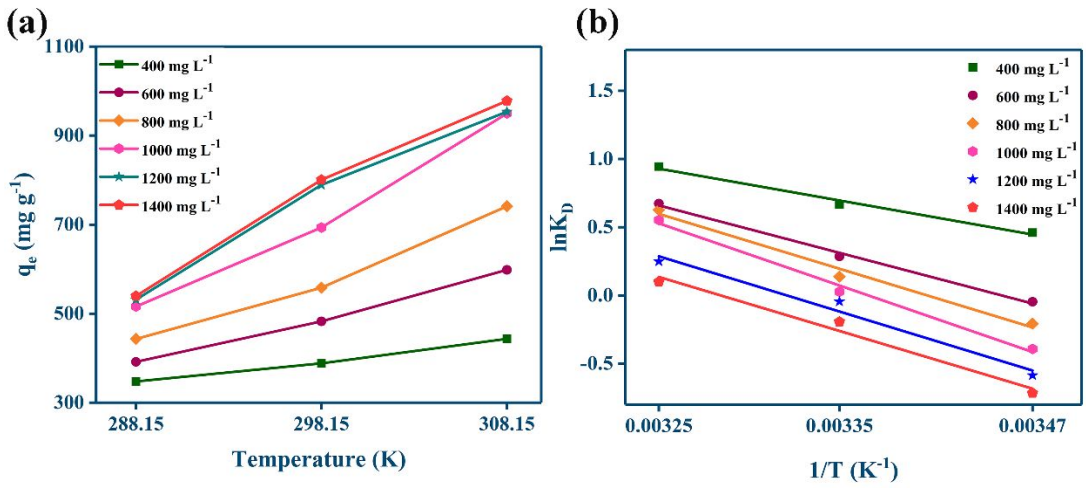

Figure S4. (a) Effect of temperature on the Pb(II) adsorption capacity of PCGt. (pH=5, dose: 0.5 g L^{-1}, contact time: 30 h) (b) Relationship between 1/T and lnK_D for the Pb(II) adsorption.

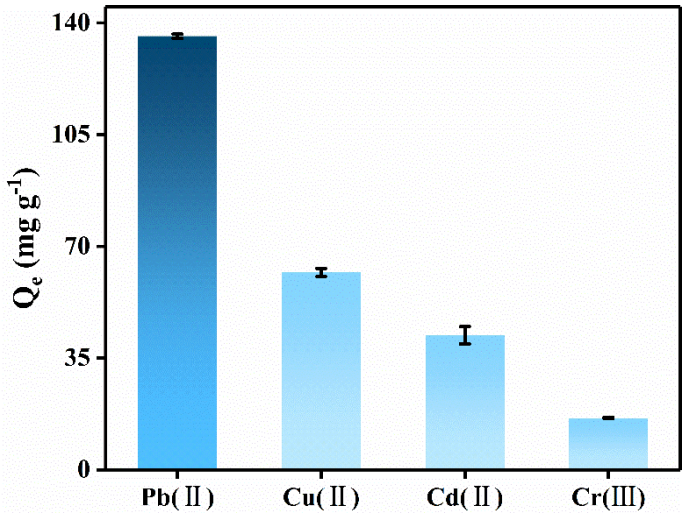

Figure S5. Adsorption capacity of PCGt on different ions. (adsorbent dose: 0.5 g L^{-1}, time: 24 h, initial ions concentration: 100 mg L^{-1}, temperature: 298 K)

Table S1. The reaction conditions of the orthogonal experiment.

Sample	PEI/g	GA/ml	GO/mg	Temperature/K	Q_e/mg g^{-1}
1	0.5000	0.2500	2.000	293.2	46.97
2	0.5000	0.5000	4.000	303.2	47.93
3	0.5000	0.7500	6.000	313.2	30.71
4	0.5000	1.000	8.000	323.2	36.36
5	1.000	0.2500	4.000	313.2	32.21
6	1.000	0.5000	2.000	323.2	67.46
7	1.000	0.7500	8.000	293.2	87.18
8	1.000	1.000	6.000	303.2	84.55
9	1.500	0.2500	6.000	323.2	37.36
10	1.500	0.5000	8.000	313.2	54.22
11	1.500	0.7500	2.000	303.2	122.5
12(PCGt)	**1.500**	**1.000**	**4.000**	**293.2**	**127.3**
13	2.000	0.2500	8.000	303.2	26.17
14	2.000	0.5000	6.000	293.2	45.79
15	2.000	0.7500	4.000	323.2	50.38
16	2.000	1.000	2.000	313.2	82.07

Table S2. The adsorption isotherm fitting parameters for Pb (II) adsorption on PCGt.

Type			288.15K	298.15K	308.15K
Langmuir	Linear	q_{max} (mg g^{-1})	565.0	869.6	1180
		K_L (L mg^{-1})	0.01144	0.006434	0.005046
		R^2_{adj}	0.9835	0.9343	0.9351
	Nonlinear	q_{max} (mg g^{-1})	551.4	1064	1428
		K_L(L mg^{-1})	0.01064	0.002830	0.002750

		R^2_{adj}	0.9612	0.9652	0.9854
Freundlich	Linear	K_F (mg g^{-1})	34.80	29.49	24.11
		n	2.449	2.067	1.787
		R^2_{adj}	0.9796	0.9971	0.9924
	Nonlinear	K_F (mg g^{-1})	52.75	29.71	30.22
		n	2.961	2.077	1.906
		R^2_{adj}	0.9844	0.9953	0.9754

Table S3. The adsorption thermodynamics fitting parameters of PCGt on Pb (II) adsorption.

C_0 (mg L^{-1})	ΔH (kJ mol^{-1})	ΔS (J mol^{-1} K^{-1})	ΔG (kJ mol^{-1})			R_{adj}^2
			288.15 K	298.15 K	308.15 K	
400	17.82	65.57	−1.071	−1.727	−2.382	0.9782
600	26.55	91.65	0.1407	−0.7759	−1.692	0.9915
800	30.72	104.7	0.5603	−0.4865	−1.533	0.9720
1000	34.81	117.4	0.9913	−0.1825	−1.356	0.9860
1200	30.91	102.7	1.317	0.2903	−0.7367	0.9555
1400	30.23	99.23	1.635	0.6433	−0.3490	0.9604