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Click Functionalization of Poly(glycidyl methacrylate) Resins with 4-Triazolecarboxylic Acid for Effective Adsorption of Pb(II) Ions

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S1. Experimental Section

S1.1 Grafting density of PA onto the PGMA microspheres

The grafting yield (GY) of the PA onto the PGMA microspheres via click chemistry can be precisely controlled by varying reaction time and the initial monomer concentration. The GY values were determined using the previously-reported equations.[1] The GY were determined by measuring the increase in the mass percentage of the PGMA-c-PA microspheres as follows:

$$GY = \frac{W_g - W_0}{W_0} \times 100\% \quad (1)$$

where W_o and W_g were the weights of the dry PGMA microspheres before and after the grafting of PA , respectively.

S1.2 Effect of solution pH

To determine the optimal solution pH for the PGMA-*c*-PA microspheres from 24 h of ring-opening reaction, the adsorption profiles of Pb(II) ion in an initial solution pH range of 1.0–6.0 was investigated. An aliquot 100 mg of the PGMA microspheres was immersed in 100 mL of Pb(II) ions with an initial concentration of 0.12 mmol·L^{-1} (i.e. 25 mg· L^{-1}), and the adsorption was allowed to proceed at 150 rpm and 25 ^{o}C for 24 h. The solution pH was adjusted by adding 0.1 mol·L^{-1} HNO_3 or NaOH solution every 2 h to remain relatively constant throughout the adsorption experiment. The equilibrium adsorption capacity was calculated by the following equation: [2]

$$q_e = \frac{(c_0 - c_e) \cdot v}{m} \quad (2)$$

where q_e is the equilibrium adsorption capacity (mg·g^{-1}), C_o and C_e are the

concentrations of the initial Pb(II) solution and the final solution at equilibrium, respectively, *m* is the mass of the PGMA microspheres (g), and *v* is the solution volume (L), which remained constant throughout the adsorption period.

S1.3 Adsorption kinetics

To determine the adsorption kinetics of Pb(II) ions, a aliquot 100 mg of PGMA-*c*-PA microspheres was immersed in 100 mL of Cu(II) solution with an initial concentration of 0.12 mmol·L^{-1} (i.e. 25 mg· L^{-1}). The initial solution pH values was 5.0, and no pH adjustment was performed throughout the adsorption process. The adsorption of Pb(II) ions on the pristine and functionalized PGMA microspheres was allowed to proceed at 25 ^{o}C at 150 rpm for a predetermined period. The residual concentration of Pb(II) ions was analyzed by taking 1.0 mL aliquot of the Pb(II) solution at different time intervals. The adsorbed amounts of Pb(II) ions per unit weight of the microspheres at time *t*, q_t (mg·g^{-1}), were calculated from the following equation: [3]

$$q_t = \frac{(c_0 - c_t) \cdot v}{m} \tag{3}$$

where c_o and c_t correspond to the initial concentration of Pb(II) ions and the Pb(II) concentration at time *t* (mg·L^{-1}), respectively. *v* is the volume of the residual volume at time t, and *m* is the weight of the microspheres added.

S1.4 Adsorption isotherms

The adsorption isotherms were obtained by varying adsorption temperatures of 25, 35, 45, and 55 ^{o}C. The adsorption solution pH was adjusted at 5.0 ± 0.1

throughout the experimental periods with a series of initial concentration of Pb(II) from C_0 = 0.096–0.48 mmol·L^{-1} (i.e. 20–100 mg·L^{-1}). At a predetermined temperature, an aliquot 100 mg of the PGMA-*c*-PA microspheres were added into 100 mL of Pb (II) solutions under continuous stirring at 150 rpm for 2 h. The adsorption amount of Pb (II) ions onto the microspheres at equilibrium was calculated from the above Equation 2. To quantitatively interpret the adsorption isotherms, the Langmuir, Freundlich and Temkin adsorption isotherm models were applied to simulate the experimental data. The Langmuir, Freundlich, and Temkin isotherm models are expressed as the following equations, respectively:[66]

$$q_e = \frac{(K_L \cdot q_{\max} \cdot C_e)}{(1 + K_L \cdot C_e)} \tag{4}$$

$$q_e = K_F \cdot C_e^{1/n} \tag{5}$$

$$qe = \frac{RT}{B_T} \ln A_T + \frac{RT}{B_T} \ln C_e \tag{6}$$

where q_{max} is the maximum adsorption capacity (mmol g^{-1}), K_L represents the adsorption equilibrium constant of Langmuir isotherm model (mmol L^{-1}), C_e is the equilibrium concentration of Pb(II) ions in the solution (mmol L^{-1}), q_e corresponds to the equilibrium adsorption amount (mmol g^{-1}), n is the Freundlich constant depicting the adsorption intensity, K_F is an empirical constant of Freundlich isotherm models, which represent adsorption capacity (mmol$^{(1-1/n)}$ $L^{1/n}$ g^{-1}), A_T is the equilibrium binding constant corresponding to the maximum binding energy (L g^{-1}), B_T is the Temkin constant related to the heat of adsorption (kJ mol^{-1}), R is the gas constant (8.314 ×10^{-3} kJ mol^{-1} K^{-1}), and T is the absolute temperature (K).

S1.5 Competitive adsorption of the coexisting heavy metal ions

To determine the effect of coexisting heavy metal ions on the adsorption behavior of Pb(II) ions on the microspheres, the competition adsorption experiment

was conducted in a quinary ion system with Pb(II), Cu(II), Mg(II) and Ca(II) ions as the coexisting heavy metal ions. Typically, a 100 mg aliquot of the PGMA-*c*-PA microspheres was added to 100 mL of the quinary heavy metal ion solution at 25 ^{o}C and at 150 rpm for 24 h. The initial concentration of each heavy metal ion was 0.12 mmol·L^{-1}, i.e., 25, 7.6, 4.8 and 2.9 mg·L^{-1} for Pb(II), Cu(II), Ca(II) and Mg(II) ions, respectively. The solution pH value remained constant at 5.0 ± 0.1 throughout the sorption periods by adjusting with 0.1 mol·L^{-1} HNO_3 or NaOH solution for every 2 h.

S1.6 Regeneration and recycle of the PGMA-c-PA microspheres

To regenerate the Pb(II)-adsorbed PGMA microspheres for recycle use, the desorption of the PGMA microspheres was performed in a 3 mol·L^{-1} HNO_3 solution. The adsorption experiments were carried out by adding 100 mg of the microspheres in 100 ml of 0.24 mmol·L-1 (i.e., 50 mg·L-1) Pb(II) solution with pH at 5.0 at 25 ^{o}C for 5 h. The desorption of the Pb(II)-loaded PGMA microspheres was conducted in 50 mL of 3 mol·L^{-1} HNO_3 solution at 25 ^{o}C at 150 rpm for 1 h. The sorption-desorption experiments were conducted for five cycles to evaluate the regeneration capacity of the functionalized PGMA microspheres.

S2. Results and Discussion

Table S1 Comparison adsorption of Pb(II) ions on various adsorbent materials

Adsorbents	Equilibrium time (hours)	C_0 (ppm)	pH values	q_{max} (mmol·g^{-1})	Refs
Ethylenediamine-modified silica	6	50-600	5-6	0.184	23
succinic anhydride-modified Sugarcane bagasse	10	430-650	2.6-5.5	2.011	30
P(MMA-HEMA) adsorbent	8	10-350	5	0.152	36
Mesoporous carbon stabilized alumina	6	250	5.0	1.137	20
Magnetic Fe_3O_4 nanoparticles	3	25-100	5.0	0.256	14
Phosphoric acid-modified PS-EDTA resin	24	50-500	6.0	0.921	31
Magnetic amine-modified activated carbon	20	20-250	5.2	0.503	15
Poly(3-sulfopropyl methacrylate) modified PVBC microspheres	24	50-200	5.0	0.82	66
PGMA-c-PA microspheres	**5**	**20-100**	**5.0**	**0.335**	**This study**

Table S2. The fitted kinetic parameters for the desorption of the Pb(II)-loaded PGMA-*c*-PA microspheres at a temperature of 298.15K

Models	Model parameters				
	k_f (min^{-1})	k_s ($g \cdot mmol^{-1}min^{-1}$)	q_{max} ($mmol \cdot g^{-1}$)	χ^2	R^2
PFO	1.866	--	0.169	$4.565E^{-4}$	0.998
PSO	--	72.742	0.171	$2.208E^{-6}$	0.999

Table S3 Thomas Fitted parameters of the breakthrough curves for the column adsorption of Pb(II) ions on the PGMA-*c*-PA microspheres at different hydraulic loading rates of 3 and 5 mL·min^{-1}

Sample	Parameters				
	θ (mL·min^{-1})	K_T (min^{-1})	q_b (mmol·g^{-1})	χ^2 (x 10^{-4})	R^2
PGMA-*c*-PA	3	0.130	0.749	1.78	0.993
	5	0.197	0.432	0.997	0.997

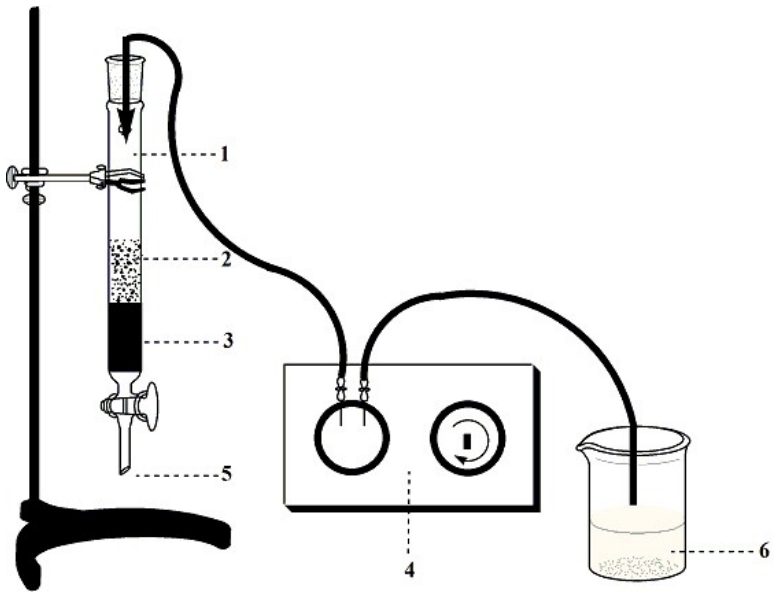

Fig. S1 Schematic illustration of the column adsorption apparatus for Pb(II) ions.

1 Glass column, 2 adsorbent resin, 3 glass sand, 4 peristaltic pump, 5 column outlet, 6 water bath

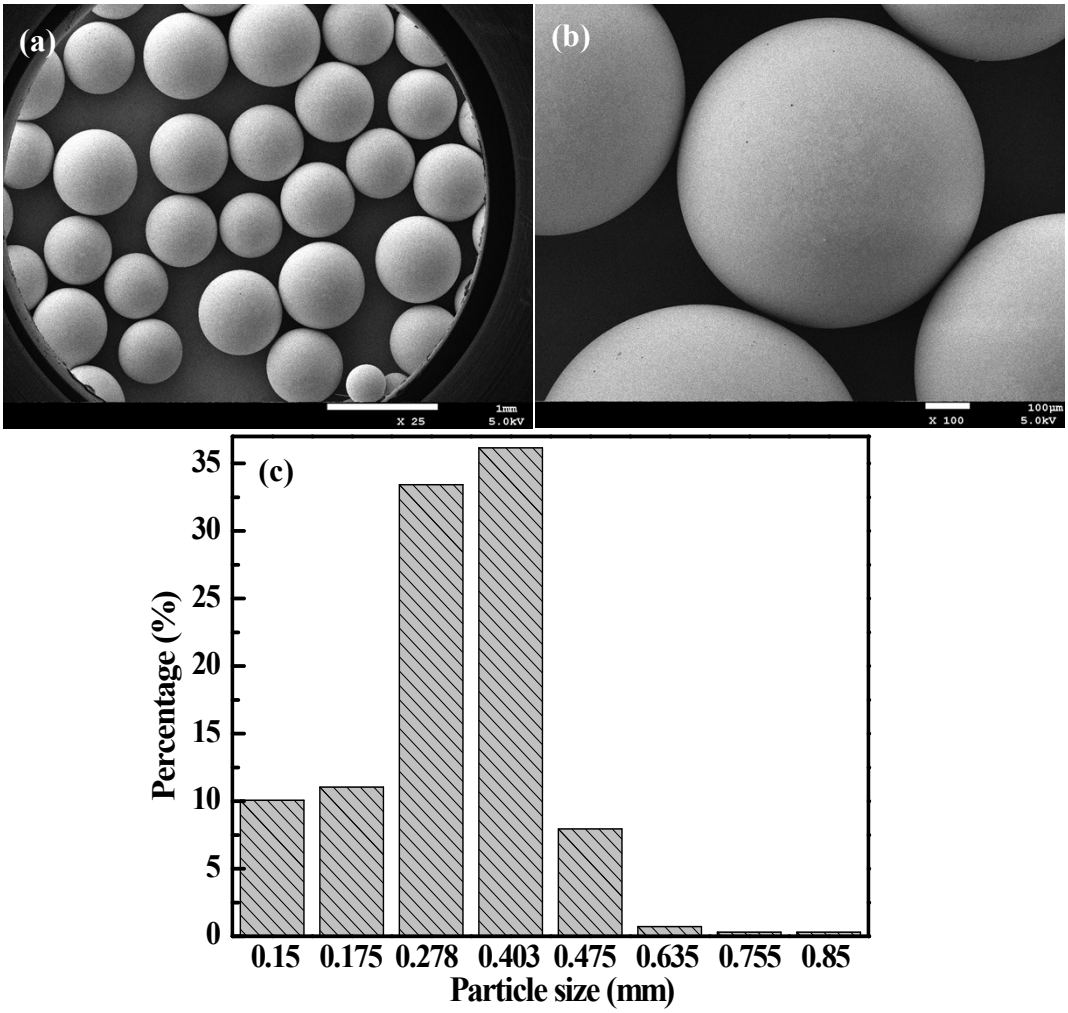

Fig. S2 SEM images of the as-synthesized PGMA microspheres at different magnifications of (a) 20× and (b) 100× using suspension polymerization, (c) the size distribution of the as-synthesized PGMA microspheres. Reaction conditions: temperature 373.15 K, stirring speed 400 rpm, reaction time 8 h.

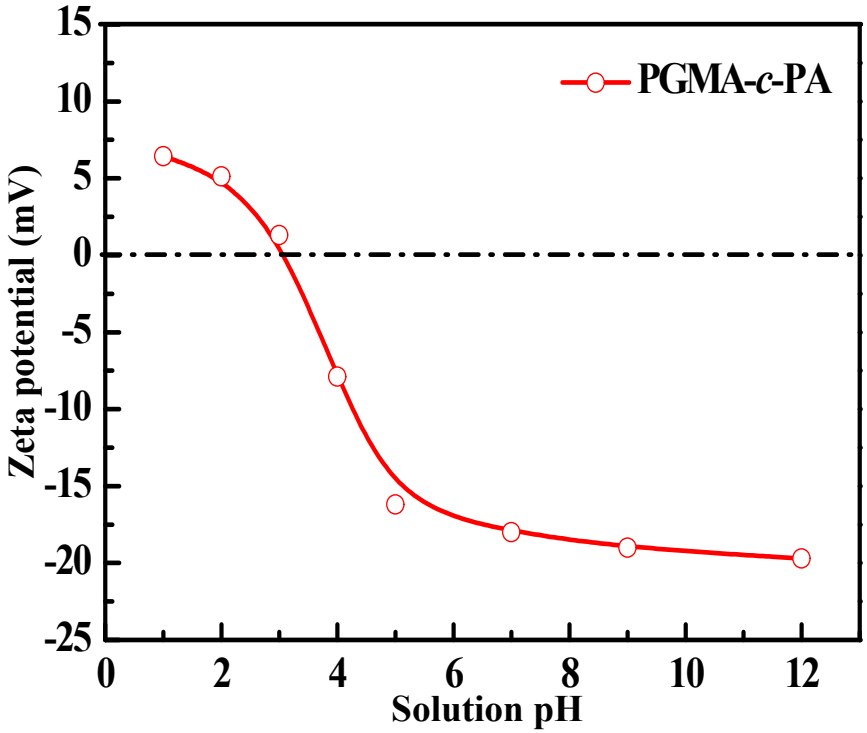

Fig. S3 The change in zeta potential of the PGMA-*c*-PA microspheres as a function of solution pH. The point of zero charge (pzc) of the adsorbent appears at solution pH of 3.2.

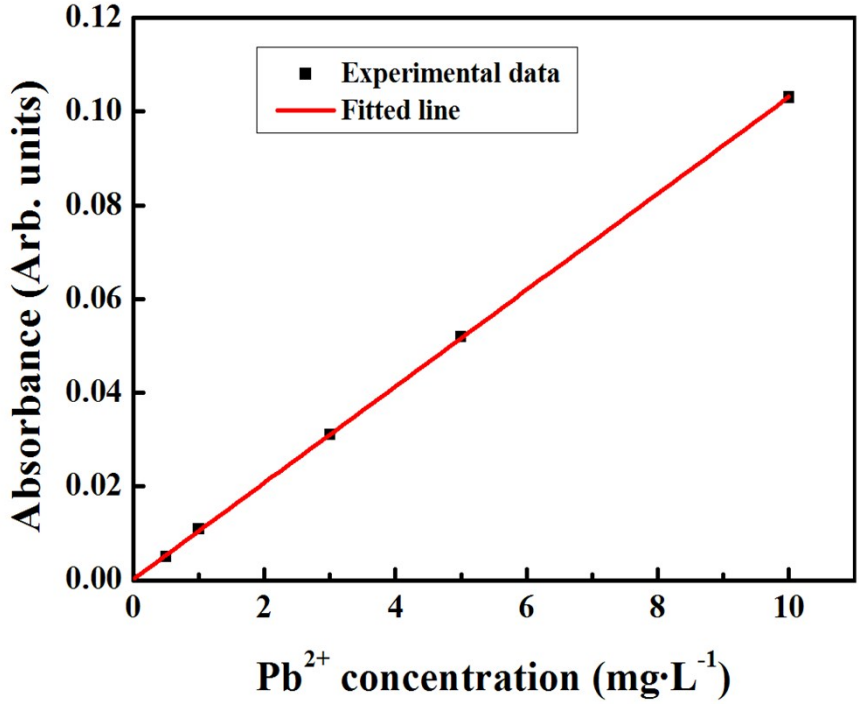

Fig. S4 The linearly-fitted calibration curve of Pb(II) ions in a concentration ranges from 0 to 10 mg·L^{-1}.

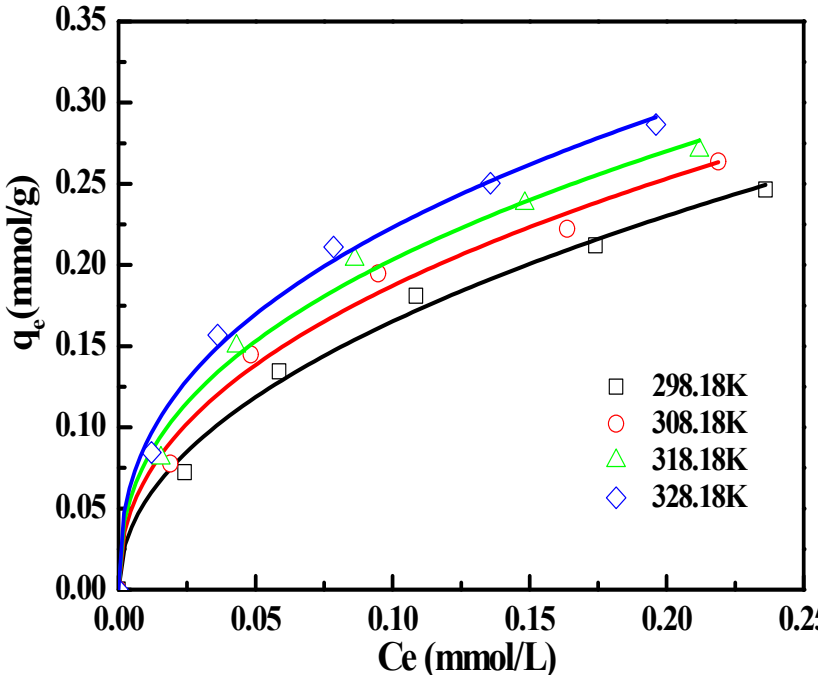

Fig. S5 Freundlich-fitted adsorption isotherms of Pb(II) on the PGMA-*c*-PA resins at different temperatures. Experimental conditions: C_0 = 0.096 - 0.48 mmol·g^{-1} (i.e., 20 - 100 ppm), m = 100 mg, v = 100 ml, t = 5 h, and initial solution pH = 5.0.

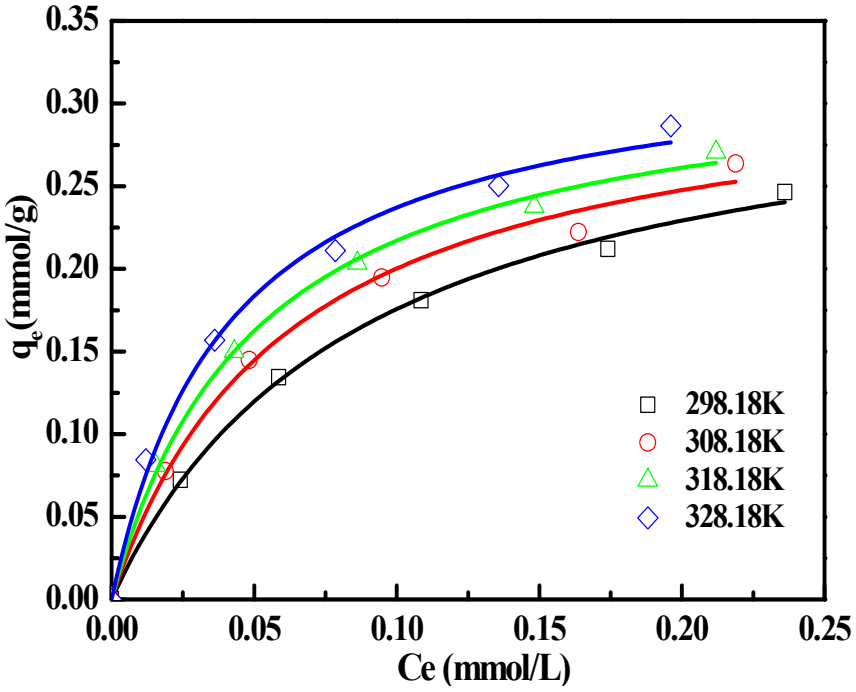

Fig. S6 Temkin-fitted adsorption isotherms of Pb(II) on the PGMA-*c*-PA resins at different temperatures. Experimental conditions: C_0 = 0.096 - 0.48 mmol·g^{-1} (i.e., 20 - 100 ppm), m = 100 mg, v = 100 ml, t = 5 h, and initial solution pH = 5.0.

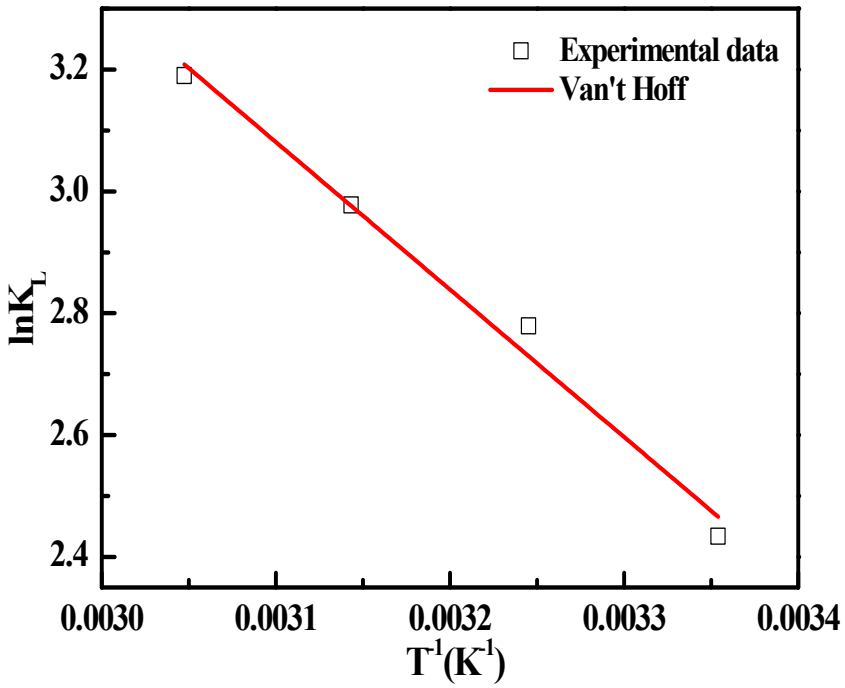

Fig. S7 Van't Hoff plot for the adsorption of Pb(II) ions on the PGMA-*c*-PA resins

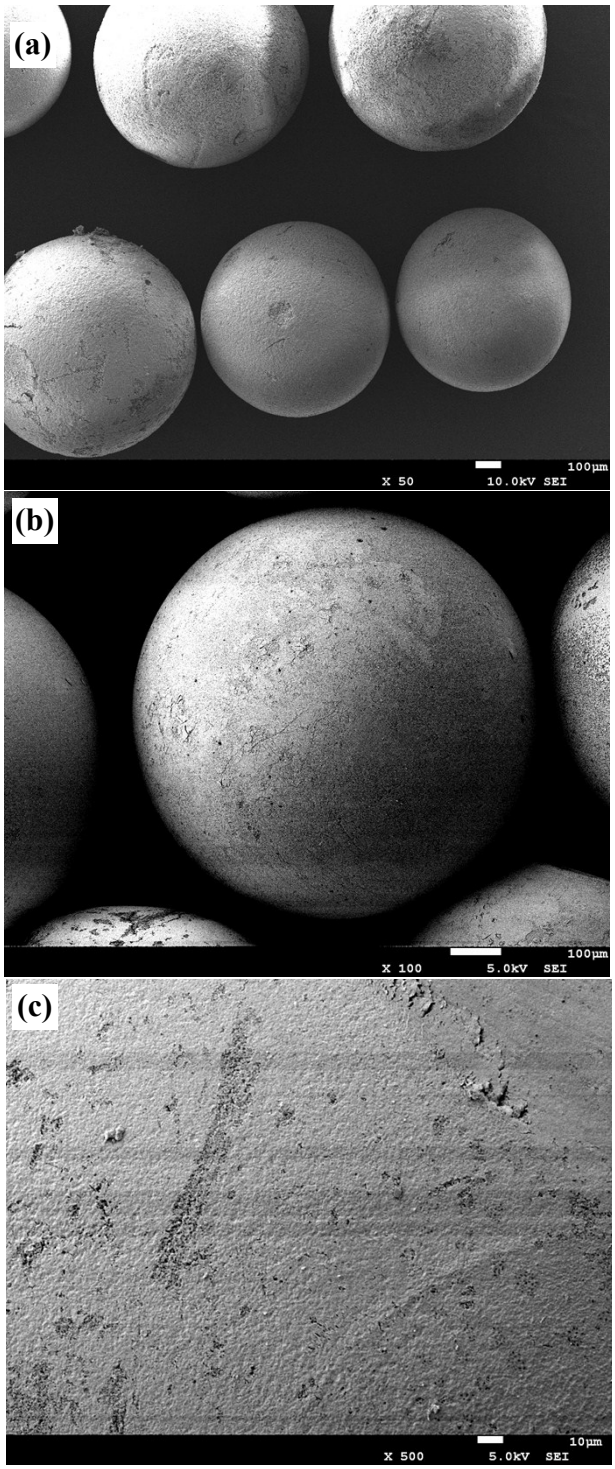

Fig. S8 Representative SEM images of the PGMA-*c*-PA microspheres after desorption in a 3 $mol^{\cdot -1}$ of HNO_3 solution for 180 min.

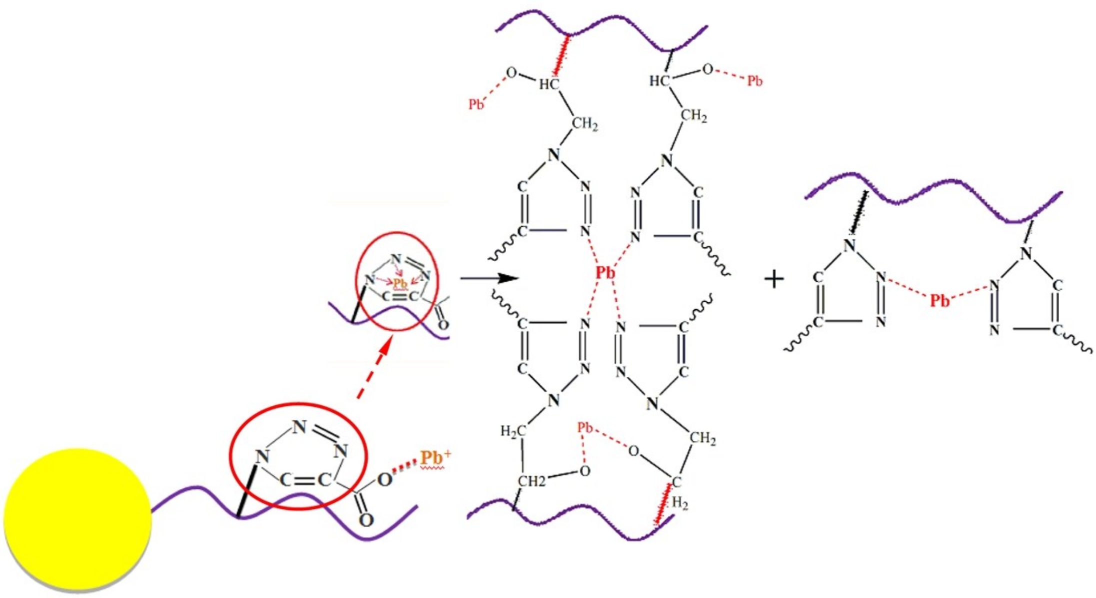

Fig. S9 Schematic illustration of the postulated mechanism of Pb(II) adsorption on the PGMA-*c*-PA microspheres via ion exchange and surface chelation (complexation).

Reference

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