Supporting Information For

Selective removal Pb(II) ions form wastewater using Pb(II) ion-imprinted polymers with bi-component polymer brushes

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Experimental

Materials and chemicals

2-Phenyl-2-propyl benzodithioate(CDB), 3-allylrhodanine was obtained from Sigma Aldrich(Shanghai, China). Styrene, 2-hydroxyethyl methacylate(HEMA) were obtained from J&K Scientific Ltd.(Beijing, China). Ethylene glycol dimethacrylate(EGDMA), 2,2-azobisisobutyronitrile(AIBN) were bought from J&K Scientific Ltd.(Beijing, China). Lead nitrate ($Pb(NO_3)_2$), chromium nitrate nonahydrate($Cr(NO_3)_2•9H_2O$), zinc nitrate hexahydrate ($Zn(NO_3)_2•6H_2O$) and nickel nitrate hexahydrate ($Ni(NO_3)_2•6H_2O$) were purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). All chemicals used in the experiments were of

analytical grade or better. Reagent water (18.2 MΩ-cm at 25°C) was purified by a Millipore water purification system (Bedford, USA).

Apparatus

The morphology of all samples were studied by a SSX-550 scanning electron microscope (SEM, Shimadzu, Japan). X-ray photoelectron spectroscopy (XPS, Kratos, UK) were record by a Kratos XSAM800 spectrometer using Al target (1486.6 eV) X ray source. Infrared (IR) spectroscopy measurements were recorded with a Bruker (Ettlingen, Germany) Vertex 70 FTIR spectrophotometer. The particle sizes of adsorbents were measured by Nano ZS90 Zeta potential analyzer (Malvern, UK). TGA Q600 SDT thermogravimetric analyzer (TA, New Castle, USA). A ContrAA 700 (AAS, Analytik Jena, Germany) high-resolution continuum source atomic absorption spectrometer was used for determination of Pb(II) ion. The wavelength was set at 217.0005 nm, all measurements were performed in an air/acetylene flame.

A gel permeation chromatograph (GPC) which was equipped with a Waters 2414 refractive index detectors, Waters 515 Pump and two Waters UltraStyragel columns with 500–30 K and 100–10 K molecular ranges (the temperature of the column oven was 35℃).A solution of THF was used as the mobile phase with a flow rate of 1.0 mL min-l, and the calibration curve was obtained by using polystyrene (PS) standards.

Synthesis of RAFT-IIP/NIP and grafted-IIP/NIP microspheres by RAFTPP

RAFT-IIP/NIP microspheres surface immobilized dithioester groups by adding chain transfer reagent. The detail steps are as follows: monomer 3-allylrhodanine, template ion Pb(II), and a mixture of methanol and water were added into round bottom flask and stirring 30 min at room temperature. Following added EGDMA, AIBN and CDB into flask then being purged with argon for 30 min, the reaction system was sealed and stirred in an oil bath 70°C for 24 h. The resulting polymer particles were collected by filtration. For comparison, the RAFT-NIP were also prepared and treated under identical conditions without adding Pb(II) ion.

Synthesis of the grafted-IIP/NIP microspheres with surface grafted with PHEMA and PS bi-component brushes (grafted-IIP/NIP) by the surface initiated RAFT polymerization as following procedure: the RAFT-IIP/NIP microspheres, HEMA and styrene (according to mole ratio of 9:1), CDB, AIBN, methanol were added into round-bottom flask following, then sealed and immersed in an oil bath at 70°C and stirred for 24 h. The resulting solid products were then dried at 30°C under vacuum to the constant weights, leading to light pink RAFT-IIP/NIP microspheres grafting bi-components polymer brushes with a weight increase.

Synthesis of three kinds of particle sizes of SiO_2

The detail synthesized steps are as follows: 230 ml anhydrous ethanol, 90 g deionized water and 1.2 g strong aqua ammoniac were added into 500 ml round bottom flask, stirring at room temperature 20 min to mixed into a homogeneous solution. Then 2.08 g, 2.5 g and 3.0 g ethyl orthosilicate (TEOS) were dispersed in 10 ml anhydrous ethanol and mixed into a homogeneous solution, and then put into a constant voltage funnel, respectively. Then the homogeneous solutions were slowly driped into the 500 ml round bottom flask, using mechanical stirring until the reaction systems changed into plained and stable inverted micelles solution, then centrifugal separation, washing three times with ethanol under ultrasonic after reaction. The three kinds of particle size of SiO_2 white powder were prepared well after drying.

Bi-component polymer brushes characterize of A gel permeation chromatograph (GPC)

The average surface grafting densities of bi-component polymer brushes (β) was defined as an equation: $\Delta W\% = (S_{BET} \times M_n \times \beta) / N_A$ □ (2)

where ΔW is the increased weight percentage for RAFT-IIP, N_A is the Avogadro constant, M_n is the molecular weight of bi-component polymer brushes, and S_{BET} is the BET of the RAFT-IIP detected using N_2 adsorption–desorption isotherms.

Batch adsorption experiments

To assess the selectivity of the RAFT-IIP/NIP and graft-IIP/NIP toward Pb(II) ions in presence of various ion, Pb(II), Cr(II), Zn(II), Co(II) and Ni(II) ions were chosen to make up a mixture solution with each of metal ion concentration 500 mg/L. After a competitive adsorption experiments, the concentrations of Pb(II), Cr(II), Zn(II), Co(II) and Ni(II) ions in the remaining samples were detected by AAS. The following equations were used to evaluate the selectivity of sorbents.

Static distribution coefficient:

$$K_D = \frac{Q_e}{C_e} \tag{3}$$

Selectivity coefficient:

$$\alpha = \frac{K_{D_1}}{K_{D_2}} \tag{4}$$

Relative selectivity coefficient :

$$\beta = \frac{\alpha_1}{\alpha_2} \tag{5}$$

where Q_e (mg/g) represents the adsorption equilibrium capacity and C_e (mg/L) is the equilibrium concentration; K_{D1} and K_{D2} were represent the distribution coefficients of Pb(II) ions and the distribution ratio of Cr(II), Zn(II), Co(II) and Ni(II); β is the relative selectivity coefficient; $\alpha_1$and α_2 represent the selectivity factor of imprinted sorbents and nonimprinted sorbents, respectively.

Adsorption isotherm Experiments

The Langmuir and Freundlich nonlinear isotherms model were used to evaluate the potential use of imprinting polymers for specific metal ions adsorption applications. The Langmuir model was applied to describe adsorption have occurred on specific uniform monolayers on homogeneous surfaces and adsorption capacity is the amount of the metal to take up all the available sites per unit mass of the sample.[50] while the Freundlich model is an empirical formula, it corresponds to the type and the

nonuniform adsorption theories of the relationship between the adsorption capacity and adsorption considers the heterogenic nature of adsorbent surfaces and could represent mono and multilayer adsorption.[51] Nonlinear regression was applied to determine the adsorption parameters for isotherm models according to the following:

Langmuir model:

$$q_e = \frac{q_m K_L C_e}{1 + K_L C_e} \tag{6}$$

Freundlich model:

$$q_e = K_f C_e^{1/n} \tag{7}$$

Where q_e (mg/g) and C_e (mg/L) are the equilibrium metal ion concentration on imprinted polymer and the equilibrium metal ion concentration in the solution at equilibrium, respectively. q_m (mg/g) is the monolayer maximum adsorption capacity at equilibrium and K_L (L/mg) is a constant related to the free energy of adsorption. K_f (mg/L) is an adsorption capacity related constant and n is an adsorption strength related constant.

Adsorption kinetic Experiments

Adsorption kinetics is important in the prediction of the rate at which Pb(II) can be removed by RAFT-IIP/NIP and grafted-IIP/NIP. To research the sorption rate of Pb(II) the pseudo-first-order (Eq. (8)) and the pseudo-second-order (Eq. (9)) models were applied to depict the sorption kinetic data.

$$q_t = q_e(1 - \exp(-k_1 t)) \tag{8}$$

$$q_t = q_e\left(1 - \frac{1}{1 + q_e k_2 t}\right) \tag{9}$$

where q_t (mg/g) and q_e (mg/g) are the amounts of Pb(II) adsorbed onto the RAFT-IIP/NIP and grafted-IIP/NIP at any time and at equilibrium, respectively, and k_1

(L/min) and k_2 (g/(mg·min)) are pseudo-first-order and pseudo-second-order kinetic rate constant.

Adsorbents regeneration

The RAFT-IIP and grafted-IIP was eluted with 0.5 M HCl until Pb(II) ion was not determined in elution solutions, then the RAFT-IIP and grafted-IIP were washed three times using deionized water.

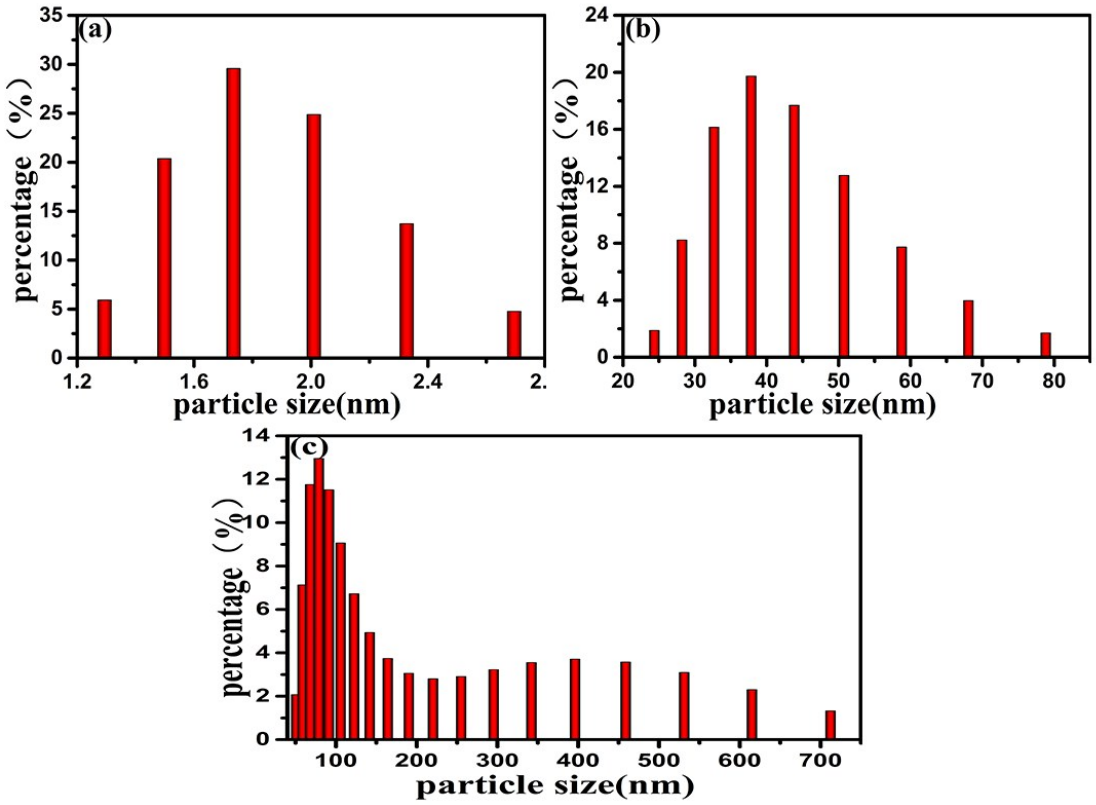

Fig.S1 the size distribution of SiO_2, the 1~3 nm particle size of SiO_2 (a), the 30~70 nm particle size of SiO_2 (b), the 70~700 nm particle size of SiO_2 (c).

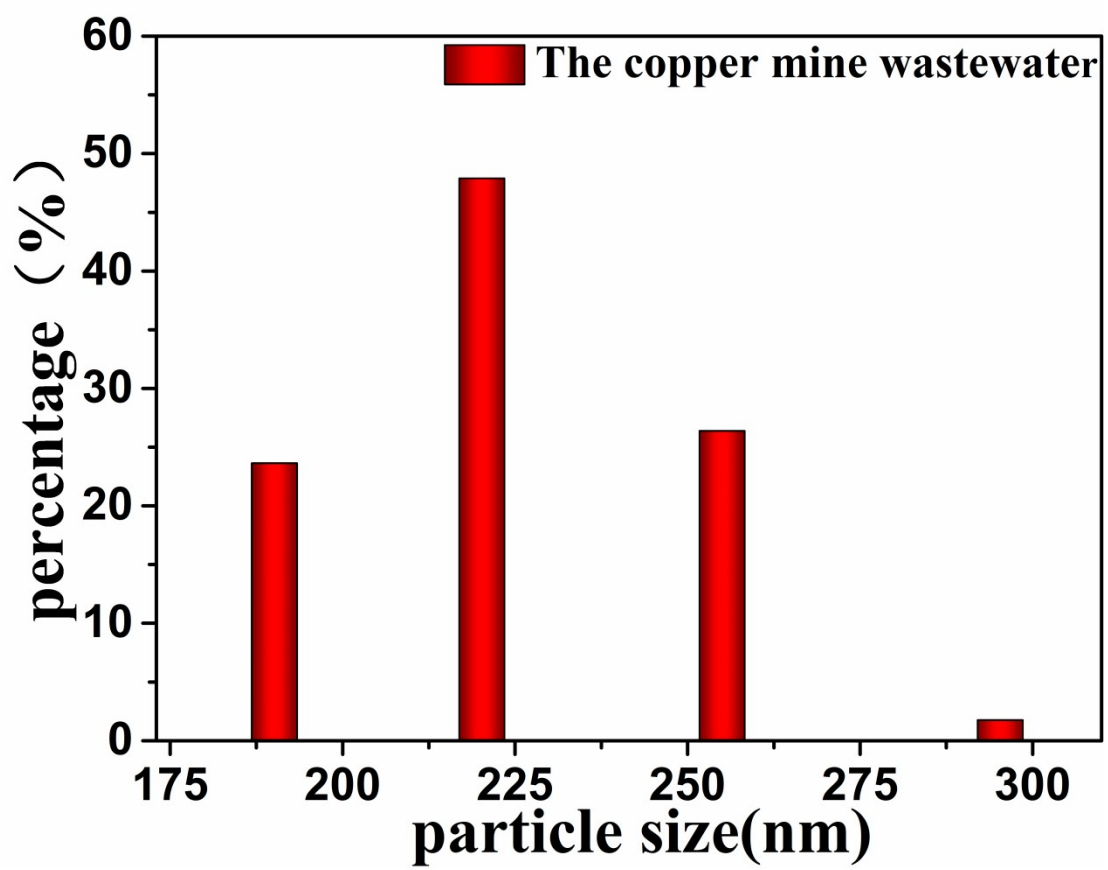

Fig.S2 the solid particles distribution of the Copper wastewater.

Fig.S3 the digital image of the products before and after adsorption process

Table S1 Bi-component properties of grafted RAFT-IIP/NIP via RAFT Polymerization

	RAFT-IIP	grafted-IIP/NIP		
	S_{BET} (m^2/g)	Mn, GPC	PDI	β
grafted-IIP	1.7677	55907	36266	0.72
grafted-NIP	1.5259	1.01	1.02	1.10