Supplementary Information

Simultaneous Removal of Phenol and Pb^{2+} from the Mixed Solution by Zwitterionic Poly(sulfobetaine methacrylate)-grafted PVBC Microspheres

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S1. Experimental Section

S1.1 Materials

Sulfobetaine methacrylate (SBMA, 97%), ethylene glycol dimethacrylate (EGDMA, 98%), *N,N,N′,N″,N″*-pentamethyldiethylenetriamine (PMDETA, 99%), 4-vinylbenzyl chloride (VBC, 90%), poly(vinyl alcohol) (PVA, 87–89% hydrolyzed average MW 20,000), cupric chloride ($CuCl_2$, 99%), cuprous chloride (CuCl, 97%) and Pb(II) standard solution (1000 $mg \cdot L^{-1}$) were obtained from Sigma-Aldrich Chemical Co. (St. Louis, MO, USA). Chemical reagents such as 4-aminoantipyrine, potassium ferricyanide ($K_3Fe(CN)_6$, 99.95%) and 2,2'-azobis-(2-methylpropionitrile) (AIBN, 97%) were purchased from Best Reagent Co. (Chengdu, China). Other chemical reagents, including *N,N′*-dimethylformamide (DMF, 98%), phenol, sodium hydroxide, nitric acid, ethanol, tetrahydrofuran (THF), and toluene were obtained from Kelong Chemical Co. (Chengdu, China). All the reagents were analytical grade and were used as received, unless otherwise stated. An Ulupure reverse osmosis system (Ultrapure Technology Co., Chengdu, China) were utilized to collect deionized water for all the following experiments.

S1.2 Grafting density of PSBMA brushes on the PVBC mictrospheres

The grafting yield (GY) of PSBMA brushes on the surfaces of PVBC microspheres was controlled by varying the polymerization time. The increase in the mass percentage of the PVBC-*g*-PSBMA microspheres was determined to calculate the GY values using the previously-established equation:

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

where W_g and W_o denoted the mass of the dry microspheres before and after grafting of PSBMA brushes, respectively. The change in grafting density (GD) of the PSBMA brushes

as a function of ATRP reaction time was calculated by the previously-established equation:

$$GD = \frac{\mathrm{GY}}{M} \tag{2}$$

where M was the molecular weight of the SBMA repeat unit at 279.35 g·mol^{-1} of the PSBMA chains. The GY and GD values were averaged from at least three replicate measurement.

S1.3 Adsorption kinetics

To determine adsorption kinetics of the PVBC-*g*-PSBMA2 microspheres towards phenol and Pb(II) ions, the initial concentration of phenol and Pb(II) ion were 2.13 and 0.48 mmol·L^{-1} (i.e., 200 and 100 ppm), respectively. The 0.1 mol·L^{-1} NaOH and nitric acid were used to adjust the solution pH. The adsorption was allowed to proceed at 298.15 K for a predetermined time. The residual concentrations of Pb(II) and phenol were analyzed by taking aliquots of 1.0 mL solution at diffferent time intervals. The adsorbed amount of Pb(II) and phenol per unit weight of the as-synthesized microspheres at time t, q_t (mg·g^{-1}), were derived from the following equation:

$$q_t = \frac{(\mathrm{C}_o - C_t)V}{m} \tag{3}$$

where C_o and C_t denoted the initial concentraiton of Pb(II) and phenol, as well as the concentration of Pb(II) and phenol at time t, V was the residual volume of adsorption solution at time t, and m was the added microsphere mass.

S1.4 Adsorption isotherms

To determine the adsorption isotherms of PVBC-*g*-PSBMA2 microspheres towards phenol and Pb(II) ions, the initial concentration of phenol was between 0.53-4.25 mmol·L^{-1} (50-400 mg·L^{-1}), and that of Pb(II) ion was about 0.12-0.97 mmol·L^{-1}(50-200 mg·L^{-1}). The adsorption reaction temperature was controlled at 298.15 K, 308.15 K and 318.15 K, respectively. The equilibrium adsorption capacity (q_e, mg L^{-1}) and adsorption capacity (q_t, mg L^{-1}) at certain time of phenol and Pb(II) ion from solutions was calculated by equations

as follows:

$$q_e = \frac{(C_o - C_e)V}{m} \quad (4)$$

where C_0 (mg L^{-1}) is the initial concentration, C_t and C_e (mg L^{-1}) are the concentrations of phenol and Pb(II) ion at time t (min) and at equilibrium, respectively. V (L) is the aqueous solution volume, m (g) is the adsorbents mass.

S1.5 Regeneration of the PVBC-*g*-PSBMA2 microspheres

The target pollutants-loaded PVBC-*g*-PSBMA2 was regenerated with 1 mol·L^{-1} nitric acid and 0.1 mol·L^{-1}sodium hydroxide solution in turn described as below. Briefly, the adsorption experiments were conducted with 50 mg of the fresh PVBC-*g*-PSBMA2 in 100 mL of 2.13 mmol·L^{-1}phenol and 0.48 mmol·L^{-1} Pb(II) ion solution (pH at 5) at 25 ^{o}C for 120 min. Subsequently, the target pollutants-loaded PVBC-g-PSBMA2 was reclaimed by filtration, and was in turn infused in 200 mL of 1 mol·L^{-1} nitric acid solution and 200 mL of 0.1 mol·L^{-1} sodium hydroxide solution to desorb the target pollutants. At last, the refreshed absorbents reclaimed, washed, and reused for adsorption of phenol and Pb(II) ion solution under the same condition. The adsorption-desorption cycle test was performed for five times.

S2. Results and Discussion

Table S1 Equilibrium constant of Pb(II) hydrolysis reactions

Hydrolysis reactions	*LogK*
$Pb^{2+} + H_2O \rightarrow PbOH^+ + H^+$	-7.597
$Pb^{2+} + 2H_2O \rightarrow Pb(OH)_2 + 2H^+$	-17.12
$Pb^{2+} + 3H_2O \rightarrow Pb(OH)_3^- + 3H^+$	28.06
$Pb^{2+} + 4H_2O \rightarrow Pb(OH)_4^{2-} + 4H^+$	-39.70
$2Pb^{2+} + 3H_2O \rightarrow Pb_2(OH)_3^+ + H^+$	-6.397
$3Pb^{2+} + 4H_2O \rightarrow Pb_3(OH)_4^{2+} + 4H^+$	-23.888
$4Pb^{2+} + 4H_2O \rightarrow Pb_4(OH)_4^{4+} + 4H^+$	-19.988

Table S2 Comparison of adsorption capacity of Pb(II) and phenol-type pollutants by different bifunctional adsorbents reported in the literatures.

Adsorbents	pH	q_{max} of phenol and derives (mg/g)	q_{max} of Pb(II) (mg/g)	Equilibrium time (hours)	Reference
Carbon nanotubes/$CoFe_2O_4$ magnetic hybrid material	6.0	42.5	140.1	10	[53]
Organoclays	6.0	96.2	33.8	0.5	[54]
β-cyclodextrin modified graphene oxide nanosheets	6.0	207.6	149.6	24	[55]
Porous PU@PDA@MSNs sponge	6.0	184.2	104.2	10	[56]
Amino and thiol-modified magnetic multi-walled CNTS	6.0	39.0	195.8	0.5	[57]
Amphiphilic hybrid material ATP-P(S-b-DVB-g-AO)	5.0	18.2	131.6	6	[58]
Ammonium-functionalized activated carbon micro-/nano-fibers	6.8	290	40.0	12	[59]
Anaerobic granular sludge	4.0	30.8	101.8	24	[60]
Nitrogen-functionalized magnetic ordered mesoporous carbon	7.0	185.5	159.9	1.0	[13]
PVBC-g-PSBMA2	**5.0**	**134.6**	**205.1**	**2.0**	**This work**

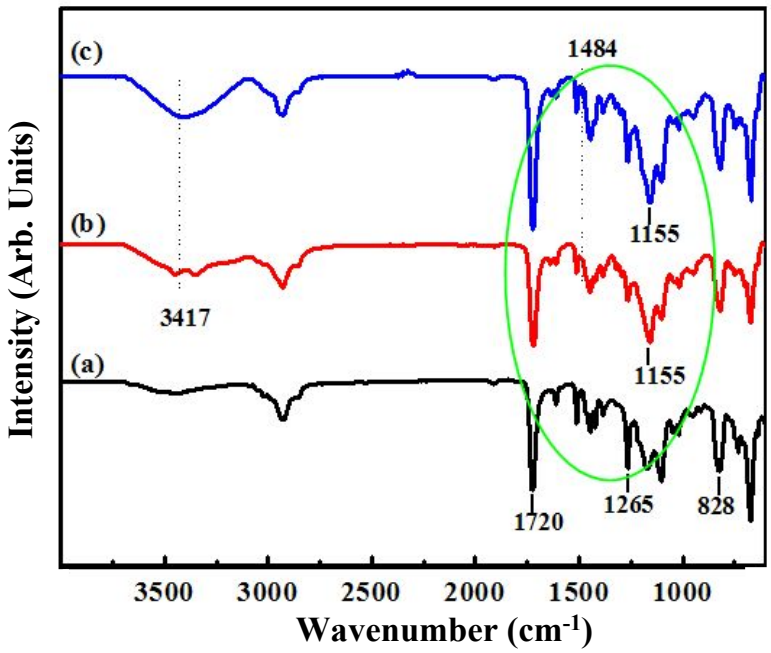

Figure S1 The ATR-FTIR spectra for the surfaces of (a) the cross-linked PVBC microspheres, (b) the PVBC-*g*-PSBMA1 microspheres from 2 h of ATRP reaction, and (c) the PVBC-*g*-PSBMA2 microspheres from 8 h of ATRP reaction.

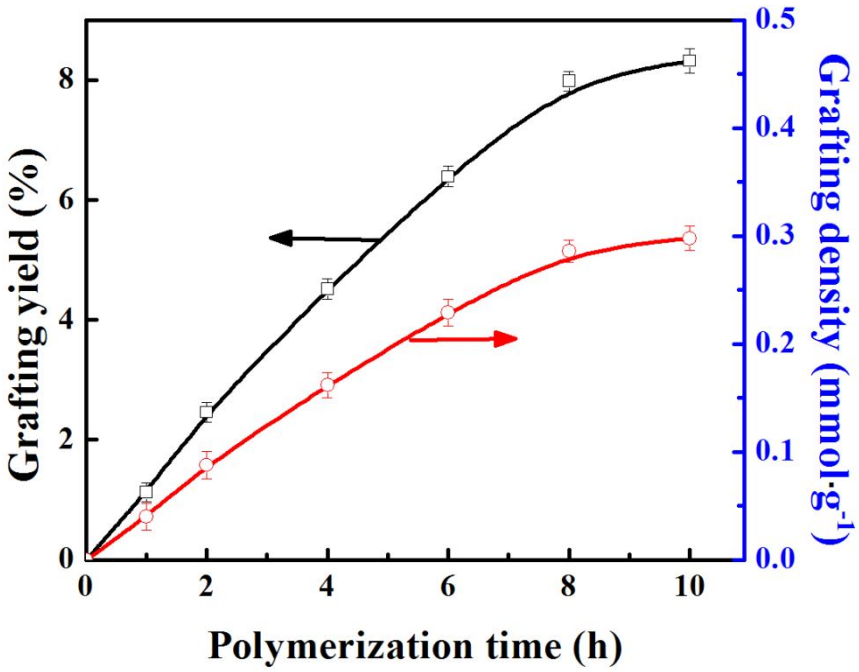

Figure S2 The change in the graft yield (GY) and grafting density (GD) of the zwitterionic PSBMA brushes grafted on the PVBC-*g*-PSBMA surfaces as a function of ATRP time.

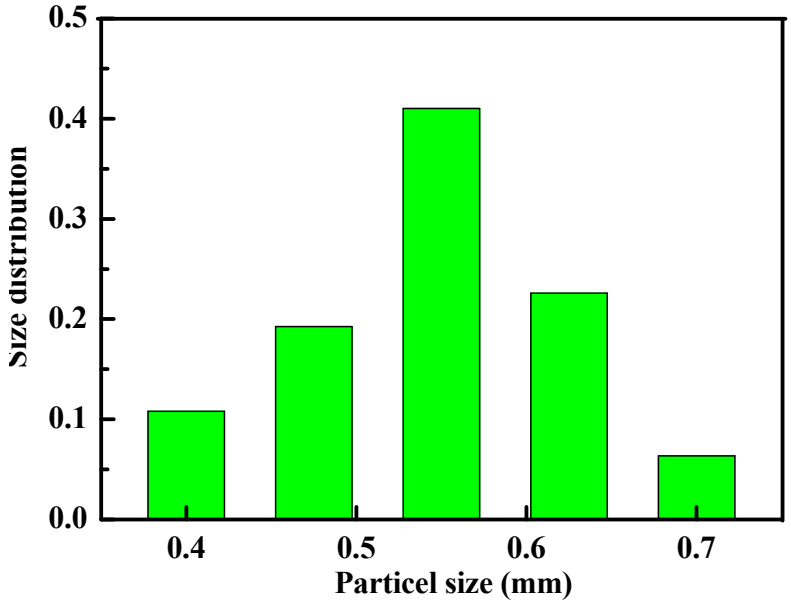

Figure S3 The particle size and size distribution of the pristine PVBC microspheres upon sieving with Tyler Standard Sieve in a range of 400-700 μm

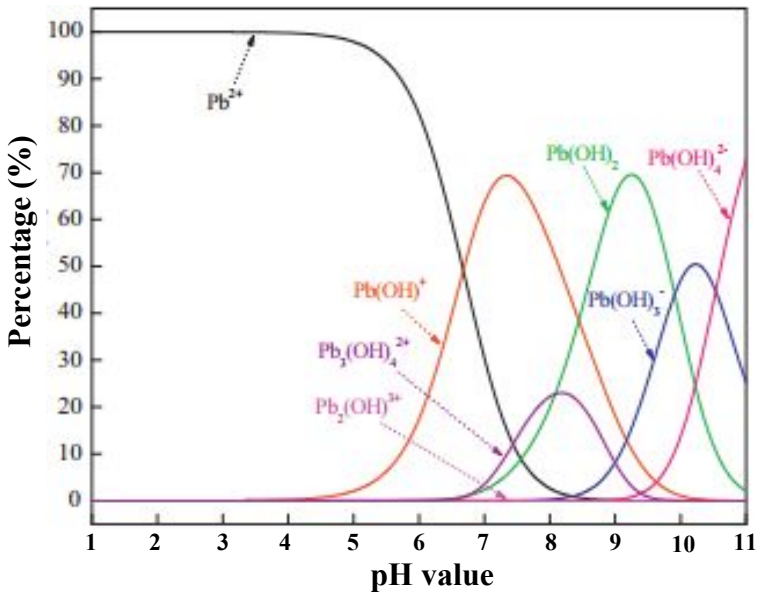

Figure S4 The distribution of Pb(II) species as a function of pH value in a 0.483 mmol·L^{-1} $Pb(NO_3)_2$ solution at the initial concentration of Pb(II) ions at 100 mg/L (ppm).

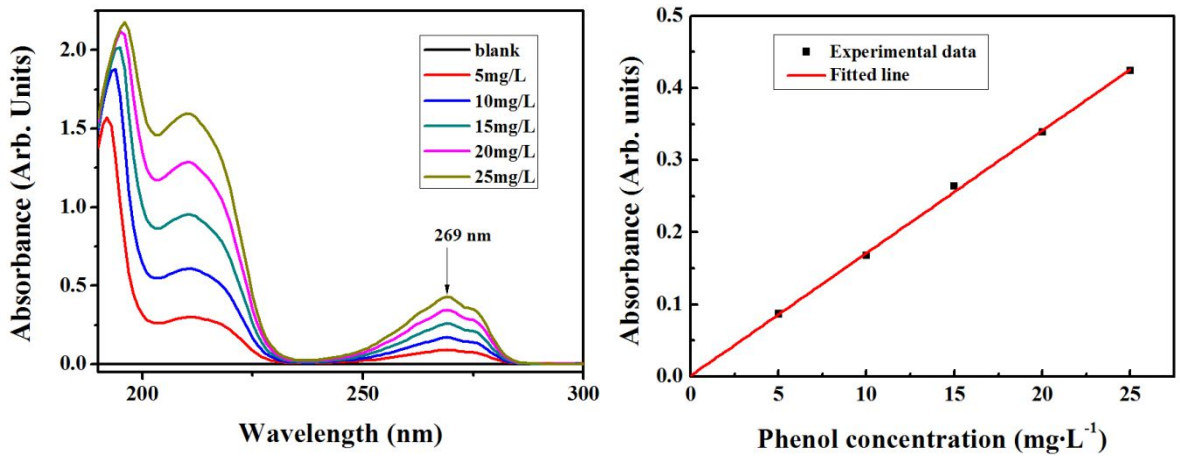

Fig. S5 (a) The UV spectrum profiles as a function of the concentration of aqueous phenol solution and (b) the calibration curves of the aqueous phenol solution at a concentration of 5, 10, 15, 20 and 25 mg·L^{-1}.

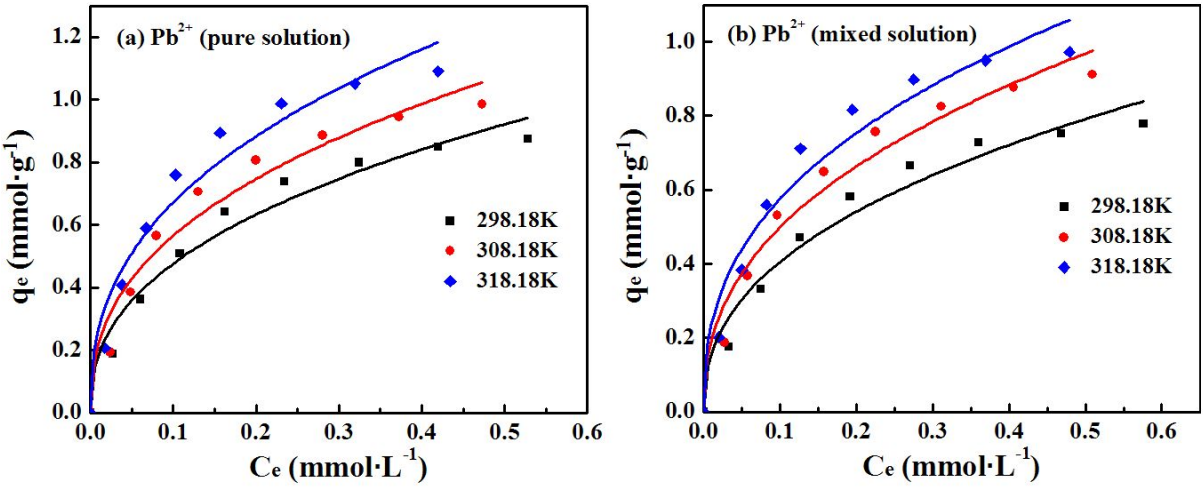

Figure S6. Freundlich-fitted adsorption isotherms of Pb(II) on the PVBC-*g*-PSBMA2 microspheres at 298.15, 308.15 and 318.15 K in (a) pure solution, (b) mixed solution. Experimental conditions: $C_0(Pb^{2+})$ = 0.12 – 0.97 mmol·L^{-1} (i.e. 50 - 200 mg·L^{-1}), C_0 (phenol) = 2.13 mmol·L^{-1} (i.e. 200 mg·L^{-1}), m = 50 mg, v = 100 mL, t = 2 h, and initial pH =5.0.

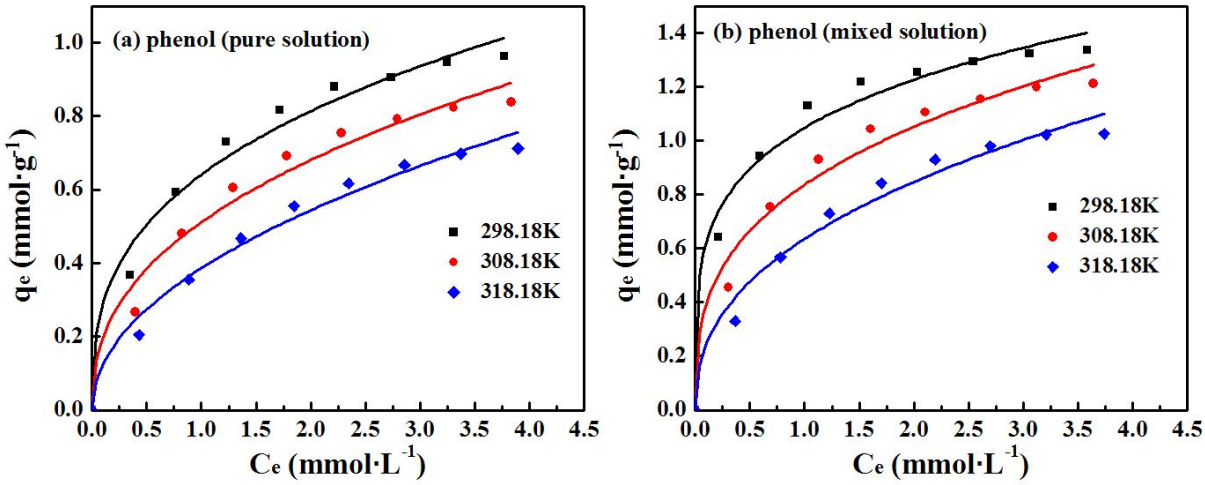

Figure S7. Freundlich-fitted adsorption isotherms of phenol on the PVBC-*g*-PSBMA2 microspheres at 298.15, 308.15 and 318.15 K in (a) pure solution, (b) mixed solution. Experimental conditions: $C_0(Pb^{2+})$ = 0.483 mmol·L^{-1} (i.e. 200 mg·L^{-1}), C_0(phenol) = 0.53 – 4.25 mmol·L^{-1} (i.e. 50 - 400 mg·L^{-1}), m = 50 mg, v = 100 mL, t = 2 h, and initial pH =5.0.