Electronic Supplementary Information

In situ decoration of La(OH)₃ on polyethyleneimine linked dendritic mesoporous silica nanospheres targeting at efficient and simultaneous removal of phosphate and Congo red

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S1 Experimental

1.1 Materials

Cetyltrimethylammonium bromide (CTAB, 99%), tetraethyl orthosilicate (TEOS, 98%), sodium trifluoroacetate (TFC) and polyethylenimine (PEI, molecular weight: 10000) were purchased from Aladdin Industrial Corporation (Shanghai, China). Triethanolamine (TEA, 98%) and La(NO₃)₃·6H₂O (99.9%) were purchased from Aladdin Industrial Corporation (Shanghai, China). Ethanol, glutaraldehyde, methyl alcohol, NaOH, concentrated HCl, concentrated H₂SO₄, KH₂PO₄, and CR were analytical grade and purchased from Sinopharm Chemical Reagent Co. (Shanghai, China). All the chemicals and reagents were used without further purification.

1.2 Synthesis of adsorbents

1.2.1 Synthesis of DMS

Typically, 380 mg CTAB and a certain amount of TFC (molar ratio of TFC : CTAB = 0.2, 0.4, and 0.5) were added to 25 mL DI water in which 68 mg TEA was dissolved. The mixture was stirred in a water bath at 80 °C for 1 h and then 4 mL TEOS was added. Afterwards, it was kept stirring for another 2 h at 80 °C. The solids were collected by centrifugation at 7500 rpm for 40 min, washed thoroughly with 50% ethanol/water solution for three times and dried overnight at 60 °C. The final product was obtained after calcinating the solids at 550 °C in air for 6 h and named as DMS-x (x = 0.2, 0.4, and 0.5, respectively), where x refers to the molar ratio of TFC to CTAB.

1.2.2 Synthesis of PEI-DMS-La

Typically, 0.5 g DMS were added to 10 mL methanol solution containing a certain amount of PEI (5, 10 or 20 w/v%). After being stirred at 30 $^{\circ}$ C for 10 h, the above mixture was quickly added to 20 mL of 1% (w/v) glutaraldehyde/methanol solution for cross-linking. After continuous stirring at 30 $^{\circ}$ C

for 1 h, centrifugation at 7500 rpm for 40 min and washing with deionized (DI) water, the obtained solids were dried at 60 °C overnight.

DMS-PEI-La was obtained by treating DMS-PEI-10% with La^{3+} solution which was prepared using $La(NO_3)_3$ 6H₂O. Briefly, 1.5 g DMS-PEI-10% was added to a 20 mL solution with a given La^{3+} concentration (e.g. 0.1 mol/L, 0.5 mol/L and 1.0 mol/L). The mixture was vigorously stirred at room temperature for 10 h. The product was obtained by centrifugation at 7500 rpm for 40 min, washed for three times with DI water, and dried at 60 °C overnight. Subsequently, the obtained powders were stirred in 0.01 mol/L NaOH solution for 10 h. The final product was obtained after centrifugation at 7500 rpm for 40 min, washed with DI water, and dried at 60 °C overnight. The sample was named as DMS-PEI-La1, DMS-PEI-La2, and DMS-PEI-La3, corresponding to La^{3+} concentration 0.1 mol/L, 0.5 mol/L and 1 mol/L, respectively.

1.3 Characterization

The morphologies, chemical compositions, and surface structures of samples were examined by a scanning electron microscopy with energy dispersive spectroscopy (SEM-EDS; FEG250, FEI) and transmission electron microscopy (TEM; F20, FEI). The crystal phases were investigated by X-ray diffraction (XRD, Bruker D8-advance) using Cu K α radiation ($\lambda = 0.15418$ Å) in 2 θ range of 10°– 80 °. Nitrogen adsorption–desorption isotherms were measured at 77 K over an automatic analyzer (ASAP 2020, Micromeritics). Fourier transform infrared (FT-IR) spectra were collected using a Nicolet 5700 FT-IR spectrometer; the sample was pressed by a KBr disk preparation apparatus. The surface chemical compositions of N, Si, O, C, La, P and S were analyzed by X-ray photo-electron spectroscopy (XPS, ESCALab 250 Xi) using Mg Ka (1253.6 eV) X-rays as the excitation source. Perkin Elmer's inductively coupled plasma optical emission spectrometer (Optima 7000 DV) determined the content

of La. The sample was dissolved in 0.1 M HCl, and the supernatant was used for detection. TG analysis was done on differential thermogravimetric synchronous thermal analyzer under N₂ atmosphere on TA Instruments TGA/SDTQ 600 with stare software, at a heating rate of 10 °C/min from 25 °C to 1000 °C. DMS-PEI-La2 was treated in 1.0 mol/L HCl solution to fully leach all La in the sample and then the La loading was determined using inductively coupled plasma atomic emission spectrophotometry (ICP-AES, OptimaTM 2000 DV, PerkinElmer).

1.4 Batch sorption experiments

The adsorption kinetics were carried out as follows: 25 mg of the adsorbent was added to 50 mL of 40 mg P /L solution in an Erlenmeyer flask with glass stopper, and then the flask was placed in a reciprocating shaker at 288 K, 298 K, and 308 K under 200 rpm, respectively. 3 mL of the reaction solution was removed at a given period of time and the filtrate was collected to analyze the residual P in the solution. As for CR adsorption, the experimental process was similar to the above, except that 10 mg of the adsorbent and 100 mL CR solution (with concentration of 20 mg/L, 40 mg/L, and 60 mg/L) were used.

To study P adsorption isotherms, 25 mg of the adsorbent was added to 50 mL P solution with different initial concentrations (1 mg/L – 50 mg/L), and then the mixtures were placed in reciprocating shakers at 288 K, 298 K, and 308 K for 8 h, respectively. On the other side, to study CR adsorption isotherms, 10 mg of the adsorbent and 100 mL CR solution with different initial concentrations (10 mg/L – 250 mg/L) were employed.

The effect of pH on P and CR adsorption was measured at 25 °C. The initial solution pH (pH = 2.0 – 11.0 and 4.0 - 11.0, respectively) was adjusted using 0.1 M HCl or NaOH. The effect of co-existing ions, such as SO₄²⁻, HCO₃⁻, F⁻, NO₃⁻, and Cl⁻, on the adsorption process was studied by dissolving their

corresponding sodium salts to P or CR solution. The effect of humic acid on the adsorption was also conducted. To evaluate the regeneration capability of adsorbent, 25 mg of the adsorbent was firstly added into 50 mL of 40 mg/L P solution at 25 °C for 12 h adsorptive removal. Afterwards, the desorption was performed by immersing the spent adsorbent in 100 mL of 0.01 M NaOH solution for 24 h. The desorbed adsorbent was collected and re-treated in 0.5 mol/L La³⁺ solution. Finally, the obtained regenerated adsorbent was reused for the next cycle of adsorption–desorption. On the other side, to regenerate the spent adsorbent after CR adsorption, 50 mL absolute ethanol was used as desorption solution instead of NaOH solution.

The adsorption capacity of P and CR in adsorption-desorption cycles were studied. In the P adsorption-desorption cyclic test, 25 mg of the adsorbent was added to 50 mL of 20 mg/L P solution; while in the CR adsorption-desorption cyclic test, 10 mg of the adsorbent was added to 100 mL of 100 mg/L CR solution. Then the mixtures were placed in reciprocating shakers at 298 K for 8 h. The spent adsorbent was collected by centrifugation and then desorbed in 0.1 M NaOH solution for 4 h (P adsorption-desorption cyclic test) or in ethanol solution for 2 h (CR adsorption-desorption cyclic test). The adsorbent was collected and re-used in the subsequent adsorption-desorption cycles.

Meanwhile, a set of control tests was also conducted by re-treating the spent adsorbent in a given La^{3+} concentration (0.5 mol/L) for regeneration. The mixture was vigorously stirred at room temperature for 10 h. The product was obtained by centrifugation at 7500 rpm for 40 min, washed for three times with DI water, and dried at 60 °C overnight. Subsequently, the obtained powders were stirred in 0.01 mol/L NaOH solution for 10 h. The final product was collected after centrifugation at 7500 rpm for 40 min, washed with DI water, and dried at 60 °C overnight. The regenerated adsorbent was then reused for the next round of adsorption test.

Figures:



Fig. S1. TEM image of DMS-PEI-La2 (a) and elemental mapping images of O, Si, N and La (b-e).



Fig. S2. Comparison of P adsorption capacities of as-prepared samples.



Fig. S3. (a) Pseudo-first-order fitting plots and (b) Elovich fitting plots of P removal by using DMS-PEI-10%, DMS-PEI-La1, DMS-PEI-La2, and DMS-PEI-La3; (c) pseudo-first-order fitting plots and (d) Elovich fitting plots of CR adsorption using DMS-PEI-La2



Fig. S4. Dubinin–Radushkevich adsorption isotherms of DMS-PEI-La2 towards P (a) and CR (b); Van't Hoff plots for adsorption of P (c) and CR (d) by using DMS-PEI-La2.



Fig. S5. Effect of co-existing anions and humic acid on CR adsorption using DMS-PEI-La2.



Fig. S6. Final CR concentration after adsorption using DMS-PEI-La2 in binary solution (C₀: 100 mg/L CR + (5 - 100) mg/L P, adsorbent dosage: 0.5 g L⁻¹, contact time: 12 h, 25 °C).



Fig. S7. pH of point zero charge (pH pzc) curves for DMS-PEI-La2 in P (a) and CR (b) solution.



Fig. S8. (a) Change of pH for P solution during adsorption; (b) La leaching from DMS-PEI-La2 in P solution (C₀: 20 mg P/L, adsorbent dosage: 0.5 g L⁻¹, contact time: 36 h, pH: 2 ~ 10, 25 °C).



Fig. S9. XRD patterns (a) and FTIR spectra (b) of DMS-PEI-La2 after adsorption in single P and binary (P+CR) solution systems.



Fig. S10. XPS survey of DMS-PEI-La2 before and after adsorption from phosphate solution and binary P-CR solution systems.

Schemes



Scheme S1. Structure of PEI.

Tables

Table S1. List of kinetic and isothem models used in this study.

Model	Equation		Ref.
Adsorption capacity	$q_t = \frac{(C_0 - C_t) \times V}{m}$	(1)	[1]
Pseudo-first-order	$\ln(q_e - q_t) = \ln q_e - k_1 t$	t (2)	[2,3]
Pseudo-second-order	$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e}$	(3)	[2, 3]
Elovich	$q_t = \beta \ln(\alpha\beta) + \beta \ln t$	(4)	[4]
Langmuir	$q_e = q_m K_L \frac{C_e}{1 + K_L C_e}$	(6)	[2,5]
	$R_{L} = \frac{1}{1 + K_{L}C_{0}}$	(7)	[1,5]
Freundlich	$q_e = K_F C_e^{1/n}$	(8)	[2]
Dubinin-Radushkevich	$q_e = q_m exp(-K_{DR}\epsilon^2)$	(9)	[1]
	$\varepsilon = \operatorname{RT}\ln(1 + \frac{1}{C_e})$	(10)	[1]
Van't Hoff	$\Delta G = -RT \ln K_d$	(11)	[1]
	$\Delta G = -RT\ln(b)$	(12)	[1]
	$\ln(b) = \frac{\Delta S}{R} - \frac{\Delta H}{RT}$	(13)	[1]

In Table S1, q_t is the adsorption capacity at a given period of time (mg/g); C_0 is the initial concentration (mg/L) of P or CR before adsorption; C_t is the P or CR concentration (mg/L) at a given period of time; V is the volume of solution (L), and m is the mass of adsorbent (g); q_e (mg/g) is the amount of P or CR adsorbed at equilibrium; t (min) is the time of adsorption; k_1 (min⁻¹) and k_2 (g/mg-min) are reaction rate constants of pseudo-first-order and pseudo-second-order; α and β is the initial adsorption rate (mg/g·min) and desorption constant (g/mg), respectively; C_i is a constant related to boundary layer thickness; C_e (mg/L) is the concentration of solution containing P or CR at equilibrium; q_m (mg/g) is the maximum adsorption capacity; K_L (L/mg) is an isotherm constant related to the adsorption site affinity in the Langmuir model; K_F (mg/g) is the maximum adsorption capacity; n is Freundlich constant related to adsorption strength in the Freundlich model; K_{DR} (mol²/kJ²) is the constant in Dubinin-Radushkevich isotherm model; R (8.314 J/mol·K) is the gas constant; and T (K) is the absolute temperature; K_d is the thermodynamic constant of adsorption process, indicating how

P or CR distributes between both the liquid and solid phases; ΔH and ΔS are the values of enthalpy and entropy, calculated as Eq. (1); b (L/mol) is the Langmuir model constant.

Sample	$S_{BET}(m^2/g)$	D (nm)	V_{total} (cm ³ /g)
La(OH) ₃	15.4	14.6	0.06
DMS-0.2	236.7	11.2	0.66
DMS-0.4	317.5	8.2	0.65
DMS-0.5	222.6	9.9	0.55
DMS-PEI-5%	104.0	14.4	0.37
DMS-PEI-10%	103.9	16.6	0.43
DMS-PEI-20%	103.8	15.2	0.41
DMS-PEI -La1	124.9	13.5	0.42
DMS-PEI-La2	130.0	13.4	0.44
DMS-PEI-La3	112.0	14.6	0.41

Table S2. Structural properties of as-prepared samples.

Model Pseudo-First-Order			Pseudo-Second-Order				Elovich						
	q_e^{exp}	q_e^{cal} /	k_1 /	\mathbb{R}^2	F valve	q_e^{cal}	k ₂ /	\mathbb{R}^2	F value	α/	β/	\mathbb{R}^2	F value
	(mg/g)	(mg/g)	(min ⁻¹)			(mg/g)	(g/mg·min)			(mg/g·min)	(g/mg)		
DMS-PEI-10%	21.8	7.1	0.010	0.84	54.8	23.7	0.012	0.99	30342.9	652.1	1.9	0.82	43.7
DMS-PEI-La1	27.3	5.8	0.010	0.80	41.4	29.1	0.016	0.99	65723.1	33910.8	1.8	0.64	17.5
DMS-PEI-La2	38.3	6.6	0.012	0.85	58.7	39.9	0.019	0.99	962167.8	23716.4	2.5	0.68	20.2
DMS-PEI-La3	35.1	6.4	0.011	0.83	52.6	37.2	0.016	0.99	464794.0	12479.6	2.4	0.64	17.3

 Table S3. Kinetic parameters for P adsorption.

Model		Pseudo-First-Order			Pseudo-Secon	d-Order		Elovich						
	q_e^{exp}	$q_e^{cal}/$	$k_{1}/$	\mathbb{R}^2	F value	 q_e^{cal} /	k_2 /	\mathbb{R}^2	F value		α/	β/	\mathbb{R}^2	F value
	(mg/g)	(mg/g)	(min ⁻¹)			(mg/g)	(g/mg·min)				(g/mg·min)	(g/mg)		
20mg/L	191.5	84.9	0.025	0.81	18.3	193. 8	0.00092	0.99	538949.5		0.83	22.3	0.68	25.3
40mg/L	397.4	184.2	0.013	0.95	165.8	406.5	0.00021	0.99	59453.0		0.42	44.4	0.87	66.9
60mg/L	591.2	397.2	0.008	0.97	358.0	617.3	0.00005	0.99	10845.8		0.02	89.8	0.98	535.3

Table S4. Kinetic parameters for CR adsorption using DMS-PEI-La2.

Model		Langmuir				Freund	Freundlich				D-R			
		q _{max} /(mg/g)	$K_L/$	R _L	\mathbb{R}^2	F value	K _F /	n	\mathbb{R}^2	F value	q _m /	K _{DR} /	\mathbb{R}^2	F value
			(L/mg)				(mg/g)				(mg/g)	$(10^{-8} \text{ mol}^2/\text{kJ}^2)$		
	15℃	55.5	2.5	0.018	0.88	124.6	40.8	6.6	0.88	122.5	53.1	9.7	0.88	121.1
Р	25℃	58.1	3.8	0.013	0.90	150.1	45.3	7.1	0.89	139.0	56.3	5.9	0.90	150.2
	35℃	59.3	5.4	0.008	0.91	155.3	47.3	7.3	0.90	143.6	57.8	3.4	0.90	154.3
	25℃	926.4	0.2	0.390	0.97	756.8	264.0	3.9	0.82	108.3	819.8	307.6	0.94	391.6
CR	35℃	1053.3	0.8	0.009	0.97	759.2	477.3	5.6	0.72	56.9	977.8	20.1	0.96	475.2
	45℃	1493.8	2.8	0.004	0.91	152.6	734.2	5.5	0.76	64.6	1441.4	4.3	0.90	146.6

Table S5. Langmuir, Freundlich and Dubinin-Radushkevich isotherm parameters in the P and CR adsorption by using DMS-PEI-La2.

Adsorbate	Temperature	b×10 ⁻³	ΔG	$\Delta S (kJ/mol \cdot K)$	ΔH (kJ/mol)
	(3 °)	(L/mol)	(kJ/mol)		
	15	77.46	-26.97		
Р	25	116.12	-28.91	0.19	28.62
	35	168.19	-30.83		
	25	106.65	-21.96		
CR	35	587.09	-26.30	0.48	115.01
	45	1962.48	-29.89		

Table S6. Thermodynamic parameters for P and CR adsorption onto DMS-PEI-La2.

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