Supporting Information for

Enhanced Phosphate Removal by Nanosized Hydrated La(III) Oxide Confined in Crosslinked Polystyrene Networks

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This file contains 14 pages, including Appendix S1-S4, Table S1-S5, and Figure S1-S8.

Appendix S1

Thermogravimetric analysis of $LaPO_4{\cdot}xH_2O$, heat from 25°C to 750°C at 20°C/min. The water content of $LaPO_4{\cdot}xH_2O$ was determined by calculation as follows: $xH_2O = \frac{M_{initial} - M_{LaPO4}}{M_{H2O}}$; $M_{initial} = \frac{M_{LaPO4}}{(1 - weightloss)}$.

Table S1 Thermogravimetric analysis of model compound $LaPO_4{\cdot}xH_2O$

Temperature °C	Weight loss %	xH_2O
25-750	10.20-13.80	1.47-2.08

Appendix S2

Equations used in this study are Langmuir model (1), Freundlich model (2), Double Langmuir model (3), Sips model (4), Pseudo-first-order model (5) and Pseudo-second-order model (6)

$$q_e = q_m \frac{k_L c_e}{1 + k_L c_e} \quad (1)$$

$$q_e = K_F C_e^{1/n} \quad (2)$$

Where q_m (mg/g) represents the adsorption capacity and K_L is the Langmuir constant. K_F (L/mg) represents the heterogeneity of the sorbent and n is the Freundlich constant.

$$q_e = q_1 \frac{k_1 c_e}{1 + k_1 c_e} + q_2 \frac{k_2 c_e}{1 + k_2 c_e} \quad (3)$$

Where q_1 and q_2 (mg/g) represents the adsorption capacity of site 1 and 2, and k_1 and k_2 (L/mg) are the Double Langmuir constants

$$q_e = \frac{q_m (bc_e)^{\beta}}{1 + (bc_e)^{\beta}} \quad (4)$$

Where q_m and b are the same as q_m and K_L in the Langmuir model, β is similar to K_F in the Freundlich model

$$q_t = q_e \left(1 - e^{-k_1 t}\right) \quad (5)$$

$$q_t = \left(\frac{1}{q_e} + \frac{1}{k_2 q_e^2} t^{-1}\right)^{-1} \quad (6)$$

Where q_e and q_t are the adsorption amounts extracted in equilibrium and at time t respectively, and k_1 and k_2 are the pseudo-first-order and pseudo-second-order constant, respectively

Table S2 The pseudo-first-order, pseudo-second-order kinetic model parameters for phosphorus adsorption onto La-201 in sulfate free solution and in background solution containing 500 mg/L sulfate.

Background solution	Pseudo-first-order model			Pseudo-second-order model		
sulfate free	q_e mg • g^{-1}	k_1 min^{-1}	R^2	q_e $mg \cdot g^{-1}$	k_2 $mg \cdot g^{-1} \cdot min^{-1}$	R^2
	52.95	0.68	0.982	56.92	0.017	0.994
500 mg/L	q_e	k_1	R^2	q_e	k_2	R^2

sulfate	mg·g^{-1}	min^{-1}		mg·g^{-1}	mg·g^{-1}·min^{-1}	
	45.01	0.11	0.969	51.55	0.0023	0.988

Table S3 Comparison of phosphorus adsorption capacity and La usage efficiency for different La-based materials

Materials	pH	La content %	q_m mg/g	Molar ratio P/La	Ref
Lanthanum-treated lignocellulosic	6.39, 6.05	2.75, 4.20	6.54, 10.88	**1.77, 2.58**	1
La(III)-chelex resin	3.1	12.38	3.04	**0.11**	2
Nanocrystalline La_2O_3	-	-	57.80	**-**	3
Synthesized Lanthanum hydroxide	-	-	107.53	**-**	4
Zeolite/lanthanum hydroxide	-	21.80	71.94	**1.48**	5
Lanthanum hydroxide doped activated carbon fiber	-	5.29	15.30	**1.30**	6
Lanthanum loaded mesoporous silica SBA-15	-	23.29	45.63	**0.**	7
Lanthanum modified macroporous silica foams	-	32.3	70.43	**0.98**	8
$La(OH)_3$ modified exfoliated vermiculites	5.0	41.55	79.60	**0.85**	9
La-201	6.7	15.80	113.64	**1.43**	This study

Appendix S3

The molar P/La ratio of the reference adsorbents was calculated on the basis of their maximum adsorption capacity and La content, which is possibly higher than the real values because the role of the host in phosphate adsorption was not excluded. As for La-201 in this study, since the host D-201 could adsorb phosphate considerably (Table S4), we deliberately excluded its contribution to phosphate adsorption by employing the background sulfate solution (Table S5) and the molar P/La ratio 1.43 reflected the real La usage.

Table S4 Double Langmuir adsorption isotherm parameters for phosphorus adsorption onto La-201 at 25℃ in sulfate free solution.

Double Langmuir				
q_1 mg/g*	k_1 L/mg P	q_2 mg P/g*	k_2 L/mg P	R^2
69.78	0.017	43.86	11.25	0.991

Table S5 Langmuir and Freundlich adsorption isotherm parameters for phosphorus adsorption onto La-201 at 25℃ at the presence of 500 mg/L sulfate

Langmuir			Freundlich		
q_m mg/g*	K_L L/mg P	R^2	n	K_F L/mg	R^2
318.37	1.05	0.980	7.81	173.93	0.766
Langmuir			Freundlich		
q_m mg/g#	K_L L/mg P	R^2	n	K_F L/mg	R^2
50.30	1.05	0.980	7.81	27.48	0.766

* mg P/g La; # mg P/g La-201

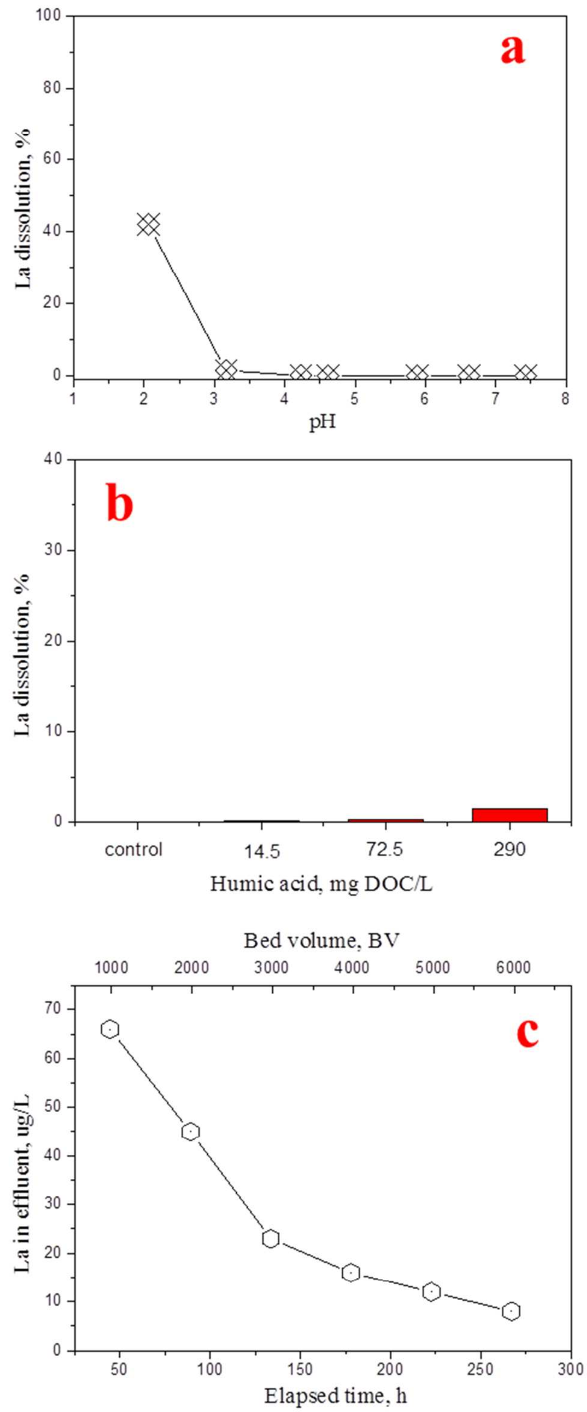

Figure S1 La dissolution from La-201 (a) at varying pH, (b) in the presence of different HA concentration for 20 days, (c) during column adsorption

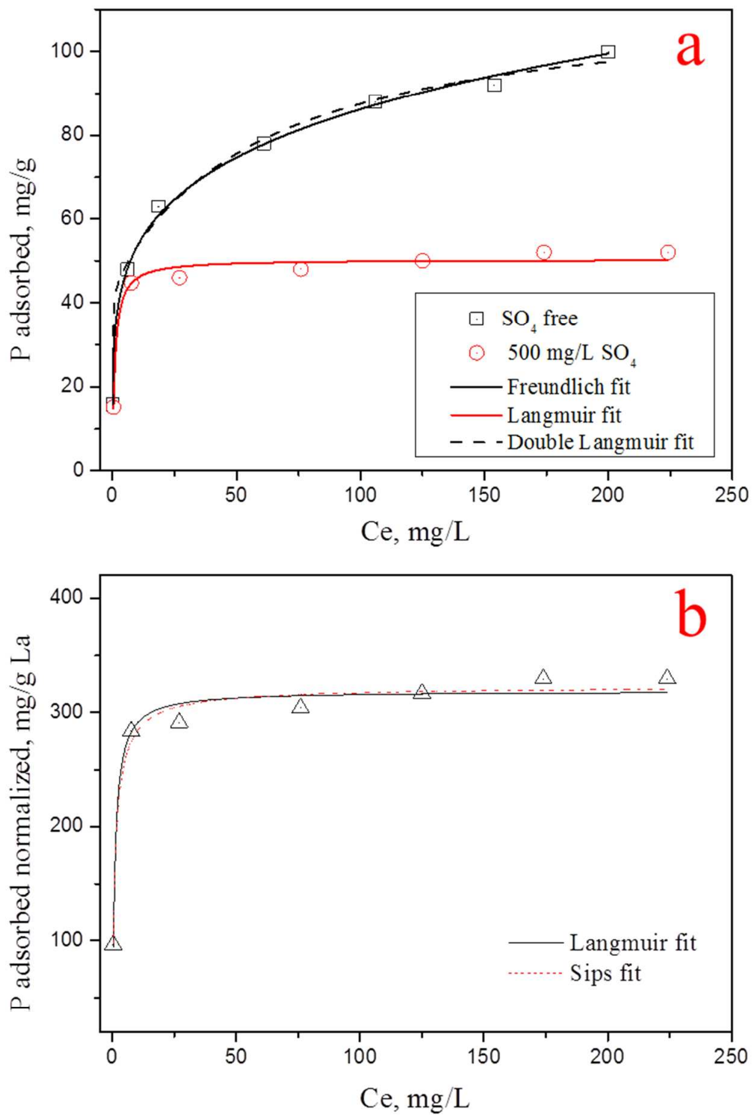

Figure S2 Phosphate adsorption isotherm onto La-201 in the background solution of sulfate free or sulfate at 25°C (a). Normalized adsorption isotherm in background sulfate solution (b) (S/L ratio, 0.5 g/L; time, 96 h).

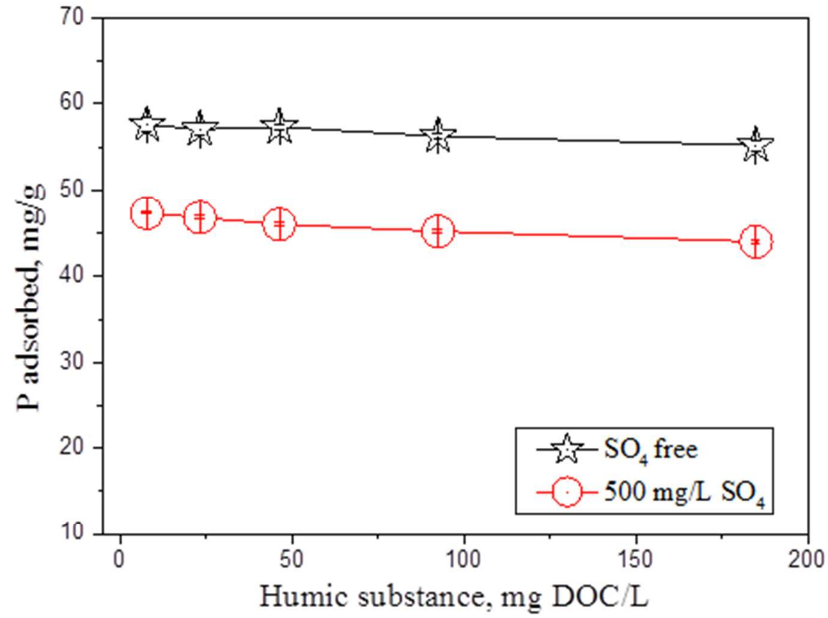

Figure S3 Effect of humic acid on the phosphate adsorption by using La-201 (25°C, pH=6.7, adsorbent dosage = 0.5 g/L, reaction time: 96 h, C_0=30 mg P/L).

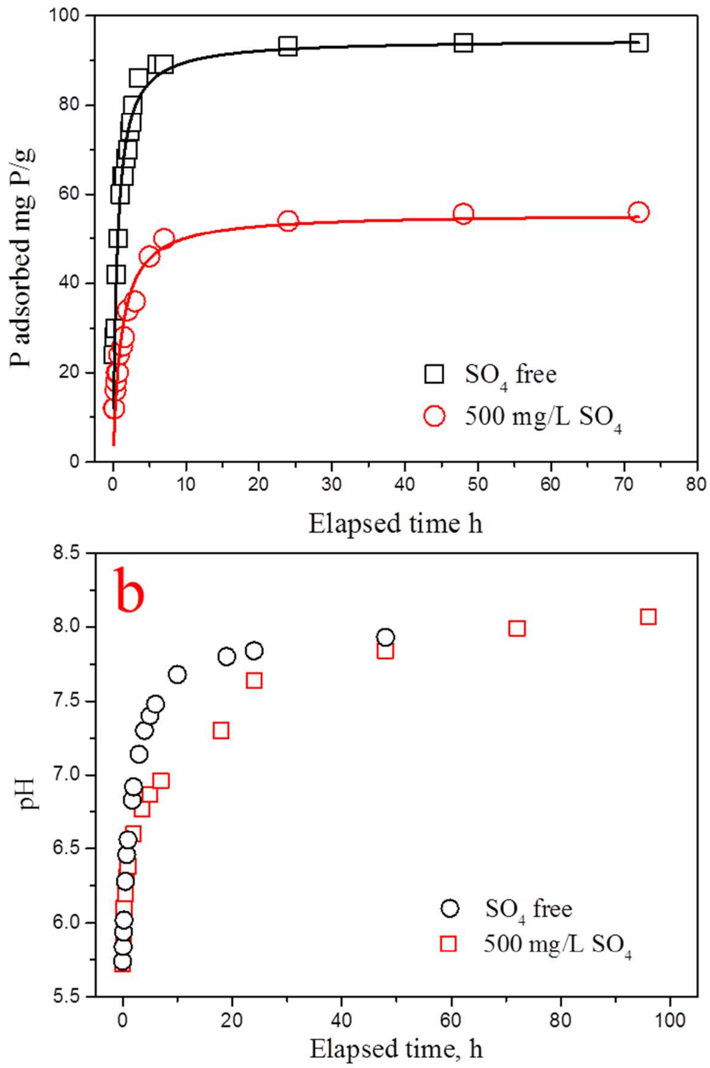

Figure S4 Phosphate uptake kinetics (C_0=150 mg P/L, *a*) and pH variation (*b*) in the background of sulfate and sulfate free solution (25°C, C_0=30 mg P/L, adsorbent dosage = 0.5 g/L).

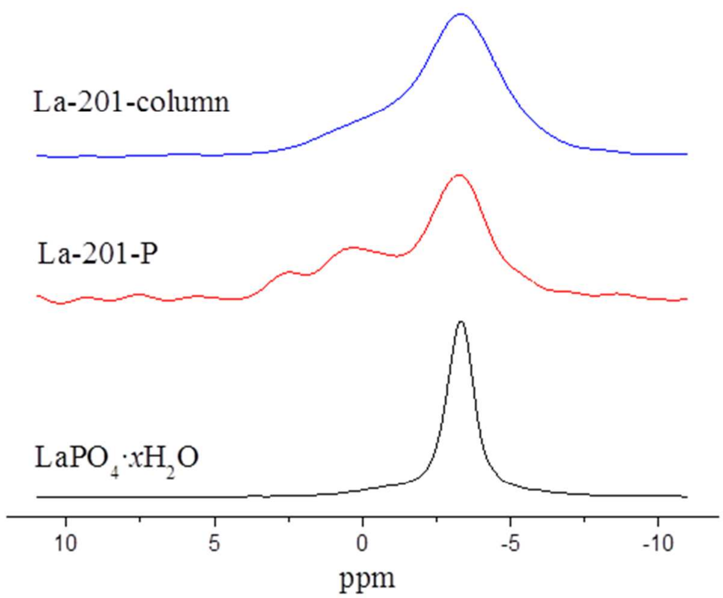

Figure S5 ^{31}P MAS NMR spectra of La-201 after P saturation and after column adsorption, and $LaPO_4 \cdot xH_2O$.

Appendix S4

The NMR spectrum of La-201-P has two additional resonance at $\delta(^{31}P)$= 0.33 and 2.47 ppm, which could reflect P adsorbed by ammonium groups and P species formed on the surface of $LaPO_4 \cdot xH_2O$ [10, 11], respectively.

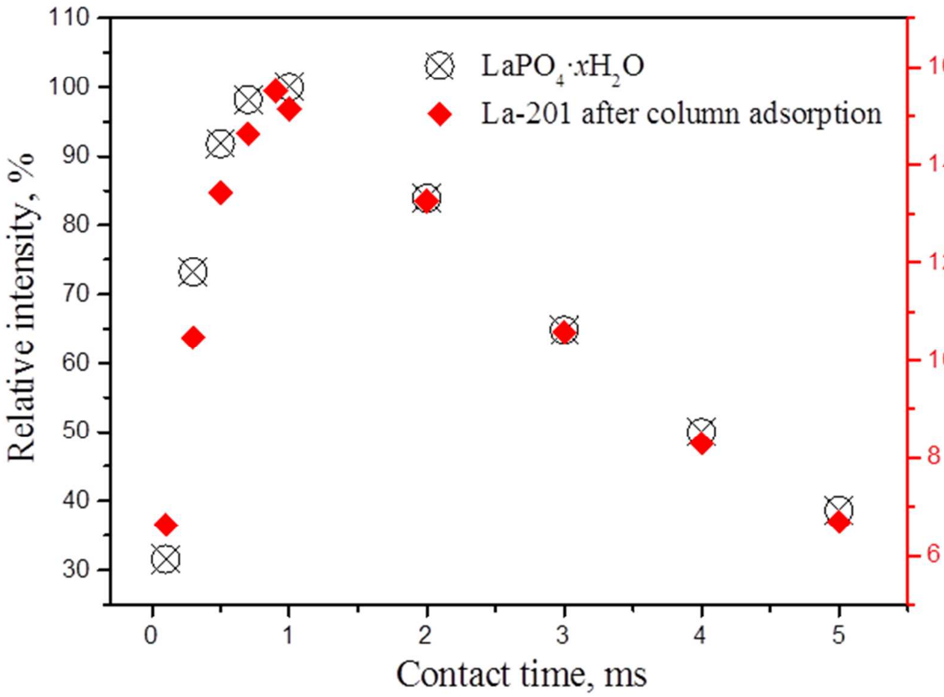

Figure S6 Relative intensity of $LaPO_4 \cdot xH_2O$ (left Y axis) and La-201 after column adsorption (right Y axis) determined from $^{31}P\{^1H\}$ CP MAS NMR experiments as a function of contact time. The intensities are normalized relative to the most intense value for $LaPO_4 \cdot xH_2O$.

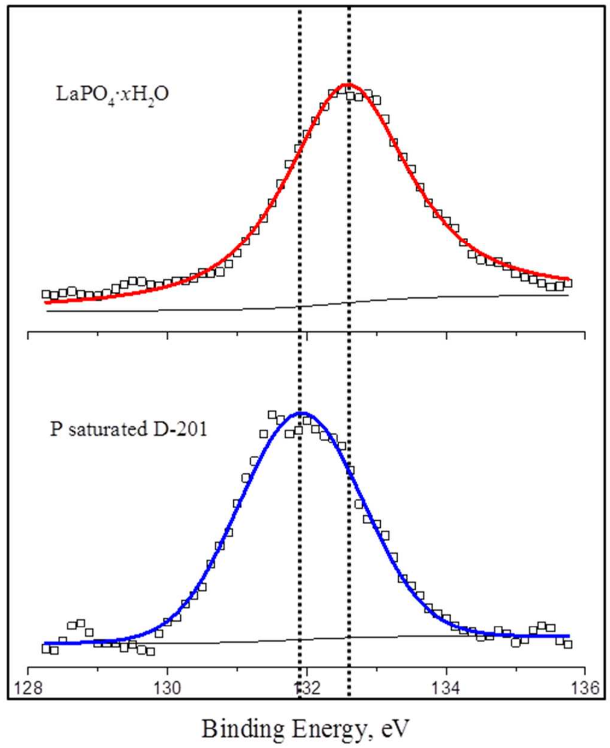

Figure S7 P2p XPS scan spectra of $LaPO_4 \cdot xH_2O$ and P saturated D-201

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