Supporting Information

Efficient capture of phosphate from wastewater by a recyclable ionic liquid functionalized polyacrylonitrile fiber: Atypical "Release and Catch" mechanism

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1. Reagents and instruments

The supplier of Polyethyleneimine (PEI, Mw=10000) was Shanghai Dibo Biotechnology Co., LTD. KH_2PO_4, ascorbic acid and ammonium molybdate were purchased from Shanghai Aladdin Biochemical Technology Co., Ltd. NaOH, $NaHCO_3$ and Na_2CO_3 were provided by Shanghai SuYi Chemical Reagent Co., Ltd. Antimonyl potassium tartrate, $K_2CO_3$and NaCl were bought from Saan Chemical Technology Co., Ltd, Tianjin Guanfu Technolicy Devel Opment Co., Ltd and Shanghai Pilot Chemical Corporation, respectively. H_2SO_4, HCl and HNO_3 were supplied by Xilong Scientific Co., Ltd. Sinopharm Group Chemical Reagent Co., Ltd provided K_2SO_4 and KCl.

2. Synthesis of ionic liquid functionalized polyacrylonitrile fiber

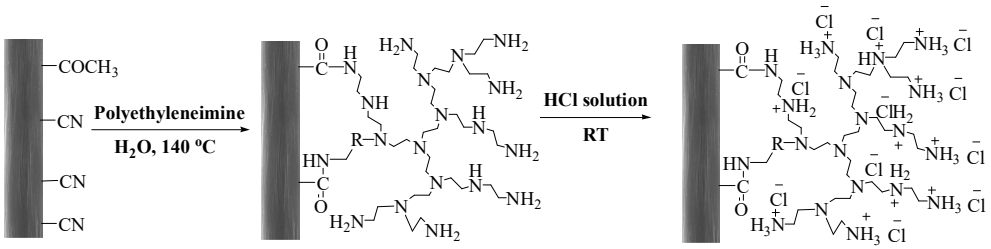

Fig. S1. Synthesis of ionic liquid functionalized polyacrylonitrile fiber.

3. The picture of various fibers

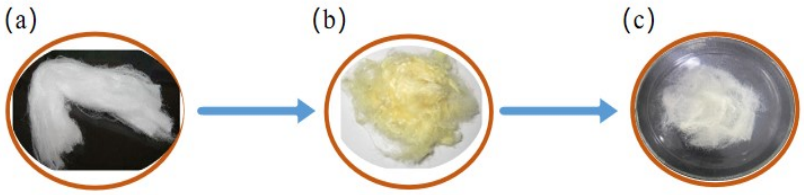

Fig. S2. The picture of (a) PANF, (b) PAN_AF, and (c) PAN_AF-Cl.

4. Typical procedure for the acid exchange capacity (Amine content)

Dried PAN_AF (100 mg) was immersed into 100 mL of 0.0200 mol L^{-1} prepared HCl for 40 min. The neutralized fiber was then filtered out and the acid concentration of the remaining

solution was determined by titration with 0.0200 mol L^{-1} prepared NaOH. The exchange capacity was calculated based on the consumption of the acid amount. The final concentration of HCl was calibrated with standard Na_2CO_3 solution, and the concentration of NaOH was calibrated with the calibrated HCl.

5. Weight gain and acid exchange

Table S1 The weight gain and acid exchange capacity of the prepared fibers.

Entry	Fiber	Weight gain (%)	Acid exchange capacity (mmol g^{-1})
1	PANF	--	--
2	PAN_AF	4.3	0.73
3	PAN_AF	8.7	1.20
4	PAN_AF	18.2	1.76
5	PAN_AF	20.9	1.87
6	PAN_AF	26.6	2.29
7	PAN_AF	33.4	2.48
8	PAN_AF-Cl	2.52	--

6. X-ray diffraction spectroscopy (XRD) and thermostability analysis

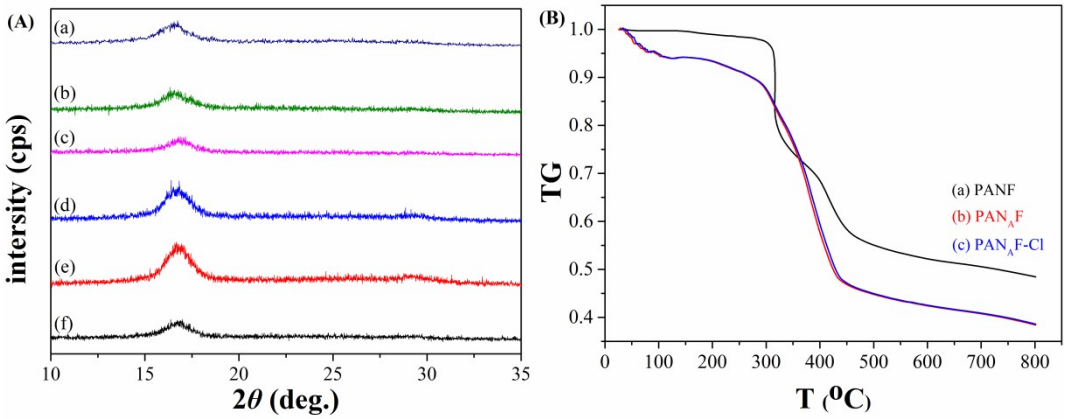

Fig. S3 (A). The XRD patterns of (a) PANF, (b) PAN_AF, (c) PAN_AF-Cl, (d) PAN_AF -P, (e) PAN_AF-Cl-1, and (f) PAN_AF-Cl-5; (B) The TGA spectra of (a) PANF, (b) PAN_AF, and (c) PAN_AF-Cl.

7. Adsorption kinetics

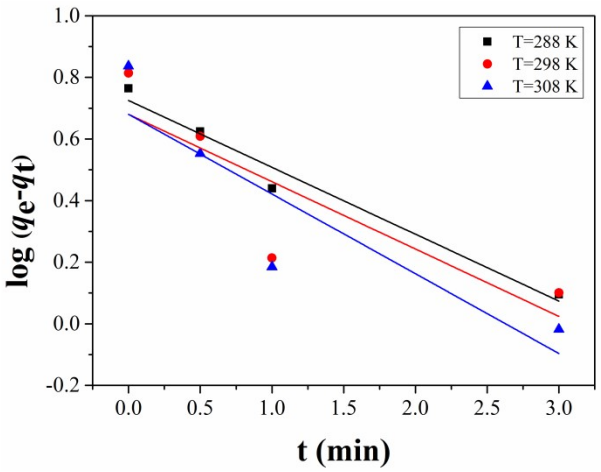

Fig. S4. The fitting curve of pseudo-first-order kinetic model for adsorption phosphate.

8. Adsorption kinetics

Table S2 Kinetic parameters for the adsorption of phosphate by PAN_AF-Cl.

Temperature (K)	$q_{e,exp}$ (mg P g^{-1})	First order kinetic		Second order kinetic		
		k_1 (min^{-1})	R^2	qe	k_2 (g ·mg^{-1}·min^{-1})	R^2
288	5.81	0.5000	0.9603	6.1335	0.1592	0.9979
298	6.52	0.5038	0.6117	6.7449	0.2796	0.9980
308	6.87	0.5962	0.7006	7.0427	0.3072	0.9993

9. Adsorption thermodynamic

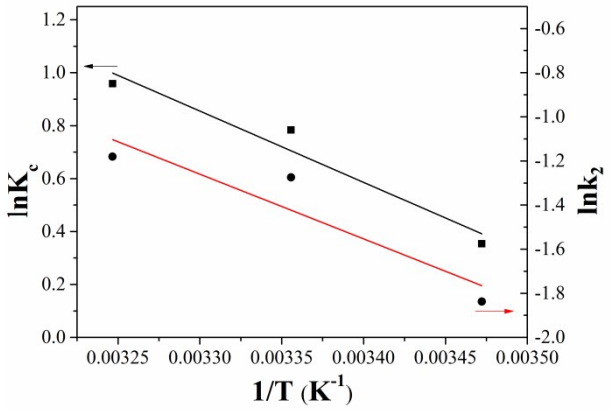

Fig. S5. The plot of lnK_c vs. 1/T and plot of lnK_2 vs. 1/T for thermodynamic parameters.

10. Parameters of theadsorptionthermodynamic

Table S3 Parameters of theadsorptionthermodynamic.

T(K)	△G° (kJ mol^{-1})	△H°(kJ mol^{-1})	△S° (J mol^{-1} K^{-1})	E_a(kJ mol^{-1})
288	-0.8463			
298	-1.9409	22.39	81.01	24.42
308	-2.4539			

11. Adsorption isotherm

Table S4 Parameters of the adsorption isotherm models.

Isotherm model	Parameter	Value
Langmuir	q_{max} (mg P g^{-1})	15.49
	K_l (L mg^{-1})	2.8468
	R^2	0.9869
Freundlich	n	1.9069
	K_f (L mg^{-1})	2.3658
	R^2	0.9768

12. Coexisting anions

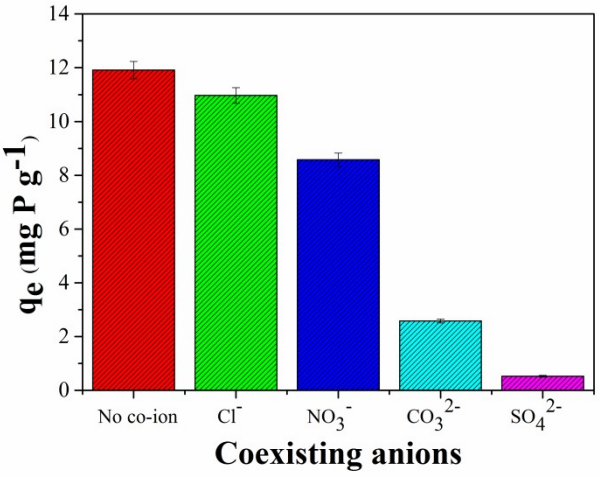

Fig. S6. Effect of coexisting anions on phosphate adsorption.

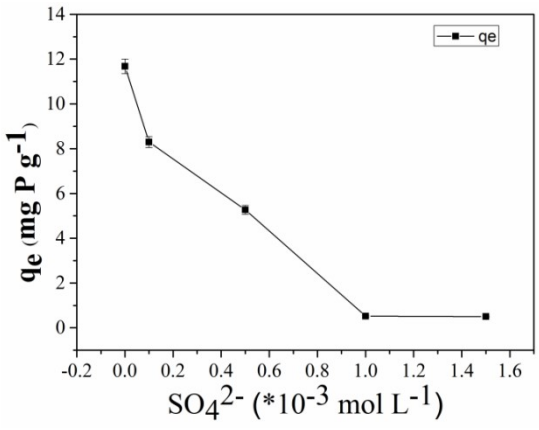

Fig. S7. Effect of SO_4^{2-} with different concentration on phosphate adsorption

13. The atomic percent of the fibers tested by XPS

Table S5 The atomic percent of the fibers tested by XPS.

Entry	Sample	Atomic percent (%)				
		C	N	O	Cl	P
1	PANF	73.78	7.71	18.51	0	0
2	PAN_AF	72.80	7.69	19.51	0	0
3	PAN_AF-Cl	70.40	7.2	20.96	0.44	0
4	PAN_AF-P	63.80	9.26	26.49	0.02	0.45

14. The mass percentage of the fibers determined by EDS

Table S6 The mass percentage of the fibers determined by EDS.

Entry	Sample	Wt (%)				
		C	N	O	Cl	P
1	PANF	67.3	27.8	4.9	0	0
2	PAN_AF	66.9	22.6	10.5	0	0
3	PAN_AF-Cl	69.6	18.1	9.3	2.9	0
4	PAN_AF-P	61.2	21.9	14.4	1.9	0.5
5	PAN_AF-Cl-1	64.5	19.0	11.8	1.8	0
6	PAN_AF-Cl-5	68.9	19.3	7.8	4.1	0

15. Optimization of HCl eluent

Table S7 Desorption of phosphate from the PAN_AF-Cl using HCl solution[a].

Eluent solutionconcentration (mol L^{-1})	Volume (mL)	T (h)	Desorption ratio (%)
0.05	30	5	76.87
0.10	30	5	81.89
0.20	30	5	89.63
0.30	30	5	95.66
0.30	10	5	90.69
0.30	20	5	91.34
0.30	30	1	88.51
0.30	30	3	89.41

[a]Dried 20 mg of phosphate adsorbed PAN_AF-Cl was immersed in HCl solution.

16. The adsorption limit test of PAN_AF-Cl on phosphate.

Table S8 Effect of adsorbent dosage on adsorption efficiency of the PAN_AF-Cl for phosphate[a].

Entry	Fiber weight (mg)	Ce (mg P L^{-1})	Removal efficiency
1	10	0.0519	89.0%
2	20	0.0497	89.5%
3	30	0.0426	91.0%
5	50	0.0326	93.1%
6	60	0.0184	96.1%

[a]The fiber adsorbent was put into 10 mL of phosphate (0.4733 mg P L^{-1}) solution for 8 h under 25 °C.

17. The practical application of PAN_AF-Cl in domestic sewage

Table S9 The content of main anions in domestic sewage[a].

Anions	Cl^-	F^-	Br^-	NO_3^-	SO_4^{2-}	CO_3^{2-}	PO_4^{3-}
Concentration	35.5 mg L^{-1}	0.98 mg L^{-1}	6.92 mg L^{-1}	2.47 mg L^{-1}	12.40 mg L^{-1}	9.58 mg L^{-1}	4.11 mg P L^{-1}

[a]The real wastewater is taken from waste water treatment plantin Hefei (pH=7.51), the concentration of Cl^-, F^-, Br^-, NO_3^- and SO_4^{2-} were measured by ion chromatograph (ICS 1100, Thermo Fisher), the PO_4^{3-} was tested by molybdenum blue colorimetry using visible spectrophotometer, the CO_3^{2-} was measured by titration.

Table S10 Practical application of PAN_AF-Cl with different weights in domestic sewage.

Entry	Fiber weight (mg)	Ce (mg P L^{-1})	Removal efficiency
1	10	3.40	17.3%
2	20	1.97	52.1%
3	30	1.12	72.7%
4	40	0.65	84.2%
5	50	0.36	91.2%
6	60	0.046	98.8%

[a]The fiber adsorbent was put into 10 mLof phosphate (4.11mg P L^{-1}) solution for 8 h under 25 °C.

18. Comparison with other phosphate removal adsorbents in the literature

Table S11 Comparison with other phosphorus removal adsorbents in the literature.

Adsorbent	Equilibrium time	q_{max} (mg P g^{-1})	Run	Reference
Al-crosslinked PVA hydrogel beads	8 h	11.5	5	[1]
Poly-aluminum chloride sludge	48 h	1.78	--	[2]
Fe(H)O-PsAX@75	4h	4.12	--	[3]
Quaternary amine modified chitosan beads	45min	11.37	10	[4]
Hybrid anion exchanger	24 h	4	5	[5]
hybrid anion exchange resin	5 min	7.17	--	[6]
Anion exchange resin (ZMAE)	24h	26.1	5	[7]
Renewable molybdate complexes	500min	26.58	5	[8]
PAN_AF-Cl	5 min	15.49	5	This study

Reference

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