

Electronic Supplementary Material

Fabrication of recyclable Fe³⁺ chelated aminated polypropylene fiber for efficient clean-up of phosphate wastewater

Shangyuan Zhao^{1,2*}, Fangjia Wang^{3*}, Rui Zhou^{1,2}, Peisen Liu^{1,2}, Qizhong Xiong^{1,2}, Weifeng Zhang^{1,2}, Chaochun Zhang^{1,2}, Gang Xu (✉)^{1,2}, Xinxin Ye^{1,2}, Hongjian Gao^{1,2}

1 Anhui Province Key Lab of Farmland Ecological Conservation and Pollution Prevention;
Engineering and Technology Research Center of Intelligent Manufacture and Efficient
Utilization of Green Phosphorus Fertilizer of Anhui Province, College of Resources and
Environment, Anhui Agricultural University, Hefei 230036, China

2 Key Laboratory of JiangHuai Arable Land Resources Protection and Eco-restoration, Ministry
of Natural Resources, College of Resources and Environment, Anhui Agricultural University,
Hefei 230036, China

3 Institute of Soil Science, Chinese Academy of Sciences, Nanjing 210008, China

E-mail: gangxu@ahau.edu.cn

* These authors contributed equally to this work.

1. The sources of reagents

PPF was purchased from Fushun Petrochemical Corporation of China (long fiber was cut into approximately 10 cm pieces before its application). All chemical reagents were analytically pure. Acrylic amide, polyethyleneimine (PEI, Mw = 10000), ammonium molybdate, ascorbic acid, antimonyl potassium tartrate, disodium ethylenediamine tetraacetic acid (EDTA), FeCl₃·6H₂O, KH₂PO₄, K₂SO₄, K₂CO₃, KCl, NaCl, inorganic acids (HCl, HNO₃, H₂SO₄), and bases (Na₂CO₃, NaHCO₃, and NaOH) were all used without purification. Deionized water was used in this work.

Acrylic amide was obtained from Shanghai Aladdin Biochemical Technology Co., Ltd.

Polyethyleneimine (PEI, Mw=10000) was provided by Shanghai Dibo Biotechnology Co., LTD. Ammonium molybdate, ascorbic acid and KH_2PO_4 were purchased from Shanghai Aladdin Biochemical Technology Co., Ltd. Antimonyl potassium tartrate was provided by Saan Chemical Technology Co., Ltd. $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ was obtained from Shanghai Macklin Biochemical Co., Ltd. EDTA, Na_2CO_3 , NaHCO_3 and NaOH were purchased from Shanghai SuYi Chemical Reagent Co., Ltd. NaCl and K_2CO_3 were supplied by Shanghai Pilot Chemical Corporation and Tianjin Guanfu Technology Development Co., Ltd, respectively. K_2SO_4 and KCl were provided by Sinopharm Group Chemical Reagent Co., Ltd. HCl, HNO_3 and H_2SO_4 were supplied by Xilong Scientific Co., Ltd.

2. Apparatus and instruments

Characterization of the functional groups on fiber surface by Fourier transform infrared (FTIR) spectrometer (Nicolette is50, USA), the fibers were cut with scissors as much as possible and mixed with dried potassium bromide, and then measured by pressing them into sheets. Surface morphology of fibers was characterized by scanning electron microscope (SEM, S-4800, Hitachi), cut the fiber material to less than 5 mm, and then place the fiber on the conductive adhesive as evenly as possible, in order to enhance the test effect, it is necessary to spray gold before the test. The elemental distribution was characterized by energy dispersive X-ray spectroscopy (EDS, X-Max N 150), Three points were randomly selected on the fiber with a magnification of 2000 times to test the energy spectrum. The change of carbon, nitrogen and hydrogen content before and after fiber modification was measured by elemental analyzer (VarioELCube, Germany), accurately weigh 2 mg of fiber and wrap it in a tin boat, acetanilide was used as the standard sample for correction. The surface structure and elemental composition of fibers were detected by

X-ray photoelectron spectroscopy (XPS, PERKIN ELMZR), cut the fiber sample of appropriate size (5mm in length) and paste it on the sample tray, then put the sample into the sample chamber. The pressure in the sample chamber is less than 2.0×10^{-7} mbar, the sample is sent to the analysis chamber, and the spot size is 400 μm , working voltage 12 kV, filament current 6 Ma. The full spectrum scanning power is 150 eV and the step size is 1eV. Fiber crystal structure was characterized by X-ray diffractometer (XRD, Beijing Purkinje General Instrument Co., Ltd.), the fibers were pressed into discs (about 1cm in diameter) with a tablet press, and the scanning rate of the test was $4^\circ/\text{min}$. FE20 pH meter (METTLER TOLEDO) was employed to measure solution pH. Vis spectro-photometer (722G, Shanghai) was used to measure phosphate concentration at 700 nm wavelength. The sample with low concentration was measured with inductively coupled plasma emission spectrometer (ICP-OES, Thermo jarrell-ash, USA).

3. The synthetic route for PP_{AMA}F-Fe

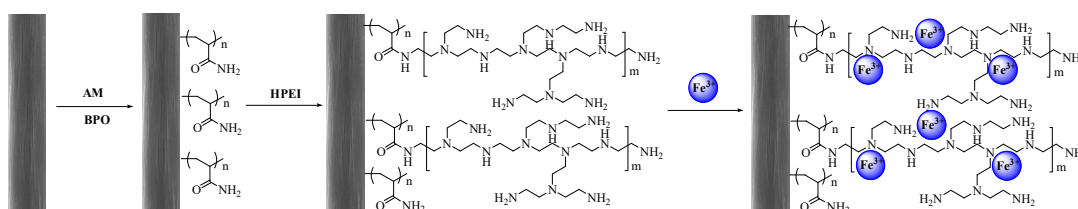


Fig. S1 Synthesis diagram of iron loaded amine-functionalized polypropylene fiber.

4. The picture of various fiber

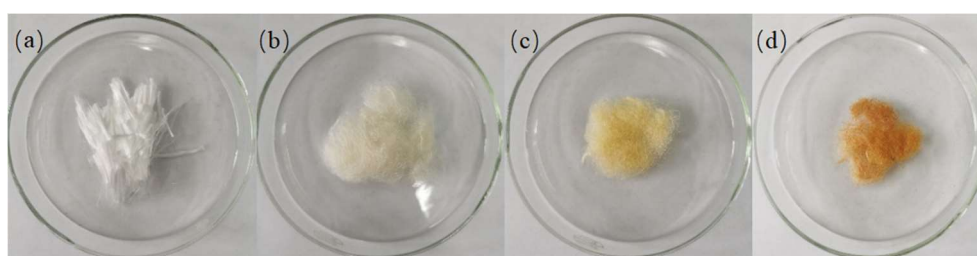


Fig. S2. The picture of (a) PPF, (b) PP_{AM}F, (c) PP_{AMA}F and (d) PP_{AMA}F-Fe.

5. Preparation of PP_{AMA}F with different weight gain

Table S1 Synthesis optimization of the PP_{AMAF} with different weight gain

Fiber	Dosage of HPEI/g	Weight gain/%
PP _{AMAF}	0.05	2.46
PP _{AMAF}	0.10	5.16
PP _{AMAF}	0.20	7.00
PP _{AMAF}	0.50	12.16
PP _{AMAF}	2.00	13.50
PP _{AMAF}	2.50	15.86

Note: Dried PP_{AMF} (0.2 g, weight of 17.66%) and HPEI were immersed into 15 mL of deionized water in reaction kettle at 110 °C for 6 hours.

6. The water uptake of the functionalized fiber

General steps: Dried fiber (20 mg) was placed in 10 mL deionized water at room temperature for 12 hours. After taking out the fiber, a vacuum pump was used to filter the excess water. Subsequently, the filtered fiber was then placed in a centrifuge tube (2 mL) with a small hole at the bottom, the fiber was centrifuged for five minutes to further remove the water adhering to their surface. Finally, the fiber after centrifugation was removed to weigh. The water uptake was calculated using the formula as follow:

$$\text{Water uptake} = (m_2 - m_1) / m_1 \times 100\%$$

Where the m_1 is the mass of the fiber before adsorption of water, and the m_2 is the mass of the fiber after adsorption of water.

Table S2 The water uptake of the PPF, PP_{AMF}, PP_{AMAF} and PP_{AMAF}-Fe

Entry	Fiber	Water uptake /%
1	PPF	4.74
2	PP _{AMF}	12.62
3	PP _{AMAF}	28.93
4	PP _{AMAF} -Fe	23.30

7. The optimization of the synthesis process for PP_{AMAF}-Fe

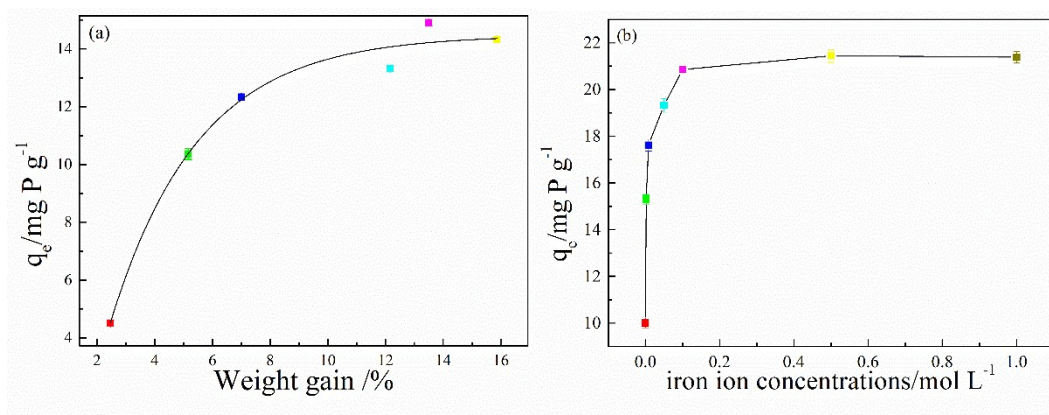


Fig. S3 (a) The adsorption capacity of phosphate by iron ion (0.1 mol L^{-1}) chelated aminated fibers different weight gain in phosphate solution (10 mg P L^{-1}), (b) Phosphate adsorption capacity of aminated fibers (weight gain of 13.5%) modified with different concentrations of Fe^{3+} (phosphate concentration of 20 mg P L^{-1}).

8. Drawing of phosphate standard curve

The experiment used the simulated wastewater prepared by the laboratory. Put 0.8788 g of dried KH_2PO_4 into a 1 L volumetric bottle and dilute the fixed capacity with deionized water to obtain a phosphate solution with a concentration of 200 mg P L^{-1} . Taking a certain volume of the liquid can be diluted to the desired concentration. We diluted a standard phosphate solution with a concentration of $0\text{-}1.4 \text{ mg P L}^{-1}$ to draw the standard curve. The phosphate absorbance was measured using a spectrophotometer at a 700 nm wavelength, and a standard curve of R^2 to 0.999 was drawn. Besides, the standard curve is affected by environmental factors such as temperature, we need to redraw before each test.

9. General steps of desorption and reusability

The desorption experiment was carried out with 30 mL of 0.1 mol L^{-1} EDTA. First, 10 mg of $\text{PP}_{\text{AMAF}}\text{-Fe}$ was added to a phosphate solution with an initial concentration of 5 mg P L^{-1} . The mixed solution is stirred for 1.5 h and then taken out, washed with deionized water and then transferred into the desorption agent. After stirring for 3 h at room temperature, the fiber was

washed with deionized water to neutrality. After that, the fiber was bonded to Fe^{3+} again, and then used it for the next absorption experiment.

10. Elemental analysis data of the fibers.

Table S3 Elemental analysis data of the fibers

Entry	Sample	C/%	H/%	N/%
1	PPF	85.76	13.35	1.46
2	PP _{AMF}	74.23	11.57	6.33
3	PP _{AMF}	69.94	11.46	9.35
4	PP _{AMF} -Fe	61.42	10.18	7.80
5	PP _{AMF} -Fe-P	58.92	9.92	7.30

11. Adsorption kinetics

Table S4 The parameters of pseudo-first-order and pseudo-second-order models for the adsorption of phosphate by PP_{AMF}-Fe

Temperature (K)	$q_{e,exp}$ /mg P g ⁻¹	First order kinetic		Second order kinetic		
		k_1/min^{-1}	R ²	$q_e/\text{mg P g}^{-1}$	$k_2/\text{g mg}^{-1} \text{min}^{-1}$	R ²
288	18.08	0.0089	0.922	18.78	0.0533	0.9985
298	21.77	0.0092	0.939	22.04	0.0458	0.9992
308	24.53	0.0105	0.908	25.05	0.0399	0.9998

12. Adsorption thermodynamics

Table S5 Thermodynamic parameters of phosphate adsorption by PP_{AMF}-Fe

T (K)	$\Delta G^\circ/\text{kJ mol}^{-1}$	$\Delta H^\circ/\text{kJ mol}^{-1}$	$\Delta S^\circ/\text{kJ K}^{-1}$	$E_a/\text{kJ mol}^{-1}$
288	-3.10			
298	-4.10	9.64	3.38	22.27
308	-4.86			

13. Adsorption isotherm

Table S6 The parameters for the Langmuir and Freundlich models

Isotherm model	Parameter	Value
Langmuir	$q_{max}/\text{mg P g}^{-1}$	33.944
	$K_l/\text{L mg}^{-1}$	0.677
	R ²	0.983
	n	4.103

Freundlich

 $K_f/L\text{ mg}^{-1}$

16.440

 R^2

0.828

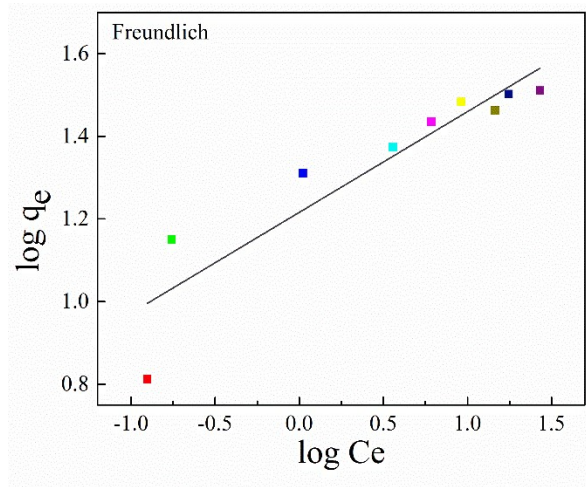


Fig. S4 Freundlich isotherm model to fit phosphate adsorption by PP_{AMAF}-Fe.

14. Adsorption of phosphate in the simulated wastewater by PP_{AMAF}-Fe

Table S7 The content of main anions in actual environmental water^a

Anions	Cl ⁻	NO ₃ ⁻	SO ₄ ²⁻	HCO ₃ ⁻	PO ₄ ³⁻
Concentration	59.11 mg L ⁻¹	0.38 mg L ⁻¹	23.53 mg L ⁻¹	140.6 mg L ⁻¹	0.014 mg L ⁻¹

^aThe real water is taken from Chaohu lake (pH=6.97), the concentration of Cl⁻, NO₃⁻ and SO₄²⁻ were measured by ion chromatograph (ICS 1100, Thermo Fisher), the PO₄³⁻ was tested by molybdenum blue colorimetry using visible spectrophotometer, the HCO₃⁻ was measured by titration.

Table S8 The adsorption limit test of PP_{AMAF}-Fe on phosphate

Dosage of PP _{AMAF} -Fe /mg	V /mL	T /h	The concentration of phosphate / $\mu\text{g P L}^{-1}$
0	15	24	4510
5	15	24	3290
10	15	24	1980
20	15	24	820
30	15	24	30
40	15	24	20
50	15	24	10

15. Reusability of the functionalized fiber

Table S9 Optimization of EDTA eluent

Concentration /mol L ⁻¹	V /mL	T /h	Desorption ratio /%
0.05	30	3	72.14 %
0.1	30	3	99.28 %
0.2	30	3	95.37 %
0.3	30	3	84.13 %
0.1	30	1	68.22 %
0.1	30	2	90.12 %
0.1	30	3	99.30 %
0.1	30	4	98.54 %
0.1	30	24	99.00%

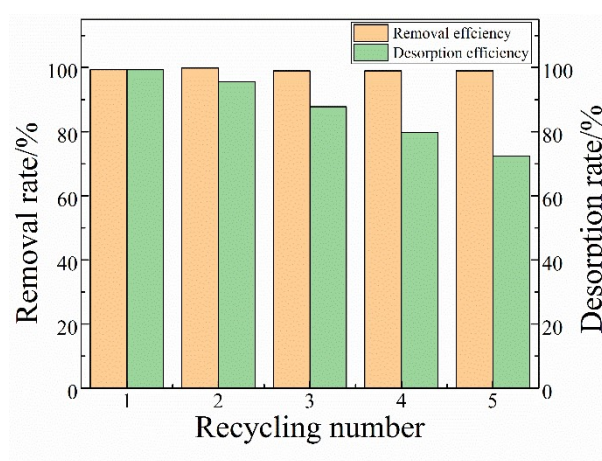


Fig. S5 Reusability of PP_{AMA}F-Fe during 5 cycles ($C_0 = 5 \text{ mg L}^{-1}$, $T = 25 \text{ }^\circ\text{C}$, $m = 10 \text{ mg}$, $V = 15 \text{ mL}$, $\text{pH} = 6$, $t = 90 \text{ min}$).

16. The mass and atomic percentage of the functionalized obtained by EDS

Table S10 The mass and atomic percentage of the functionalized obtained by EDS

Fiber	Weight /%						Atomic /%					
	C	N	O	Cl	Fe	P	C	N	O	Cl	Fe	P
PPF	100	0	0				100					
PP _{AM} F	94.11	1.17	4.72				95.39	1.01	3.59			
PP _{AMA} F	93.95	1.90	4.15				95.20	1.65	3.16			
PP _{AMA} F-Fe	84.03	1.09	4.52	8.16	2.21		91.74	1.02	3.70	3.02	0.52	
PP _{AMA} F-Fe-P	96.49	0.25	2.00	0.12	0.47	0.67	97.85	0.22	1.52	0.04	0.10	0.26

17. The mass and atomic percentage of the functionalized obtained by XPS

Table S11 The mass and atomic percentage of the functionalized obtained by XPS

Fiber	Atomic /%					
	C	N	O	Cl	Fe	P
PPF	100	0	0			
PP _{AMF}	71.83	21.71	6.46			
PP _{AMAF}	58.79	30.55	10.65			
PP _{AMAF} -Fe	62.80	8.79	26.81	0.76	0.71	
PP _{AMAF} -Fe-P	59.57	8.27	29.35	0.11	0.62	2.07

18. The proposed adsorption mechanism

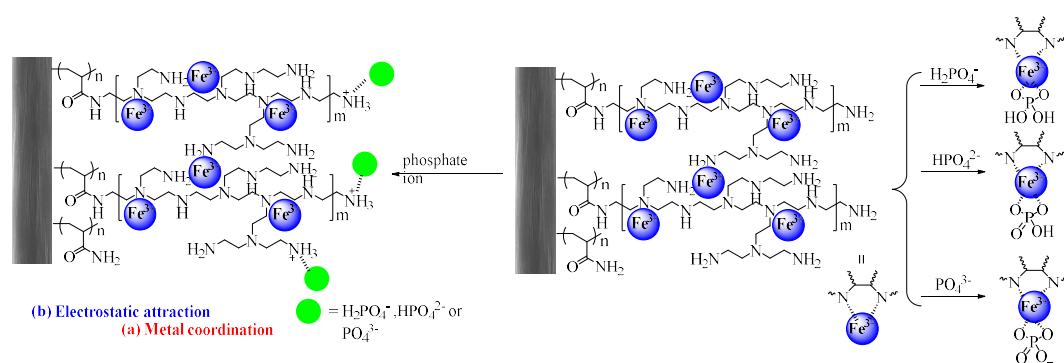


Fig. S6 The possible adsorption mechanism of PP_{AMAF}-Fe for phosphate ion.