Electronic Supplementary Material (ESI) for RSC Advances.

Supporting Information

Construction of Phosphate-rich polyacrylonitrile Fiber Surface Microenvironment for Efficient Purification of Crystal Violet Wastewater

Gang Xu*[a,b], Mengcan Jin[a,b], Fangjia Wang[a], Yusef Kianpoor Kalkhajeh[a,b], Qizhong Xiong[a,b], Liangliang Zhang[a,b], Minli Tao*[c], Hongjian Gao*[a,b]

[a]Anhui Province Key Lab of Farmland Ecological Conservation and Pollution Prevention, School of Resource and Environment, Anhui Agricultural University, Hefei, 230036, P. R. China.

[b]Research Centre of Phosphorous Highly Efficient Utilization and Water Environment Protection Along the Yangtze River Economic Zone.

[c]Department of Chemistry, School of Sciences, Tianjin University, Tianjin, 300072, P. R. China.

*Corresponding author. E-mail: gangxu@ahau.edu.cn; hjgao@ahau.edu.cn.

1. Reagents and instruments

Polyacrylonitrile fiber purchased from the Fushun Petrochemical Corporation of China, the average molecular weight for spinning solution is about 53000 to 106000, which contains 93.0% of acrylonitrile, 6.5% of methyl acrylate and 0.4-0.5% sodium styrene sulfonate. Some chemical reagents such as rhodamine B, methyl green, vitoria blue B, methylene blue, and neutral red, $POCl_3$, ethanolamine, and the other reagents (HNO_3, NaOH etc.) were all of analytical grade. The H_2O used in this work is deionized.

The UV was determined by a TU-1901 UV spectrophotometer, the solid UV was determined with Integrating sphere IS19-1(Beijing Purkinje General Instrument Co.,Ltd., China). The model of YG(B)001A electronic single fiber strength tester was used to test the breaking strength of the PANF and the functionalized fiber adsorbents. A model PHS-3C pH meter purchased from Shanghai Leici Instrument Factory of China was used to adjust the pH of the solution. Determination of phosphorus content in fibers by an ICP-9000 (N+M) inductively coupled plasma optical emission spectrometer (Thermo Jarrell-Ash, USA). Elemental analysis for the fiber before and after modification was determined by a vario micro cube (Elementar, Germany). The FTIR of the fiber samples were tested by AVATAR360 Fourier Transform infrared spectroscopy spectrometer (Thermo Nicolet, USA). Specific surface area and aperture analysis of the fibers is determined by Auto-sorb-iQA3200-4 surface area analyzer (Connor, USA). A model of S-4800 scanning electron microscopy was utilized to observe the surface morphology of fibers (Hitachi). A D/MAX-2500 X-ray diffractometer (XRD) was used to test the crystal structure of the different fibers (Rigaku Corporation). The chemical structure in the fiber surface was analysed by 300 MHz Solid-^{13}C NMR (Infinityplus 300, Varian, USA).

2. The effect of pH on the adsorption of CV by B-PAN$_{EAP}$F

Fiber sample 10 mg and 20 mL of CV solution was put into a 50 mL bottle, the pH of the solution was adjusted from 3 to 11, respectively. The above solution was full contact 4 h under magnetic stirring at room temperature. The fiber was then removed and the concentration of CV in the solution was measured by UV–vis spectrometer. It should note that before testing, the pH of dye solution was adjusted the same as that of standard curve.

3. Determine the point of the zero charge (pH_{PZC}) of B-$PAN_{EAP}F$

Firstly, different KNO_3 solutions were prepared to adjust the pH of the solution to 3-8, respectively. Then 10 mg functionalized fiber was put into each KNO_3 aqueous solution and stirred for 4 h. The pH of each KNO_3 solution after interacting with fibers was determined. Finally, a plot pH_{final} and $pH_{initial}$ was built to determine the zero charge (pH_{PZC}) of B-$PAN_{EAP}F$.

4. The photo of (a) B-$PAN_{EAP}F$ and (b) B-$PAN_{EAP}F$-CV

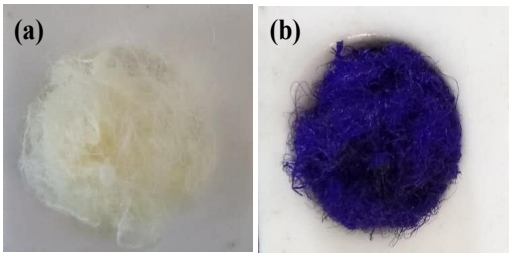

Fig. S1. The photo of (a) B-$PAN_{EAP}F$ and (b) B-$PAN_{EAP}F$-CV.

5. The specific surface area and porosity of the fiber

Table S1 Specific surface area and porosity of the PANF, $PAN_{EA}F$ and B-$PAN_{EAP}F$

Entry	Fiber	S_{BET} (m^2 g^{-1})	V_{Tot} (cm^3 g^{-1})	Average pore diameter (nm)
1	PANF	15.6	0.05	2.3
2	$PAN_{EA}F$	20.4	0.10	2.8
3	B-$PAN_{EAP}F$	10.2	0.05	2.2

6. The FTIR spectra of CV

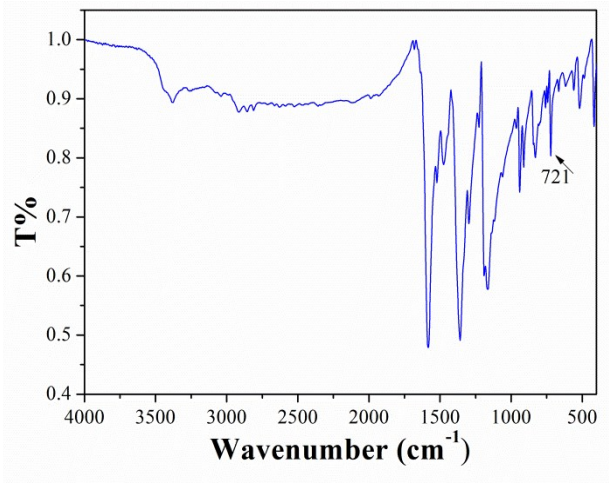

Fig. S2. The FTIR spectra of CV.

7. The solid UV-vis spectra

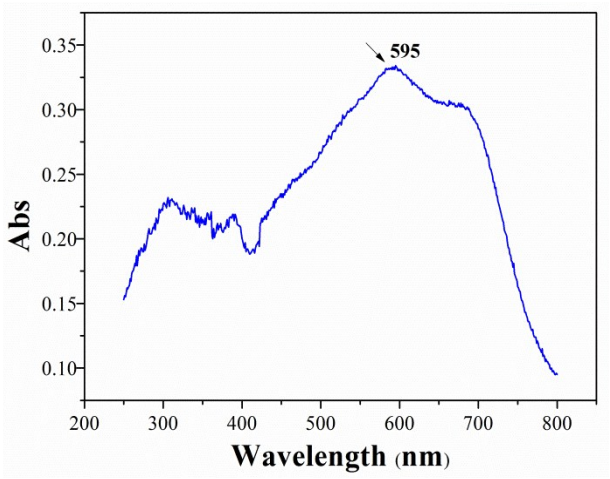

Fig. S3. The solid UV-vis spectra CV.

8. The effect of adsorbent dosage on the removal ability of B-PAN$_{EAP}$F

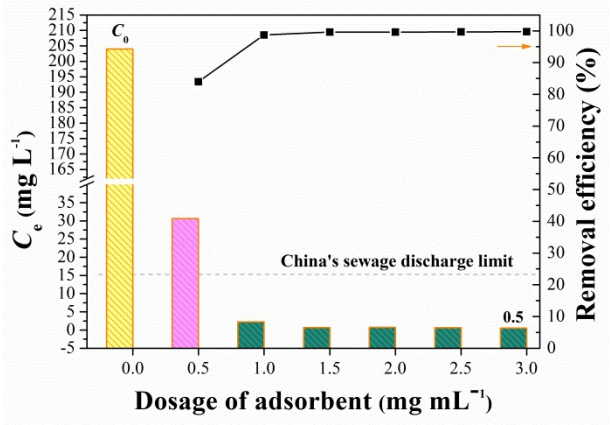

Fig. S4. The effect of adsorbent dosage on the removal ability of B-PAN$_{EAP}$F (the initial concentration is 204 mg L^{-1}, in 10 mL solution with pH of 6 for 2 h).

9. The pseudo first-order adsorption kinetic

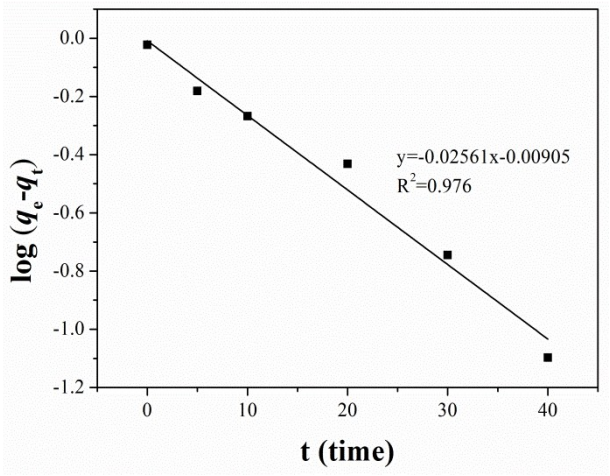

Fig. S5. The pseudo first-order adsorption kinetic.

10. Freundlich isotherm models of B-PAN$_{EAP}$F for CV

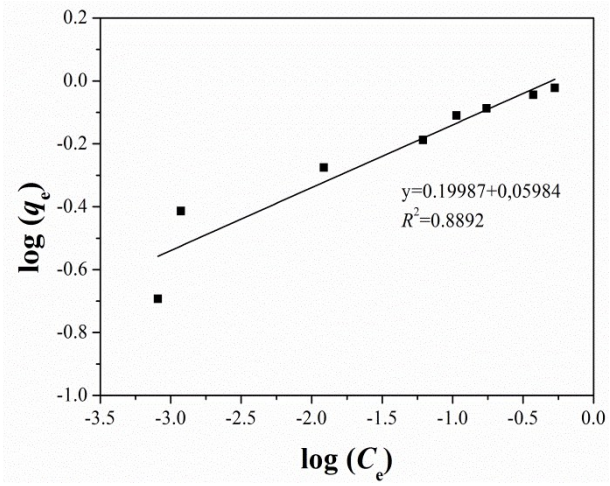

Fig. S6. Freundlich isotherm models of B-PAN$_{EAP}$F for CV.

11. Adsorption kinetics and adsorption isotherm constants for the adsorption of CV on B-$PAN_{EAP}F$.

Table S2 Adsorption kinetics and adsorption isotherm constants for the adsorption of CV on B-$PAN_{EAP}F$.

Kinetic model	First order kinetic			Second order kinetic		
	q_e (mg g^{-1})	k_1 (min^{-1})	R^2	k_2 (g ·$mmol^{-1}$·min^{-1})		R^2
	364.82	0.0560	0.976	0.06828		0.994
Isotherm model	Langmuir			Freundlich		
	q_{max} (mg g^{-1})	K_L (L $mmol^{-1}$)	R^2	n	K_F (mmol g^{-1})	R^2
	354.46	73.3842	0.996	5	1.1477	0.8892

12. Thermodynamic studies

Table S3 Parameters of the sorption isotherm models

T(K)	△G° (kJ mol^{-1})	△H°(kJ mol^{-1})	△S° (J mol^{-1} K^{-1})	E_a (kJ mol^{-1})
283	1.15			
293	0.64	13.90	45.13	11.46
303	0.25			

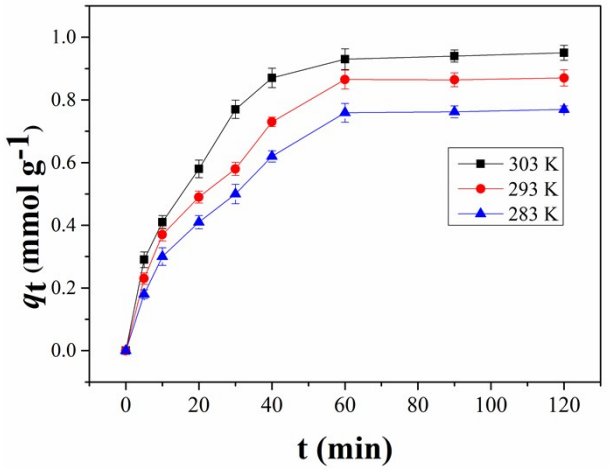

Fig. S7 The effect of temperature on the adsorption of CV by B-$PAN_{EAP}F$.

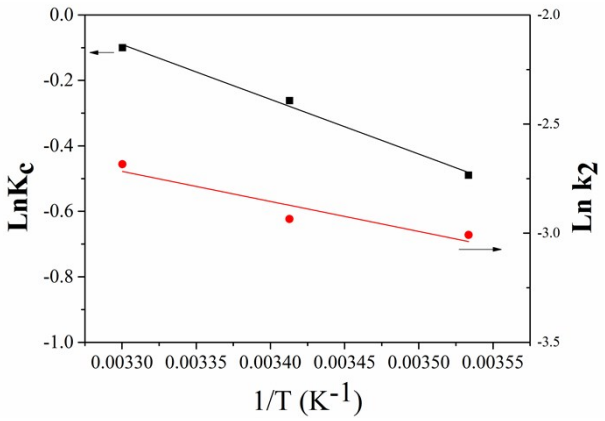

Fig. S8. Estimation of thermodynamic parameters (plot of ln*Kc* vs. 1/T) and activation energy (plot of ln*k*2 vs. 1/T) for the CV onto B-PAN$_{EAP}$F.

13. Possible adsorption mechanism

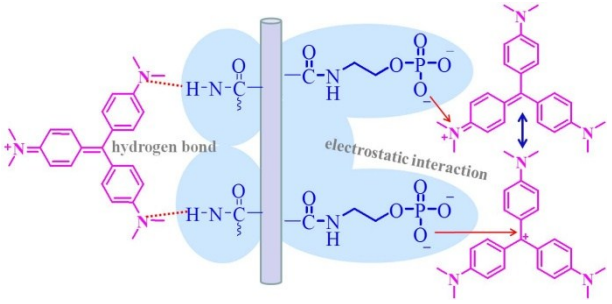

Fig. S9. Possible adsorption mechanism of CV onto B-PAN$_{EAP}$F.

14. Atomic composition of B-PAN$_{EAP}$F before and after the absorption of CV as determined by XPS

Table S4 Atomic composition of B-PAN$_{EAP}$F before and after the absorption of CV as determined by XPS.

Entry	Sample	Atomic percent (%)				
		C	N	O	P	Na
1	B-PAN$_{EAP}$F	70.44	9.23	18.28	0.54	1.5
2	B-PAN$_{EAP}$F-CV	72.92	7.44	18.58	0.55	0.5

15. Diagram of the continuous flow process

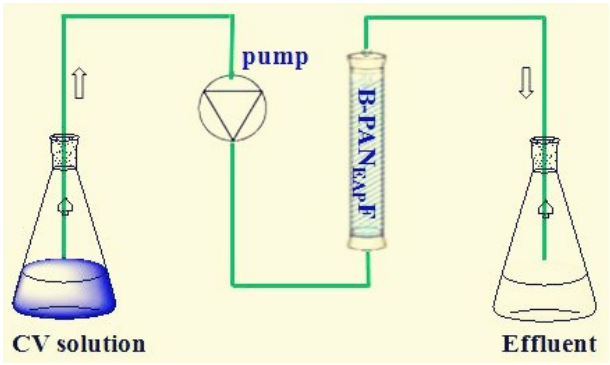

Fig. S10. Diagram of the continuous flow process.