Electronic supplementary information for

Electrospun nanofibrous polyethyleneimine mat: a potential adsorbent for removal of chromate and arsenate from drinking water

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Experiments and Characterizations

S1 Chemicals and materials

Branched Polyethyleneimine (M.W. 10,000) and glycidyl methacrylate (GMA) were purchased from Sigma-Aldrich Co., Ltd, USA. Polyvinylidene fluoride (PVDF) powder (M.W. 420,000) was purchased from Solvay Chemicals Co., Ltd, Belgium. The $NaHAsO_4 \cdot 7H_2O$ was purchased from Chem. Service Inc. While $K_2Cr_2O_7$, N, N-dimethyl formamide (DMF), sodium hydroxide (NaOH), hydrochloric acid (HCl) and other chemicals of analytical grade were purchased from Sinopharm Chemical Reagent Co., Ltd., China. All chemicals were used without further purification. Ultrapure water was used for all experiments unless otherwise stated.

S2 Preparation of nanofibrous adsorbent

The first step is to reduce water solubility of branched polyethyleneimine (b-PEI) inspired of previous research which is gently modified considering of the properties of b-PEI.[1] In view of solvent used in the subsequent electrospinning process, 20 mL N, N-dimethylformamide (DMF) was used to dissolve 4g b-PEI in a brown glass vial, 2mL glycidyl methacrylate (GMA) was added dropwise to the solution of b-PEI with magnetically stirred. 4-methoxyphenol was also added to the b-PEI solution previously at 10 mmol L^{-1} to prevent GMA from homopolymerization. Then the mixture was continuously stirred and shielded from light during the synthesis process bathing in ice water. After reaction, the methacrylated b-PEI (m-PEI) was then precipitated from the DMF with n-hexane leaving the free and self-polymerized GMA in solution. The residue was washed with n-hexane three times then vacuum filtered, dried, and characterized by FT-IR spectroscope and Thermogravimetric (TG) analyser.
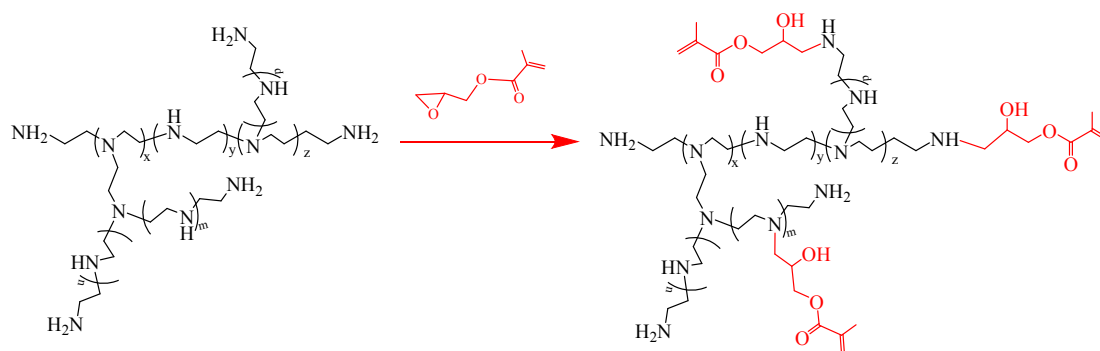
Scheme S1. Scheme of the ring opening reaction between b-PEI and GMA.

In order to avoid the m-PEI insoluble due to cross-linking of the purified m-PEI, which makes it difficult to be re-dissolved in DMF to prepare feed solution of electrospinning, the mixture was immediately mixed with 40 g of 10 wt% PVDF (the mass ratio of PVDF/m-PEI was 1) after reaction without separation of GMA and subsequently applied to electrospinning. The adding of PVDF was aimed at increasing the viscosity and chain entanglements of electrospinning solution and promoting mechanical property of the electrospun mat. Then the mixed solution were loaded into four glass syringes for the purpose of faster electrospinning with the same feeding rate of 0.3 mL h^{-1} and a voltage of 17 kV was applied between the needle and the rotating drum collector. During the electrospinning process, four nozzles moved from left to right repeatedly to make the electrospun mat more uniform. The indoor temperature was adjusted to above 20°C to promote the volatilization of solvent and energy saving lamp lighting was kept on during the electrospinning process. The electrospinning of an unmodified b-PEI/PVDF solution in DMF was carried out for contrast. The resulting fibrous mats were dried in vacuum at 40 °C overnight to remove residual solvent and weighted, subsequently the electrospun mats were immersed in abundant ultrapure water at 40 °C for 48h and then dried in vacuum at 40 °C to remove the unmodified b-PEI from resultant fibrous mat.

The resulted m-PEI/PVDF nanofibrous mats were digested with concentrated nitric acid from a temperature range from room temperature to 190°C using a MARS 6™ Microwave Digestion System, which has been reported in our previous work.[2] PVDF has no mass loss in the process of the microwave digestion attributing to its strong chemical corrosion resistance, thus the actual content of m-PEI in m-PEI/PVDF composite mats can be calculated as followed:

$$\chi\left(\%\right)=\frac{W_1-W_m}{W_1}\times100\left(\%\right)$$

(1)

where $\chi(\%)$ is the actual content of m-PEI in m-PEI/PVDF composite mats, W_1(g) and W_m(g) is the weight of the immersed electrospun nanofibrous mats before and after microwave digestion.

S3 Porosity of nanofibrous adsorbent

A certain length and width of m-PEI and PVDF dense films are prepared and then weighted, respectively and the inherent densities are calculated by the ratio of mass and volume. Similarly, the apparent density of m-PEI/PVDF composite mats can be calculated by the weight and volume of mats. Therefore, the porosity of m-PEI/PVDF composite mats was calculated using the following

equation through derivation:

$$p(\%) = \frac{\rho_i\rho_F - \rho_i\rho_M - x\rho_M(\rho_F - \rho_i)}{\rho_i\rho_F} \times 100\%$$ (2)

where $p(\%)$ is the porosity of electrospun m-PEI/PVDF composite mats, ρ_i and ρ_F represent the inherent densities of m-PEI and PVDF, respectively, and ρ_M is the apparent density of m-PEI/PVDF composite mats, $\chi(\%)$ is the actual content of m-PEI in the m-PEI/PVDF composite mats.

S4 Adsorption experiments

Firstly, 1000mg L^{-1} Cr(VI) and As(V) solution were prepared using $K_2Cr_2O_7$ and $NaHAsO_4 \cdot 7H_2O$ as the source of heavy metal ions and diluted to different concentrations for subsequent adsorption experiments. The PH of various solutions was adjusted by HCl and NaOH. A batch of 100 mL 35.4 mg L^{-1} Cr(VI) solution and 100mL 50 mg L^{-1} As(V) solution was adjusted to different PH range from 2 to 10 and then a dosage of 0.5 g L^{-1} m-PEI/PVDF nanofibrous mats were added to the solutions and shaken continuously for 2 hours for Cr(VI) and 4 hours for As(V) in a thermostatic water bath oscillator at 150 r/min and 25°C. After adsorption, the residual concentrations of Cr(VI) and As(V) in adsorbed solution were analyzed by a Perkin-Elmer Optima 8000 inductively coupled plasma atomic emission spectrometer (ICP-OES). The adsorption capacity can be calculated by the following equation:[3]

$$q_e = \frac{(C_0 - C_e)V}{W}$$ (2)

where C_e (mg L^{-1}) is the heavy metal ions concentration at the adsorption equilibrium, q_e (mg g^{-1}) is the equilibrium adsorption capacity, V (L) is the volume of metal solution, and W (g) is the weight of the adsorbent.

The time-dependence experiments with and without coexisting ions (**Table S1**) were conducted at the same conditions and samples were taken at interval times until the equilibrium was reached. The residual concentrations of Cr(VI) and As(V) and coexisting metal concentration were analyzed by ICP-OES and concentrations of coexisting anions were analyzed by a Thermo Fisher ICS-2100 Ion Chromatography. For the object of investigating the maximum adsorption capacity of Cr(VI) and As(V), the adsorption at different initial concentration was carried out to obtain the maximum

adsorption capacity. Additionally, the simultaneous adsorption of Cr(VI) and As(V) was conducted in 100 mL stock solution containing 50 mg L^{-1} Cr(VI) and 50 mg L^{-1} As(V) with 0.05 g m-PEI/PVDF nanofibrous mat. At last, various stock solution with low initial concentration range from 0.01 to 0.2 mg L^{-1} of Cr(VI) and 0.05 to 0.2 mg L^{-1} As(V) were prepared and disposed by 0.5 g/L of m-PEI/PVDF nanofibrous mats with the same conditions as above, then the residual concentrations of stock solutions after adsorption were analyzed by a Perkin-Elmer NexION™ 300D inductively coupled plasma mass spectrometer (ICP-MS).

S5 General Characterization

FT-IR spectra of b-PEI and m-PEI were collected by scanning the potassium bromide tablets of samples on transmission module. While the spectra of PVDF mat, b-PEI/PVDF and m-PEI/PVDF composite mats were obtained by scanning the nanofibrous mats on attenuated total reflection (ATR) module. All the FT-IR spectra were performed on a Bruker Optics TENSOR 27 FT-IR Spectrometer and were averaged over 32 scans at 4 cm^{-1} resolution obtained in the range of 600~4000 cm^{-1}. TG analysis was performed on a Perkin-Elmer Pyris 1 TGA instrument at a heating rate of 10 °C min^{-1} under nitrogen atmosphere. The microscopic morphology of nanofibrous mats were observed with a JSM-6700F scanning electron microscope (JEOL, Japan). Samples were sputtered with 10 nm gold layer to enhance the electrical conductivity.

# Tables and Figures

Table S1 Concentrations of coexisting ions.

Cl^-	NO_3^-	SO_4^{2-}	Ca^{2+}	Mg^{2+}
100 mg L^{-1}	3.1 mg L^{-1}	10 mg L^{-1}	6.8 mg L^{-1}	20 mg L^{-1}

Table S2 Comparison of adsorbent materials adsorption capacity.

Adsorbents	q_m(mg g^{-1}ads)		References
	Cr(VI)	As(V)	
PVAm modified PET fibers	26.2		4
Nanostructured BiOBr microspheres	16.5		5
Nostoc muscorum biomass	22.92		6
3-MPA-coated SPION		150	7
Iron oxide grafted TNTs		90.96	8
MWCNTs	2.32	3.38	9
Fe$_2$O$_3$@AlO(OH) superstructure Nanomaterial	41.3	75.3	10
Amino-functionalized mesoporous silica	159.2	119.6	11
m-PEI/PVDF nanofibrous adsorbents	**109.1**	**230.7**	This work

Table S3 Kinetic parameters of the adsorption of Cr(VI) and As(V) onto m-PEI/PVDF nanofibrous mats in aqueous solution with and without coexisting ions.

Heavy metals	Coexisting ions	$q_{e,exp}$ (mg g^{-1})	Pseudo-first order			Pseudo-second order		
			qe (mg g^{-1})	k$_1$ (min^{-1})	R^2	qe (mg g^{-1})	k$_2$ (g mg-1min-1)	R^2
Cr(VI)	no	69.04	81.11	0.05136	0.98843	87.72	0.000445	0.97736
Cr(VI)	yes	52.49	54.73	0.03685	0.99841	71.74	0.000375	0.94622
As(V)	no	93.01	50.25	0.02810	0.95782	96.62	0.001262	0.99984
As(V)	yes	79.20	50.56	0.01918	0.97491	85.03	0.000669	0.99978
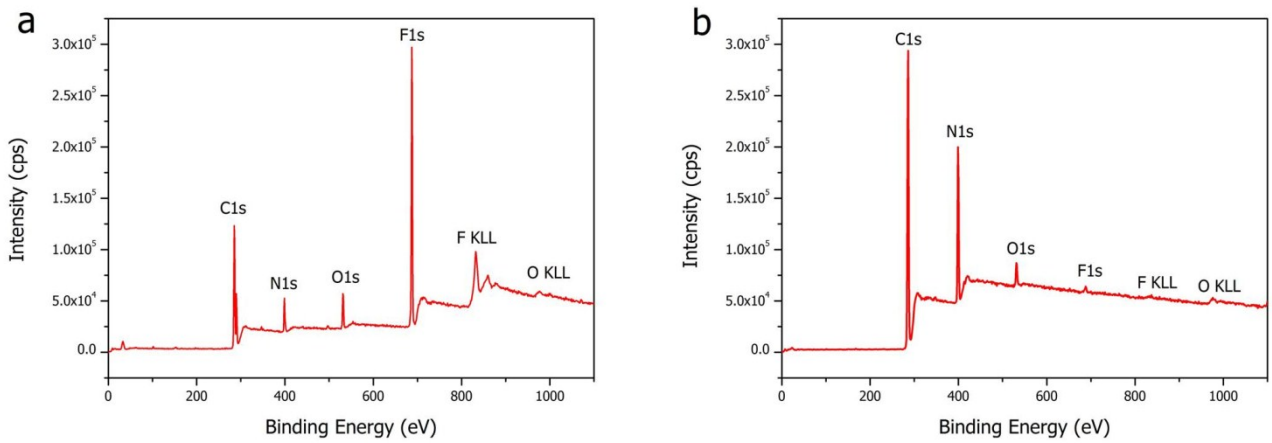
Figure S1 the wide XPS spectrum of m-PEI/PVDF composite nanofibrous mat (a) before and (b) after water immersion.
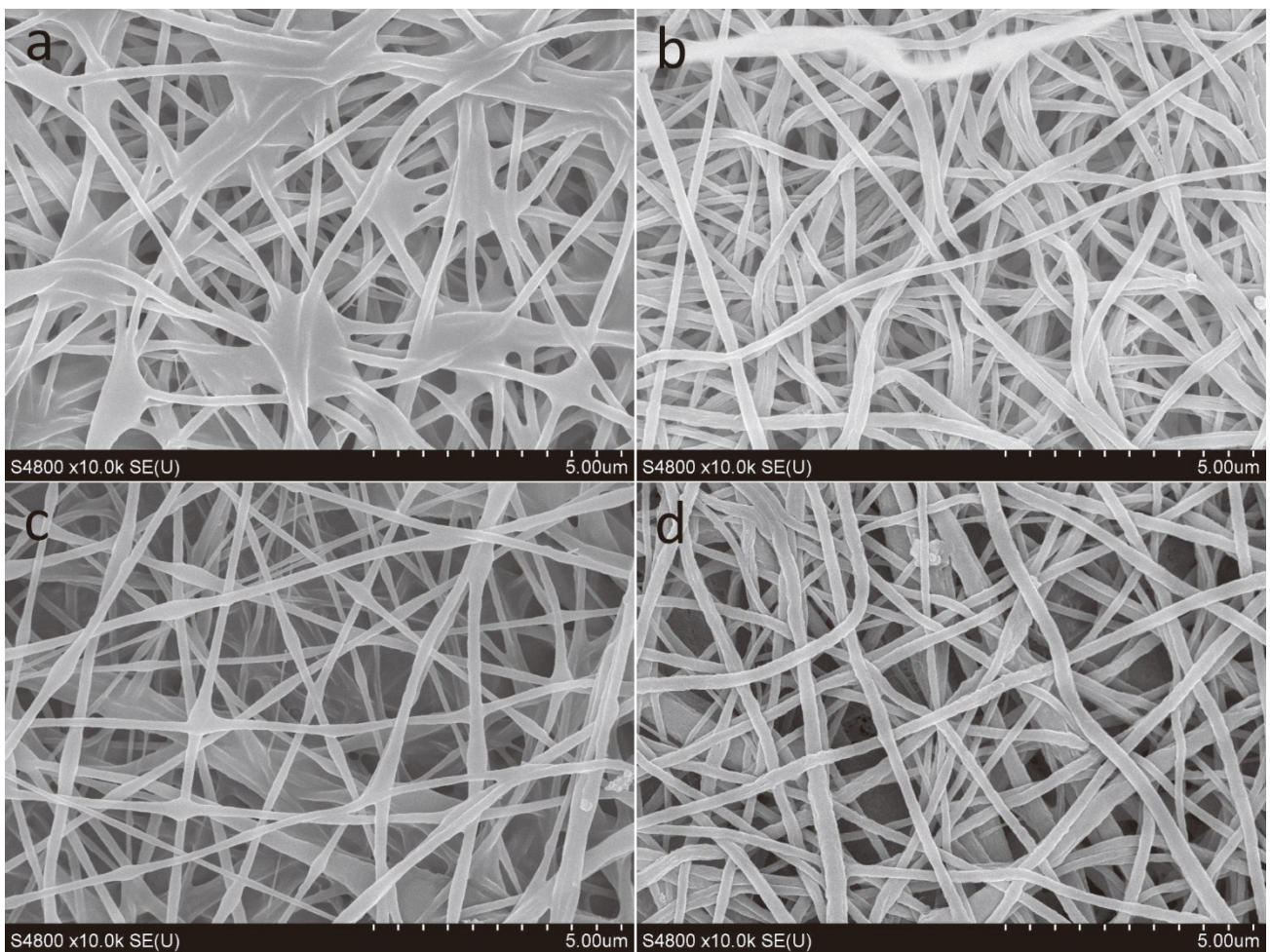
Figure S2 the SEM images of (a, b) b-PEI/PVDF and (c, d) m-PEI/PVDF composite nanofibrous mat before and after water immersion.
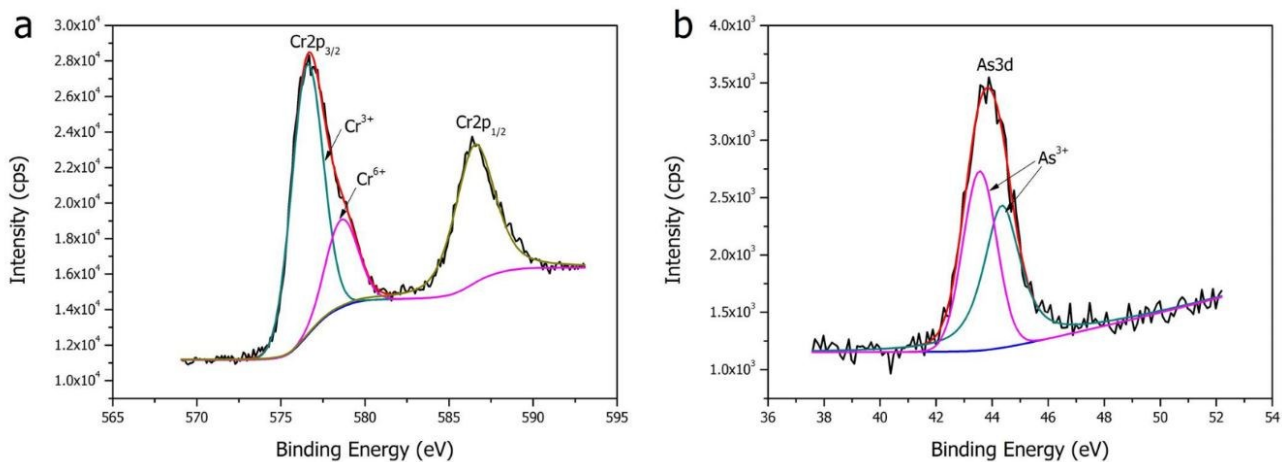
Figure S3 the XPS spectra of adsorbed (a)Cr(VI) and (b)As(V) on m-PEI/PVDF composite nanofibrous mat .
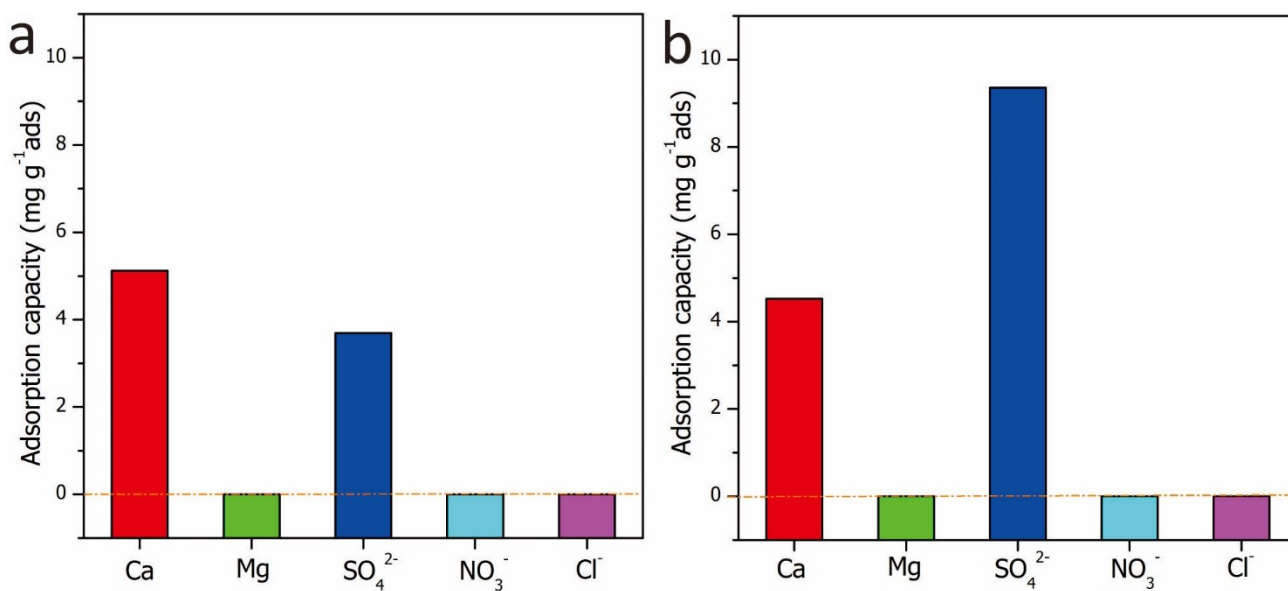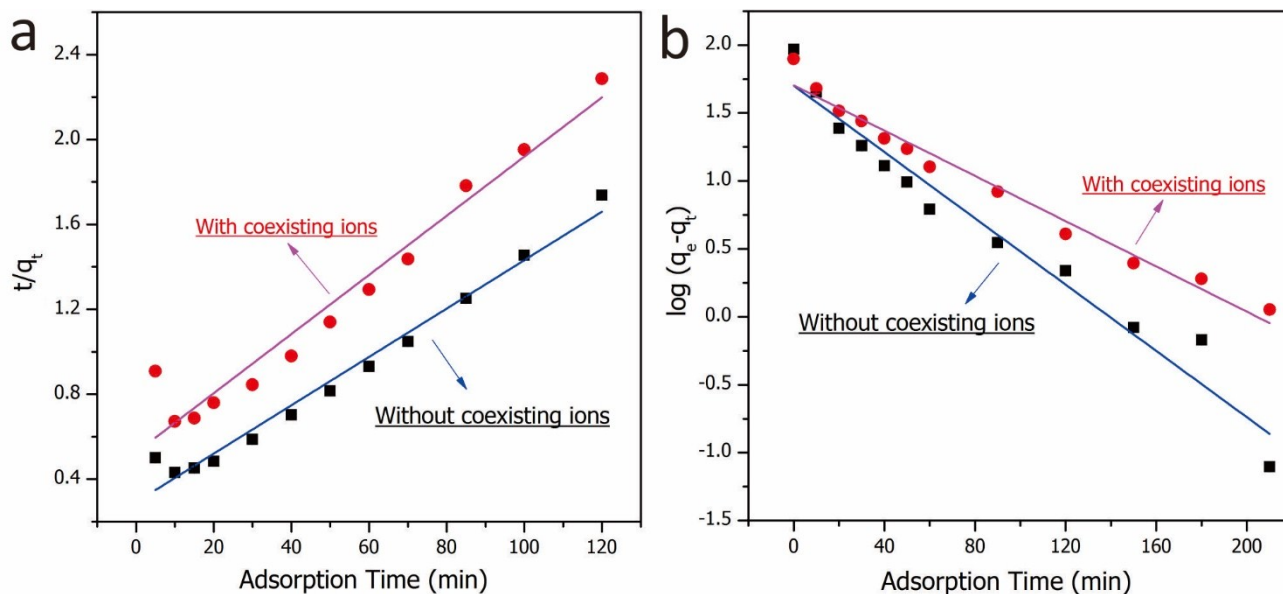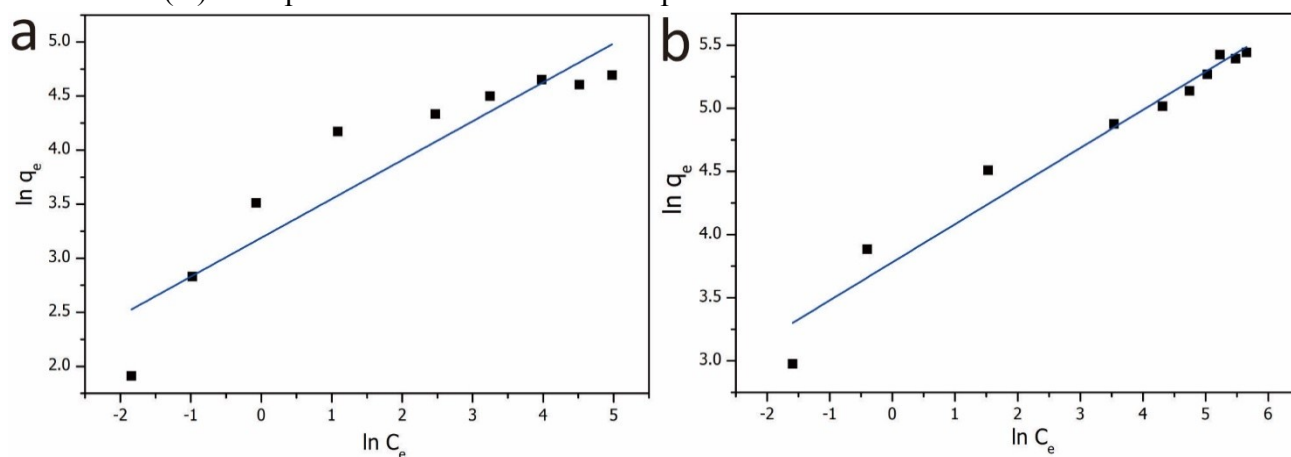

Figure S4 the uptake of co-existing ions onto m-PEI/PVDF composite nanofibrous mat in (a) Cr(VI) and (b) As(V) solution.

Figure S5 (a) the pseudo-second-order model of Cr(VI) adsorption and (b) the pseudo-first-order model of As(V) adsorption onto m-PEI/PVDF composite nanofibrous mat.

Figure S6 the Freundlich isotherm model of (a) Cr(VI) and (b) As(V) adsorption onto m-PEI/PVDF composite nanofibrous mat.

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