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Supplementary material for

Al-doping chitosan nonwoven in a novel adsorption reactor with sleeve cylinder for dye removal: Performance and mechanism

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Texts

Text S1 Kinetic models

The kinetic models are given as follows:

The pseudo first-order kinetic model:

$$\log(q_e - q_t) = \log q_e - \frac{K_1}{2.303} t \quad (1)$$

The pseudo second-order rate model:

$$\frac{t}{q_t} = \frac{1}{h} + \frac{1}{q_e} t, \quad h = K_2 q_e^2 \quad (2)$$

where *qe* and *qt* are the amounts of dye adsorbed (mg/g) at equilibrium and at different intervals, respectively; *K*1 (1/min) and *K*2 (g/mg•min) are the pseudo-first-order and second-order rate constants; and *h* represents the initial adsorption rate (mg/g•min).

Text S2 Three isotherm equations

The Langmuir isotherm was originally proposed to describe the adsorption of gas molecules onto metal surfaces. The model assumes uniform energy of the adsorption onto the surface and no migration of the adsorbate in the plane of the surface. It is expressed as

$$q_e = \frac{abC_e}{1 + bC_e} \tag{3}$$

where q_e is the amount of dyes adsorbed at equilibrium (mg/g) and C_e is the adsorbate concentration at equilibrium in aqueous solution (mg/L). The Langmuir isotherm parameters are *a* and *b*. The capacity of the adsorbent can be evaluated by *a*, and the parameter *b* includes various physical constants.

The Freundlich isotherm describes heterogeneous systems as the surfaces with nonenergetically equivalent sites. The equation can be written as follows:

$$q_e = K_f C_e^{1/n} \tag{4}$$

where K_f is the Freundlich constant, which is indicative of the extent of adsorption, and *1/n* is the heterogeneity factor, an indicator of adsorption effectiveness. Another useful equation is the Langmuir-Freundlich isotherm, which is based on the generalized Langmuir and generalized exponential isotherms and is the most promising extension of the Langmuir and Freundlich isotherms. It is expressed as

$$q_e = \frac{q_m (K_{lf} C_e)^v}{1 + (K_{lf} C_e)^v} \tag{5}$$

where q_m is the maximum adsorption (mg/g), K_{lf} is the Langmuir-Freundlich constant, and *v* is the Langmuir-Freundlich heterogeneity constant. The Langmuir-

Freundlich isotherm is essentially the Freundlich isotherm approaching a maximum at high concentrations.

Text S3 Infrared spectroscopy analysis (FT-IR), Ultraviolet–Visible spectroscopy analysis (UV-Vis) and H-NMR analysis

The Fourier-transform infrared (FT-IR) spectra of initial chitosan nonwoven and Al-doping chitosan nonwoven before and after adsorption are shown in **Fig. S3**, respectively. For pure chitosan nonwoven, a broad band at 3429 cm^{-1} is attributed to the stretching of –OH and $–NH_2$ groups. The N-H antisymmetric stretching vibration of primary amine is 3357 cm^{-1} and 3292 cm^{-1}. A band at 2917 cm^{-1} corresponds to the stretching of C-H groups. The absorption band at 1652 cm^{-1} and 1591 cm^{-1} are assigned as amide I vibrations and $–NH_2$ stretching vibration, respectively. The symmetric deformation of methyl groups are presented at 1373 cm^{-1}. The fingerprint of chitosan is between 1144 and 895 cm^{-1} corresponding to the polysaccharide skeleton (including the vibrations of the glycoside bonds, C–O and C–O–C stretching vibrations) [1-4]. FTIR spectrum of CSNW-AR73, Al-CSNW and Al-CSNW- AR73 complex show much similar bands of chitosan nonwoven.

Fig. S4 shows the UV-Vis absorption spectra of initial chitosan nonwoven and Al-doping chitosan nonwoven before and after adsorption. The dye maximum adsorption peak occurred at the 510 nm wavelength. When initial chitosan nonwoven and Al-doping chitosan nonwoven after adsorption, there also appear the dye maximum adsorption peak at 510 nm. It proves that the dyes combine with the adsorption materials. While the absorbance at 510 nm of Al-doping chitosan nonwoven after

adsorption is lower than initial chitosan nonwoven after adsorption, which implies its much higher capacity.

The ^{1}H NMR spectra of chitosan nonwoven and Al-doping chitosan nonwoven in CD_3COOD/D_2O were shown in **Fig. S5**. According to the published studies [5-7], a small peak about at 2.03 ppm assigned to the presence of $-CH_3$ of the N-alkylated glucosamine (GlcN) residue. The singlet at 3.16 ppm was assigned to H2 of GlcN and N-alkylated GlcN, and the multiplet peaks from 3.6 to 3.9 ppm were attributed to H3, H4, H5, and H6 of GlcN and N-alkylated GlcN. There existed a peak at around 4.8 ppm because of the presence of H1 of GlcN and N-alkylated GlcN. Although the Al species were supported on nonwoven successfully in loading from about 0.2267% by the modification processes according to the SEM-EDS result, no obvious difference between initial chitosan nonwoven and Al-doping chitosan nonwoven were observed. This result might be attributed to the low content of Al species on chitosan nonwoven, which is in agreement with the results of FTIR and UV-Vis spectra (**Figure S3 and S4**).

Tables

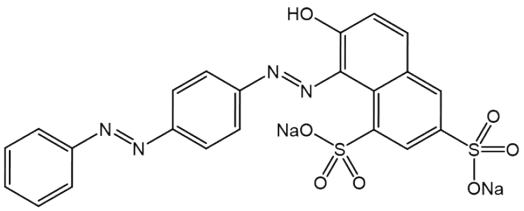
Table S1. Parameters of kinetics study for AR73 adsorption onto Al-doping chitosan nonwoven

Initial Concentration (mg/L)	Pseudo first-order equation			Pseudo second-order equation		
	q_e (mg/g)	K_1 (1/min)	R^2	q_e (mg/g)	K_2 (g/mg•min)	R^2
20	7.9646	0.3205	0.9983	8.1526	0.06183	0.9989
50	20.0220	0.1943	0.9957	20.9161	0.01083	0.9960
100	37.8800	0.09737	0.9259	42.5532	0.001804	0.9725
150	54.1056	0.01925	0.9234	61.4628	0.001103	0.9619
200	59.8149	0.02142	0.9584	66.9344	0.001586	0.9893

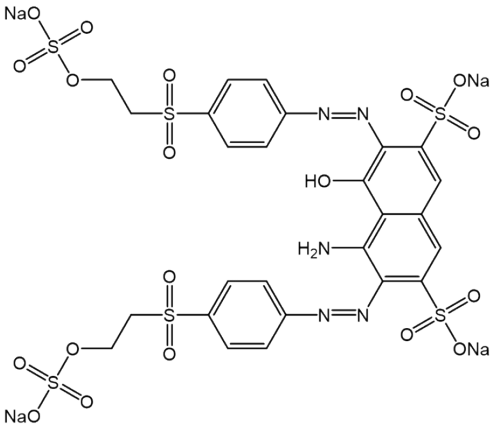
Table S2. Parameters of isotherm models for AR73 adsorption

Adsorption Isotherm Model	Initial chitosan nonwoven		Al-doping chitosan nonwoven	
	Parameters	R^2	**Parameters**	R^2
Langmuir	a = 78.37 mg/g b = 0.13529 L/g	0.9414	a = 144.67 mg/g b = 1.2168 L/g	0.85794
Freundlich	K_f= 25.82 $mg^{1-1/n}L^{1/n}/g$ n =5.86447	0.9216	K_f= 61.07 $mg^{1-1/n}L^{1/n}/g$ n = 6.9518	0.95076
Langmuir-Freundlich	q_m = 88.43mg/g K_{lf} =0.08682 v = 0.51724	0.9774	q_m =260.03mg/g K_{lf} =0.00725 v = 0.23468	0.95251

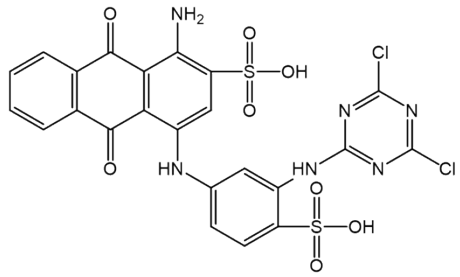
Figures



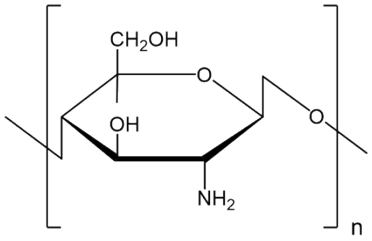
C. I. Acid Red 73



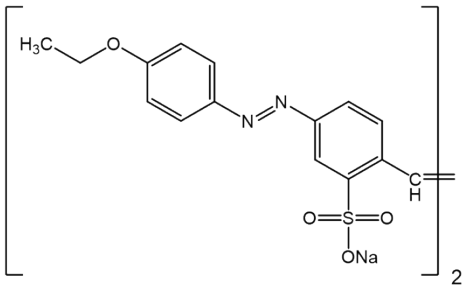
C. I. Reactive Black 5



C. I. Reactive Blue 19



Chitosan



C. I. Direct Yellow 12

Figure S1. The chemical structures of dyes and chitosan.

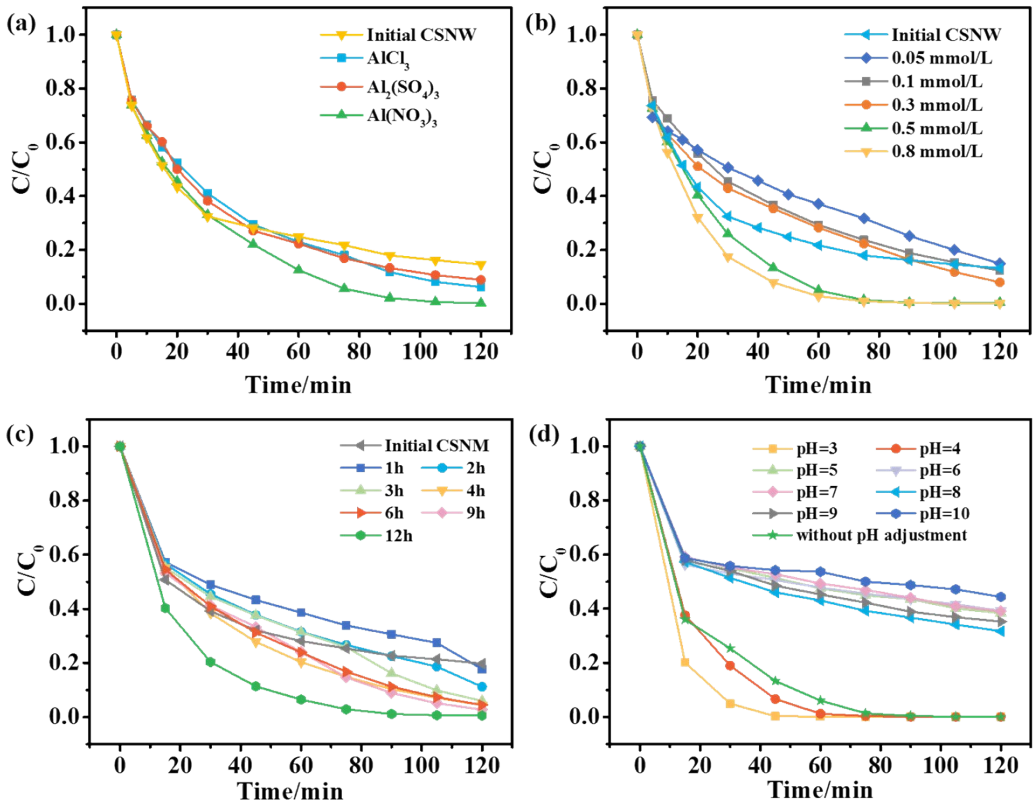


Figure S2. Effect of (a) aluminum source, (b) content of Al^{3+}, (c) modification time and (d) modification pH on AR73 removal by Al-doping chitosan nonwoven (initial concentration 100 mg/L, 2 L, adsorbent 5 g).

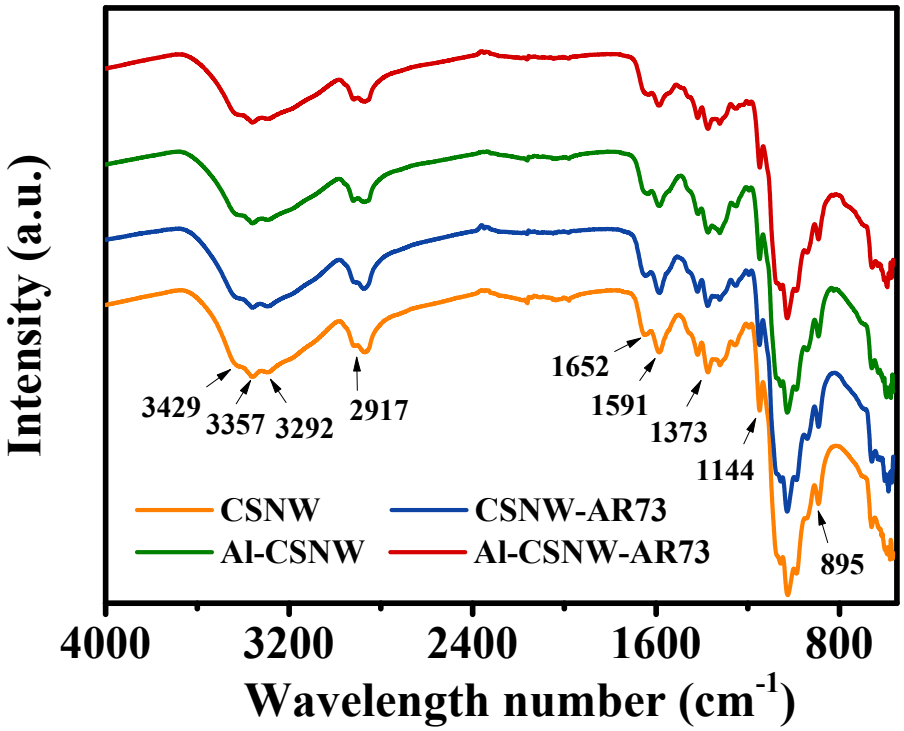


Figure. S3 FTIR spectra of initial chitosan nonwoven (CSNW), initial chitosan nonwoven after adsorption (CSNW-AR73), Al-doping chitosan nonwoven (Al-CSNW), and Al-doping chitosan nonwoven after adsorption (Al-CSNW-AR73).

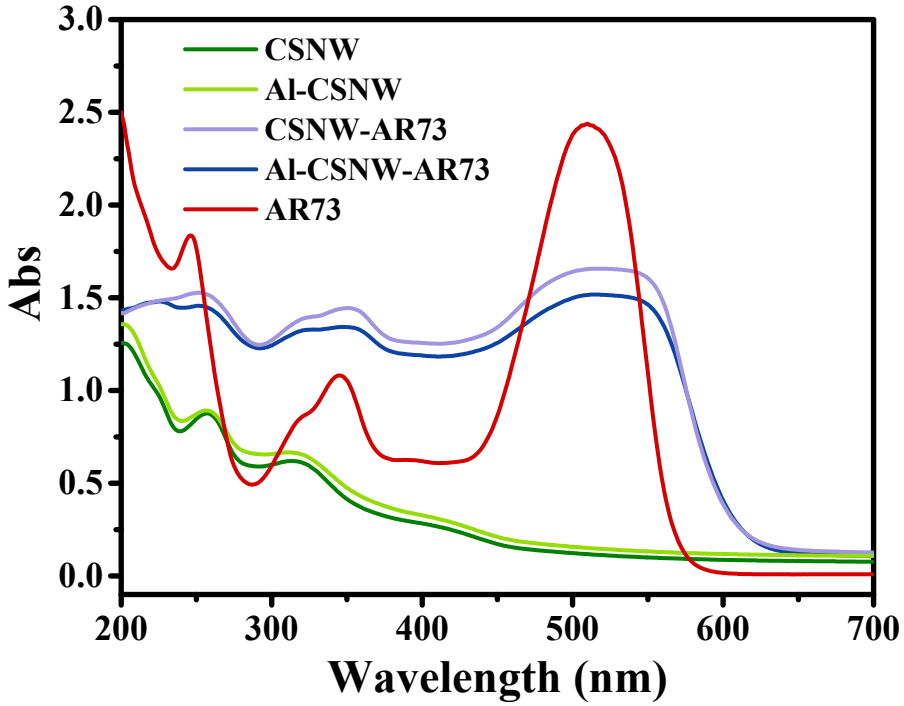


Figure. S4 UV-vis diffuse reflection spectra of C. I. Acid Red 73 (AR73), initial chitosan nonwoven (CSNW), initial chitosan nonwoven after adsorption (CSNW-AR73), Al-doping chitosan nonwoven (Al-CSNW) and Al-doping chitosan nonwoven after adsorption (Al-CSNW-AR73).

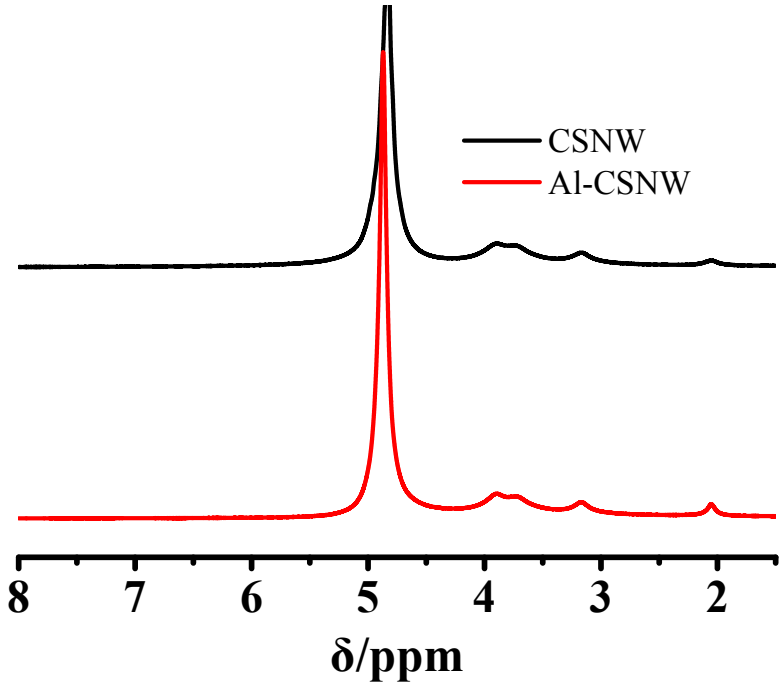


Figure. S5 ^{1}H NMR spectra of chitosan nonwoven (CSNW) and Al-doping chitosan nonwoven (Al-CSNW) in D_3CCOOD/D_2O

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