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Supplementary Information

Cotton fiber supported layered double hydroxides for highly efficient adsorption of anionic organic pollutants in water

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Influence of Ni:Al rations on adsorption performance

The adsorption performance of LDHs modified cotton fiber prepared under Ni:Al ratios of 3:1, 2:1, 1:1, 1:2, 1:3 was investigated and the results were shown in Fig. S1. The results indicated that the ratio of Ni and Al would influence the adsorption performance and the molar ratio of 2:1 NiAl had the best performance in removal of ketoprofen and congo red.

The main reason is that the general formula of LDHs is $[M^{2+}_{1-x}M^{3+}_{x}(OH)_2]^{x+}(A^{n-})_{x/n}\cdot mH_2O$, in which M^{2+} and M^{3+} stand for divalent and trivalent cation. When x is larger which means the higher Al^{3+} content in the experiment, metal oxides and/or metal hydroxides may appear in LDHs and decrease adsorption efficiency of the composite. However, too lower content of Al^{3+} can cause disorder of LDHs layer and irregular shapes of LDHs structure and influence the adsorption efficiency. Finally, the ratio of 2:1 NiAl was chosen in our experiment and both free-standing and supported LDHs were synthesized at this ratio for adsorption experiments.

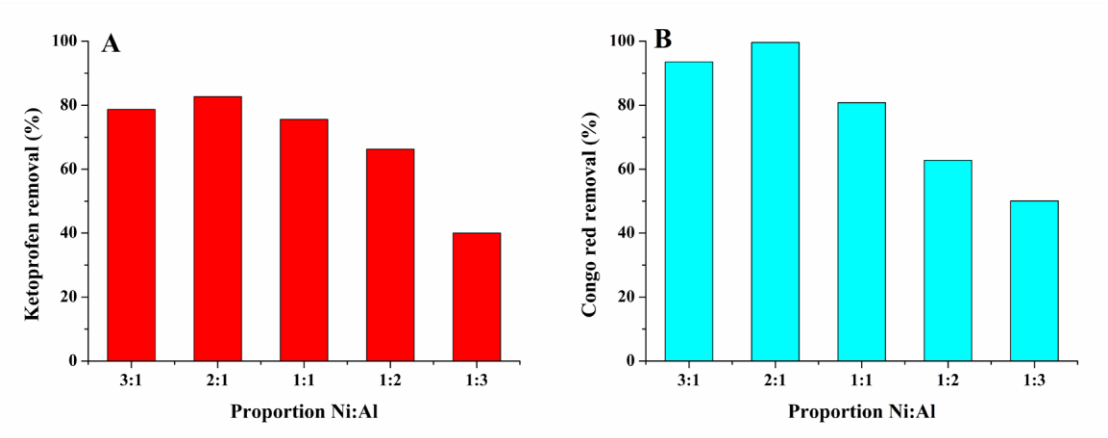

Fig. S1. The removal percentage of (A) ketoprofen and (B) congo red at different proportion Ni:Al (Initial concentration: 200 mg/L; Contact time: 10 h).

Preparation of LDHs crystal

Based on the synthetic method reported by literature, LDHs crystal was synthesized by coprecipitation method. 5.80 g $Ni(NO_3)_2\cdot 6H_2O$, 3.80 g $Al(NO_3)_3\cdot 9H_2O$ and 4.20 g urea were dissolved in 50 mL deionized water and then the solution was reacted under 95 ℃ for 18 h. To obtain uniform LDHs crystal in size, the reaction solution was

under continuous stirring. The resulting slurry was centrifuged at 8000 rpm for 10 min, washed by water and then the process above was repeated three times to remove reactant residuals. Finally the precipitate was collected and dried overnight under 60 ℃ in the oven.

Characterization

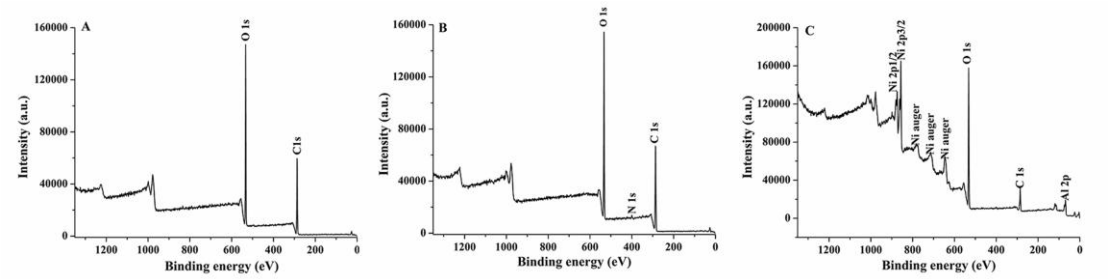

Fig. S2. XPS spectra of (A) bare cotton and (B) PD@cotton and (C) LDHs@PD@cotton.

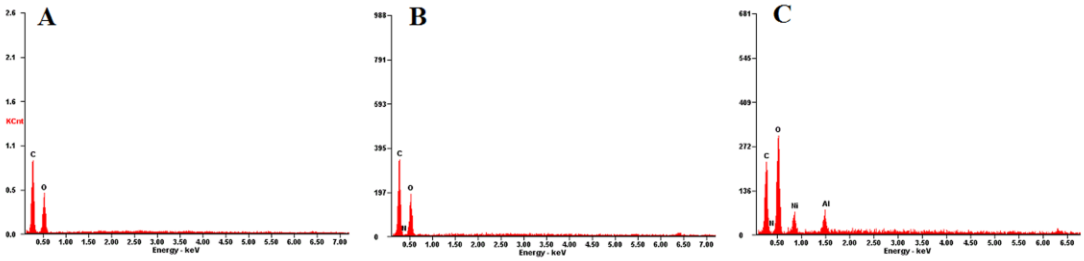

Fig. S3. EDS spectra of (A) bare cotton and (B) PD@cotton and (C) LDHs@PD@cotton.

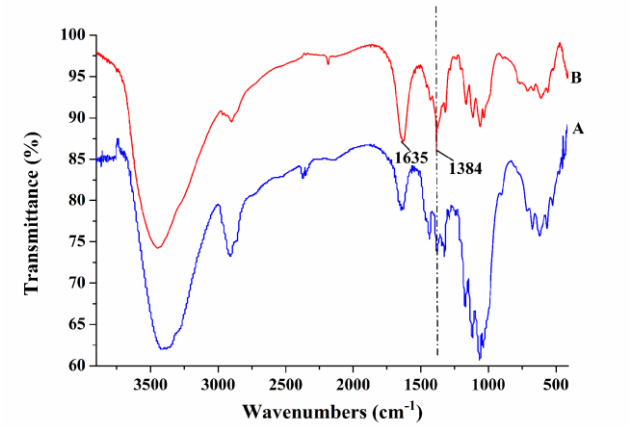

Fig. S4. FTIR spectra of (A) bare cotton and (B) LDHs@PD@cotton.

Adsorption kinetic

The liner form of pseudo-second-order kinetic model was expressed as follows:

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

Where q_e and q_t (mg/g) are the amount of adsorbates absorbed on LDHs-C and LDHs@PD@cotton at equililibrium and time t (min), respectively, and k is the the equilibrium rate constant. The values of k and $q_{e,cal}$ could be calculated from the slope and intercept of the plot of t/q_t *versus* t, respectively. The linear relationship of t/q_t *versus* t was presented in Fig. S5 and the detailed parameters were presented in Table S1.

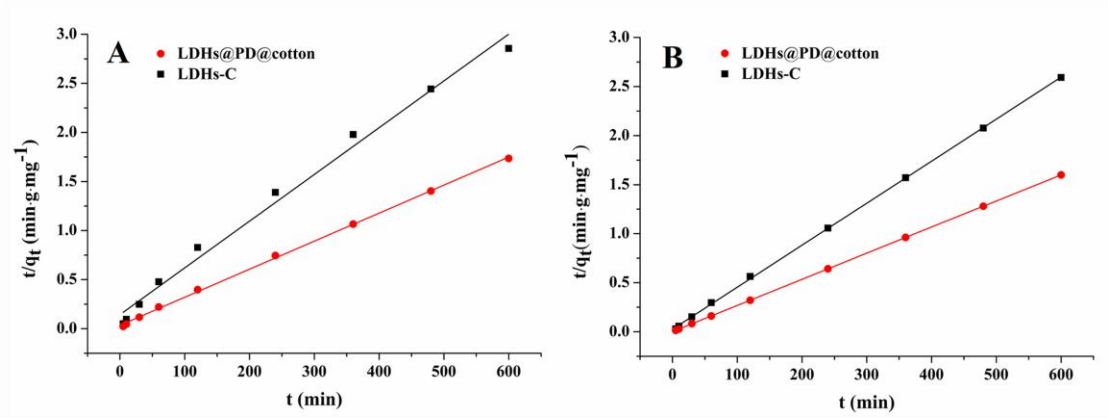

Fig. S5. Pseudo-second-order kinetics for adsorption of (A) ketoprofen and (B) congo red over LDHs-C and LDHs@PD@cotton.

Table S1

Parameters of the pseudo-second-order adsorption kinetics of ketoprofen and congo red samples (Initial concentration : 200 mg/L)

Adsorbents	Sample	$q_{e,exp}$ (mg/g)	Pseudo-second-order model				
			$q_{e,cal}$	k ($\times 10^{-4}$ g/mg·min)	R^2	S.D.(%)	h (mg/g·min)
LDHs-C	ketoprofen	210	208	1.61	0.991	0.31	7.10
	congo red	231	232	7.34	0.999	0.17	39.17
LDHs@PD	ketoprofen	346	345	2.44	0.999	0.09	29.21
@cotton	congo red	375	370	56.08	1.000	0.44	788.63

Test of kinetics models

Normalized standard deviation, S.D.(%), is a parameter to decide which kinetic model will describe the adsorption kinetic behavior better. It can be obtained by the following equation:

$$S.D.(\%) = 100 \times \left\{ \sum \frac{[(q_{e,exp} - q_{e,cal})/q_{e,exp}]^2}{N-1} \right\}^{1/2} \quad (2)$$

Where N is the number of data points, $q_{e,exp}$ is the equilibrium absorption capacity obtained from experiments and $q_{e,cal}$ is the calculated values by kinetics models.

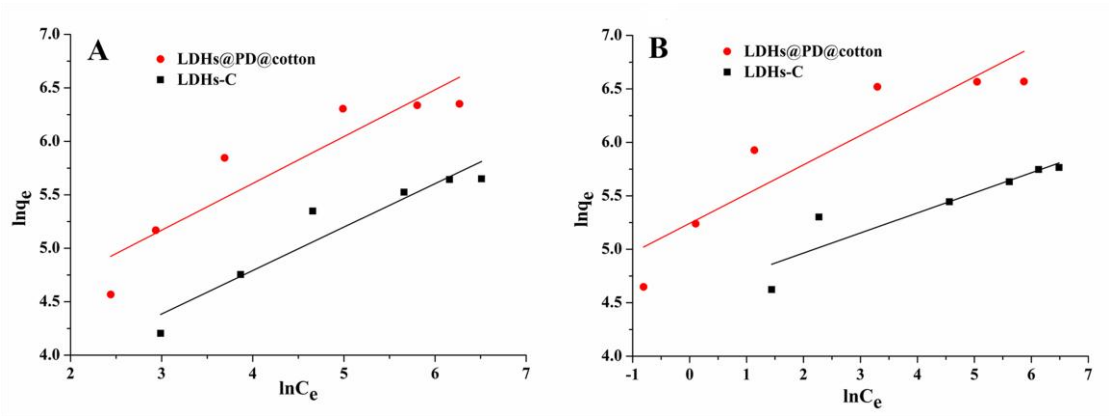

Fig. S6. Freundlich plots of the isotherms for (A) ketoprofen and (B) congo red over LDHs-C and LDHs@PD@cotton.

Separation factor

Separation factor: The separation factors (R_L) for different adsorbents toward ketoprofen and congo red were calculated as follows:

$$R_L = \frac{1}{1+K_L C_0} \quad (3)$$

Where, C_0 is the initial concentration of ketoprofen and congo red (mg/L) and K_L is the Langmuir constant (L/mg). The R_L values for LDHs@PD@cotton and LDHs-C towards ketoprofen and congo red were depicted in Fig. S7.

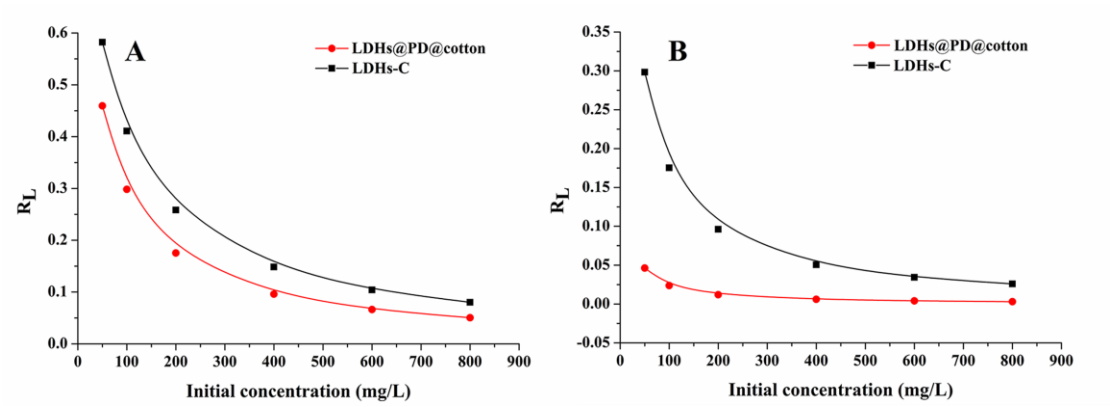

Fig. S7. Effect of initial concentrations of (A) ketoprofen and (B) congo red on the separation factor R_L over LDHs-C and LDHs@PD@cotton.

Adsorption performance of LDHs@PD@cotton packed pipette tips

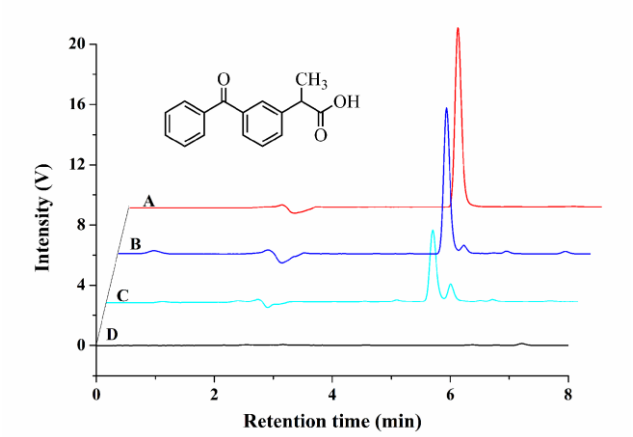

Fig. S8. HPLC chromatogram of (A) original ketoprofen solution (1 mg/L) and after treated by (B) cotton and (C) LDHs-C and (D) LDHs@PD@cotton.

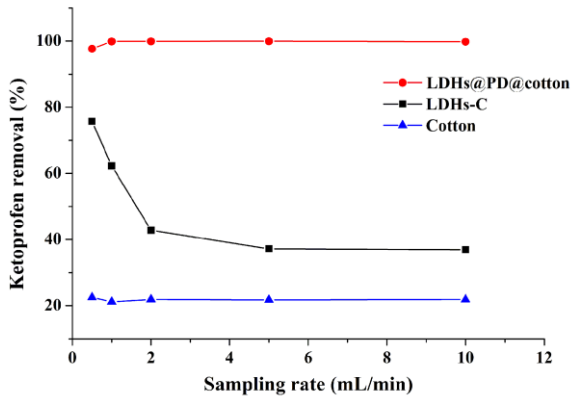

Fig. S9. The influence of sampling rate on the adsorption of ketoprofen (1 mg/L) over bare cotton fiber, PD@cotton and LDHs@PD@cotton.

Reusability experiment

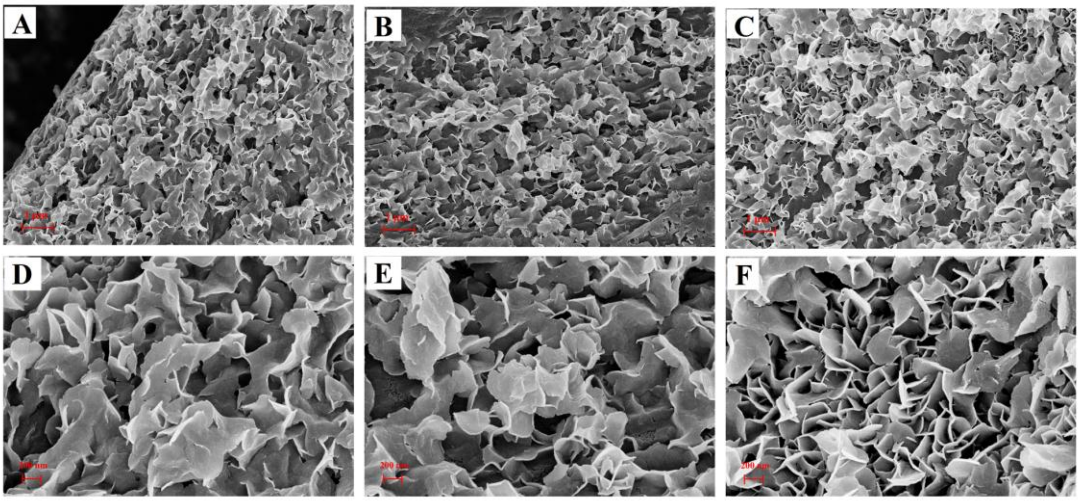

Fig. S10. SEM images of LDHs@PD@cotton (A, D) before adsorption and (B, E) after adsorption of ketoprofen and (C, F) after regeneration in 5 recycles.

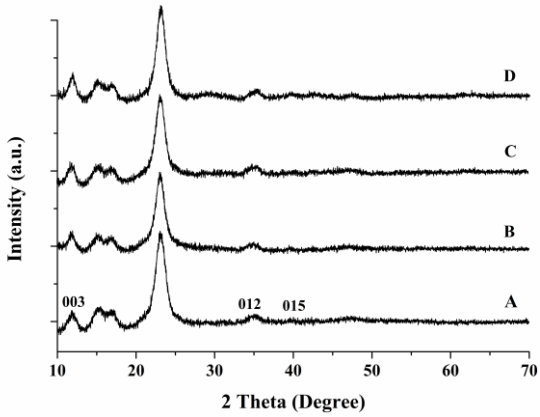

Fig. S11. XRD patterns of LDHs@PD@cotton (A) before adsorption and (B) after adsorption of ketoprofen and (C) after adsorption of congo red and (D) after regeneration in 5 recycles.

Adsorption performance of LDHs@PD@cotton on other anionic pharmaceuticals and organic dyes

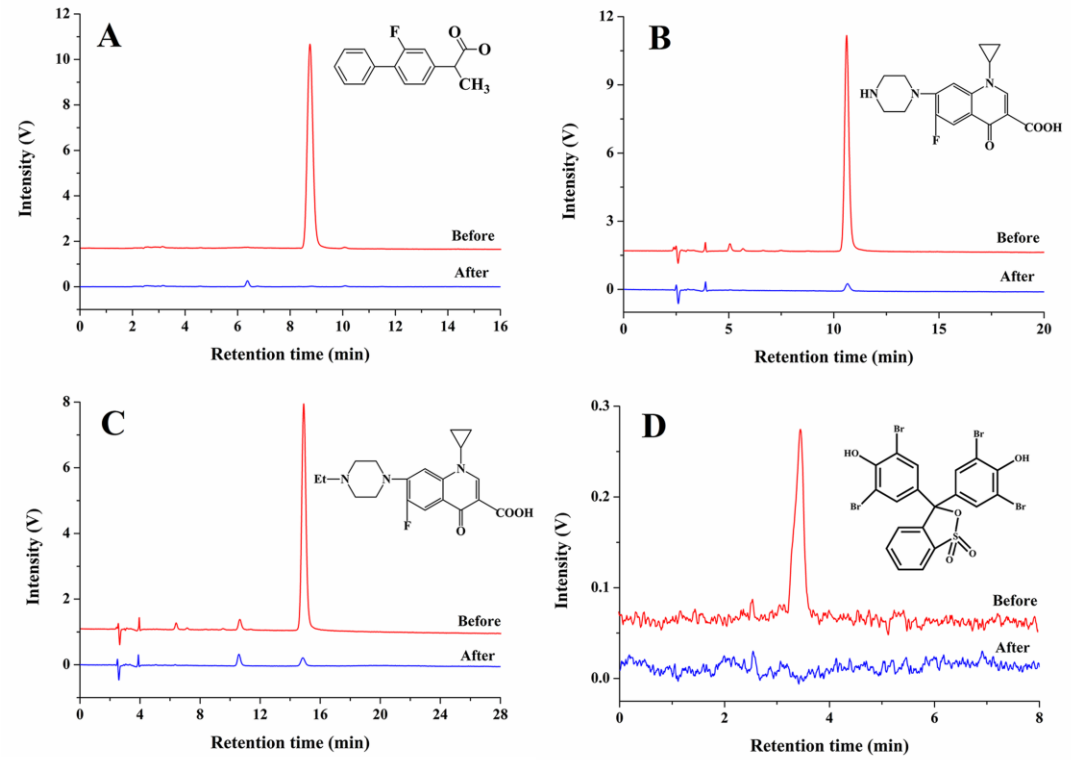

Fig. S12. Adsorption behavior of other anionic pharmaceuticals and dyes over LDHs@PD@cotton from water: (A) Flurbiprofen and (B) Ciprofloxacin and (C) Enrofloxacin and (D) Bromophenol blue.