Supplementary Information for

Preparation of Poly (acrylic acid) Based Hydrogel with Fast Adsorption Rate and High Adsorption Capacity for Removal of Cationic Dyes

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1. ^{1}H NMR spectrum of Dex-MA

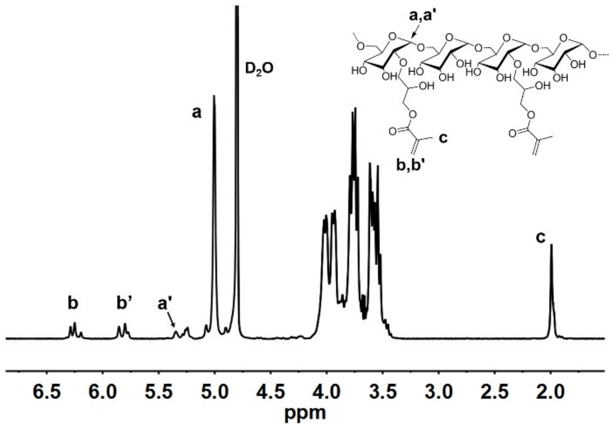

Fig S1 ^{1}H NMR (400 MHz) spectrum of Dex-MA in D_2O.

2. pH_{PZC} of Dex-MA/PAA hydrogel

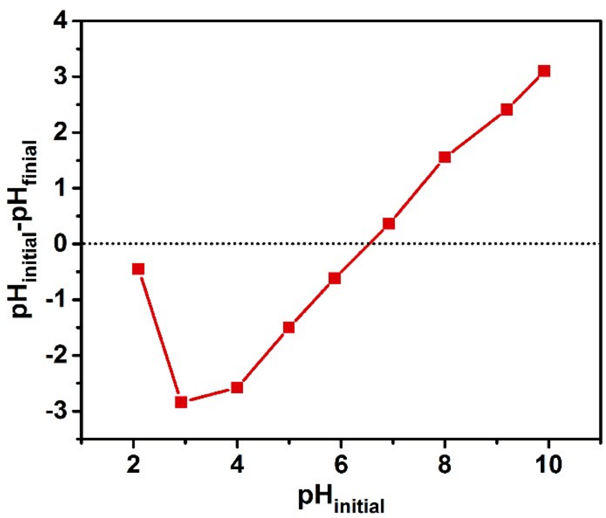

Fig. S2 Plot of $pH_{(initial)}$ - $pH_{(final)}$ against $pH_{(initial)}$. The intercept $pH_{(PZC)}$ = 6.6 is the pH at which the Dex-MA/PAA hydrogel has zero charge.

3. The effect of degree of substitution (DS) and AA content on adsorption ability

The effect of degree of substitution (DS) on the adsorption rate was investigated before systematically studying the adsorption properties of hydrogels. When the DS of Dex-MA was 3.5% (m_{AA}/m_{Dex-MA}=4), the strength of the resulting hydrogel was very soft due to the low crosslink degree, which cannot be applied as the adsorbent.

As shown in Fig. S3, the adsorption rate was slightly decreased when the DS increased from 10.5% to 13.6. The hydrogel network was more compact due to the increased crosslink degree, resulting in the increase of diffusion resistance for MB and CV.

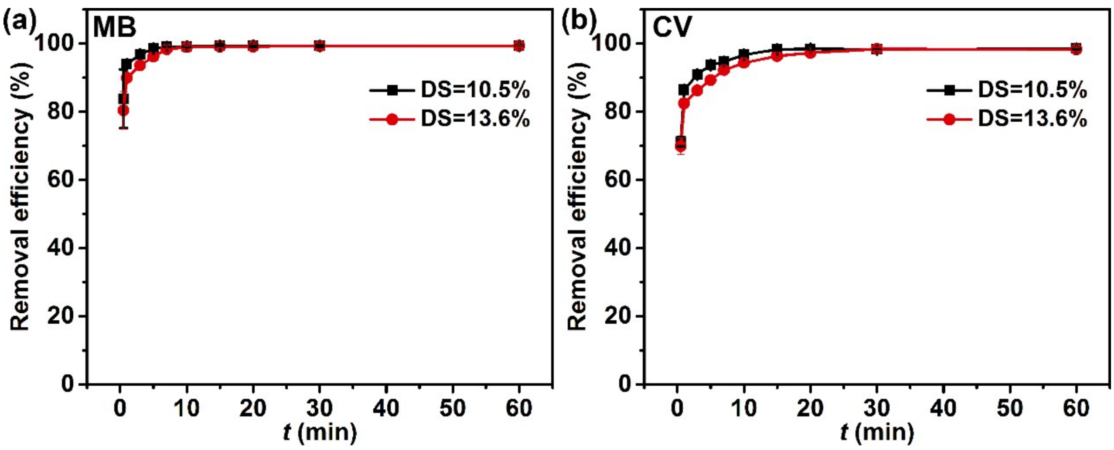

Fig. S3 The effect of degree of substitution on the adaorption rate of (a) MB and (b) CV.

The effect of AA content on the maximum adsorption capacity (q_m) was also studied, and the results was shown in Fig. S4. The q_m was dramatically improved with the increase of AA content. However, the q_m did not increase linearly when the $m_{AA}/m_{Dex\text{-}MA}$ was increased to 6, which was ascribed to the low polymerization yield at high concentration of AA.[1] The hydrogel obtained at high concentration of AA presented poor mechanical strength when applied in adsorption application. Besides, the hydrogel was easily suspended in dye solutions with poor settling property, which is an important factor for adsorbent. The separation of adsorbent with poor settleability requires extra flocculation, which will increase the cost of water treatment.

Therefore, considering the factors above, the $m_{AA}/m_{Dex\text{-}MA}$=4 was selected for preparing the Dex-MA/PAA adsorbent.

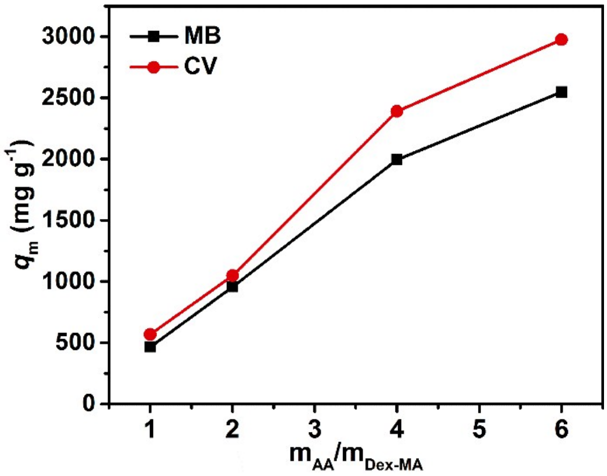

Fig. S4 The effect of AA content on the $q_{m.}$

4. Response surface methodology (RSM) studies of optimal conditions

Response surface methodology (RSM) and Box-Benhnken design (BBD) was applied to determine the optimal parameters of pH, salt concentration and temperature. The experimental responses were removal efficiency of MB and CV (50 mg/L). The statistical significance was evaluated by variance analysis (ANOVA)and the programs Design Expert were used to study all the parameters and experiment data. The values of three factors were shown in Table S1 and the experimental values of removal efficiency of MB and CV were listed in Table S2.

Table S1. Actual levels for independent factors used in the experimental design

Factors		Values		
		-1	0	1
A	pH	2	6	10
B	Concentration of NaCl (mM)	0	200	400
C	Temperature (°C)	20	40	60

Table S2. Box-Benhnken design of three factors and three levels.

Order	Factors			Removal efficiency (%)	
	A	B	C	MB	CV

2	1	0	1	10.24	53.04
1	0	-1	-1	97.96	97.46
14	-1	1	0	1.98	18.45
13	1	1	0	3.03	42.79
10	1	0	-1	12.42	55.22
6	0	0	0	12.33	54.04
17	0	0	0	13.56	52.37
11	1	-1	0	98.04	96.9
4	0	-1	1	96.15	95.25
16	0	1	1	2.28	41.1
9	-1	0	1	5.98	22.56
12	-1	0	-1	7.98	24.78
5	0	0	0	11.56	57.13
7	0	0	0	12.88	52.68
15	0	0	0	9.29	55.92
3	-1	-1	0	47.52	54.19
8	0	1	-1	3.46	43.32

The variance analysis of all of the linear, quadratic, and interaction effects of the three factors for MB and CV were shown in Table S3 and S4, respectively. According to *p* value, the A, B, AB, B^2 were significant for removal efficiency of MB, and the C, AC, BC, A^2， C^2 were not significant. A, B, AB, A^2, B^2 were significant for removal efficiency of CV and C, AC, BC, C^2 were not significant. The *F* also confirmed these effects. Based on the results above, the removal efficiency of MB and CV were significantly influenced by the pH and salt concentration.

For a model to be significant and have a good fit, the *F*-value must be higher than 3.02, and for lack of fit, lower than 5.05. In addition, the *p* value must be lower than 0.05 and the *p* value for lack of fit, higher than 0.05. Therefore, the regression model for MB was significant, however, the lack of fit was also significant. The removal efficiency of CV shows a significant regression model without lack of fit, which were also confirmed by *p* values. The determination coefficient (R^2) for the models indicates that they explain 94.01 and 98.36% of the variations around the average for removal efficiency of MB and CV, respectively.

Table S3 Variance analyses (ANOVA) table for MB

Source	Sum of squares	DF	Mean square	F Value	p-value	R^2
Model	19559.36	9	2173.26	28.89	0.0001	0.9401
A	454.06	1	454.06	6.04	0.0437	
B	13523.55	1	13523.55	179.77	< 0.0001	
C	6.43	1	6.43	0.09	0.7785	
AB	611.82	1	611.82	8.13	0.0246	
AC	8.10×10^{-3}	1	8.10×10^{-3}	1.08×10^{-4}	0.9920	
BC	0.10	1	0.10	1.32×10^{-3}	0.9720	
A^2	239.66	1	239.66	3.19	0.1174	
B^2	4658.64	1	4658.64	61.93	0.0001	
C^2	96.02	1	96.02	1.28	0.2958	
Residual	526.58	7	75.23			
Lack of Fit	515.75	3	171.92	63.52	0.0008	
Pure Error	10.83	4	2.71			
Cor Total	20085.94	16				

Table S4 Variance analyses (ANOVA) table for CV

Source	Sum of squares	DF	Mean square	F value	p-value	R^2
Model	8899.09	9	988.79	107.86	< 0.0001	0.9836
A	2047.04	1	2047.04	223.30	< 0.0001	
B	4907.43	1	4907.43	535.33	< 0.0001	
C	9.75	1	9.75	1.06	0.3368	
AB	84.36	1	84.36	9.20	0.0190	
AC	0.0004	1	0.0004	4.36×10^{-5}	0.9949	
BC	2.5×10^{-5}	1	2.5×10^{-5}	2.73×10^{-6}	0.9987	
A^2	1059.65	1	1059.65	115.59	< 0.0001	
B^2	887.52	1	887.52	96.82	< 0.0001	
C^2	0.48	1	0.48	0.05	0.8264	
Residual	64.17	7	9.17			
Lack of Fit	47.20	3	15.73	3.71	0.1189	

Pure Error	16.97	4	4.24
Cor Total	8963.26	16	

Fig. S5 shows the influence of NaCl and pH on the removal efficiency of MB and CV. The increase of pH and decrease of NaCl concentration cause an increase of removal efficiency of MB and CV. Based on the programs Design Expert, the optimal conditions for adsorption of MB and CV was obtained, which was pH 10, 20 °C, 0 mM NaCl. In this model, the removal efficiency is gradually increased with the increase of pH at 20 °C without NaCl, which is inconsistent with the result. In our studies, the pH effect on the removal efficiency was studies at 20 °C without NaCl. At $pH_{initial}$ 2.0 the removal efficiency for MB and CV were 47.8 % and 56.9 %, respectively. When the $pH_{initial}$ slightly increased to 3.0, the removal efficiency for both dyes were dramatically increased to ~96%. Further increases in $pH_{initial}$ to 10.0 produced no additional increase in the removal efficiency for the dyes. Although the prediction of pH is not accurate, we can still get more information about the impact of different parameters. Considering the real pH effect, pH 8, 20 °C, 0 mM NaCl was selected as the adsorption conditions.

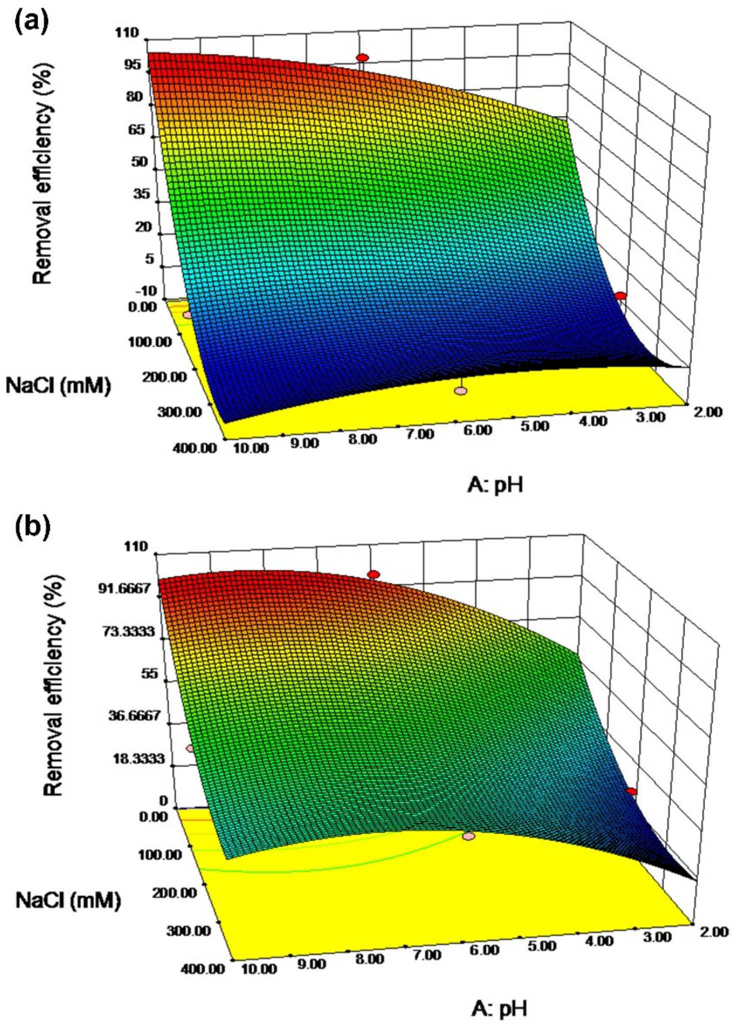

Fig. S5 Influence of pH and NaCl on removal efficiency of (a) MB and (b) CV

5. Dye solutions before and after adsorption.

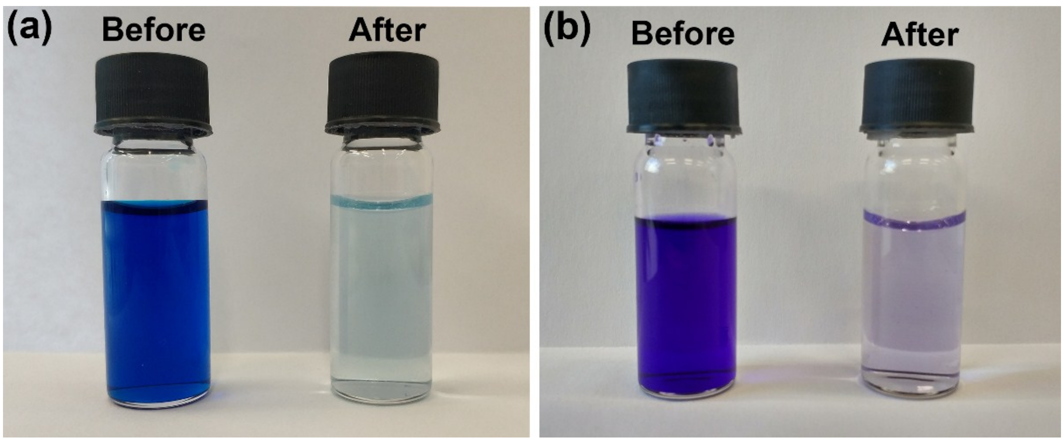

Fig. S6 Solutions of (a) MB and (b) CV before and after adsorption.

6. Adsorption kinetics at 100 mg L^{-1} of dyes

We also confirmed the e kinetics at concentration of 100 mg/L. As shown in Fig. S7, within the first minute the removal efficiencies of MB and CV have reached 91.1 % and 82.6 %, respectively, which was a little lower than that of 50 mg/L. The equilibrium time of MB and CV at 50 mg/L and 100 mg/L were similar. The experimental data were also fitted to pseudo-first order, pseudo-second order, Elovich kinetic model, and intra-particle diffusion model (Fig. S8) and their corresponding kinetic parameters were listed in Table S5. The experimental data were also well fitted by PSO kinetic model due to the high R^2. Besides, the kinetic parameters obtained by the intra-particle diffusion model at 100 mg/L presented the similar adsorption process ($k_{d1} > k_{d2} > k_{d3}$, $C_1 < C_2 < C_3$) with that of 50 mg/L.

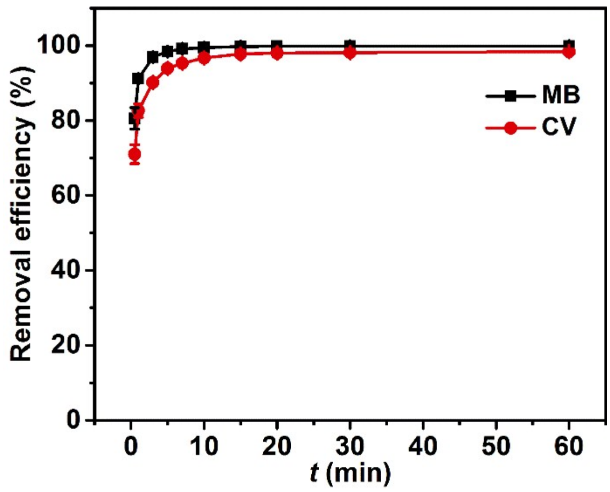

Fig. S7 Effect of contact time, *t*, on the dye removal efficiency. Hydrogel adsorbent dose: 1 g L^{-1}, dye concentration: 100 mg L^{-1}, $pH_{initial}$ 8.0.

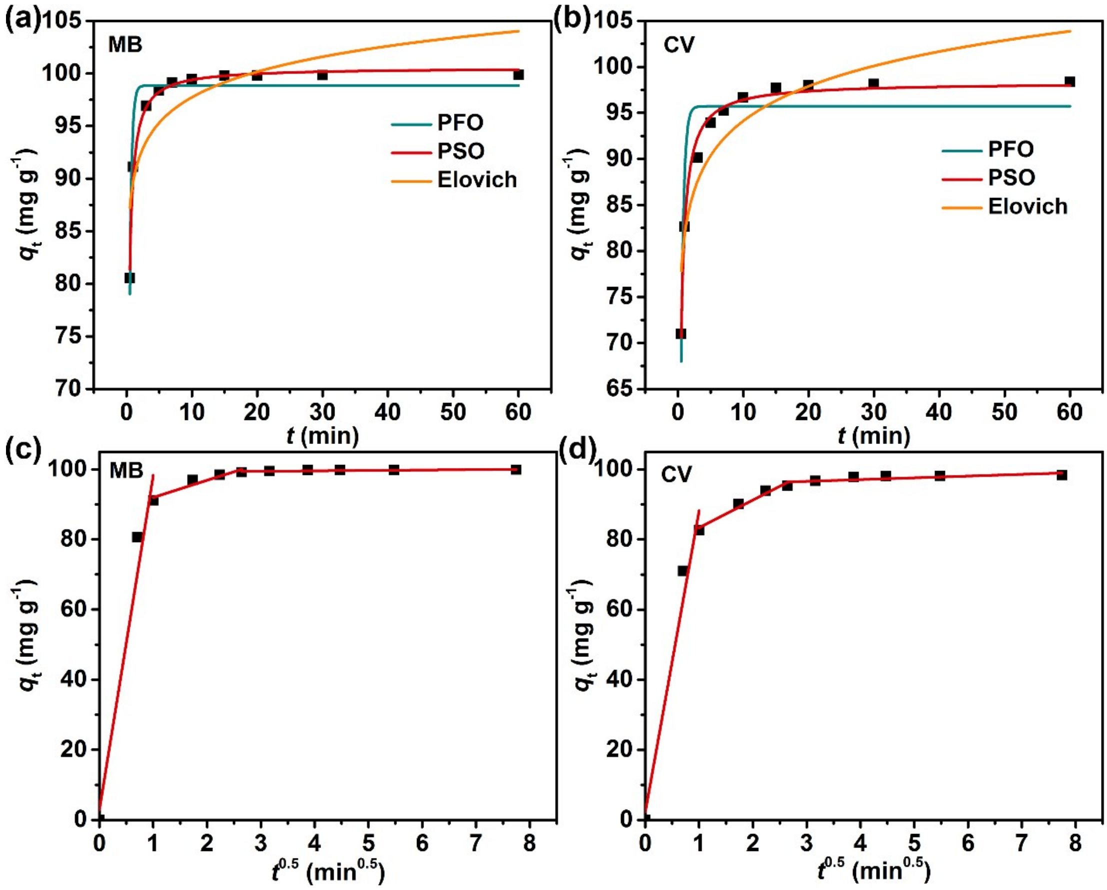

Fig. S8 Dye adsorption on Dex-MA/PAA as a function of time: pseudo-first order (PFO), pseudo-second order (PSO) and Elovich kinetic plots of (a) MB and (b) CV; intra-particle diffusion kinetic plots of (c) MB and (d) CV. (Dyes concentration:100 mg/L)

Table S5 Parameters for pseudo-first order, pseudo-second order and Elovich kinetic models, and intra-particles diffusion model for MB and CV adsorption (Dyes concentration: 100 mg/L).

	Parameter	Adsorbing dye	
		MB	CV
Pseudo-first order	$q_{e(cal)}$	98.8	95.7
	k_1	3.22	2.48

	R^2	0.9201	0.8560
Pseudo-second order	$q_{e(cal)}$	99.8	98.3
	k_2	0.085	0.052
	R^2	0.9912	0.9893
Elovich	α	4.42×10^{11}	1.80×10^{7}
	β	0.28	0.18
	R^2	0.6799	0.8125
Intra-particle diffusion			
Stage 1	k_{d1}	95.3	85.9
	C_1	2.98	2.32
	R^2	0.9339	0.9501
Stage 2	k_{d2}	4.90	7.87
	C_2	87.1	75.5
	R^2	0.8662	0.9481
Stage 3	k_{d3}	0.12	0.50
	C_3	99.1	95.1
	R^2	0.4349	0.5154

7. Adsorption in the presence of both cationic dyes

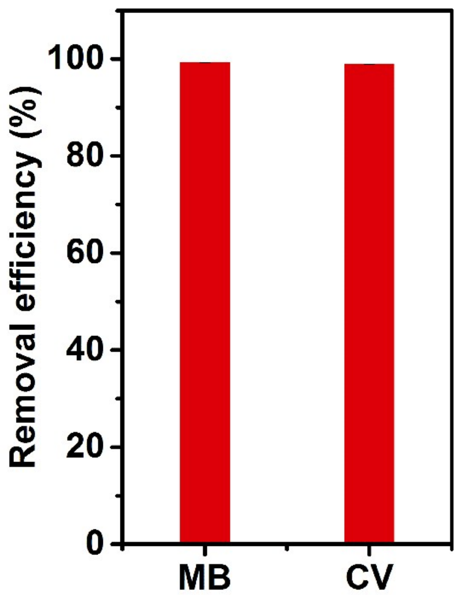

Fig. S9 Adsorption MB and CV onto Dex-MA/PAA hydrogel in their mixer solution (Dye concentration: MB 50 mg/L, CV 50 mg/L, contact time 3 h, pH 8.0)

5. Effect of Humic acid on the adsorption of MB and CV

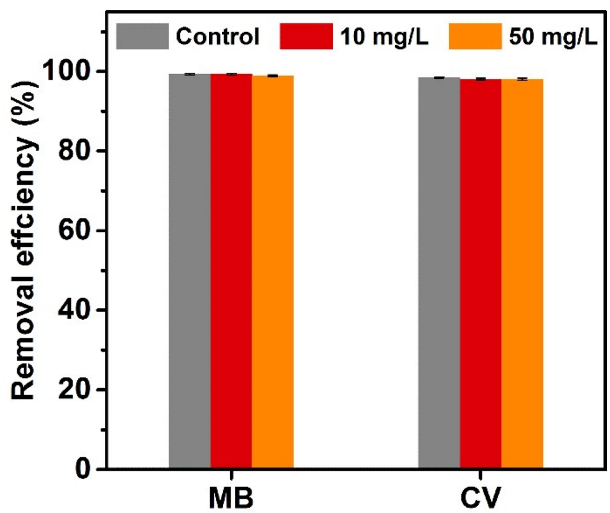

Fig. S10 Effects of different concentrations of humic acid on the removal efficiencies of MB and CV. Hydrogel adsorbent dose: 1 g L^{-1}, dye concentration: 50 mg L^{-1}, $pH_{initial}$ 8.0.

References

1 H. C. Chiu, Y. F. Lin and Y. H. Hsu, *Biomaterials*, 2002, **23**, 1103-1112.