Supplementary Information

Characterizing the Interactions between Humic Matter and Calcium Ions during Water Softening by Cation-Exchange Resins

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Text S1. Resin Pretreatment.

The resins were subjected to wash by 10 bed volumes of 1M HCl and 1M NaOH, respectively in fixed-bed column runs in order to remove residual impurities. After washing resins with acid and base, distilled water was passed through the column to reach neutral pH in the effluent. The effluent flow rate was adjusted to 5 mL/min using a constant-flow pump to provide sufficient contact time between resin and solution. After column wash, the resins were transferred to a Soxhlet apparatus to be extracted with methanol for 8 hours for removing organic residues.

Table S1. Basic parameters of the cation exchange resins

Parameters	D113
Type	Macroporous
Type of the matrix	Polyacrylic
Cross-linker	Divinylbenzene
Moisture (%)	55
Total exchange capacity (mmol/g)	10.8
Average bead diameter (315-125 um)	≧96

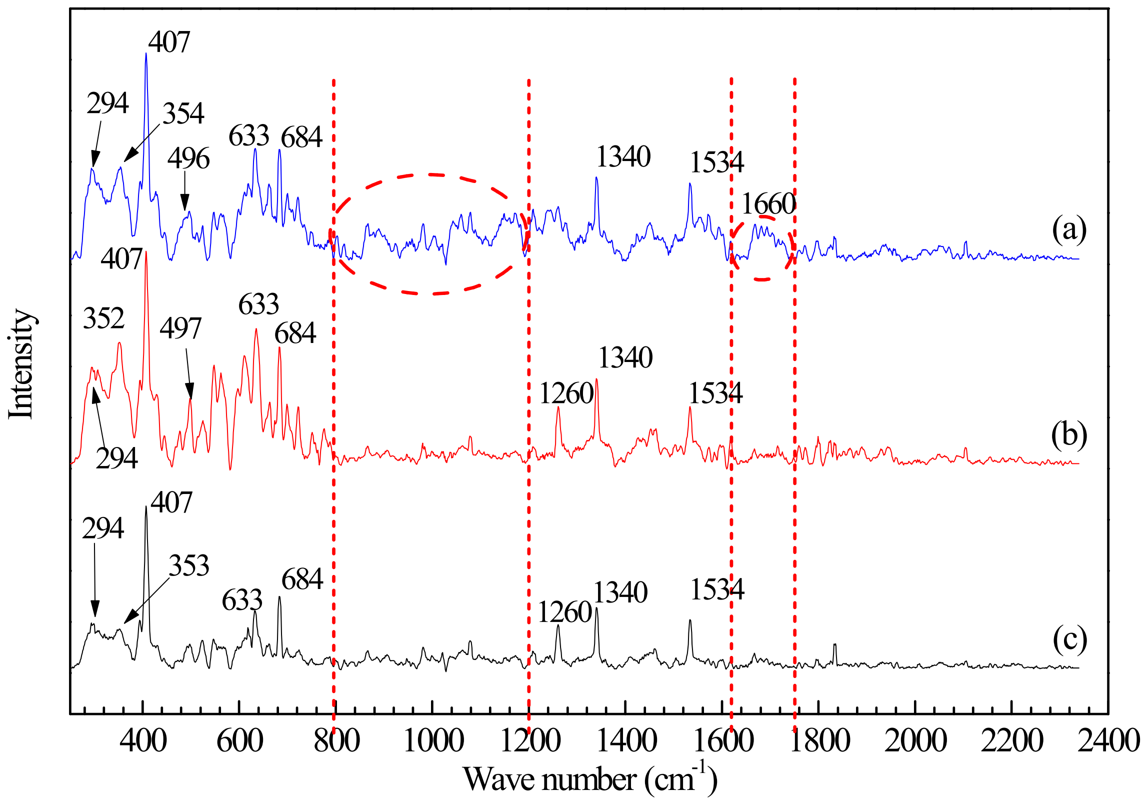


Figure S1. Raman spectrums of three resins: (a) CER-HM/Ca; (b) CER-Ca; (c) CER-Na

In the Figure S1, C=N bond of the Pyrrolines and Oxazolines is from the HM at 1645-1695 cm^{-1}, and the 1660 cm^{-1} from the spectrum of CER-HM/Ca was in the ranges. It is indicated that the HM was deposed on the surface of the resins. C-O stretching vibration of the unidentate carboxylate occurs in the range 1260-1420 cm^{-1}, the 1260 cm^{-1} was found in both of the spectrums of CER-Ca and CER-Na, while it disappeared in the spectrums of CER-HM/Ca. These results suggest that HM could react with unidentate carboxylate. More importantly, the aromatic carboxylic acids and -(NO_2)-Ca-O- bridging can be found by the ranges 900-1000 cm^{-1} and 1000-1200 cm^{-1}, respectively. These results indicate that Ca ion can be as a bridge between HM and CERs.

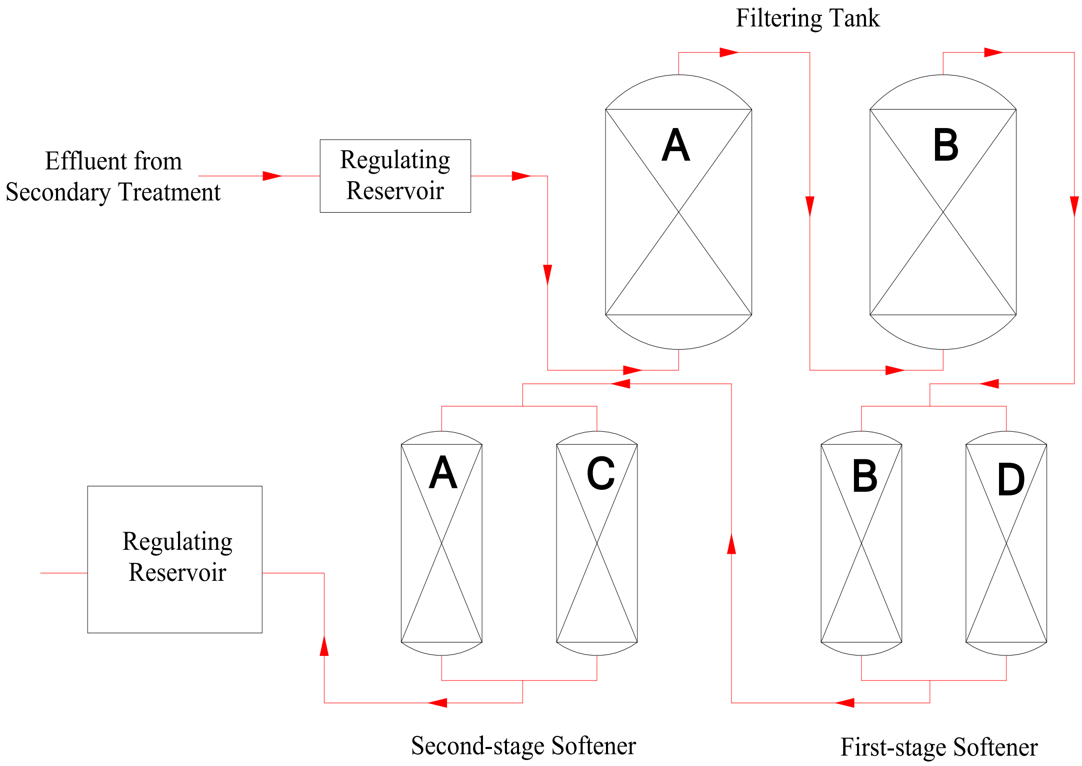
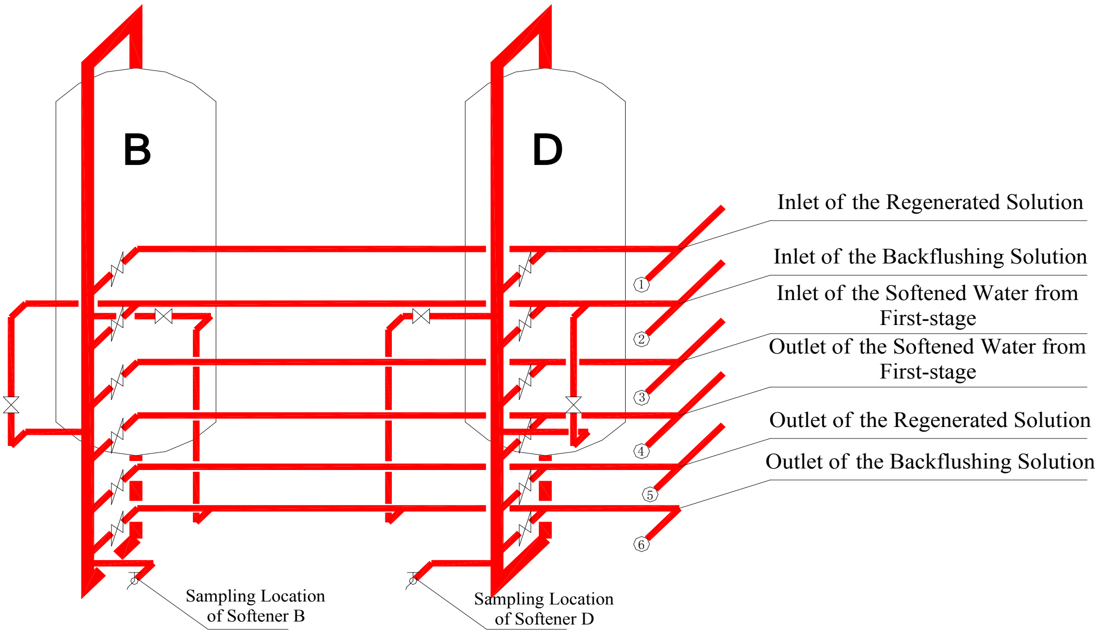
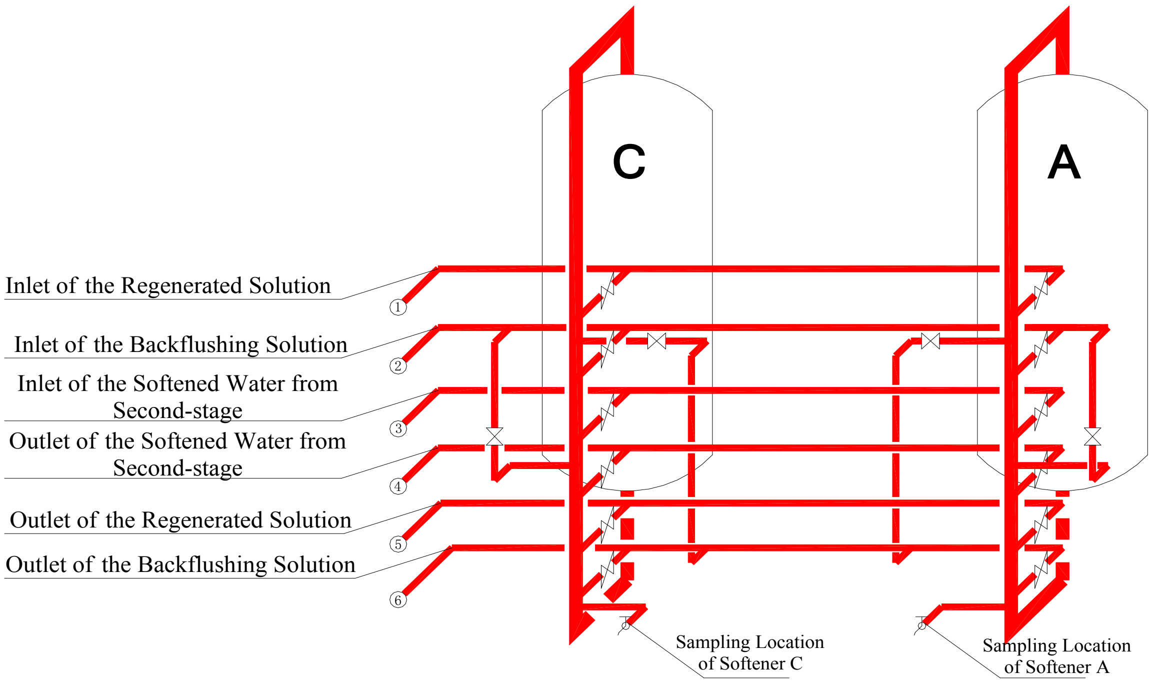


Figure S2. Flow diagram of the softening process in the pilot-scale test



(a)



(b)

Figure S3. Schematic diagram of the two stage softeners in the pilot-scale test: (a) Schematic diagram of the first-stage softeners; (b) Schematic diagram of the second-stage softeners.

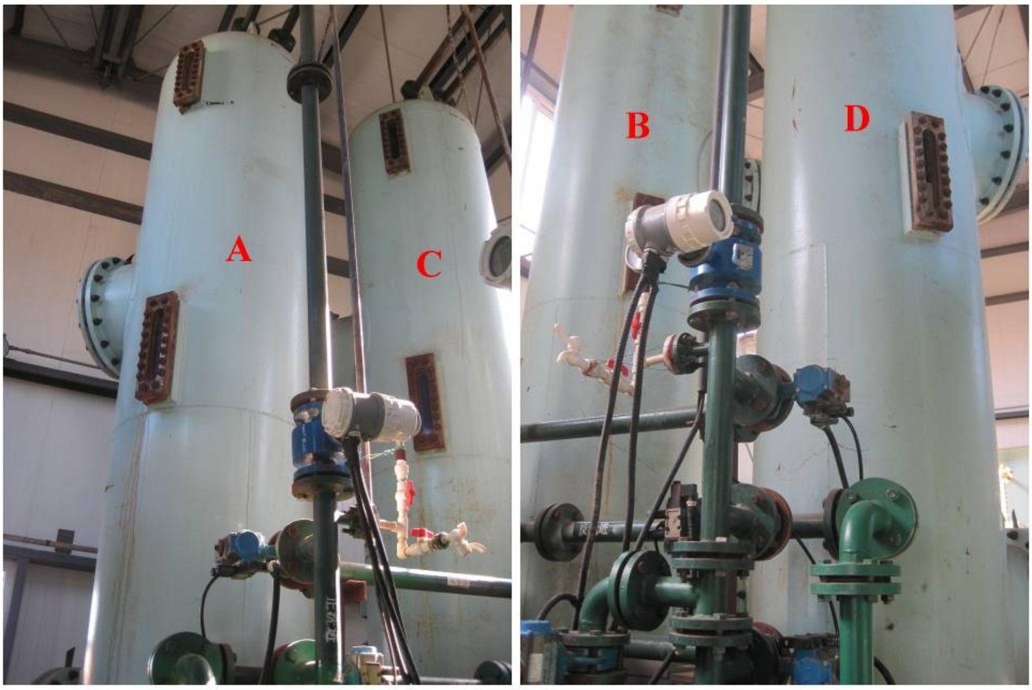


Figure S4. Photo of the two stage softeners in the pilot-scale test

Table S2. Basic characteristics of the raw oilfield produced water and the effluent from the secondary treatment in the pilot-scale test

	Raw Oilfield-produced Water		Effluent from Secondary Treatment	
	Average	SD	Average	SD
Oil Content（mg/L）	680	±45	6.2	±1.1
Sulfide（mg/L）	43.8	±10.7	8.65	±0.03
TOC（mg/L）	1760	±120	127.5	±3.1
UV_{254}	TH	TH	6.81	±0.23
pH（25℃）	8.54	±0.68	7.46	±0.41
SS（mg/L）	1340	±108	5	±2
TDS（mg/L, 25℃）	8000	±500	1770	±59
DO（mg/L, 25℃）	2.51	±1.19	2.10	±0.15
Ca（mg/L）	539	±30	100	±24
Mg（mg/L）	128	±15	20	±8
Fe（mg/L）	6.24	±1.31	1.6	±0.3
Mn（mg/L）	0.41	±0.03	0.05	±0.002

a SD = Standard Deviation; a TH = Too High

Table S3. Basic parameters of the two stage softeners in the pilot-scale test

Parameters	Resin Softeners			
	B	D	A	C
Mass of the CERs (kg)	770	770	720	720
Superficial Liquid Velocity (m/h)	0.5~0.8	0.5~0.8	0.5~0.8	0.5~0.8
Radius of the Softener (mm)	750	750	750	750

Table S4. Removal rates of $SUVA_{254}$ and total hardness by the CERs in the pilot-scale test

Parameters	Effluent from Secondary Treatment	Softened Water	Removal Rate (%)
$SUVA_{254}$ (L/mg C·m)	3.20~5.60	2.18~3.24	30~60
Total hardness ($CaCO_3$, mg/L)	200~350	0.020~0.080	99

Table S5. Basic characteristics of the model water

Sample	HM Content (mg/L)	$SUVA_{254}$ (L/mg C·m)	UV_{254}		DOC (mg/L)		pH
			AV	SD	AV	SD	
0	0	/	/	/	/	/	7.5
1	5	4.0	0.102	± 0.0042	2.510	± 0.1480	7.3
2	10	5.3	0.178	± 0.0102	3.372	± 0.1674	7.6
3	15	6.2	0.251	± 0.0177	4.038	± 0.1607	7.4
4	20	6.8	0.347	± 0.0321	5.080	± 0.1908	7.3
5	25	7.3	0.430	± 0.0489	5.872	± 0.2610	7.5
6	30	7.6	0.483	± 0.0207	6.338	± 0.1821	7.6

a AV=Average Value; a SD=Standard Deviation

Table S6. Ca Q_e of CERs with different dosages of HM

Sample	HM Content (mg/L)	Q_e (mg/g)	Standard Deviation
0	0	189.21	±3.7319
1	5	206.46	±2.7706
2	10	209.22	±1.3972
3	15	219.80	±8.7919
4	20	221.23	±6.2515
5	25	232.86	±5.7251
6	30	246.32	±7.4879

a Q_e= Equilibrium adsorption quantity

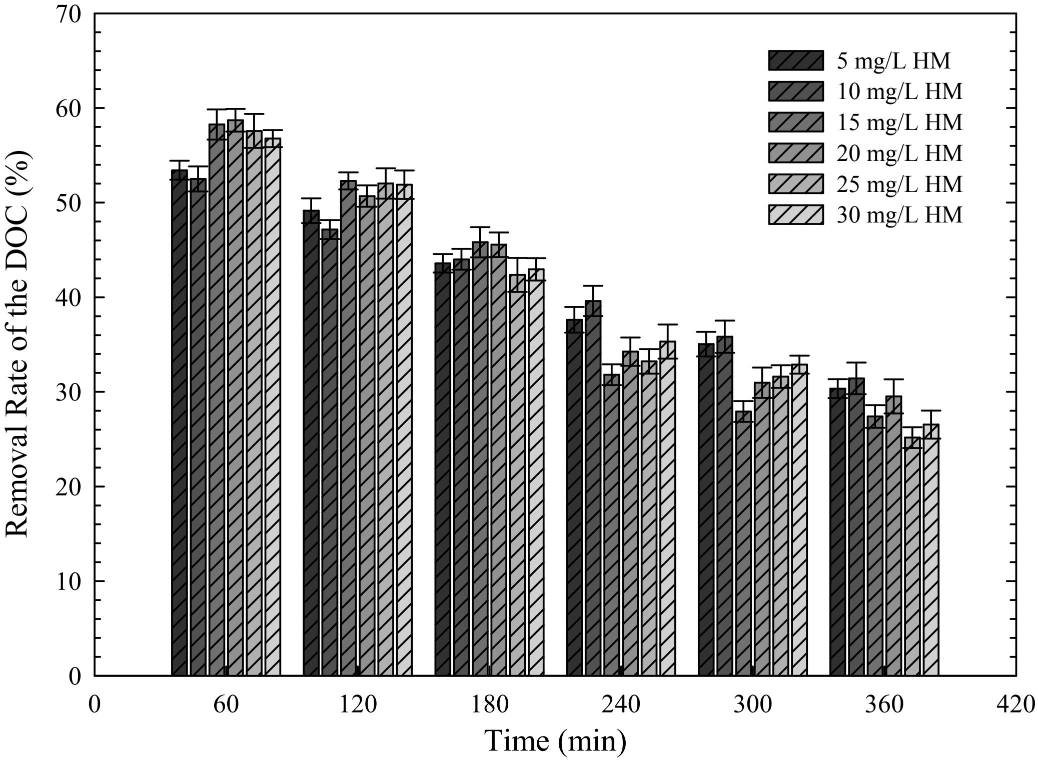
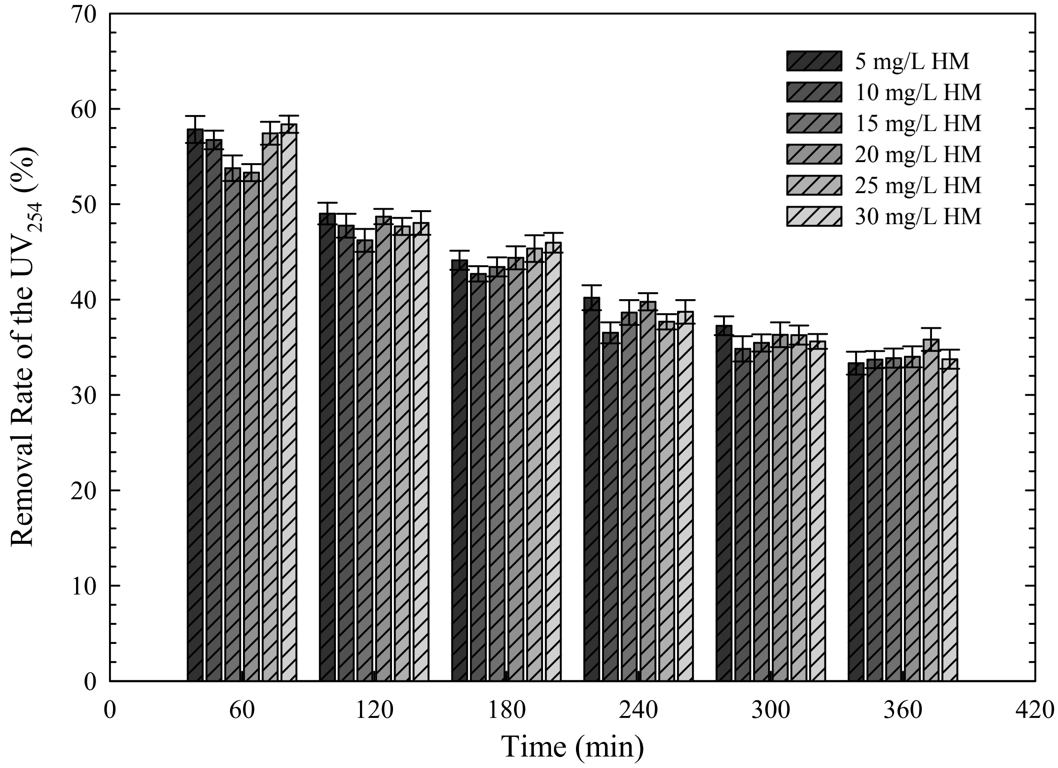
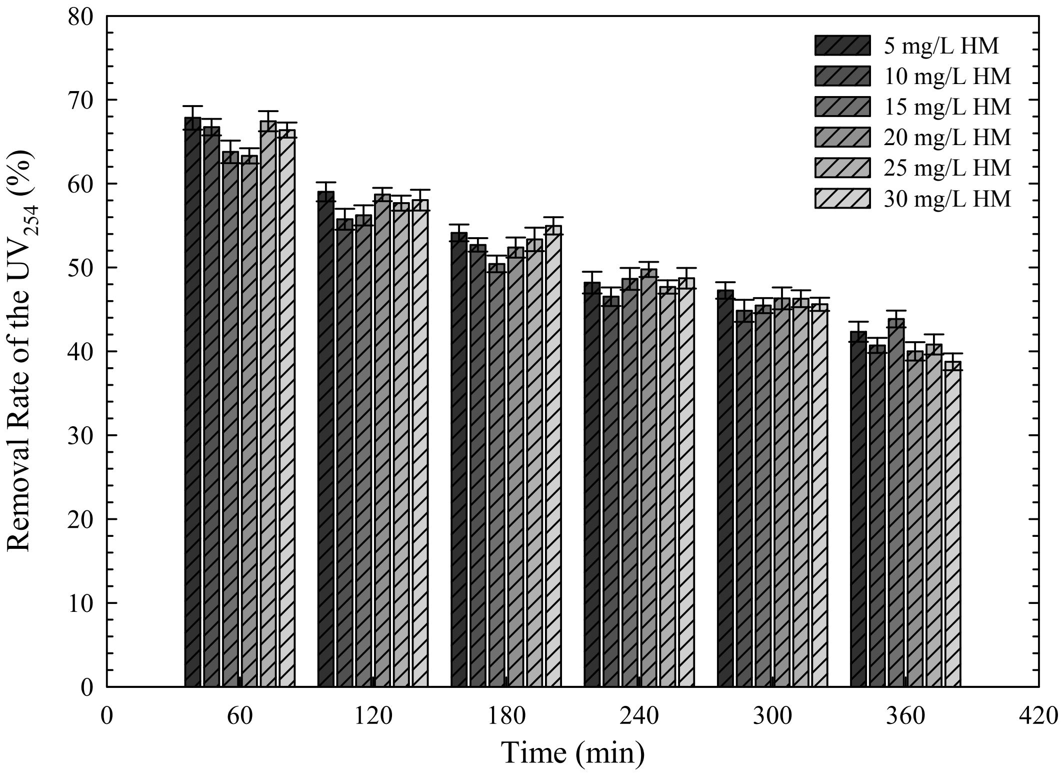


Figure S5. Removal rates of the DOC of the HM with different dosages and time by CERs



(a)



(b)

Figure S6. Removal rates of the UV_{254} of the HM with different dosages and time by CERs: (a) the SLV was 1.0 ± 0.2 m/h; (b) the SLV was 0.5 ± 0.2 m/h.

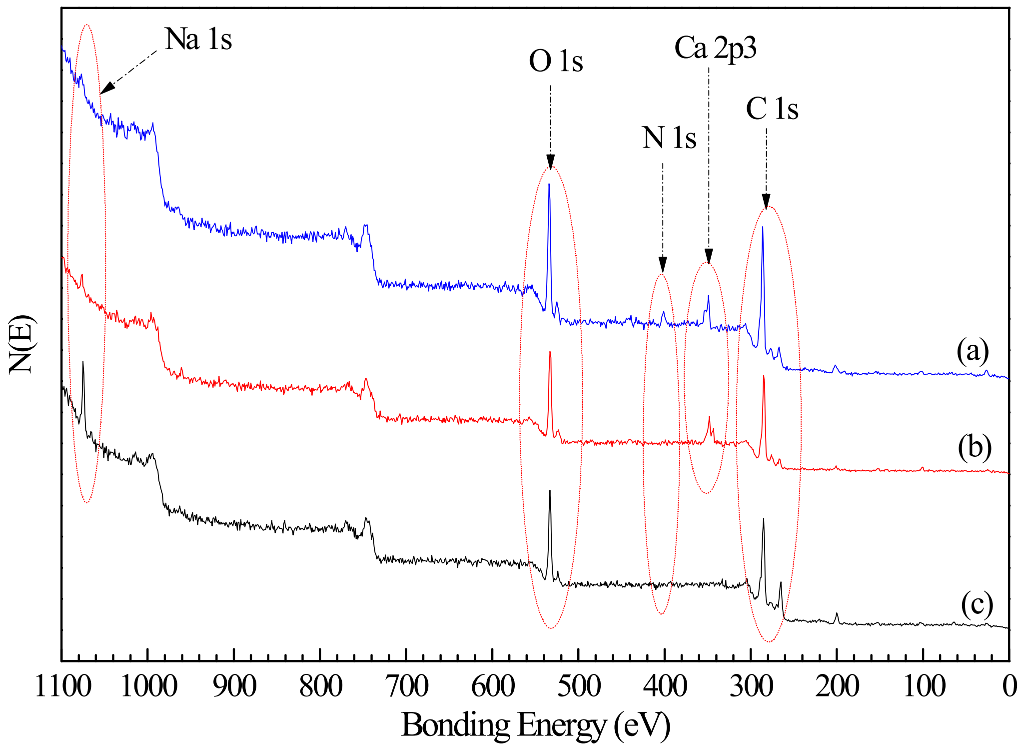


Figure S7. XPS survey scans of CER-HM/Ca (a), CER-Ca (b), and CER-Na (c)

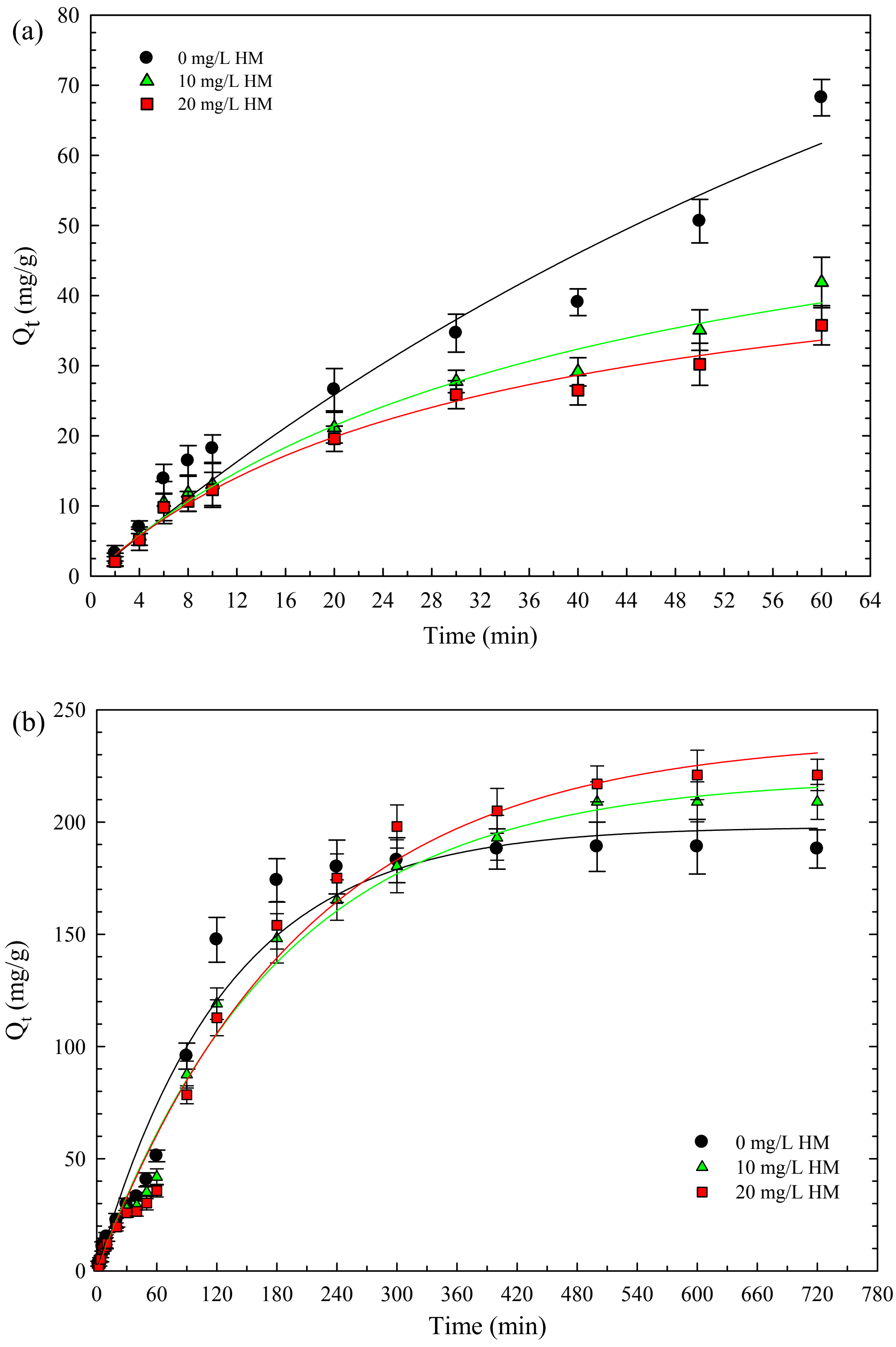
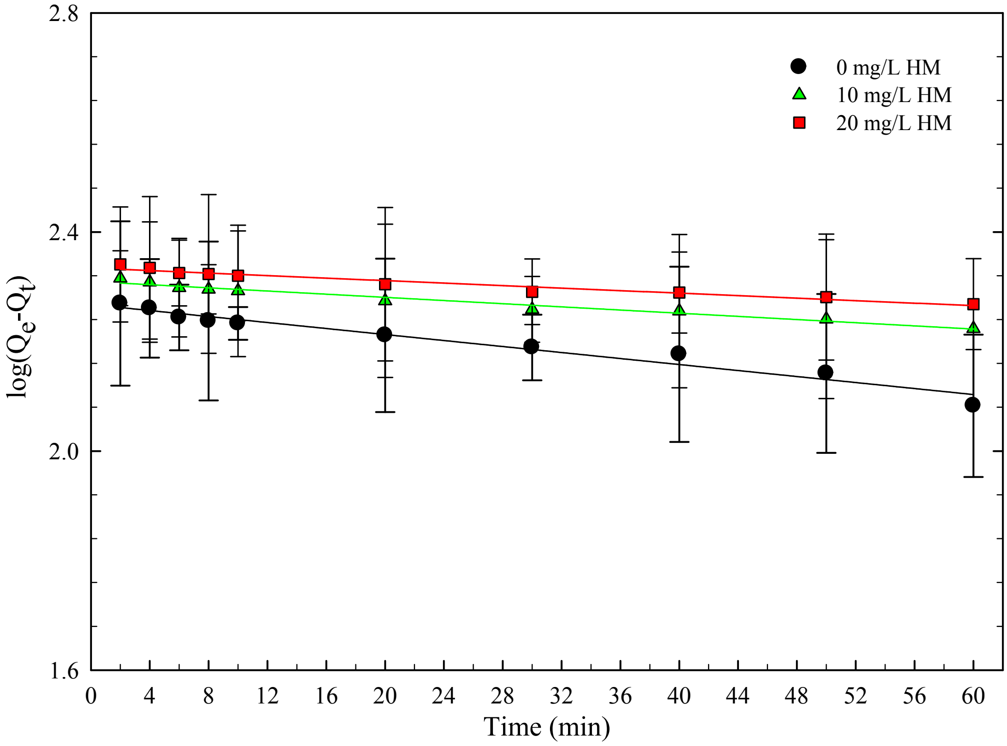
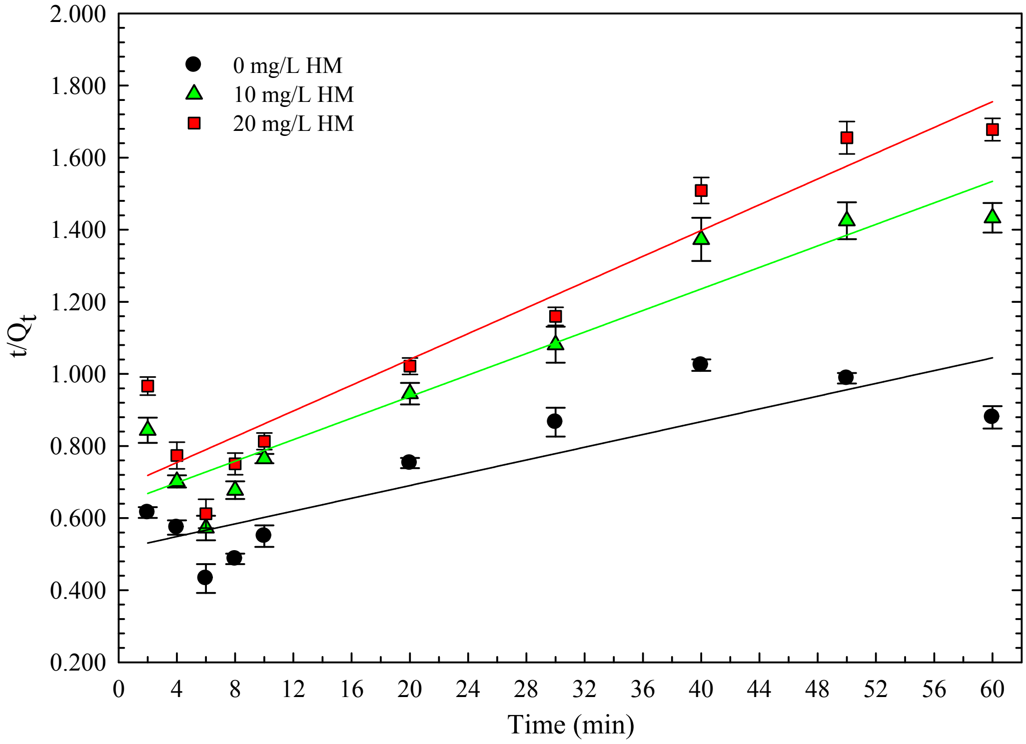


Figure S8. Kinetics of Ca adsorption with different HM dosages on resins: (a) the kinetics of Ca adsorption at initial stage (0~60 mins); (b) the kinetics of Ca adsorption at whole stage (0~720 mins).

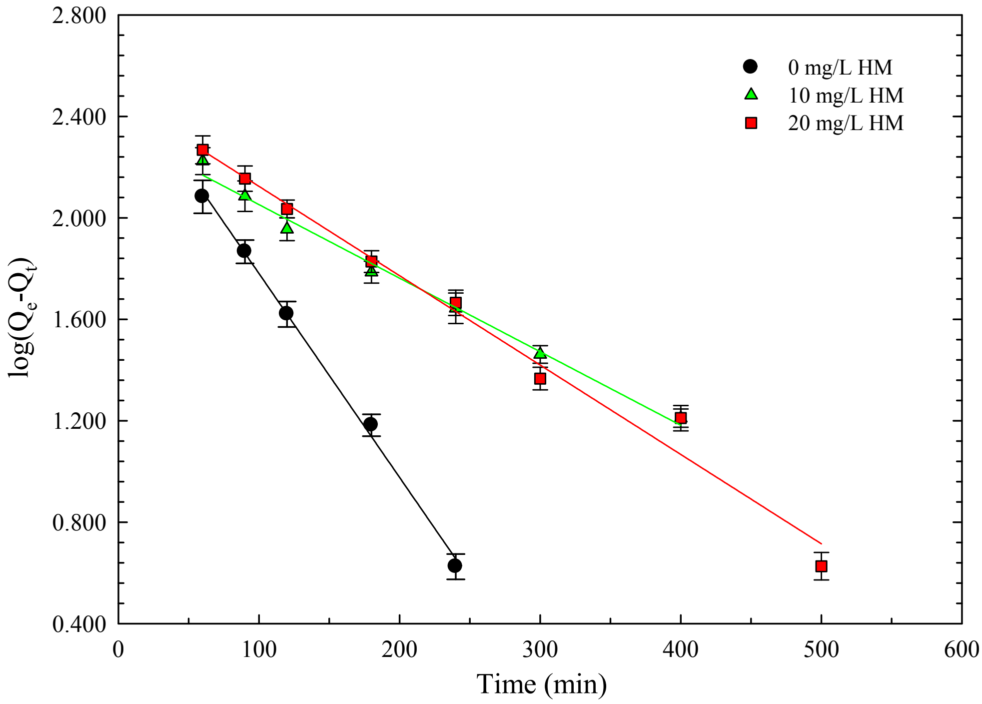


(a)

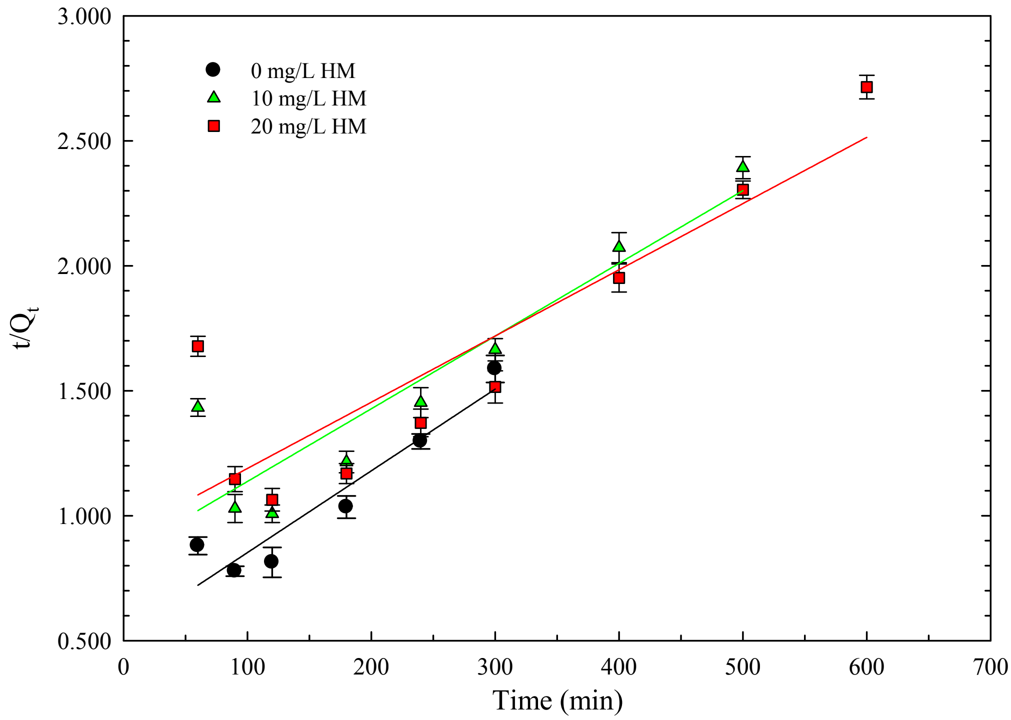


(b)

Figure S9. The fitting curves for adsorption of Ca ions at initial stage (0-60 mins): (a) the Pseudo-first-order fitting; (b) the Pseudo-second-order fitting.



(a)



(b)

Figure S10. The fitting curves for adsorption of Ca ions after 60-min of adsorption: (a) the Pseudo-first-order fitting; (b) the Pseudo-second-order fitting.