Supplementary materials

Sodium carbonate (0.200 mmol/L) was introduced to control the ion strength and alkalinity. Hydrochloric acid (0.100 mol/L) and sodium hydroxide (0.100 mol/L) were used to adjust the pH of the simulated algae-laden water. The coagulation procedure was consistent with what was stated in the text. Aluminum sulfate octadecahydrate (with hydrophobic silica or ferrous sulfate heptahydrate) was added into the solution at the beginning of rapid stirring, Water samples were collected 2 cm underwater to determine Zeta potential when stirring for 1 min using a Zeta potential analyzer (Zetasizer Nano ZS90, Malvern, UK).

As shown in Fig. S1, the coagulation performance of aluminum sulfate octadecahydrate in neutral conditions was prior to that in acid conditions. Restabilization was more likely to occur in acid conditions, which was unfavorable for coagulation. Residual Al of aluminum sulfate octadecahydrate decreased a lot with the addition of hydrophobic silica, both in neutral and acidic conditions (Fig. S2).

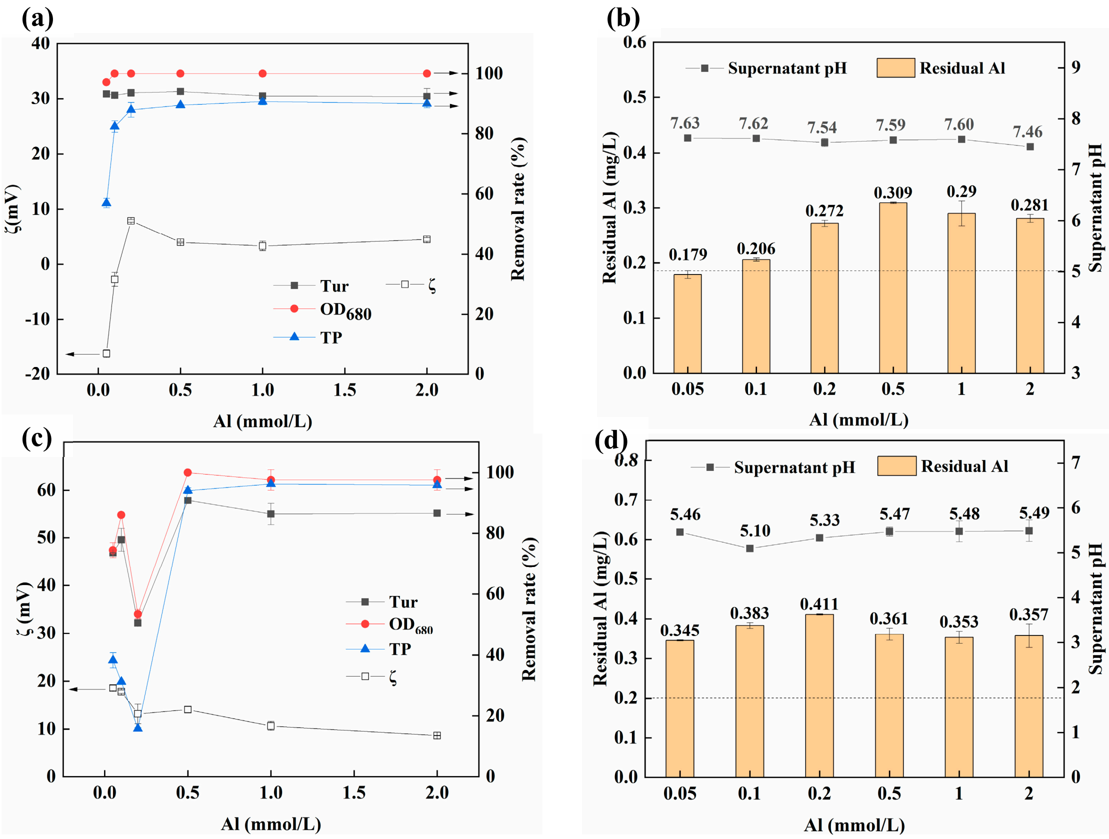

Figure S1. Coagulation performance of aluminum sulfate octadecahydrate in (a) (b) neutral conditions and (c) (d) acid conditions.

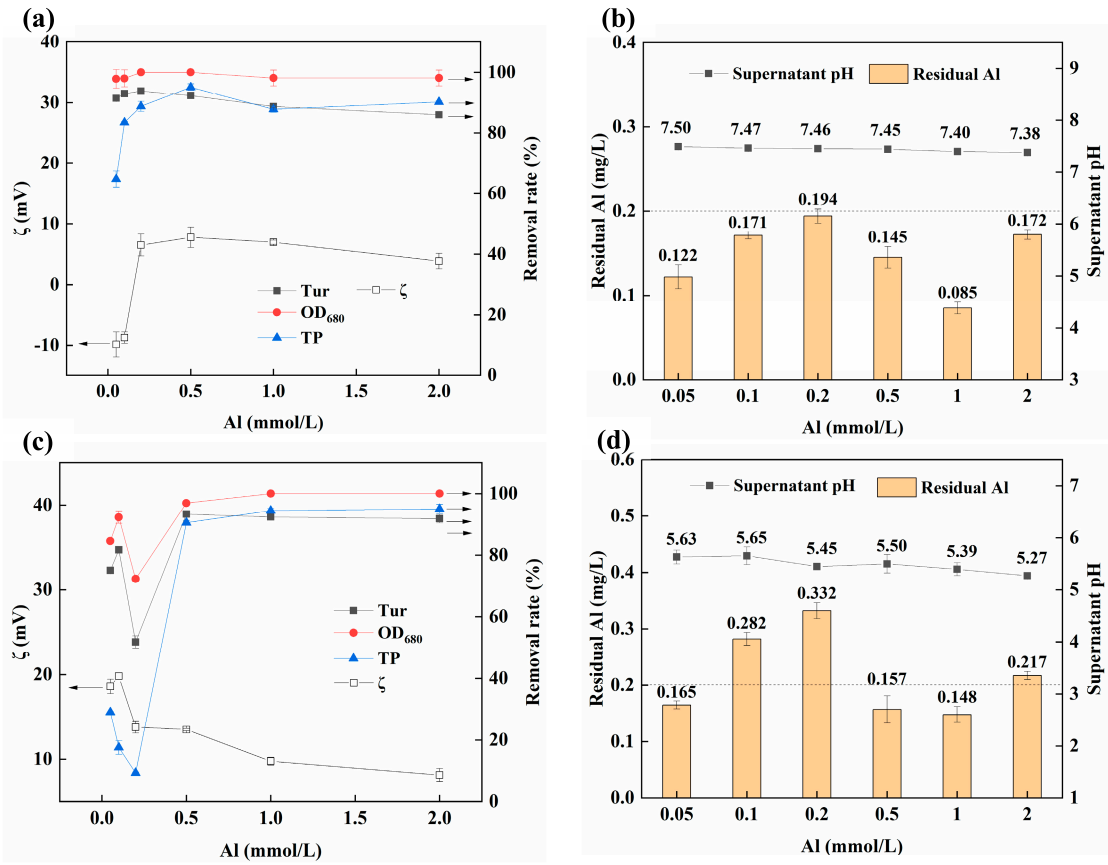

Figure S2. Coagulation performance of hydrophobic silica-assisted aluminum sulfate octadecahydrate in (a) (b) neutral conditions and (c) (d) acid conditions.

Ferrous sulfate heptahydrate was introduced for synergistic coagulation to further improve the removal efficiency of TP. As can be seen in Fig. S3a, with the increase of n(Fe):n(Al) from 0:1 to 1:1, the removal rate of TP increased from 70.05% to 80.71%. When it continued to rise to 3:1, the removal rate of TP was basically maintained at 89.01%. When n(Fe):n(Al) was 2:1, concentration of residual Al dropped to 0.208 mg/L. n(Fe):n(Al) in the range of 1:1 to 3:1 was chosen for the subsequent three-variable three-level experiments.

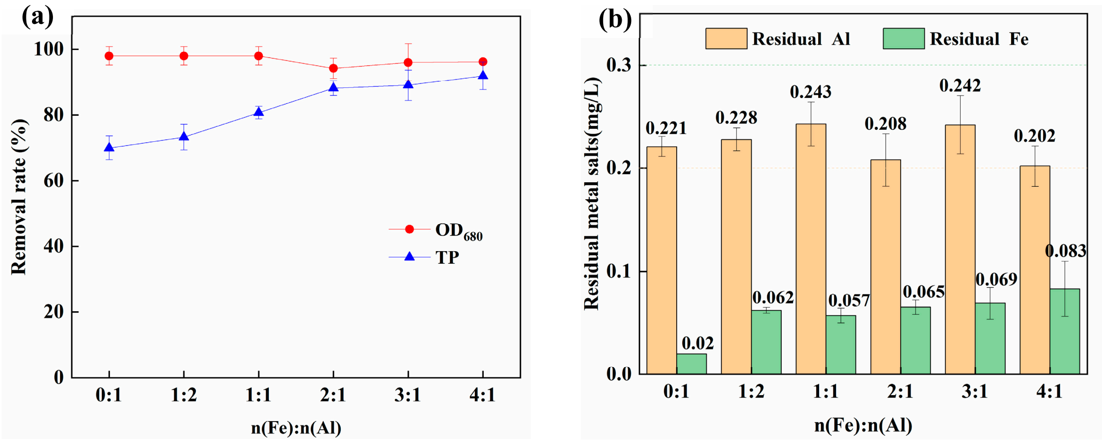

Figure S3. Coagulation performance of different n(Fe):n(Al) in neutral conditions.

Where the concentration of aluminum was fixed at 0.05 mmol/L, and the concentration of ferrous iron varied according to the value of n(Fe):n(Al).

Table S1. Details from BBD for 17 runs of jar tests [a].

Run	Input variables			Output responses							
	A	B	C	R1 [b]		R2 [c]		R3 [d]		R4 [e]	
				EV [f]	PV [g]	EV	PV	EV	PV	EV	PV
1	−1	−1	0	0.166	0.160	0.078	0.066	83.46	85.30	94.64	94.44
2	1	−1	0	0.128	0.130	0.090	0.047	88.72	86.12	96.49	94.16
3	−1	1	0	0.158	0.156	0.086	0.129	81.89	84.36	94.64	96.96
4	1	1	0	0.112	0.118	0.084	0.096	86.47	84.75	96.49	96.68
5	−1	0	−1	0.182	0.187	1.280	1.226	81.10	78.59	92.86	90.24
6	1	0	−1	0.148	0.146	1.154	1.194	80.45	82.25	85.96	85.46
7	−1	0	1	0.280	0.282	0.568	0.591	20.16	18.35	−7.46	−6.98
8	1	0	1	0.260	0.255	0.582	0.573	13.39	15.89	−5.36	−2.76
9	0	−1	−1	0.166	0.166	1.054	1.089	82.68	83.41	79.21	82.02
10	0	1	−1	0.158	0.155	1.254	1.234	77.95	77.91	82.14	82.44
11	0	−1	1	0.262	0.265	0.530	0.550	15.75	15.77	−12.50	−12.80
12	0	1	1	0.260	0.260	0.552	0.517	19.69	18.95	−5.36	−8.18
13	0	0	0	0.198	0.166	0.074	0.116	90.55	87.69	92.86	91.10
14	0	0	0	0.158	0.166	0.122	0.116	88.19	87.69	92.86	91.10
15	0	0	0	0.158	0.166	0.116	0.116	85.83	87.69	89.29	91.10
16	0	0	0	0.142	0.166	0.122	0.116	88.19	87.69	91.23	91.10
17	0	0	0	0.172	0.166	0.144	0.116	85.71	87.69	89.29	91.10

[a] The total molar concentration of Al and Fe was 0.20 mmol/L.

[b] Residual Al (mg/L).

[c] Residual Fe (mg/L).

[d] Removal rate of TP (%).

[e] Removal rate of OD_{680} (%).

[f] Experimental value.

[g] Predicted value.

Table S2. ANOVA for the regression coefficients and the significance test between the input variables and residual Al (R1).

Source	Sum of Squares	df	Mean Sqaure	F-value	p-value	
Model	0.0400	9	0.0044	16.21	0.0007	significant
A	0.0024	1	0.0024	8.69	0.0215	
B	0.0001	1	0.0001	0.5273	0.4913	
C	0.0208	1	0.0208	75.93	< 0.0001	
AB	0.0000	1	0.0000	0.0584	0.8160	
AC	0.0000	1	0.0000	0.1788	0.6851	
BC	9.000E-06	1	9.000E-06	0.0328	0.8613	
A^2	0.0004	1	0.0004	1.33	0.2868	
B^2	0.0010	1	0.0010	3.60	0.0997	
C^2	0.0158	1	0.0158	57.55	0.0001	
Residual	0.0019	7	0.0003			
Lack of Fit	0.0002	3	0.0001	0.1172	0.9454	not significant
Pure Error	0.0018	4	0.0004			
Cor Total	0.0419	16				

Table S3. ANOVA for the regression coefficients and the significance test between the input variables and residual Fe (R2).

Source	Sum of Squares	df	Mean Sqaure	F-value	p-value	
Model	3.33	9	0.3695	236.22	< 0.0001	significant
A	0.0013	1	0.0013	0.8314	0.3922	
B	0.0063	1	0.0063	4.01	0.0853	
C	0.7875	1	0.7875	503.42	< 0.0001	
AB	0.0000	1	0.0000	0.0313	0.8645	
AC	0.0049	1	0.0049	3.13	0.1201	
BC	0.0079	1	0.0079	5.06	0.0592	
A^2	0.0003	1	0.0003	0.2037	0.6654	
B^2	0.0067	1	0.0067	4.26	0.0778	
C^2	2.51	1	2.51	1602.91	< 0.0001	
Residual	0.0110	7	0.0016			
Lack of Fit	0.0083	3	0.0028	4.24	0.0983	not significant
Pure Error	0.0026	4	0.0007			
Cor Total	3.34	16				

Table S4. ANOVA for the regression coefficients and the significance test between the input variables and the removal rate of TP (R3).

Source	Sum of Squares	df	Mean Sqaure	F-value	p-value	
Model	14067.84	9	1563.09	197.38	< 0.0001	significant
A	0.7257	1	0.7257	0.0916	0.7709	
B	2.67	1	2.67	0.3366	0.5800	
C	8014.15	1	8014.15	1012.00	< 0.0001	
AB	0.1159	1	0.1159	0.0146	0.9071	
AC	9.37	1	9.37	1.18	0.3128	
BC	18.75	1	18.75	2.37	0.1677	
A^2	8.25	1	8.25	1.04	0.3414	
B^2	5.65	1	5.65	0.7137	0.4261	
C^2	5927.27	1	5927.27	748.47	< 0.0001	
Residual	55.43	7	7.92			
Lack of Fit	39.37	3	13.12	3.27	0.1412	not significant
Pure Error	16.06	4	4.01			
Cor Total	14123.27	16				

Table S5. ANOVA for the regression coefficients and the significance test between the input variables and the removal rate of OD_{680} (R4).

Source	Sum of Squares	df	Mean Sqaure	F-value	p-value	
Model	29870.23	9	3318.91	432.19	< 0.0001	significant
A	0.1485	1	0.1485	0.0193	0.8933	
B	12.68	1	12.68	1.65	0.2397	
C	17191.79	1	17191.79	2238.70	< 0.0001	
AB	0.0000	1	0.0000	0.0000	1.0000	
AC	20.24	1	20.24	2.64	0.1485	
BC	4.44	1	4.44	0.5782	0.4719	
A^2	107.16	1	107.16	13.95	0.0073	
B^2	1.42	1	1.42	0.1848	0.6802	
C^2	12573.93	1	12573.93	1637.37	< 0.0001	
Residual	53.76	7	7.68			
Lack of Fit	40.98	3	13.66	4.28	0.0971	not significant
Pure Error	12.77	4	3.19			
Cor Total	29923.98	16				

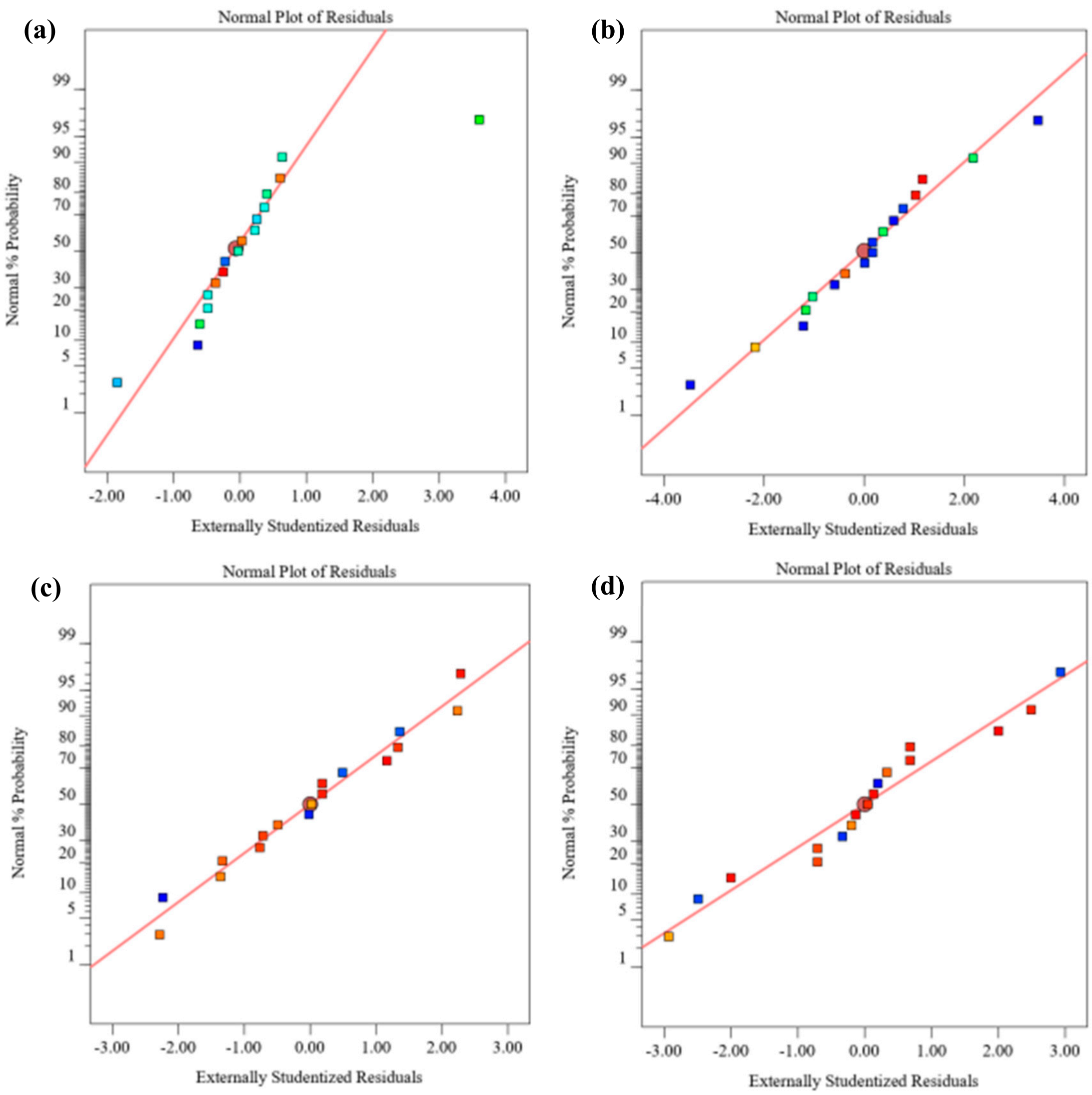

Figure S4. Normal plots of residuals of diagnostics for (a) R1: Residual Al (in mg/L), (b) R2: Residual Fe (in mg/L), (c) R3: the removal rate of TP (in %) and (d) R4: the removal rate of OD_{680} (in %).

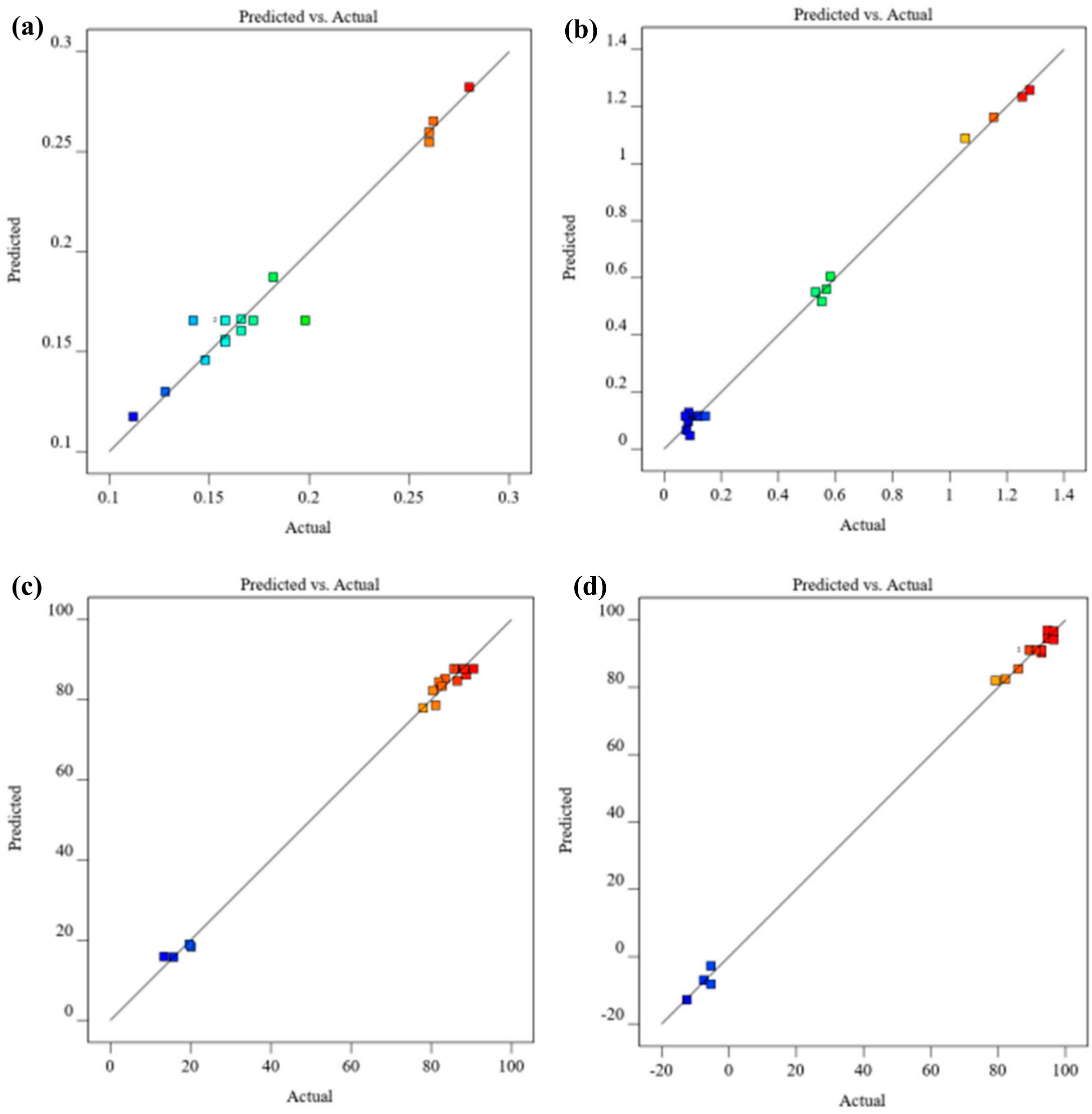

Figure S5. Predicted vs. actual plots in diagnostics for (a) R1: Residual Al (in mg/L), (b) R2: Residual Fe (in mg/L), (c) R3: the removal rate of TP (in %), (d) R4: the removal rate of OD_{680} (in %).

FAS poly-coagulants with different n(CO_3^{2-}):n(Al+Fe) were discussed to further verify its crucial effect on removal efficiencies.

Coagulation performance was highly achieved by $FAS_{1–4}$ and FAS_{13} with n(CO_3^{2-}):n(Al+Fe) of 1.75:1, and FAS_{13} was selected for comparison with that of 1:1 and 2.5:1. Residual Al and residual Fe of $FAS_{1–4}$ and FAS_{13} were below 0.200 and 0.300 mg/L, respectively, which are thresholds of standards for drinking water quality (GB5749–2006). Above 89.29% OD_{680} was removed by $FAS_{1–4}$ and FAS_{13}. Phosphorus is a key nutrient for the formation of cyanobacterial blooms, and the removal rates of total phosphorus (TP) is crucial to evaluate coagulation performances of FAS poly-coagulants. Removal efficiencies of TP increased from 81.89% to 90.55% with n(Fe):n(Al) from 1:1 (FAS_1 and FAS_3) to 2:1 (FAS_{13}), but showed a decrease tendency when n(Fe):n(Al) was up to 3:1 (FAS_2 and FAS_4). Therefore, removal efficiencies of TP of FAS_{13} were superior than $FAS_{1–4}$ and FAS_{13} was selected.

Among FAS poly-coagulants with n(CO_3^{2-}):n(Al+Fe) of 1:1, FAS_5 was selected for comparison with FAS_{13}. Residual Al of FAS_5 was 0.182 mg/L, less than 0.200 mg/L. 81.10% TP and 92.86% OD_{680} were removed by FAS_5 in coagulation. Even though the proportion of Fe was the lowest, residual Fe of FAS_5 was 1.280 mg/L, far above 0.300 mg/L, not to mention FAS_6 and FAS_{9-10} with higher n(Fe):n(Al).

Among FAS poly-coagulants with n(CO_3^{2-}):n(Al+Fe) of 2.5:1, FAS_7 was selected for comparison with FAS_{13}. By using $FAS_{7–8}$ and FAS_{11-12}, residual Al and residual Fe exceeded 0.200 mg/L and 0.300 mg/L, respectively, and the removal efficiency of OD_{680} was very poor. However, the removal efficiency of TP reached the highest of 20.16% by FAS_7 with the lowest n(Fe):n(Al).

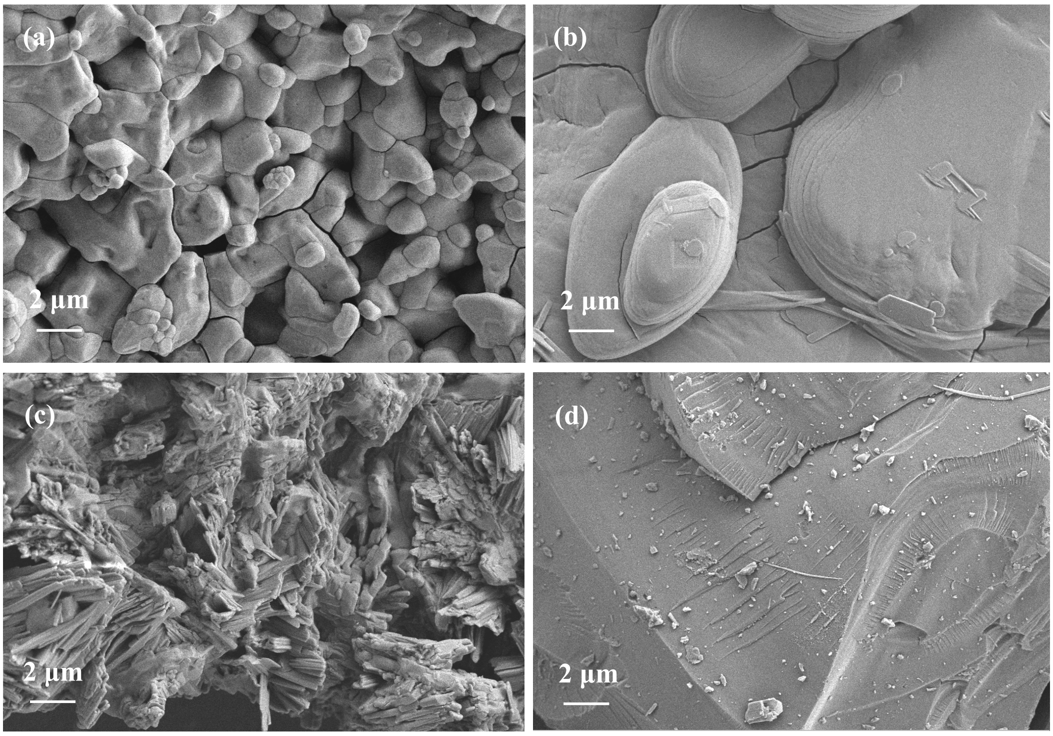

Figure S6. SEM images of raw materials: (a) $FeSO_4 \cdot 7H_2O$, (b) $Al_2(SO_4)_3 \cdot 18H_2O$, (c) Na_2CO_3 and (d) hydrophobic SiO_2.

Table S6. Details of weight loss and corresponding temperature of FAS poly-coagulants.

Samples	Stage 1		Stage 2		Stage 3		Stage 4	
	T [a] (°C)	WL [b] (%)	T (°C)	WL (%)	T (°C)	WL (%)	T (°C)	WL (%)
FAS_{13}	22.75	24.33	243.89	1.37	442.98	8.36	733.79	8.11
FAS_5	24.99	23.62	241.06	1.87	453.88	10.86	788.18	5.64
FAS_7	20.81	17.29	244.07	1.37	449.67	6.21	775.33	11.11

[a] Temperature.

[b] Weight loss.