Electronic Supplementary Material (ESI) for RSC Advances.

Supplementary Information

CONTENTS

S1. Characterization of poly (CTS-g-AM-MAPTAC)

(1) FTIR,XRD,SEM and TG/DSC

FTIR of poly (CTS-g-AM-MAPTAC) were recorded using KBr pellets on a 550Series II infrared spectrometer (BRUKER Company, Switzerland). XRD patterns were obtained with an X-ray diffractometer (DMAX/2C, Japan) using graphite monochromatized Cu Ka radiation (k = 1.54056 Å); Morphology analysis was performed on MIRA 3 LMU SEM system (TES-CAN Company, Czech Republic). TG/DSC analysis was carried out on STA449C instrument (Netzsch, Germany) under argon atmosphere at a heating rate of 10 ℃ min^{-1}.

(2) Grafting rate calculation

$$G\ (\%) = (W_2 - W_1)/W_1 \times 100\%$$

Formula: W_1 - added chitosan mass, g;

W_2 - purified poly (CTS-g-AM-MAPTAC) copolymer mass, g.

(3) Determination of intrinsic viscosity and solubility

Several 250 mL beakers were added with 100 mL distilled water, and the pH was adjusted with 0.1 M HCl or NaOH to make it rise in a gradient between 1 and 13. 0.1 g (accurate to 0.0001 g) of poly (CTS-g-AM-MAPTAC) and CTS were added to aqueous solutions with different pH values, and then stirred and dispersed on a magnetic stirrer. The solubility of the synthesized product and chitosan under different pH conditions was observed by naked eyes.

As shown in Table 1, the solubility of poly(CTS-g-AM-MAPTAC) was significantly better than that of CTS. CTS could only be dissolved in acidic solution (pH≤3.0), while poly(CTS-g-AM-MAPTAC) was partially soluble at pH = 5.0 ~ 7.0, and was soluble under other conditions. This was mainly due to the introduction of cationic hydrophilic group （N^+-$(CH_3)_3$） into the CTS molecule after graft copolymerization, which weakened the hydrogen bonding on the molecular chain of CTS to form an amorphous structure. This structure was more prone to hydration, thereby enhancing solubility, expanding the exposure of flocculant active sites in

water, and improving the flocculation effect.

Table 1 The solubility of CTS and poly（CTS-g-AM-MAPTAC）under different pH

pH	1	2	3	4	5	6	7	8	9	10	11	12	13
CTS	+	+	+	-	-	-	-	-	-	-	-	-	-
Poly（CTS-g-AM-MAPTAC）	+	+	+	+	±	±	±	+	+	+	+	+	+

+: soluble, ±: partially soluble, -: insoluble.

S2. SEM analyses

As shown in Fig.1 (a), the surface of CTS is uniform and smooth, showing a typical crystal structure. However, the surface of poly (CTS-g-AM-MAPTAC) appears wrinkles of different layers, and many holes of different sizes are distributed on it. This may be due to the introduction of cationic MAPTAC destroyed the hydrogen bond on the molecular chain of CTS, resulting in the collapse of the original crystal structure and the change of the surface structure of CTS. This porous structure can not only improve the solubility of the product but also increase the specific surface area, so as to enhance the adsorption and bridging ability [1-4].

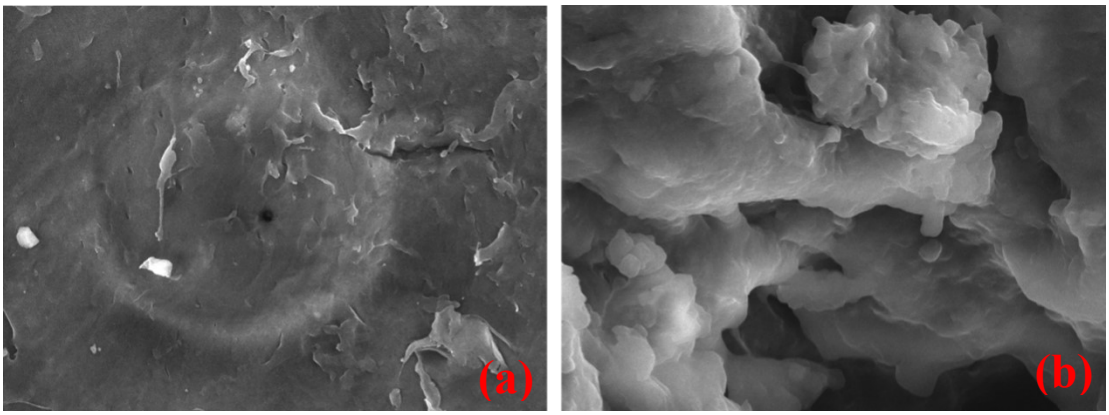

Fig. 1 SEM graphs of (a) CTS and (b) poly (CTS-g-AM-MAPTAC)

S3. Zeta potential analysis

Zeta potential can reflect the charge properties and charge amount on the surface of the material. The flocculation mechanism can be simply understood by studying the Zeta potential of flocculant and pollutant. In order to analyze the flocculation mechanism of the prepared products, the changes of Zeta potential of the prepared products under different acidic conditions were compared with those of the simulated wastewater kaolin and Escherichia coli suspensions. At the same time, CTS was taken for comparison. The results are shown in Fig.2.

It can be seen from Fig.2 that with the increase of alkalinity, the Zeta potential of all substances decreased, which was caused by the increase of OH- ions in water under alkaline conditions. Kaolin and E.coli suspensions showed negative electricity in a wide pH range, so the flocculant with higher cationic degree was more conducive to the flocculation process. The Zeta potential of poly (CTS-g-AM-MAPTAC) was significantly higher under acidic conditions than that of CTS, but slightly lower under alkaline conditions. This was due to the introduction of quaternary ammonium groups on the molecular chain of MAPTAC increased the cationic degree, which made it exhibit better electrical neutralization under acidic conditions. In addition, in order to improve the solubility of CTS, the carboxymethylation treatment was performed before the preparation of poly (CTS-g-AM-MAPTAC). The introduction of -COOH would lead to the decrease of Zeta potential, so the electrical neutralization of poly (CTS-g-AM-MAPTAC) under alkaline conditions was weaker than that of CTS [5]. However, this small difference does not affect the good decontamination ability of poly (CTS-g-AM-MAPTAC). Affected by the negative electricity of pollutants, bridging plays a major role in alkaline conditions, while poly (CTS-g-AM-MAPTAC) with large molecular weight and steric hindrance has good flocculation effect.

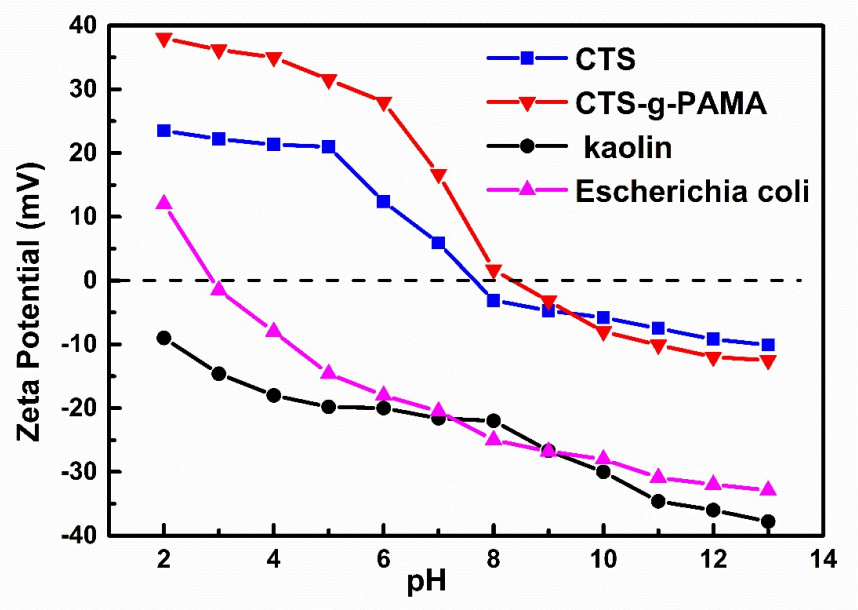

Fig. 2 ZP-pH profiles of CTS, poly（CTS-g-AM-MAPTAC), kaolin and Escherichia coli

S4. The details of flocculants used in performance evaluation test

Table 2 Grafting ratios and corresponding intrinsic viscosities of flocculant

	percent grafting rate G（%）	intrinsic viscosity [η]（dL•g^{-1}）
poly（CTS-g-AM-MAPTAC）（1#）	78	5.39
poly（CTS-g-AM-MAPTAC）（2#）	202	5.12
poly（CTS-g-AM-MAPTAC）（3#）	220	5.49
PAMA	172	5.37
PAM	0	5.90
PAC		
1277		

S5. Preparation methods of simulated wastewater

(1) Simulated kaolin wastewater（0.1 wt%）

Accurately 1.0g of dried kaolin particles were dissolved in 1.0L of distilled water.

(2) Simulated escherichia coli wastewater

Culture of E.coli: 25.0g LB agar powder was dissolved in 1.0L distilled water, then pH was adjusted to neutral with 0.1M hydrochloric acid or sodium hydroxide, and then transferred to conical flask, sealed with sterile sealing membrane, sterilized in autoclave at 121 °C for 15min, cooled at room temperature ; the original strain of E. coli was transferred into sterile liquid medium and cultured in a constant temperature biochemical incubator at 30 °C for 24 h.

E.coli suspension: E.coli suspension of three generations was centrifuged at 3000r / min for 5min, and the supernatant was removed. The remaining bacteria was washed three times with pure water and then diluted with normal saline (0.9 % wt) to obtain E.coli suspension (cell density: 1×10^{7}CFU•mL^{-1}).

S6. Determination methods of water quality indexes

(1) Subsequent turbidity

The residual turbidity percentage (RT %) was calculated as follows:

$$RT（\%）= T_i/T_0 \times 100\%$$

Formula: RT % - residual turbidity percentage, %;

T_i - Turbidity of supernatant after flocculation, NTU;

T_0 - Turbidity of original kaolin suspension, NTU.

(2) Zeta potential

The aqueous solution containing a certain amount of the substance to be measured was adjusted with 0.1M HCl or NaOH to different pH, and the supernatant was measured for the Zeta potential value using a Zeta potentiometer.

(3) OD_{600}

The bactericidal effect of poly (CTS-g-AM-MAPTAC) on Escherichia coli can be analyzed by measuring the optical density (OD_{600}) in the supernatant after flocculation. TU-1901 dual-beam UV spectrophotometer was used to determine the transmittance (T) of the supernatant after flocculation at 600 nm. LB agar in the blank sample would affect the optical density, so the relative optical density was used for calculation. In order to simplify, it is still expressed as OD_{600}, and the specific value is the value after deducting the blank sample. The optical density is calculated as follows:

$$OD_{600} = lg\frac{1}{T}$$

Formula: T - Light transmittance at 600 nm in supernatant after flocculation minus that of blank sample.

S7. The combination of experimental conditions and the grafting rate of synthetic products under various conditions

Table 3 Details of BBD model

serial number	Initiator concentration （mol / L）	Mass ratio of total monomer to chitosan	Monomer mole ratio（%）	Illumination time (min)	Percent grafting G（%）	
					Actual value	Predicted value
1	6.00	4.00	25.00	60.00	225.60	222.52
2	5.00	4.00	25.00	45.00	188.30	189.08
3	6.00	3.00	23.00	60.00	168.90	167.26
4	5.00	4.00	25.00	75.00	202.70	201.70
5	5.00	4.00	27.00	60.00	198.10	197.79
6	6.00	4.00	25.00	60.00	224.80	222.52
7	6.00	5.00	23.00	60.00	172.50	168.61
8	7.00	4.00	23.00	60.00	190.40	191.54
9	6.00	3.00	27.00	60.00	162.80	168.06

serial number	Initiator concentration （mol / L）	Mass ratio of total monomer to chitosan	Monomer mole ratio（%）	Illumination time (min)	Percent grafting *G*（%）	
					Actual value	Predicted value
10	6.00	5.00	25.00	45.00	168.90	170.45
11	6.00	4.00	25.00	60.00	219.50	222.52
12	7.00	3.00	25.00	60.00	172.90	171.80
13	7.00	4.00	25.00	45.00	188.30	190.68
14	6.00	3.00	25.00	45.00	162.70	162.00
15	6.00	4.00	27.00	75.00	195.60	193.48
16	6.00	4.00	23.00	45.00	182.30	182.22
17	6.00	5.00	25.00	75.00	172.30	173.82
18	5.00	3.00	25.00	60.00	174.30	173.20
19	6.00	4.00	25.00	60.00	219.70	222.52
20	7.00	5.00	25.00	60.00	175.10	174.00
21	7.00	4.00	25.00	75.00	193.50	194.10
22	6.00	4.00	27.00	45.00	191.80	187.87
23	6.00	4.00	23.00	75.00	190.90	192.63
24	5.00	4.00	23.00	60.00	188.90	191.64
25	6.00	4.00	25.00	60.00	223.00	222.52
26	6.00	3.00	25.00	75.00	175.40	174.67
27	7.00	4.00	27.00	60.00	193.80	191.89
28	5.00	5.00	25.00	60.00	179.70	178.60
29	6.00	5.00	27.00	60.00	171.30	174.31

S8. The statistical analysis of the model errors

The error of the model is statistically analyzed in Table 4 and Fig. 3. The R^2 of the linear regression equation is 0.9861, and the measured values in Fig. 3 (c) are basically near the predicted linear line, indicating that the linear fitting accuracy is

high. The values of R^2_{adj} and R^2_{pted} are 0.9721 and 0.9330, respectively, which are close to 1, and the difference between them is 0.03391<0.2, indicating that the established model can guide the preparation conditions well, and there are no other obvious influencing factors. CV%=1.68%1＜10%，Adeq Precision=26.583＞4, The residual normal distribution in Fig. 3(a) is basically linear, and the discrete distribution between the predicted value and the residual is irregular, indicating that the established relationship model between the response target value (grafting rate) and the four influencing factors has high accuracy and credibility.

Table 4 Analysis of error in regression model

project	value	project	value
Std. Dev.	3.17	R^2	0.9861
Mean	188.76	R^2_{adj}	0.9721
C.V. %	1.68	R^2_{pted}	0.9330
PRESS	673.70	Adeq Precision	26.583

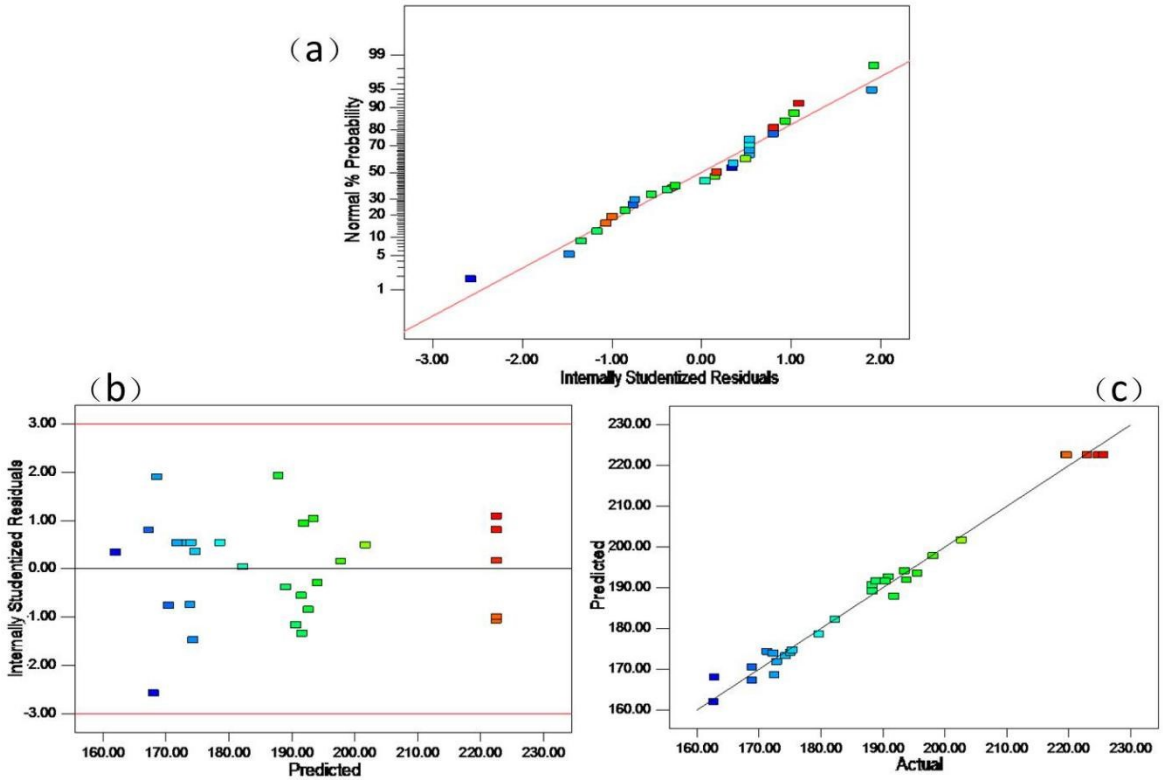

Fig .3 Analysis of error (a) Nomal plot of prediceted, (b) Residuals vs. Predicted,

(c) Predicted vs. Actual

S9. The optimum dosage of each flocculants for kaolin suspension under different pH

Table 5 The optimum dosage of each flocculants for kaolin suspension under different pH

pH / flocculant	2	3	4	5	6	7	8	9	10	11	12
poly（CTS-g-AM-MAPTAC）（2#）	0.6	0.4	0.4	0.4	0.4	0.6	0.6	0.8	1.0	1.0	1.2
PAMA	4	3	3	3	3	4	4	5	6	8	9
PAM	4	4	3	3	3	4	4	6	6	8	9
PAC	5	4	4	6	6	6	7	12	13	15	16

S10. The optimum dosage of each flocculants for Escherichia coli suspension under different pH

Table 6 The optimum dosage of each flocculants for Escherichia coli suspension under different pH

pH	2	3	4	5	6	7	8	9	10	11	12
poly（CTS-g-AM-MAPTAC）（2#）	12	10	10	10	10	12	12	12	14	14	14
PAMA	12	10	10	10	12	12	12	14	14	16	16
PAM	24	24	20	20	20	22	22	24	24	26	26
1277	16	14	10	10	10	12	12	14	14	16	20

References

[1] J. Chen, X. Xu, R. Nie, L. Feng, X. Li, B. Liu, Polymers, 2020, **12**.
[2] Y. Sun, Y. Yu, X. Zheng, A. Chen, H. Zheng, Carbohyd. Polym., 2021, **261**.
[3] Y. Wu, X. Jiang, J. Ma, J. Wen, S. Liu, H. Liu, H. Zheng, Carbohyd. Polym., 2021, **273**.
[4] Y. Yu, Y. Sun, J. Zhou, A. Chen, K.J. Shah, Water, 2021, **13**.
[5] K. Karami, P. Bayat, S. Javadian, M. Saraji, J. Mol. Liq., 2021, **342**.