

Supporting Information:

Morphology and adsorption properties of chitosan sulfate salt microspheres prepared by a microwave-assisted method

Received 00th January 20xx,
 Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

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Characterization

FTIR (US Nicolet/NEXUS-6700) was used to characterize the chemical composition of chitosan, CSS and CSS-S. FTIR spectra of samples prepared with KBr were collected using 64 scans in the range of 4000 - 400 cm⁻¹ at a resolution of 4 cm⁻¹.

Elemental analysis of chitosan and the samples were carried out on Elementar Vario EL III elemental analyzer(Germany). The samples were placed into the elemental furnace and subjected to complete combustion in a pure oxygen environment at 950 °C.

The thermostability of the samples was tested using STA449F3 simultaneous thermal analyzer (Netzsch geraetebau gmbh, Germany). Experiments were carried out in nitrogen atmosphere. And a single scan was run at 20 °C/min from 30 °C to 900°C.

Result

Figure S1 showed the FTIR spectra of unmodified chitosan, CSS and CSS-S from 400 cm⁻¹ to 1750 cm⁻¹ during 120 min of reaction. The characteristic peaks appeared in the FTIR spectra of CSS at 1519 cm⁻¹, 1104 cm⁻¹ and 621 cm⁻¹ after treatment with sulfuric acid for 30 min. The peak at 1634 cm⁻¹ (amide I) of unmodified chitosan was divided into two peaks at 1634 cm⁻¹ and 1519 cm⁻¹ after ionic cross-linking. The symmetric bending of the -NH₃⁺ group at 1519 cm⁻¹ indicated the presence of a strong protonated amino structure in the chitosan sulfate salts¹. Moreover, the peaks at 621 cm⁻¹ and 1104 cm⁻¹, which could be assigned to the asymmetric S-O

bending of SO₄²⁻ and asymmetric S-O stretching of SO₄²⁻, respectively, indicated that the presence of sulfate group in chitosan^{2,3}. However, no characteristic peak of asymmetric S-O stretching of HSO₄⁻ (at ~1200 cm⁻¹) was observed in the FTIR spectra³. This confirmed that the physical crosslinking of chitosan was caused by the sulfate anion instead of bisulfate⁴. In the first 15 min of reaction, the absence of the -NH₃⁺ group (at 1519 cm⁻¹) and the presence of SO₄²⁻ (1104 cm⁻¹ and 621 cm⁻¹) in the spectrum of CSS-15 suggested that not all of the H⁺ and SO₄²⁻ ions absorbed by chitosan acted as protonation agent and crosslinking agent. This indicated that the diffusion of SO₄²⁻ ions into chitosan was quicker than protonation and ionic crosslinking in the first 15 min. No further significant spectral change was observed after the reaction progressed from 30 min to 120 min, especially the intensity of the -NH₃⁺ group at 1519 cm⁻¹. This indicated that the protonation of free -NH₂ group in the unmodified chitosan had much quickly taken place in the first 30 min. The unchanged peaks of SO₄²⁻ (at 1104 cm⁻¹ and 621 cm⁻¹) after 30 min indicated that the SO₄²⁻ ions diffused in chitosan mainly bridged the -NH₃⁺ groups

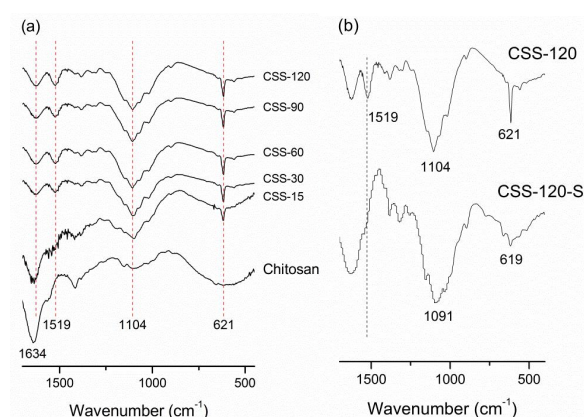


Figure S1 The infrared spectra of chitosan, CSS and CSS-S (the CSS samples were prepared at 90 °C under 1.2 mol/L H₂SO₄ for different time).

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†Electronic Supplementary Information (ESI) available: [details of any supplementary information available should be included here]. See DOI: 10.1039/x0xx00000x

Table S1 Elemental analyses of chitosan, CSS and CSS-S*

	Chitosan	CSS-30	CSS-90	CSS-120	CSS-30-S	CSS-90-S	CSS-120-S
C (%)	40.22	27.93	26.16	25.99	29.93	29.12	28.76
H (%)	7.28	6.92	6.88	6.94	7.10	7.04	6.94
N (%)	7.29	5.22	4.95	4.89	5.50	5.30	5.36
x	-	1.00	1.17	1.19	0.81	0.88	0.92

* CSS samples were prepared at 90 °C under 1.2 mol/L H₂SO₄ for different time.

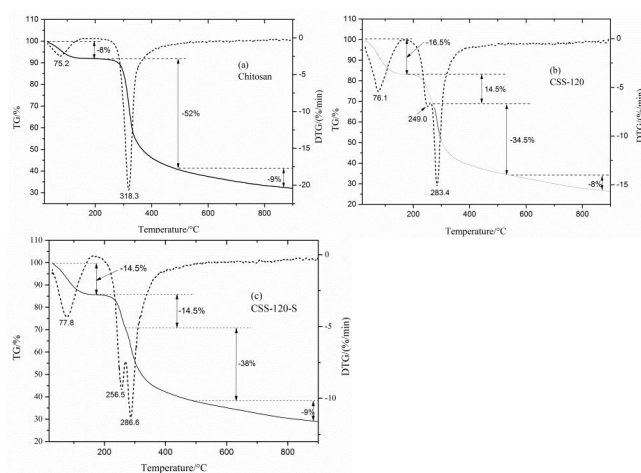
and increased the degree of ionic crosslinking after 30 min. Sample CSS-30-S, CSS-90-S and CSS-120-S were tried to be recovered from sample CSS-30, CSS-90 and CSS-120 by deacidification with NaOH solution, respectively. The resulted CSS-120-S showed that all the three characteristic peaks in CSS (at ~1519 cm⁻¹, 1104 cm⁻¹ and 621 cm⁻¹) just decreased after treated with NaOH (Figure S1b, the spectra of CSS-30-S and CSS-90-S were similar to that of CSS-120-S). The presence of peaks at about 1091 cm⁻¹ and 619 cm⁻¹ in sample CSS-120-S indicated that the sulfate group in CSS was not entirely removed².

The presence of sulfate group in the chitosan microspheres was also accurately determined by elemental analysis (Table 1)². Elemental analyses indicated that >99% of the amino groups in chitosan had reacted to form sulfate salts (set CSS formula as [(C₆H₁₂NO₄)·xSO₄]_n, the x in the formula calculated as about 1, according to carbon). The protonation degree is higher than other reported chitosan sulfate salt^{5,6}. Moreover, as the reaction time prolonged, the content of C, H, and N decreased; the value x also increased and was greater than 1 finally. This result showed that more and more sulfate ions diffused into the chitosan network with increasing the microwave-assisted heating time. This phenomena could be due to the non-thermal effect of microwave heating. The existence of sulfate group in sample CSS-30-S, CSS-90-S and CSS-120-S could be also concluded from elemental analyses (Table 1)². Although the value x decreased, it was still close to 1. This indicated that the CSS was much stable even after the alkali treatment.

The thermal stability⁷ of unmodified chitosan and chitosan sulfate salt microspheres was studied by thermogravimetric analysis in nitrogen atmosphere (Figure S2). For unmodified chitosan (Figure S2a), the first thermal event was observed at 75 °C with a weight loss of 8 %, which was assigned to the loss

of water physically adsorbed and/or weakly hydrogen-bonded to chitosan molecules⁸. The second thermal event reached a maximum at 318 °C with a weight loss of 52 %, which corresponded to the depolymerisation and decomposition of chitosan chains⁹. The third weight loss of 9 % and a residual mass of 31 % was observed.

For CSS-120 and CSS-120-S, the first thermal event was observed at about ~76 °C with a weight loss of 16.5 % and 14.5%, respectively (Figure S2b and 2c). This indicated that CSS-120 and CSS-120-S had a stronger affinity of water than the unmodified chitosan, which might be due to the presence of hydrophilic ammonium and sulfate. The second thermal event of CSS-120 showed a two-step decomposition process at 249 °C and 283 °C with a weight loss of 14.5 % and 34.5%, respectively (Figure S2b). The first step could be assigned to

**Figure S2** TG and DTG curves of chitosan, CSS-120 and CSS-120-S.

the melting of chitosan ammonium sulfate functional groups², which happened prior to the decomposition of the chitosan polymer (the second step at 283 °C). CSS-120-S also showed a similar two-step decomposition process at 256 °C and 287 °C with a weight loss of 14.5 % and 38%, respectively (Figure S2c). It was shown that the mass loss of CSS-120-S at the chitosan chain decomposition step (~287 °C) was higher than that of CSS-120 (~283 °C). This could be due to the decrease of content of ammonium sulfate functional groups in CSS-120-S after the alkali treatment. This was also in agreement with the results of FTIR, XPS and elemental analysis.

Notes and references

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