

## Electronic Supplementary Information

### Does non-thermal plasma modify biopolymers in solution? A chemical and mechanistic study for alginate

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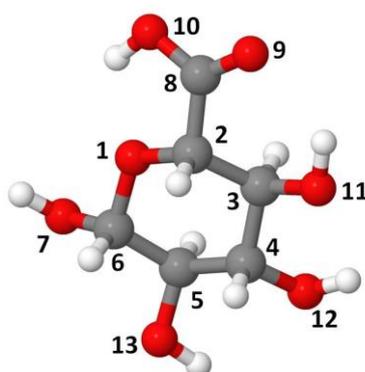
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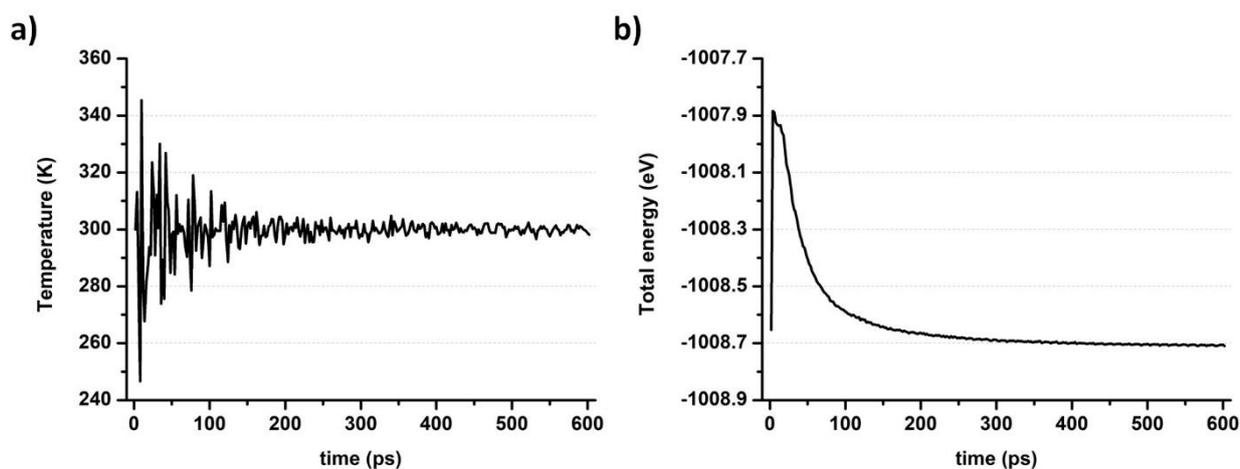
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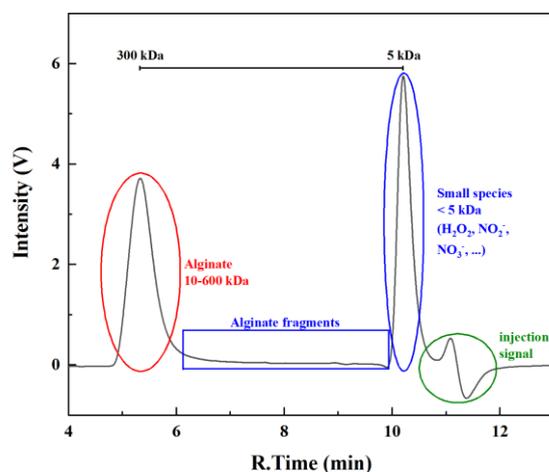
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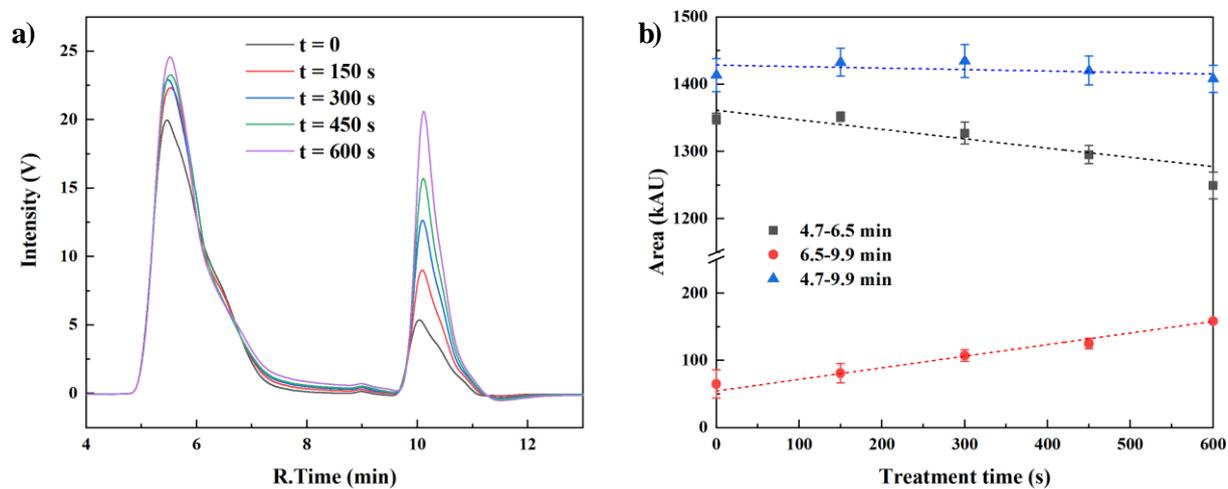
**Figure S1.** Molecular structure of the glucuronic acid. The carbon, oxygen and hydrogen atoms are illustrated in gray, red and white colors, respectively. Some atoms are numbered for reference in Table S1.



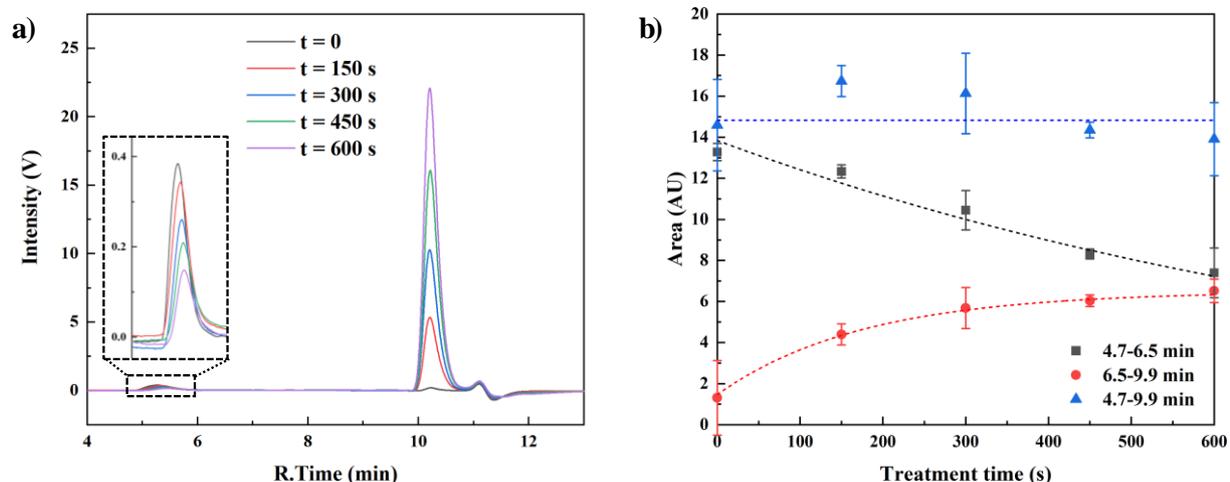
**Figure S2.** Time evolution of the temperature and total energy of the glucuronic acid model system.



**Figure S3.** Typical chromatogram of 0.5 g L<sup>-1</sup> alginate solution treated by non-thermal plasma (NTP). The different regions of the chromatogram are highlighted and assigned. The black bar on top represents the separation limits of the column.



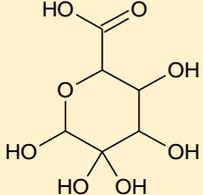
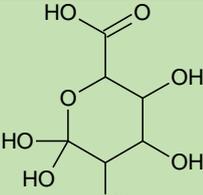
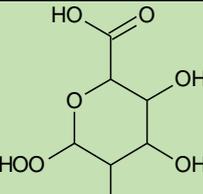
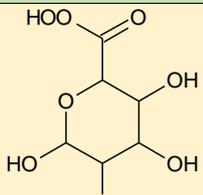
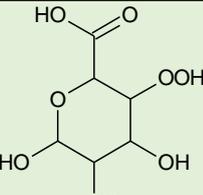
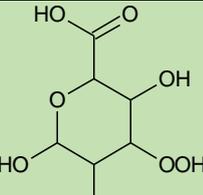
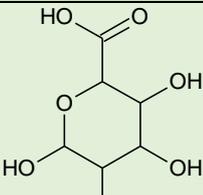
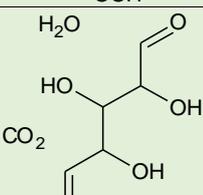
**Figure S4.** a) Chromatograms of 5 g L<sup>-1</sup> alginate solutions treated by NTP for different times; b) areas of different portions of the chromatograms as a function of the treatment time. The dashed lines are exponential (black and red) or linear (blue) fits.



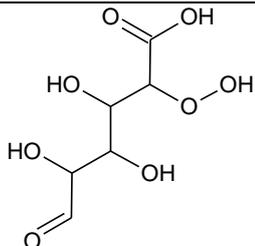
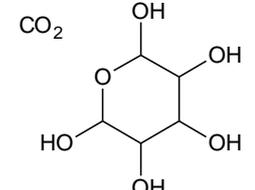
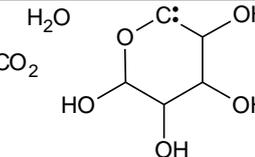
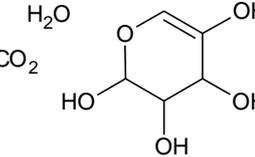
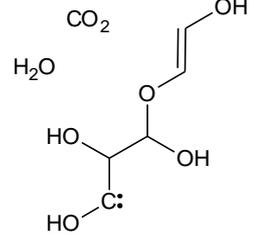
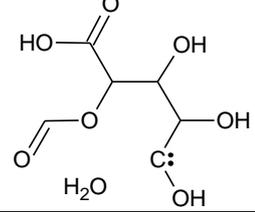
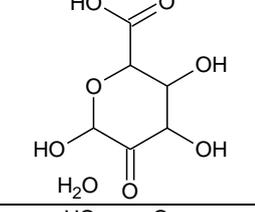
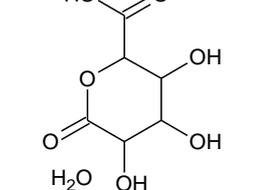
**Figure S5.** a) Chromatograms of 0.05 g L<sup>-1</sup> alginate solutions treated by NTP for different times; the inset is an enlargement of the peak at 5.5 min; b) areas of different portions of the chromatograms as a function of the treatment time; the dashed lines are exponential (black and red) or linear (blue) fits.

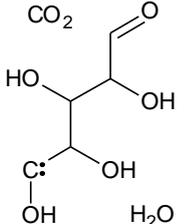
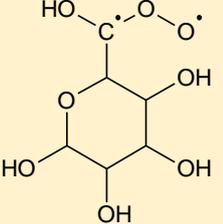
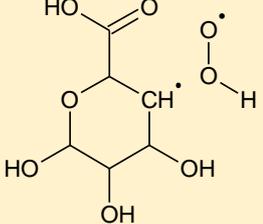
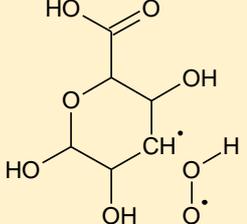
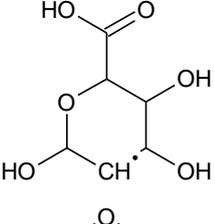
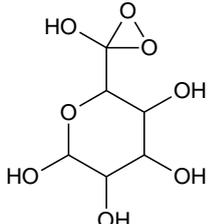
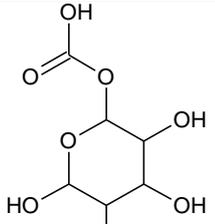
**Table S1.** Overview of all the reaction mechanisms observed in the DFTB-MD simulations after the interaction of O atoms with glucuronic acid. The numbering of the various atoms corresponds to Figure S4 below. Note that most of these reactions are initiated by H-abstraction, but the latter can occur at different C or O atoms, as indicated by the second column. Color code: dark green = events that happen with frequency higher than 7.9%; light green = events that happen with frequency between 5.0 and 7.9%; yellow = events that happen with frequency between 2.0 and 4.9%; white = events that happen with frequency lower than 2%.

No.	H-abstraction	N° events	Description	Structure	%
1	C2	16	C2-OH formation		8
2	C3	11	C3-OH formation		5.5
3	C4	9	C4-OH formation		4.5

4	C5	5	C5-OH formation		2.5
5	C6	19	C6-OH formation		9.5
6	O7	17	O7-OH formation		8.5
7	O10	6	O10-OH formation		3
8	O11	13	O11-OH formation		6.5
9	O12	19	O12-OH formation		9.5
10	O13	10	O13-OH formation		5
11	O7 and O10	12	liberation of H <sub>2</sub> O and CO <sub>2</sub> , breaking of C2-C8 and C6-O1 bonds, formation of C6=O7 and C2=O1 double bonds		6

12	O7 and O10	2	liberation of H <sub>2</sub> O and CO <sub>2</sub> , breaking of C2-C8, C5-C6 and C3-C4 bonds, formation of C4=C5, C2=C3 and C6=O7 double bonds		1
13	O7 and O11	1	liberation of H <sub>2</sub> O, breaking of C5-C6 and C3-C4 bonds, formation of C4=C5, C6=O7 and C3=O11 double bonds		0.5
14	O7 and O12	1	liberation of H <sub>2</sub> O, breaking of C5-C6 bond, formation of C5-O12 bond		0.5
15	O7 and O13	8	liberation of H <sub>2</sub> O, C5-C6 bond breaking, formation of C5=O13 and C6=O7 double bonds		4
16	O10 and O11	1	liberation of H <sub>2</sub> O and CO <sub>2</sub> , breaking of C2-C8 bond, formation of C2-O11 bond		0.5
17	O10 and O12	1	liberation of H <sub>2</sub> O and CO <sub>2</sub> , breaking of C2-C8, C4-C5 and C6-O1 bonds, formation of C2=O1, C4=O12 and C5=C6 double bonds		0.5
18	O11 and O12	9	liberation of H <sub>2</sub> O, breaking of C3-C4 bond, formation of C3=O11 and C4=O12 double bonds		4.5
19	O12 and O13	4	liberation of H <sub>2</sub> O, breaking of C4-C5 bond, formation of C4=O12 and C5=O13 double bonds		2

20	O7	3	binding to O1, breaking of C6-O1 bond, formation of C6=O7 double bond and O1-OH bond		1.5
21	O10	1	liberation of CO <sub>2</sub> , breaking of C2-C8 bond, formation of C2-OH bond		0.5
22	C2 and O10	1	liberation of H <sub>2</sub> O and CO <sub>2</sub> , breaking of C2-C8 bond		0.5
23	C3 and O10	1	liberation of H <sub>2</sub> O and CO <sub>2</sub> , breaking of C2-C8 bond, formation of C2=C3 double bond		0.5
24	C4 and O10	1	liberation of H <sub>2</sub> O and CO <sub>2</sub> , breaking of C3-C4 bond, formation of C2=C3 double bond		0.5
25	C5 and O7	1	liberation of H <sub>2</sub> O, breaking of C5-C6 bond, formation of C6=O7 double bond		0.5
26	C5 and O13	2	liberation of H <sub>2</sub> O, formation of C5=O13 double bond		1
27	C6 and O7	4	liberation of H <sub>2</sub> O, formation of C6=O7 double bond		2

28	C6 and O10	1	liberation of H <sub>2</sub> O and CO <sub>2</sub> , breaking of C2-C8 and C6-O1 bonds, formation of C2=O1 double bond		0.5
29	-	6	binding to O9		3
30	-	5	binding to O11		2.5
31	-	7	binding to O12		3.5
32	-	1	binding to O13		0.5
33	-	1	binding to C8 and O9 (C8=O9 → C8-O9 and C8-O)		0.5
34	-	1	binding to C8 and C2, breaking of C2-C8 bond, formation of C2-O-C8 bond		0.5
<b>TOTAL</b>		<b>200</b>			<b>100</b>