Electronic Supplementary Information

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

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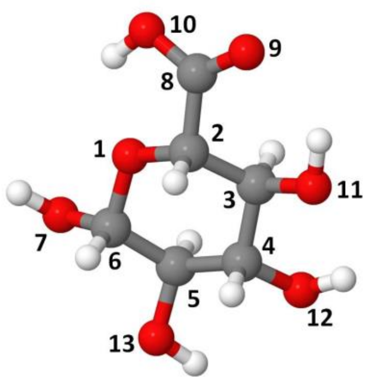


Figure S1. Molecular structure of the glucuronic acid. The carbon, oxygen and hydrogen atoms are illustrated in gray, red and white colors, respectively. Some atoms are numbered for reference in Table S1.

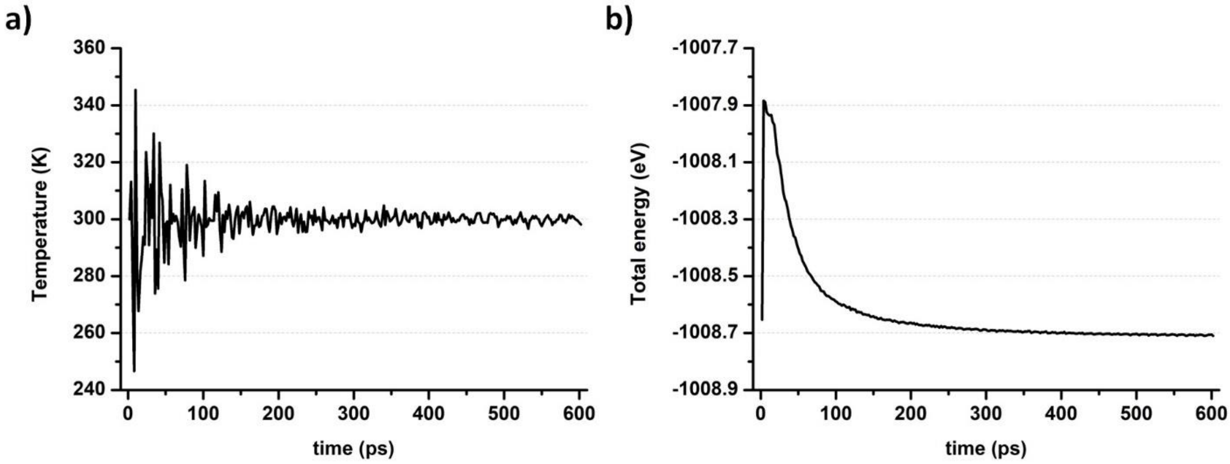


Figure S2. Time evolution of the temperature and total energy of the glucuronic acid model system.

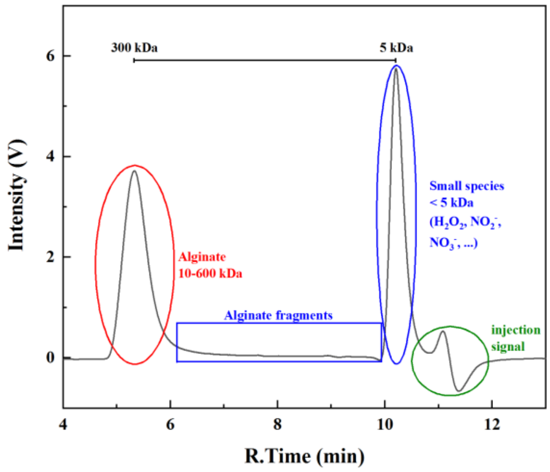


Figure S3. Typical chromatogram of 0.5 g L^{-1} alginate solution treated by non-thermal plasma (NTP). The different regions of the chromatogram are highlighted and assigned. The black bar on top represents the separation limits of the column.

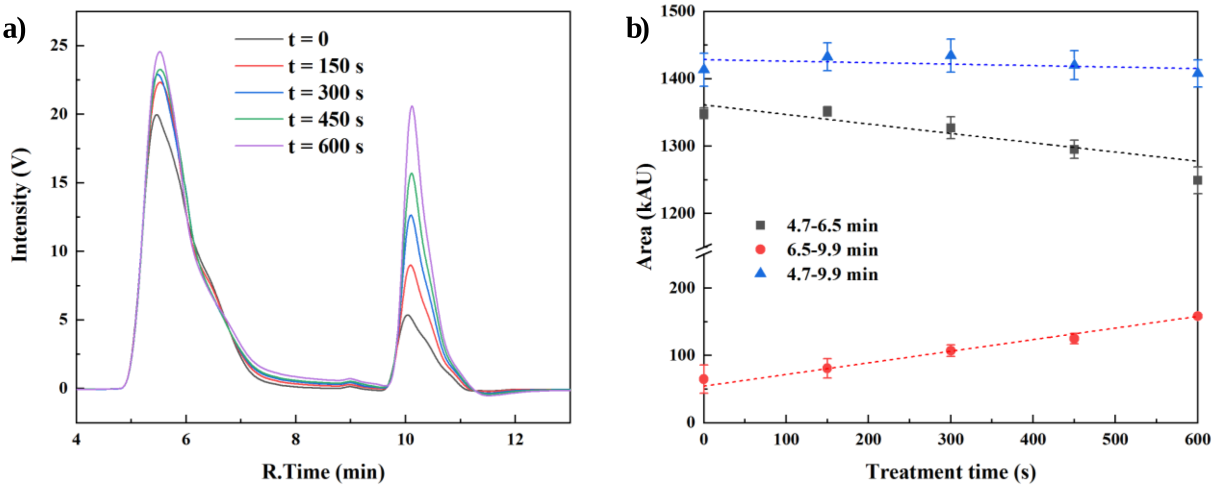


Figure S4. a) Chromatograms of 5 g L^{-1} alginate solutions treated by NTP for different times; b) areas of different portions of the chromatograms as a function of the treatment time. The dashed lines are exponential (black and red) or linear (blue) fits.

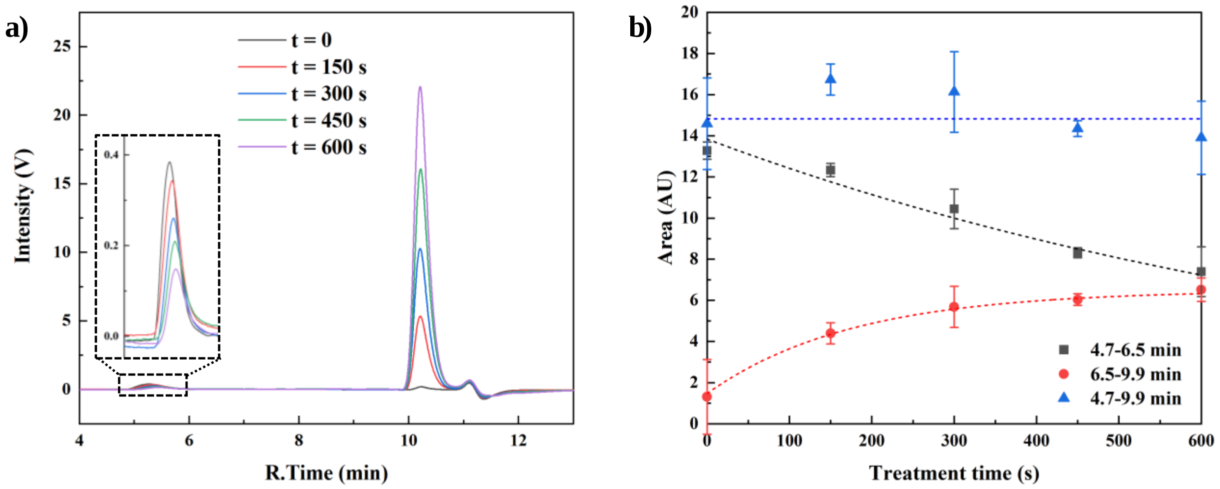
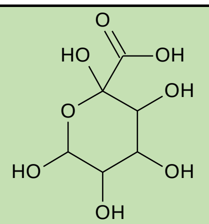
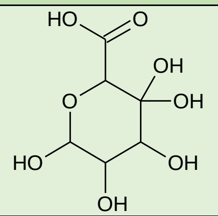
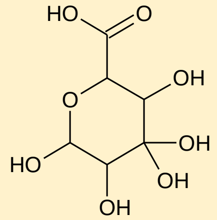
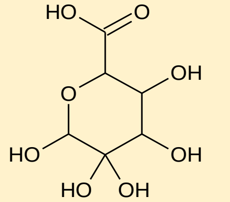
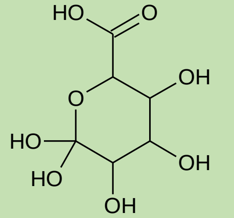
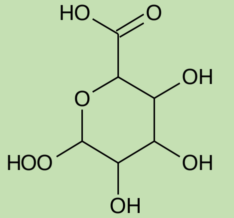
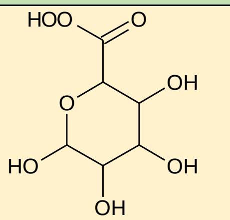
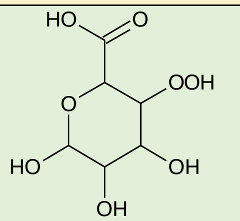
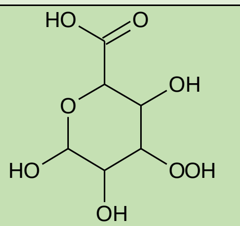
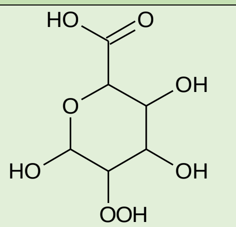
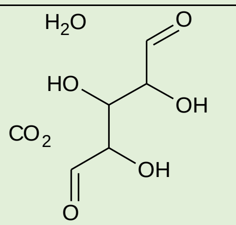
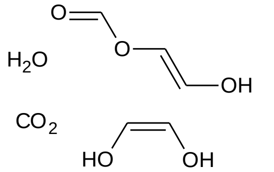
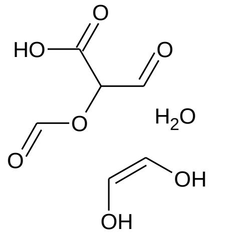
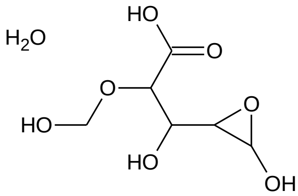
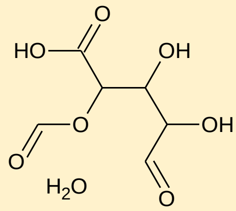
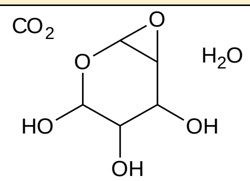
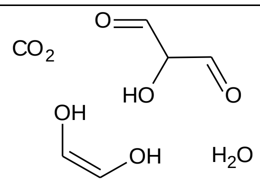
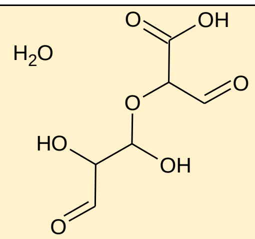
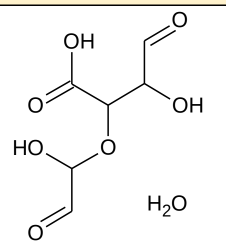


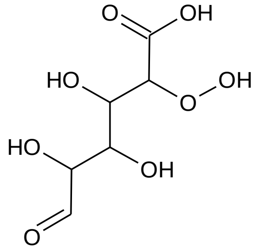
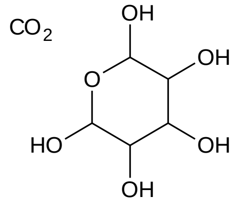
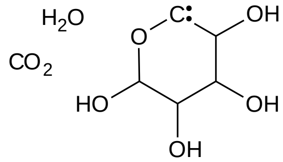
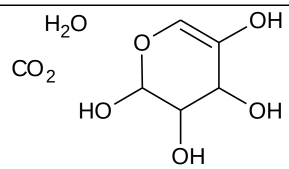
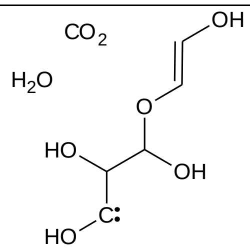
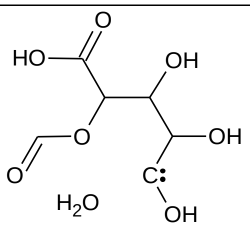
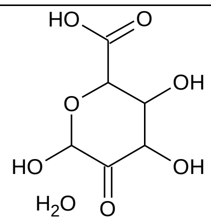
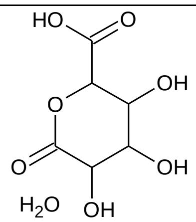
Figure S5. a) Chromatograms of 0.05 g L^{-1} alginate solutions treated by NTP for different times; the inset is an enlargement of the peak at 5.5 min; b) areas of different portions of the chromatograms as a function of the treatment time; the dashed lines are exponential (black and red) or linear (blue)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

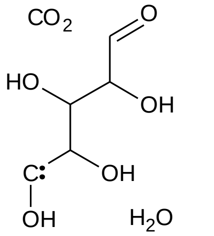
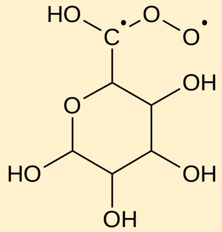
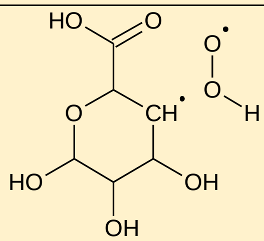
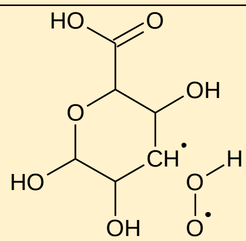
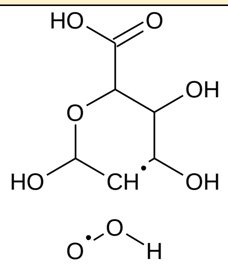
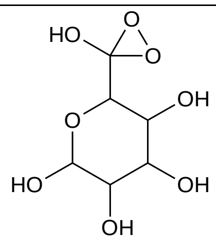
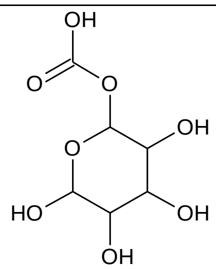
Table S1. Overview of all the reaction mechanisms observed in the DFTB-MD simulations after the interaction of O atoms with glucuronic acid. The numbering of the various atoms corresponds to Figure S4 below. Note that most of these reactions are initiated by H-abstraction, but the latter can occur at 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_2O and CO_2, 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_2O and CO_2, 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_2O, 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_2O, breaking of C5-C6 bond, formation of C5-O12 bond		0.5
15	O7 and O13	8	liberation of H_2O, C5-C6 bond breaking, formation of C5=O13 and C6=O7 double bonds		4
16	O10 and O11	1	liberation of H_2O and CO_2, breaking of C2-C8 bond, formation of C2-O11 bond		0.5
17	O10 and O12	1	liberation of H_2O and CO_2, 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_2O, breaking of C3-C4 bond, formation of C3=O11 and C4=O12 double bonds		4.5
19	O12 and O13	4	liberation of H_2O, 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_2, breaking of C2-C8 bond, formation of C2-OH bond		0.5
22	C2 and O10	1	liberation of H_2O and CO_2, breaking of C2-C8 bond		0.5
23	C3 and O10	1	liberation of H_2O and CO_2, breaking of C2-C8 bond, formation of C2=C3 double bond		0.5
24	C4 and O10	1	liberation of H_2O and CO_2, breaking of C3-C4 bond, formation of C2=C3 double bond		0.5
25	C5 and O7	1	liberation of H_2O, breaking of C5-C6 bond, formation of C6=O7 double bond		0.5
26	C5 and O13	2	liberation of H_2O, formation of C5=O13 double bond		1
27	C6 and O7	4	liberation of H_2O, formation of C6=O7 double bond		2

28	C6 and O10	1	liberation of H_2O and CO_2, 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
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