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Article:
Ahmad, A. and Martsinovich, N. (2023) Atomic-scale modelling of organic matter in soil: adsorption of organic molecules and biopolymers on the hydroxylated α-Al2O3 (0001) surface. Philosophical Transactions of the Royal Society A: Mathematical, Physical and Engineering Sciences, 381 (2250). 20220254. ISSN: 1364-503X

https://doi.org/10.1098/rsta.2022.0254

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Supplementary material

for

Atomic-scale modelling of organic matter in soil: Adsorption of organic molecules and biopolymers on the hydroxylated α-Al_2O_3 (0001) surface

Aneesa Ahmad,[a #] Natalia Martsinovich [a*]

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Figure S1. Adsorption configurations of methanol on the hydroxylated α-Al_2O_3 (0001) surface. Red spheres – O atoms, light grey – Al, dark grey – C, white – H atoms.

Table S1. Adsorption energies and hydrogen bond lengths for methanol adsorbed on the hydroxylated α-Al_2O_3 (0001) surface. Here and in the following tables, the label "m" refers to the atoms of the adsorbed molecule; "s" refers to surface hydroxyls (OH attached to surface Al atoms), and "ss" refers to surface hydroxyls formed by H atoms attached to surface O atoms.

Figure S2. Adsorption configurations of methylamine on the hydroxylated α-Al_2O_3 (0001) surface. Red spheres – O atoms, light grey – Al, dark grey – C, blue – N, white – H atoms.

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Figure S5. Adsorption configurations of acetic acid hydrogen-bonded on the hydroxylated α-Al_2O_3 (0001) surface.

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Table S6. Adsorption energies and bond lengths for acetic acid covalently adsorbed on the hydroxylated α-Al_2O_3 (0001) surface. Labels "C1, C2, C3" refer to covalently bonded acetic acid co-adsorbed with a surface hydroxyl (OH) or with a water molecule, while "P1" refers to covalently bonded acetic acid where the co-adsorbed water was desorbed but remained hydrogen bonded to the surface.

Table S7. Adsorption energies and hydrogen bond lengths of the most stable adsorbed configurations of acetic acid, methylamine, acetamide, methanol and methyl acetate calculated using PBE+D3, compared to the same configurations re-optimised using PW91+D3 and vdW-DF2, and B3LYP+D3 energies for vdW-DF2-optimised geometries.

Figure S7. Summary of adsorption energies of the most stable adsorbed configurations of acetic acid, methylamine, acetamide, methanol and methyl acetate calculated using PBE+D3, compared to these configurations' energies calculated using PW91+D3, vdW-DF2 and B3LYP+D3.

Figure S8. Adsorption configurations of cellulose on the hydroxylated α-Al_2O_3 (0001) surface.

Table S8. Adsorption energies and hydrogen bond lengths for cellulose adsorbed on the hydroxylated α-Al_2O_3 (0001) surface. In this and the following tables, labels "(m)" refer to intramolecular hydrogen bonds, labels "(s)" refer to hydrogen bonds between atoms of the surface, and all other hydrogen bonds are surface-adsorbate hydrogen bonds.

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Table S9. Adsorption energies and hydrogen bond lengths for pectin adsorbed on the hydroxylated α-Al_2O_3 (0001) surface.

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Table S11. Adsorption energies and hydrogen bond lengths for chitosan adsorbed on the hydroxylated α-Al_2O_3 (0001) surface.

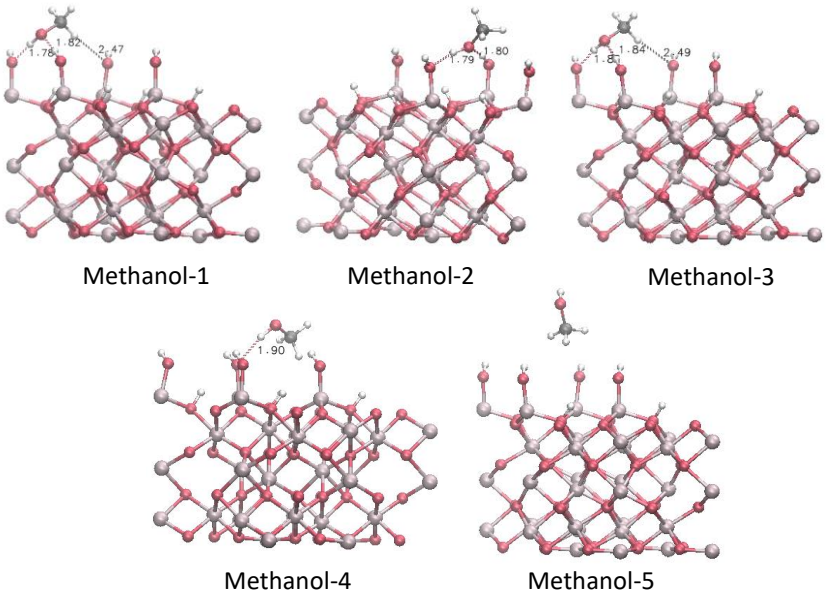

Figure S1. Adsorption configurations of methanol on the hydroxylated α-Al_2O_3 (0001) surface. Red spheres – O atoms, light grey – Al, dark grey – C, white – H atoms.

Table S1. Adsorption energies and hydrogen bond lengths for methanol adsorbed on the hydroxylated α-Al_2O_3 (0001) surface. Here and in the following tables, the label "m" refers to the atoms of the adsorbed molecule; "s" refers to surface hydroxyls (OH attached to surface Al atoms), and "ss" refers to surface hydroxyls formed by H atoms attached to surface O atoms.

Adsorbate	**Adsorption energy, eV**	**Hydrogen bonds**	**Hydrogen bond lengths, Å**
Methanol-1	-0.71	Om…HOs, OHm…OHs, CHm…OHs	1.82, 1.78, 2.47
Methanol-2	-0.70	Om…HOs, OHm…OHs	1.80, 1.79
Methanol-3	-0.70	Om…HOs, OHm…OHs, CHm…OHs	1.84, 1.88, 2.49
Methanol-4	-0.42	OHm…OHs	1.90
Methanol-5	-0.09	N/A	N/A

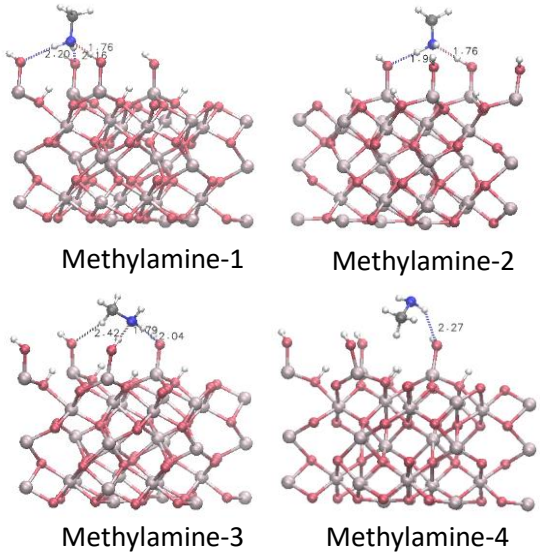

Figure S2. Adsorption configurations of methylamine on the hydroxylated α-Al_2O_3 (0001) surface. Red spheres – O atoms, light grey – Al, dark grey – C, blue – N, white – H atoms.

Table S2. Adsorption energies and hydrogen bond lengths for methylamine adsorbed on the hydroxylated α-Al_2O_3 (0001) surface.

Adsorbate	**Adsorption energy, eV**	**Hydrogen bonds**	**Hydrogen bond lengths, Å**
Methylamine-1	-0.79	Nm…HOs, NHm…OHs, NHm…OHs	1.76, 2.16, 2.20
Methylamine-2	-0.59	Nm…HOs, NHm…OHs,	1.76, 1.95
Methylamine-3	-0.58	Nm…HOs, NHm…OHs, CHm…OHs	1.79, 2.04, 2.42
Methylamine-4	-0.16	NHm…OHs	2.27

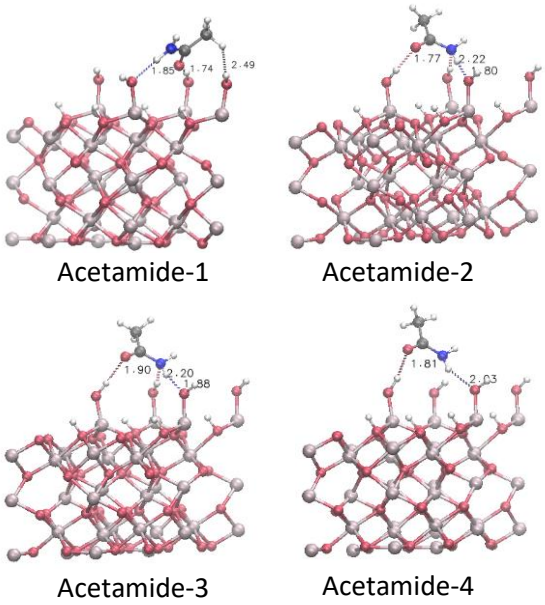

Figure S3. Adsorption configurations of acetamide on the hydroxylated α-Al_2O_3 (0001) surface.

Table S3. Adsorption energies and hydrogen bond lengths for acetamide adsorbed on the hydroxylated α-Al_2O_3 (0001) surface.

Adsorbate	**Adsorption energy, eV**	**Hydrogen bonds**	**Hydrogen bond lengths, Å**
Acetamide-1	-0.74	Om…HOs, NHm…OHs, CHm…OHs	1.74, 1.85, 2.49
Acetamide-2	-0.70	Om…HOs, NHm…OHs, Nm…HOs	1.77, 1.80, 2.22
Acetamide-3	-0.67	Om…HOs, NHm…OHs, Nm…HOs	1.90, 1.88, 2.20
Acetamide-4	-0.55	Om…HOs, NHm…OHs	1.81, 2.03

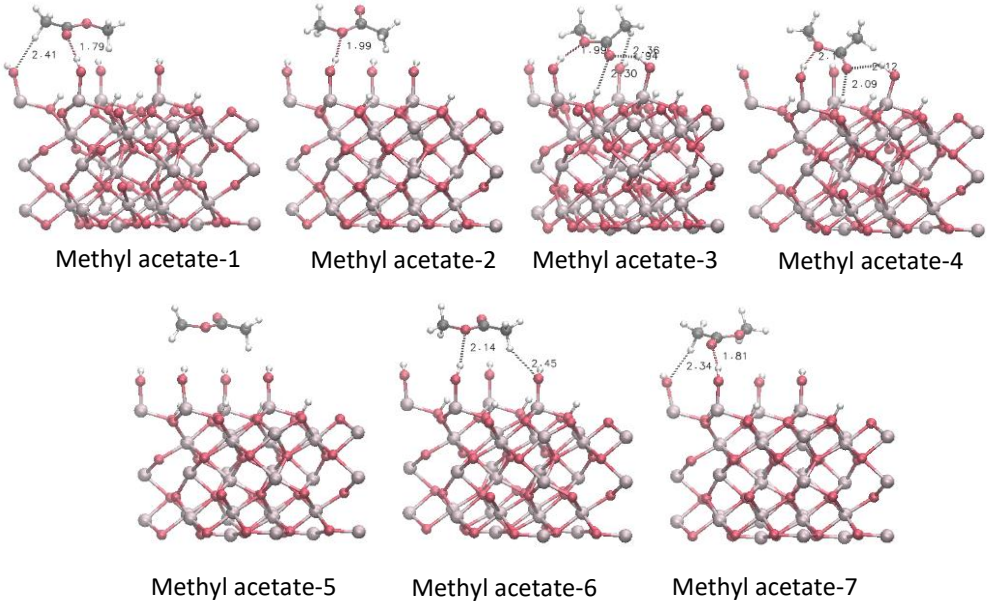

Figure S4. Adsorption configurations of methyl acetate on the hydroxylated α-Al_2O_3 (0001) surface.

Table S4. Adsorption energies and hydrogen bond lengths for methyl acetate adsorbed on the hydroxylated α-Al_2O_3 (0001) surface.

Adsorbate	**Adsorption energy, eV**	**Hydrogen bonds**	**Hydrogen bond lengths, Å**
Methyl acetate-1	-0.49	O(carbonyl)m…HOs, CHm…HOs	1.79, 2.41
Methyl acetate-2	-0.47	O(ether)m…HOs	1.99
Methyl acetate-3	-0.43	O(ether)m…HOs, O(carbonyl)m…HOs, O(carbonyl)m…HOss, CHm…OHs	1.99, 1.94, 2.30, 2.39
Methyl acetate-4	-0.37	O(ether)m…HOs, O(carbonyl)m…HOs, O(carbonyl)m…HOss	2.11, 2.12, 2.09
Methyl acetate-5	-0.25	N/A	N/A
Methyl acetate-6	-0.19	O(ether)m…HOs, CHm…HOs	2.14, 2.45
Methyl acetate-7	-0.11	O(carbonyl)m…HOs, CHm…HOs	1.81, 2.34

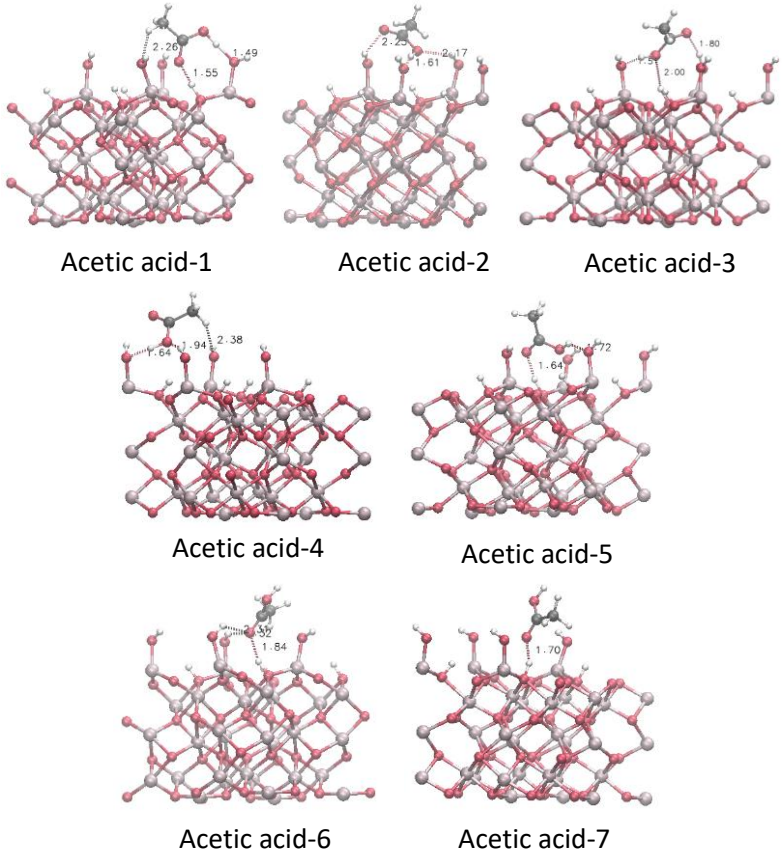

Figure S5. Adsorption configurations of acetic acid hydrogen-bonded on the hydroxylated α-Al_2O_3 (0001) surface.

Table S5. Adsorption energies and hydrogen bond lengths for acetic acid adsorbed on the hydroxylated α-Al_2O_3 (0001) surface by hydrogen bonding.

Adsorbate	**Adsorption energy, eV**	**Hydrogen bonds**	**Hydrogen bond lengths, Å**
Acetic acid-1	-1.11	OHm…OHs, O(carbonyl)m…HOss, CHm…OHs	1.49, 1.55, 2.26
Acetic acid-2	-0.98	OHm…OHs, O(carbonyl)m…HOs, O(hydroxyl)m…HOs	1.61, 2.25, 2.17
Acetic acid-3	-0.95	OHm…OHs, O(carbonyl)m…HOs, O(hydroxyl)m…HOss	1.51, 1.80, 2.00
Acetic acid-4	-0.94	OHm…OHs, O(hydroxyl)m…HOs, CHm…OHs	1.64, 1.94, 2.38
Acetic acid-5	-0.93	OHm…OHs, O(carbonyl)m…HOss	1.72, 1.64
Acetic acid-6	-0.55	O(carbonyl)m…HOss, O(carbonyl)m…HOs, O(carbonyl)m…HOs	1.84, 2.31, 2.32
Acetic acid-7	-0.45	O(carbonyl)m…HOss	1.77

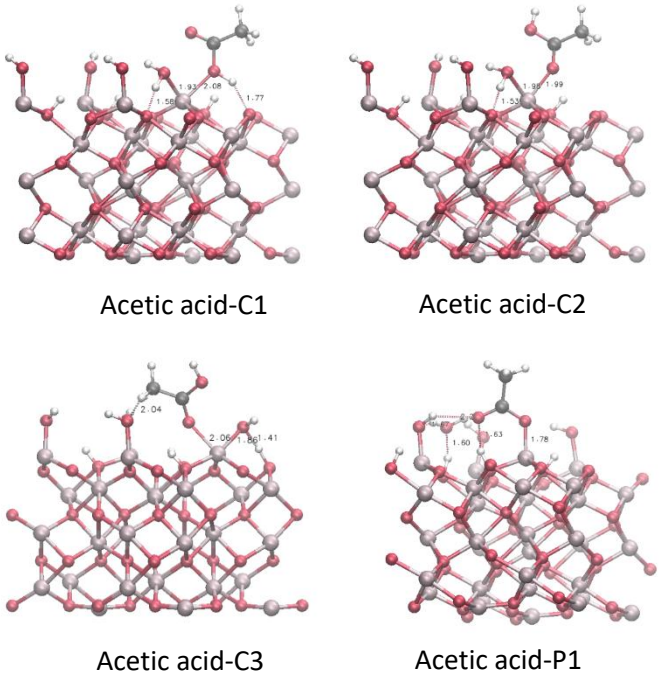

Figure S6. Adsorption configurations of acetic acid covalently bonded on the hydroxylated α-Al_2O_3 (0001) surface.

Table S6. Adsorption energies and bond lengths for acetic acid covalently adsorbed on the hydroxylated α-Al_2O_3 (0001) surface. Labels "C1, C2, C3" refer to covalently bonded acetic acid co-adsorbed with a surface hydroxyl (OH) or with a water molecule, while "P1" refers to covalently bonded acetic acid where the co-adsorbed water was desorbed but remained hydrogen bonded to the surface.

Adsorbate	**Adsorption energy, eV**	**Surface-adsorbate covalent bonds**	**Covalent bond lengths, Å**	**Hydrogen bonds**	**Hydrogen bond lengths, Å**
Acetic acid-C1	-0.64	Al-O(acid OH), Al-O(water)	2.08, 1.93	OHm…Oss, OH(water)…Oss	1.77, 1.58
Acetic acid-C2	-0.59	Al-O(acid O=), Al-O(water)	1.99, 1.98	OH(water)…Oss	1.53
Acetic acid-C3	-0.56	Al-O(acid O=), Al-O(OH)	2.06, 1.86	CHm…OHs, CHm…OHs, OHs…HOss	2.04, 2.19, 1.41
Acetic acid-P1	-1.08	Al-O(acid O=)	1.87	OHm…Oss, OH(water)…OHs, O(hydroxyl)m… HO(water), O(water)…HOs	1.63, 1.67, 2.29, 2.39

Table S7. Adsorption energies and hydrogen bond lengths of the most stable adsorbed configurations of acetic acid, methylamine, acetamide, methanol and methyl acetate calculated using PBE+D3, compared to the same configurations re-optimised using PW91+D3 and vdW-DF2, and B3LYP+D3 energies for vdW-DF2-optimised geometries.

	Adsorption energies, eV				**Hydrogen bond lengths, Å**			
Adsorbate	**PBE +D3**	**PW91 +D3**	**vdW-DF2**	**B3LYP +D3**	**Hydrogen bonds**	**PBE +D3**	**PW91 +D3**	**vdW-DF2**
Acetic acid	-1.11	-0.94	-0.73	-0.76	OHm…OHs, O(carbonyl)m…HOss	1.49, 1.55	1.49, 1.56	1.66, 1.91
Methylamine	-0.79	-0.82	-0.62	-0.61	Nm…HOs, NHm…OHs, NHm…OHs	1.76, 2.16, 2.20	1.76, 2.16, 2.22	1.84, 2.19, 2.25
Acetamide	-0.74	-0.79	-0.71	-0.68	Om…HOs, NHm…OHs	1.74, 1.85	1.73, 1.86	1,84, 1.91
Methanol	-0.71	-0.76	-0.58	-0.57	Om…HOs, OHm…OHs	1.82, 1.78,	1.83, 1.78	1.84, 1.90
Methyl acetate	-0.49	-0.52	-0.41	-0.42	O(carbonyl)m…HOs, CHm…HOs	1.79, 2.41	1.79, 2.43	1,86, 2.51

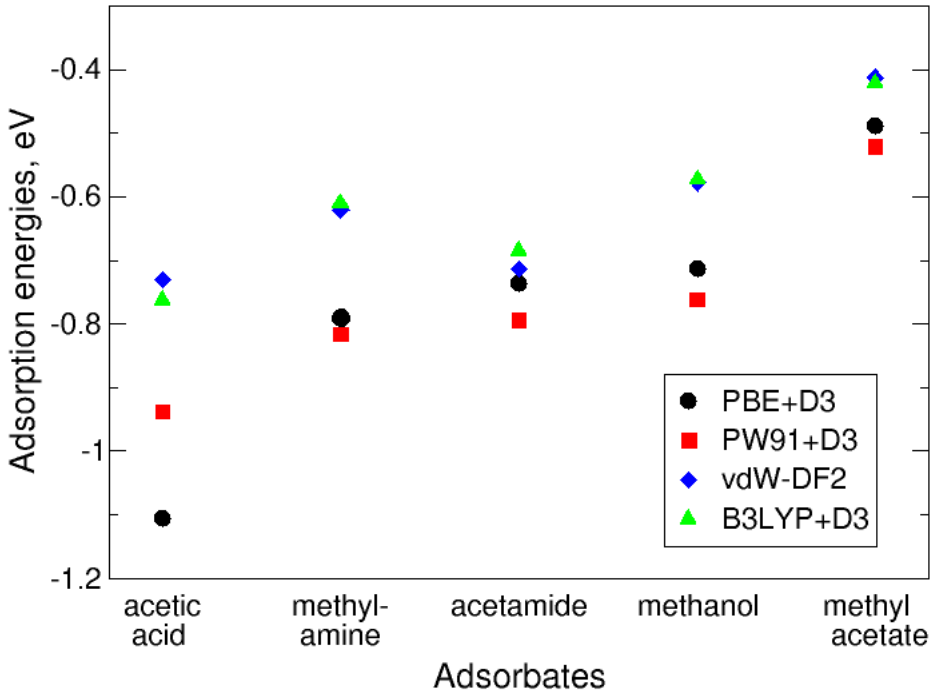

Figure S7. Summary of adsorption energies of the most stable adsorbed configurations of acetic acid, methylamine, acetamide, methanol and methyl acetate calculated using PBE+D3, compared to these configurations' energies calculated using PW91+D3, vdW-DF2 and B3LYP+D3.

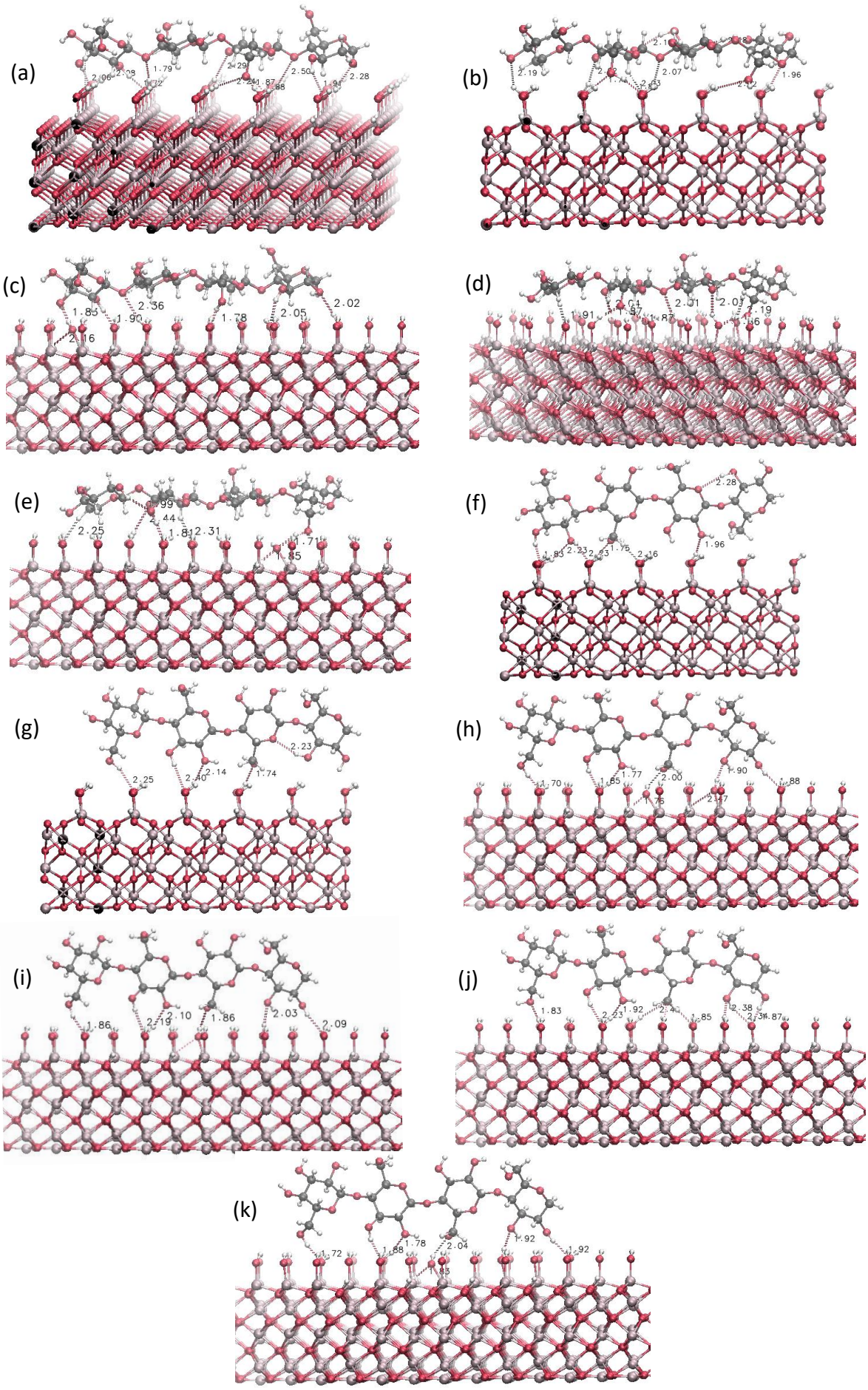

Figure S8. Adsorption configurations of cellulose on the hydroxylated α-Al_2O_3 (0001) surface.

Table S8. Adsorption energies and hydrogen bond lengths for cellulose adsorbed on the hydroxylated α-Al_2O_3 (0001) surface. In this and the following tables, labels "(m)" refer to intramolecular hydrogen bonds, labels "(s)" refer to hydrogen bonds between atoms of the surface, and all other hydrogen bonds are surface-adsorbate hydrogen bonds.

Number	Configuration	Adsorption energy, eV	Number of hydrogen bonds	Hydrogen bond lengths, Å
a	flat, along y	-2.92	11	2.06, 2.08, 1.72, 1.79, 2.29, 2.24, 1.87, 1.88, 2.50, 1.94, 2.28
b	flat, along y	-2.81	10	2.19, 2.02, 1.76, 1.85, 2.03, 2.07, 2.19(m), 2.18(m), 242, 1.96
c	flat, along x	-2.28	7	2.16(s), 1.83, 1.90, 2.36, 1.78, 2.05, 2.02
d	flat, along x	-1.90	8	1.91, 2.04, 1.87, 1.87, 2.01, 2.01, 1.86, 2.19
e	flat, along x	-1.31	7	2.25, 2.44, 1.99(m), 1.81, 2.31, 1.85(s), 1.71
f	edge (OH down), along y	-1.87	7	1.83, 2.23, 2.23, 1.75, 2.16, 1.96, 2.28(m)
g	edge (OH down), along y	-1.26	5	2.25, 2.40, 2.14, 1.74, 2.23(m)
h	edge (OH down), along x	-1.40	7	1.70, 1.85, 1.77, 1.90, 1.88, 1.76(s), 2.47(s)
i	edge (OH down), along x	-1.03	7	1.86, 2.19, 2.10, 1.86, 2.03, 2.09, 2.39(s)
j	edge (OH down), along x	-1.42	8	1.83, 2.23, 1.92, 2.43, 1.85, 2.38, 2.34, 1.87
k	edge (OH down), along x	-1.30	7	1.72, 1.88, 1.78, 1.83(s), 2.04, 1.92, 1.92

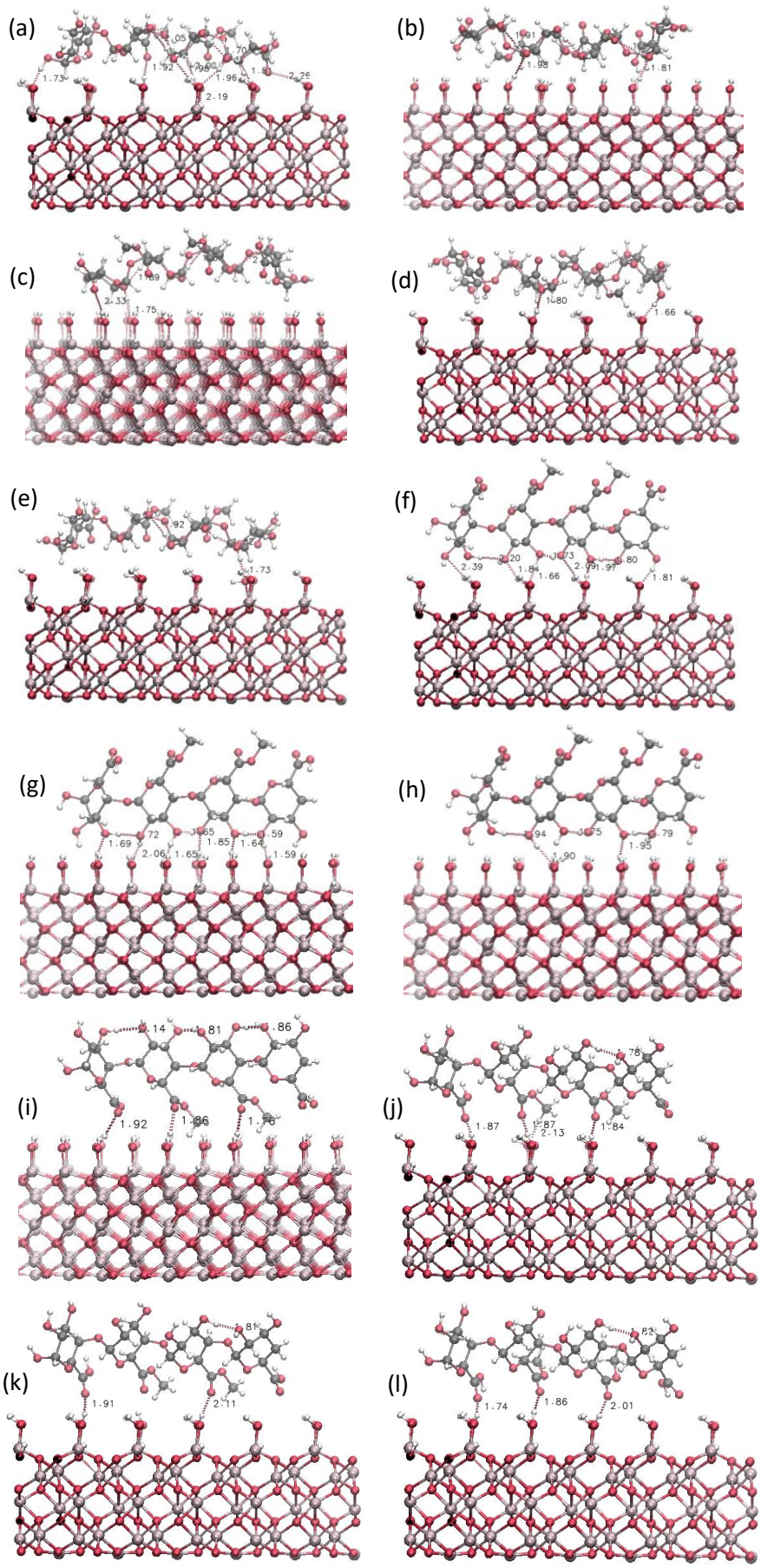

Figure S9. Adsorption configurations of pectin on the hydroxylated α-Al_2O_3 (0001) surface.

Table S9. Adsorption energies and hydrogen bond lengths for pectin adsorbed on the hydroxylated α-Al_2O_3 (0001) surface.

Number	Configuration	Adsorption energy, eV	Number of hydrogen bonds	Hydrogen bond lengths, Å
a	flat (methyl up), along y	-2.43	10	1.76, 1.92, 2.05(m), 1.98, 2.00, 1.70(m), 1.96, 2.19(s), 1.81, 2.26
b	flat (methyl down), along x	-2.05	5	1.98, 1.81, 1.91(m), 1.75(m), 1.94(m)
c	flat (methyl up), along x	-1.71	5	1.75, 2.33, 1.89(m), 1.83(m), 2.11(m)
d	flat (methyl down), along y	-1.46	3	1.66, 1.80, 1.80(m)
e	flat (methyl up), along y	-1.25	3	1.73, 1.82(m), 1.92(m)
f	edge, OH down, along y	-2.50	9	2.39, 2.20(m), 1.84, 1.66, 1.73(m), 2.09, 1.97, 1.80(m), 1.81
g	edge, OH down, along x above gap	-2.42	9	1.69, 2.06, 1.65, 1.86, 1.64, 1.59, 1.72(m), 1.65(m), 1.59(m)
h	edge, OH down, along x above OH	-1.90	5	1.90, 1.95, 1.94(m), 1.75(m), 1.79(m)
i	edge, ester down, along x above gap	-1.01	6	1.92, 1.86, 1.76, 2.14, 1.81, 1.86(m)
j	~edge, ester down, along y	-0.52	5	1.87, 1.87, 2.13, 1.84, 1.78(m)
k	~edge, ester down, along y	-0.50	3	1.91, 2.11, 1.81(m)
l	~edge, ester down, along y	-0.34	4	1.74, 1.86, 2.01, 1.82(m)

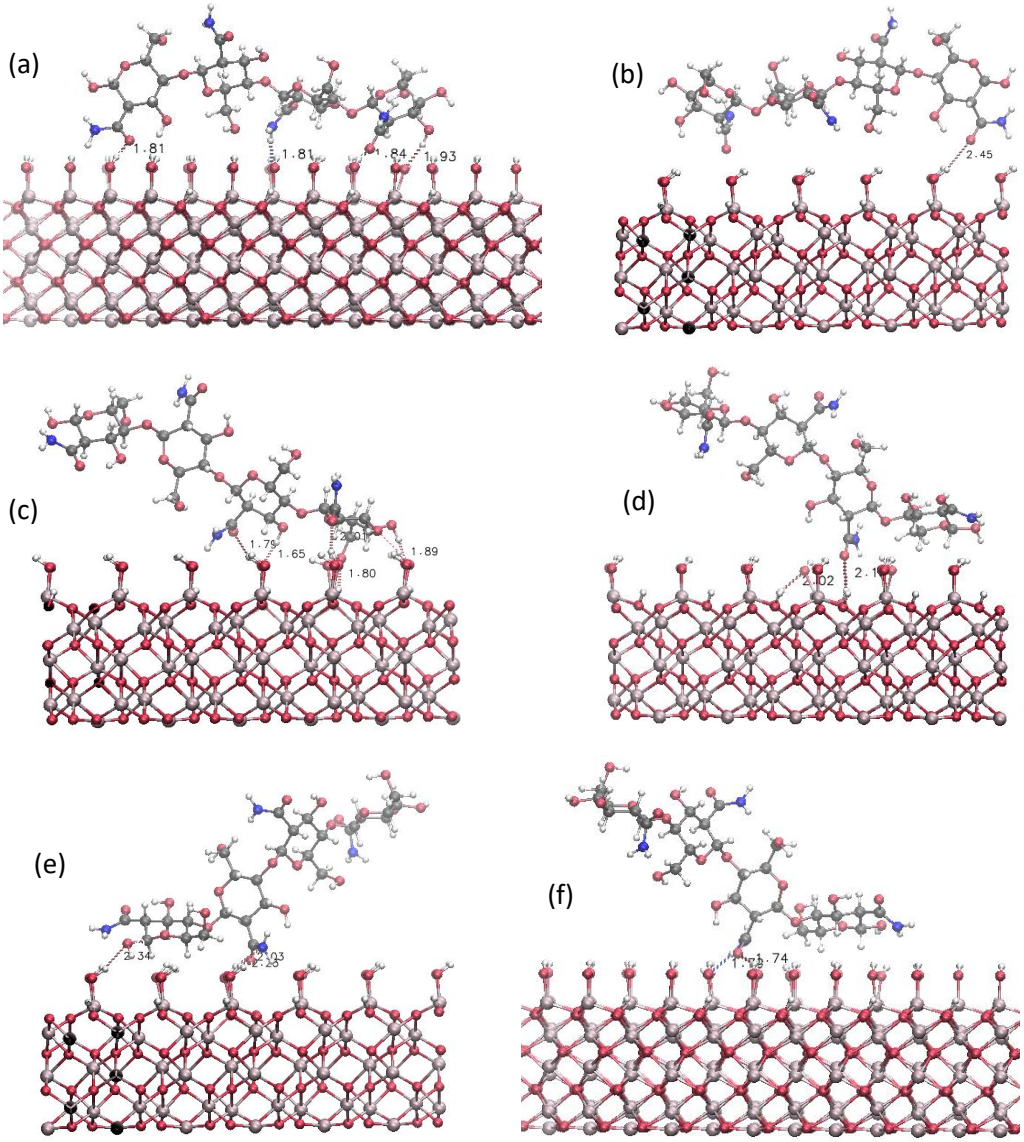

Figure S10. Adsorption configurations of chitin on the hydroxylated α-Al_2O_3 (0001) surface.

Table S10. Adsorption energies and hydrogen bond lengths for chitin adsorbed on the hydroxylated α-Al_2O_3 (0001) surface.

Number	Configuration	Adsorption energy, eV	Number of hydrogen bonds	Hydrogen bond lengths, Å
a	parallel, along x	-2.03	4	1.81, 1.81, 1.84, 1.93
b	parallel, along y	-1.05	1	2.45
c	half-adsorbed, along y	-1.71	6	1.89, 1.83, 1.80, 2.01, 1.65, 1.79
d	half-adsorbed, along x	-1.47	2	2.18, 2.02(s)
e	half-adsorbed, along y	-1.29	3	2.34, 2.23, 2.03
f	half-adsorbed, along x	-0.86	2	1.79, 1.74

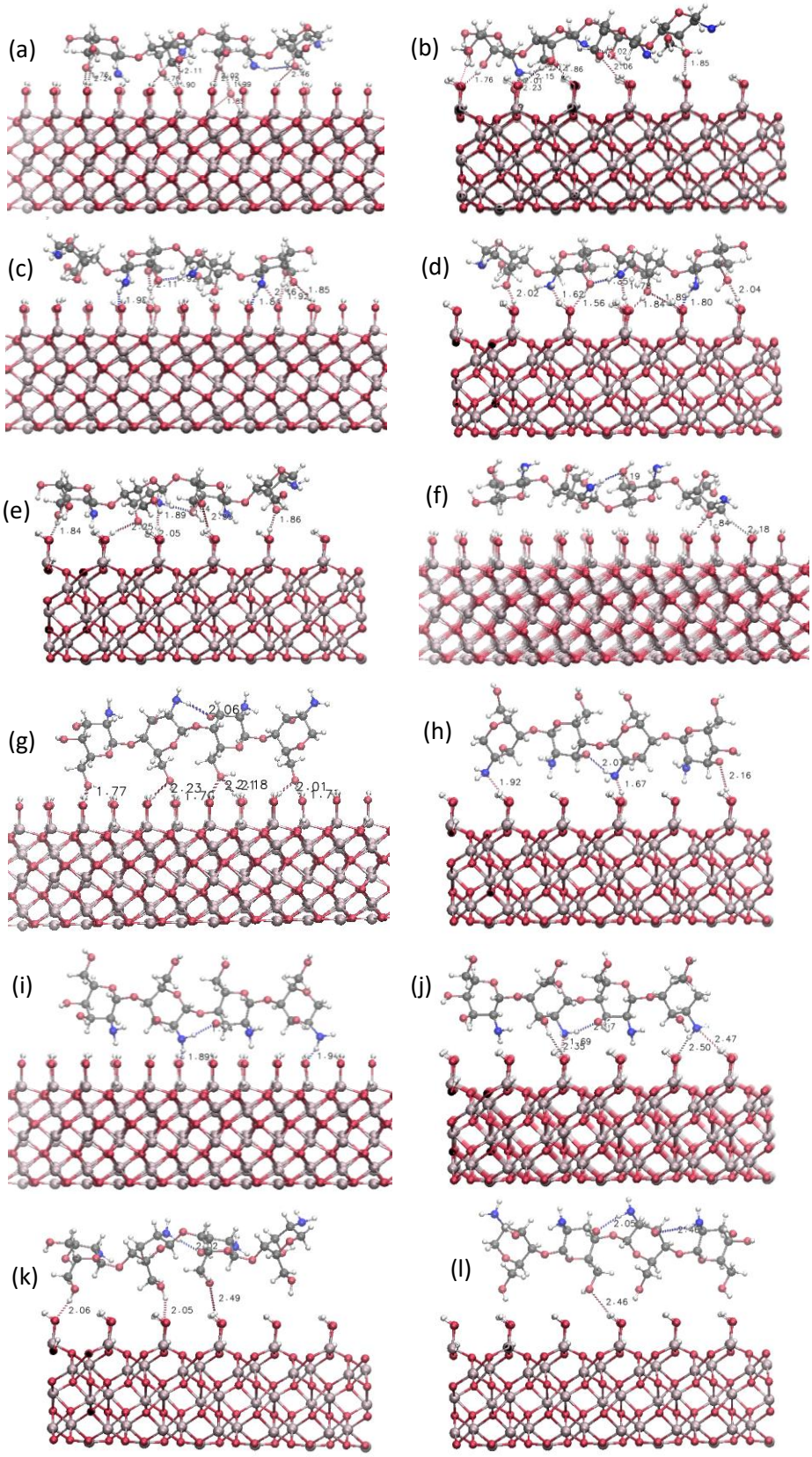

Figure S11. Adsorption configurations of chitosan on the hydroxylated α-Al_2O_3 (0001) surface.

Table S11. Adsorption energies and hydrogen bond lengths for chitosan adsorbed on the hydroxylated α-Al_2O_3 (0001) surface

Number	Configuration	Adsorption energy, eV	Number of hydrogen bonds	Hydrogen bond lengths, Å
a	flat, amine and OH down, along x	-2.66	11	1.76, 2.24, 1.76, 1.90, 2.11, 2.02, 2.15, 1.99, 1.85(s), 2.35(m), 2.46
b	flat, amine and OH down, ~along y	-2.49	9	1.76, 1.21, 2.23, 2.12, 2.15, 1.86, 2.06, 1.85, 2.03(m)
c	flat, amine and OH down, along x	-2.39	7	1.98, 2.11, 1.92(m), 1.84, 2.16, 1.92, 1.85
d	flat, amine and OH down, along y	-2.29	9	2.02, 1.62, 1.56, 1.85(m), 1.78, 1.84, 1.89, 1.80, 2.04
e	flat, amine and OH down, along y	-2.09	7	1.84, 2.25, 2.05, 1.89, 1.94(m), 2.33, 1.86
f	flat, amine and OH up, along x	-1.30	3	1.84, 2.18, 2.19(m)
g	edge, OH down, along y	-2.39	8	1.77, 2.23, 2.76, 2.21, 2.18, 2.06(m), 2.01, 1.78
h	edge, amine down, along y	-1.69	4	1.92, 2.07(m), 1.67, 2.16
i	edge, amine down, along x	-1.65	3	1.89, 1.94, 1.94(m)
j	edge, amine down, along y	-1.61	5	2.35, 1.65, 2.07(m), 2.50, 2.47
k	~edge, OH down, along y	-1.12	4	2.49, 2.05, 2.06, 2.02
l	edge, OH down, along y	-0.73	4	1.74, 1.86, 2.01, 1.82(m)