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Insights on Adsorption of Pyocyanin in Montmorillonite using Molecular Dynamics Simulation

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Supporting Information

Interatomic Potentials

Molecular dynamics simulations rely on interatomic potentials for accurately describing the interactions of atoms with each other. The total potential energy (E_{Total}) of the molecular system is a summation of the energies from the non-bonded ($E_{non\text{-}bonded}$) and bonded (E_{bonded}) components of the system:

$$E_{Total} = E_{nonbonded} + E_{bonded} \tag{1.1}$$

Non-bonded interactions — The contribution of the non-bonded components ($E_{non\text{-}bonded}$) to E_{Total} is the summation of the Columbic (or electrostatics energy) and the van der Waals energy:

$$E_{nonbonded} = E_{Coul} + E_{VDW} \tag{1.2}$$

The electrostatics energy resulting from long-range interactions is computed with Coulomb's law (equation 1.3).

$$E_{Coul} = \frac{e^2}{4\pi\varepsilon_o}\sum_{i \neq j}\frac{q_i q_j}{r_{ij}} \tag{1.3}$$

Where q_i and q_j are the charges of the two interacting atoms, e is the electron charge, and ε_o is the permittivity (dielectric constant) of a vacuum.

The van der Waals energy represents the short-range energy component associated with atomic interactions and is commonly described by the 12-6 Lennard-Jones (LJ) potentials (Lennard-Jones, 1924b; a):

$$E_{VDW} = 4\varepsilon\left[\left(\frac{\sigma}{r_{ij}}\right)^{12} - \left(\frac{\sigma}{r_{ij}}\right)^{6}\right] \qquad 1.4$$

The r_{ij}, σ, and ε, are the separation distance between two atoms, distance at which potential between particle is zero, and the depth of the potential energy well, respectively. The $1/r^{12}$ represents Pauli repulsion at short distance (overlapping of atoms) and $1/r^6$ terms represents the London dispersion energy at longer separations.

Bonded interactions — The summation of the energies associated with bond stretching (two-body), angle bending (three-body) and torsion (four-body) represents the total energy of the bonded components (i.e. E_{bonded}):

$$E_{bonded} = E_{bond\ stretch} + E_{Angle\ bend} + E_{Torsion} \qquad 1.5$$

The energy force field uses either harmonic oscillator potential (equation 1.6) or Morse potential (equation 1.7) to model the bond stretching terms. The Morse potential is more realistic in modelling covalent bonds as it could potentially allow for bond breaking.

$$E_{bond\ stretch} = k_1(r - r_0)^2 \qquad 1.6$$

Where r is the distance between bonded atoms, r_o is the equilibrium bond distance, and k_1 is an empirical force constant that can be obtained from the vibrational spectrum.

$$E_{Morse} = D_o\left(1 - e^{(1 - \alpha(r - r_o))}\right)^2 \qquad 1.7$$

Where D_o is equilibrium dissociation energy while the parameter α controls the 'width' of the potential well.

The angle bend ($E_{Angle\ bend}$) component of three sequentially bonded atoms is described by a harmonic potential (Equation 1.8).

$$E_{Angle\ bend} = k_2(\theta - \theta_0)^2 \qquad 1.8$$

The k_2, θ, and θ_0 represents force constant, the measured angle, and the equilibrium bond angle, respectively.

The $E_{Torsion}$ term for dihedral interaction can be computed from the dihedral angle φ and harmonic constant k_3.(Equation 1.9).

$$E_{Torsion} = k_3(1 + \cos 3\varphi) \qquad 1.9$$

Depending on the force field, it can also contain information for the rest of the terms in E_{bonded}—improper torsional terms, and cross terms. The improper torsional terms maintain the planarity of the aromatic rings while the cross terms describe the coupling of internal variables.

Overall, for this computational study, E_{Total} can be decomposed into:

$$E_{Total} = E_{Coul} + E_{VDW} + E_{Bond\ stretch} + E_{Angle\ bend} + E_{Torsion} \qquad 2.0$$

Arrangement of Pyocyanin in the Interlayer of Montmorillonite

To build pyocyanin–montmorillonite complexes, it was necessary to first determine the most thermodynamically favourable arrangement of pyocyanin in the interlayer of montmorillonite. An earlier study suggests that one layer of pyocyanin is oriented almost parallel to the basal surface but the arrangement of interlayer adsorbed pyocyanin is not clear (Fashina and Deng, 2022). To determine the most favourable arrangement, three types of possible arrangements were investigated using a 2x5x2 supercell. The pyocyanin molecules were arranged:

1. Tail-to-head — the methyl group of one pyocyanin points to the hydroxyl group of the next pyocyanin (Fig. S1a),
2. Head-to-head — the methyl or hydroxyl group of one pyocyanin molecule faces the methyl or hydroxyl group of the next molecule (Fig. S1b), and
3. Random — the methyl group points towards the *x, y* and *z*-directions of the basal surface (Fig. S1c).

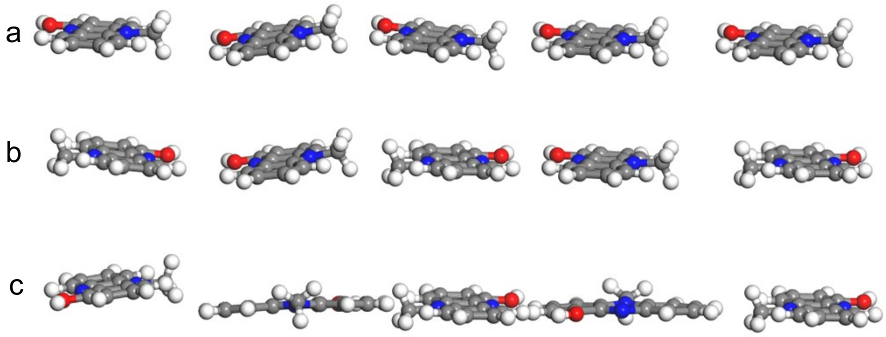

Fig. S1. Three arrangements of the pyocyanin in the interlayer of Na-montmorillonite.

Table S1. The Potential Energy for Pyocyanin as a Function of type of Arrangement

Parameter	**Tail-Head**	**Head-Head**	**Random**
a	10.36 ± 0.01	10.36 ± 0.01	10.36 ± 0.01
b	44.95 ± 0.05	44.93 ± 0.06	44.94 ± 0.05
c	25.99 ± 0.08	26.19 ± 0.1	26.022 ± 0.09
α	90	90	90
β	90	90	90
γ	90	90	90
PE (kcal/mol)	-197074.53 ±25	-197043.99 ±24	-197056.13±25

Assignment of Forcefield Parameters

Table S2. Forcefield Atom Types, Partial Atomic Charges, and Lennard-Jones Parameters Used for MD Simulations

Forcefield	**Species**	**Atom Type**	**Charge (e)**	**ε (kcal/mol)**	**σ (Å)**
SPC	SPC water hydrogen	h*	0.4100		
	SPC water oxygen	o*	-0.8200	0.1554	3.1655
Clayff	hydroxyl hydrogen	hoc	0.4250		
	hydroxyl oxygen	ohc	-0.9500	0.1554	3.1655
	hydroxyl oxygen with substitution	ohs	-1.0808	0.1554	3.1655
	bridging oxygen	ob	-1.0500	0.1554	3.1655
	bridging oxygen with octahedral substitution	obos	-1.1808	0.1554	3.1655
	tetrahedral silicon	st	2.1000	1.8405×10^{-6}	3.3020
	octahedral aluminium	ao	1.5750	1.3298×10^{-6}	4.2712
	octahedral magnesium	mgo	1.3600	9.0298×10^{-7}	5.2643
	aqueous sodium	Na	1.0	0.1301	2.3500

	ion				
CVFF (PYOH^{+})	Oxygen bonded to H	oh	-0.3430	0.2280	2.8598
	Hydrogen bonded to O	ho	0.3870		
	Sp2 N sp2 aromatic	np	-0.1830, -0.2930[a]	0.1669	3.5012
	Sp2 C sp2 aromatic	cp	0.147[b], -0.063, 0.067[c]	0.1479	3.6170
	Sp3 C methyl group	c3	-0.1530	0.0389	3.8754
	Hydrogen bonded to	h	0.1370	0.0380	2.4499
CVFF (PYO)	carbonyl oxygen	o'	-0.3586	0.2280	2.8598
	Sp2 N sp2 aromatic	np	-0.2069, -0.3169[a]	0.1669	3.5012
	Sp2 C sp2 aromatic	cp	0.1231[b], -0.0869, 0.041[c]	0.1479	3.6170
	Sp3 C methyl group	c3	-0.1769	0.0389	3.8754
	Hydrogen bonded to C	h	0.1131	0.0380	2.4499

a = methyl substituted N; b = C in the pyrazine ring; and c = carbonyl C

Table S3. Bond Parameters for the Clayff, SPC, and CVFF Force Field

Harmonic bond strength				k_1	r_o
Forcefield	Species *i*	Species *j*		(kcal/mol Å)	(Å)
SPC	o*	h*		553.9350	1.0000
Clayff	ohc	hoc		553.9350	1.0000
	ohs	hoc		553.9350	1.0000
CVFF	oh	cp		384.0000	1.3700
	o'	cp		297.4852	1.3300
	oh	ho		540.6336	0.9600
	np	cp		560.0000	1.2600
	np	c3		336.8000	1.4750
	cp	cp		480.0000	1.3400
	c3	h		340.6175	1.1050
	cp	h		363.4164	1.0800
Harmonic bond-angle bend				k_2	θ_o
	Species *i*	Species *j*	Species *k*		
SPC	h*	o*	h*	45.7696	109.47
CVFF	cp	oh	ho	50.0000	109.00
	cp	np	cp	75.1000	114.00
	cp	np	c3	75.0000	120.00
	np	cp	cp	90.0000	120.00
	cp	cp	cp	90.0000	120.00
	np	c3	h	80.0000	109.50
	h	c3	h	39.5000	106.40
	cp	cp	h	37.0000	120.00
	oh	cp	cp	60.0000	120.00
	o'	cp	cp	65.0000	120.00
	Torsion			k_3	φ

	Species *i*	Species *j*	Species *k*	Species *l*		
CVFF	ho	oh	cp	cp	0.375	180
	cp	np	cp	cp	1	180
	c3	np	cp	cp	1	180
	cp	np	c3	h	0	180
	np	cp	cp	np	3	180
	np	cp	cp	cp	3	180
	cp	cp	cp	cp	3	180
	np	cp	cp	h	3	180
	cp	cp	cp	h	3	180
	oh	cp	cp	np	3	180
	oh	cp	cp	cp	3	180
	o'	cp	cp	np	3	180
	o'	cp	cp	cp	3	180
	h	cp	cp	h	3	180
	oh	cp	cp	h	3	180
	o'	cp	cp	h	3	180
	Out-of-plane CVFF				k_4	X
CVFF	c3	np	cp	cp	0.37	180
	np	cp	cp	cp	0.37	180
	cp	cp	cp	h	0.37	180
	oh	cp	cp	cp	0	180
	o'	cp	cp	cp	0	180

	Clay component			Pyocyanin			
	Na	o*	h*	C	N	oh or o'	ho
DM	1.67 & 0.52*	-	-	-	-	-	-
HM	3.75	2.61	2.96 & 1.98	-	-	-	-
DMPH	1.10	-	-	2.94	3.22	2.63	1.69
HMPH	3.87 & 3.19†	2.65 & 1.93	2.81 & 1.63	2.65	3.87 & 3.19	2.52 & 1.93†	1.63 & 2.81
DMP	1.26	-	-	3.37	3.37	3.37	-
HMP	3.80 & 2.98	2.65 & 1.98	2.65 & 1.61	2.94	3.96	4.87 & 2.95	-

Na = interlayer sodium; o* = oxygen of water; h* = hydrogen of water; C = C of methyl; N = nitrogen; oh = protonated oxygen; ho = proton on PYOH$^+$;o' = oxygen

Table S4. The atomic profile distances (Å) from the basal (ob) oxygens

The d-spacing of a layer of montmorillonite at various moisture conditions

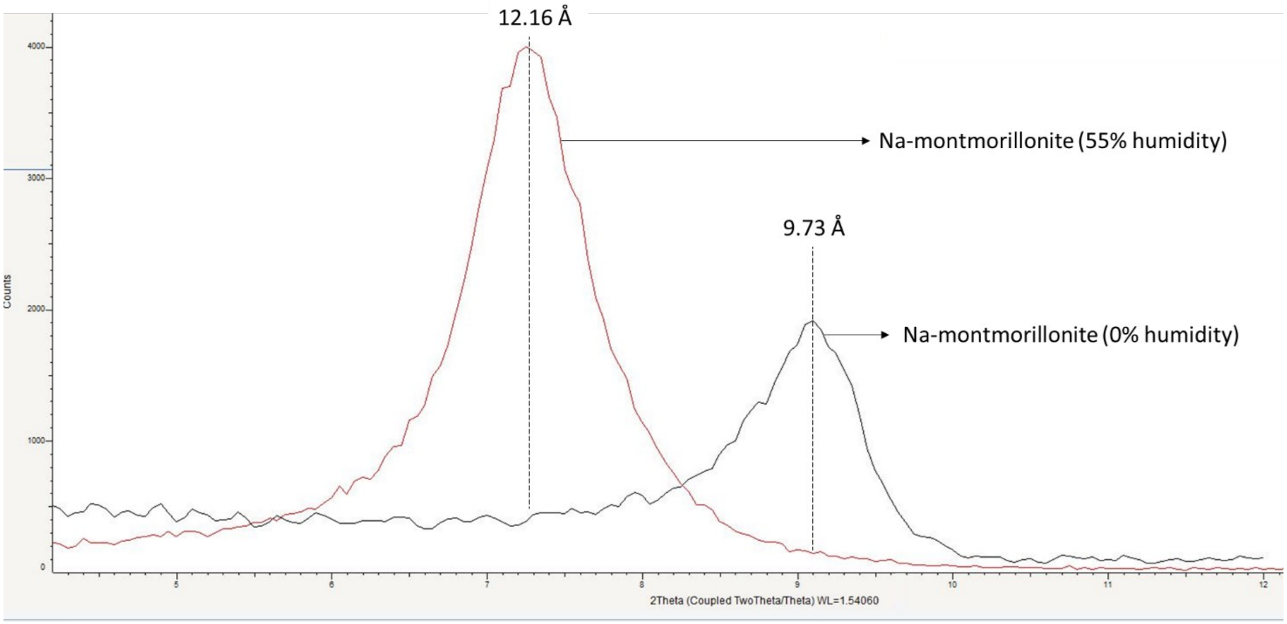

Fig. S2. XRD patterns of montmorillonite at room humidity (55%) and 0% humidity.