



MODELING OF THE SURFACE OF THE MINERAL GOETHITE

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BACKGROUND

- Goethite ($\alpha\text{-FeOOH}$) is a common component of soils.
- It belongs to the group of ferric oxyhydroxides, which are able to sorb large amounts of heavy metal cations, anions and oxyanions and also organic pollutants (e.g. polycyclic aromatic hydrocarbons).
- Even though the bulk structure of goethite is relatively simple the surface structure is complicated due to the existence of several types of adsorption surface sites.
- The surfaces of ferric oxyhydroxides are predominantly formed from hydroxyl groups.



Goethite- Hydrated iron oxide
Size: 6X8 cm
Origin: Brazil



STUDIED SYSTEMS

I- Isolated clusters: Fe_4 , Fe_6 and Fe_8

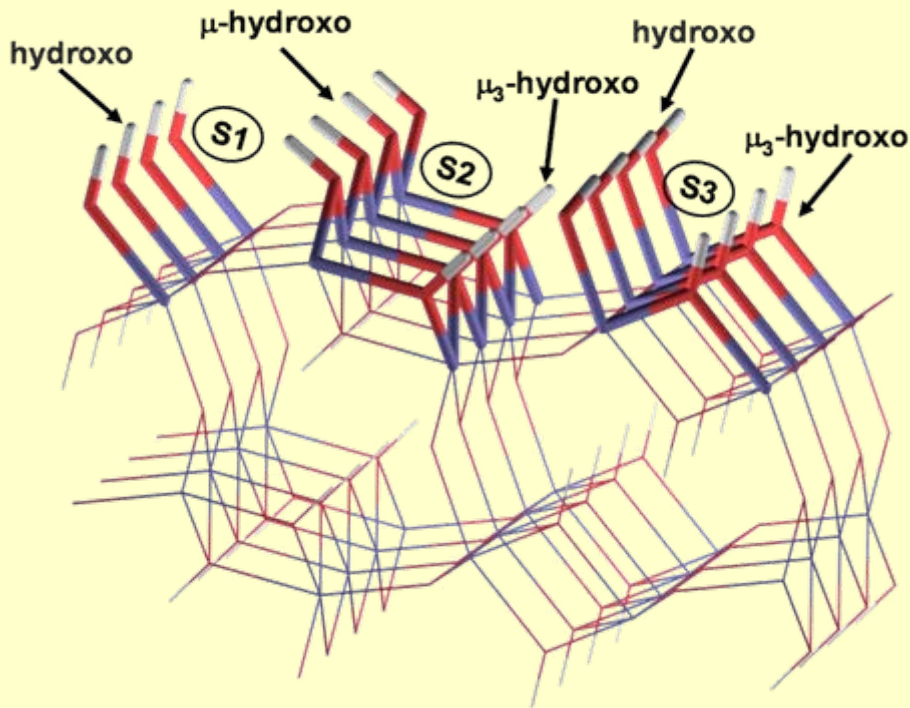
II - Complexes formed of each isolated cluster and water, acetic acid, acetate, 2,4D-dichlorophenoxyacetic acid, 2,4D-dichlorophenoxyacetate

III – $\text{Fe}_6 \cdots \text{C}_6\text{H}_6$

GOAL

The main aim of the present work is the study of adsorption complexes on goethite. We show the structural manifold of the hydroxyl groups of a goethite surface in their interaction with a set of adsorbents occurring in soil environments. For this purpose we have selected a series of molecular species containing small model molecules like water and acetic acid and acetate representing typical polar interactions in soils. Beyond that the interaction of the herbicide 2,4-dichloro-phenoxyacetic acid (2,4-D) and of benzene with the goethite surface has been studied. The latter choice resulted from the absorption capability of goethite concerning aromatic compounds.

STRUCTURAL AND COMPUTATIONAL DETAILS:



-The goethite structure consists of a network of distorted octahedra with Fe(III) cations in their centers which are connected via μ -oxo-bridges.

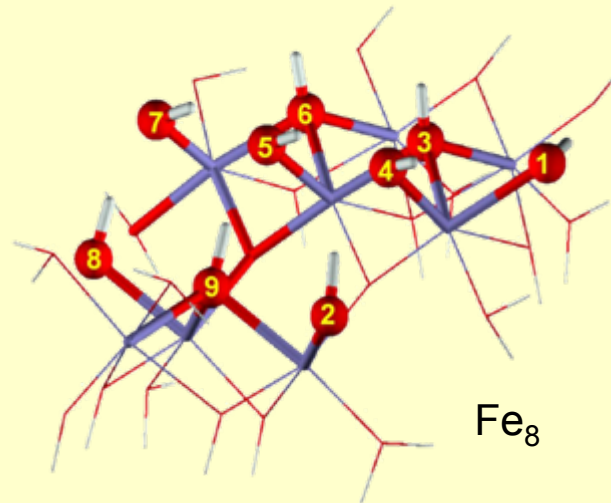
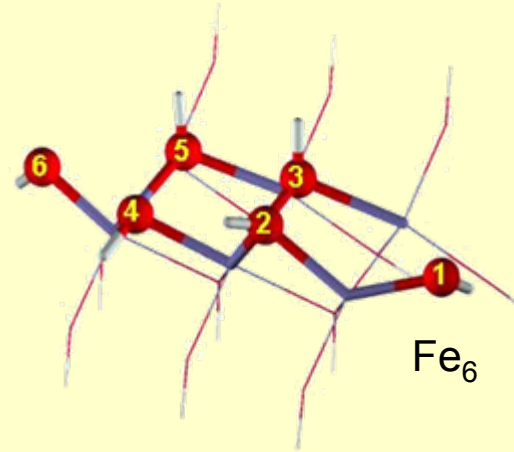
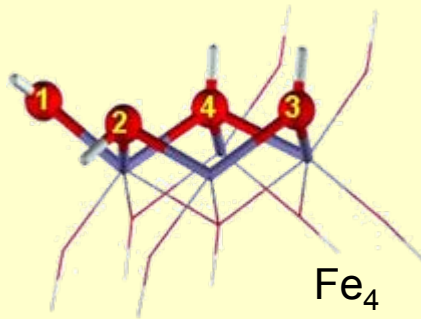
-Cluster models used in the calculations were constructed from the (110) slab surface. The surface of this model contains three different OH types.

-All calculations were performed at **DFT/B3LYP** level of theory with the **TURBOMOLE** program.

-**SCF** calculations for isolated clusters and the water complexes were carried out at low and high-spin as well as at closed shell levels.

-**Basis Set:** SVP, SVP+sp - Only the O-H groups highlighted in the cluster model picture were optimized. All other geometric parameters were kept frozen.

RESULTS

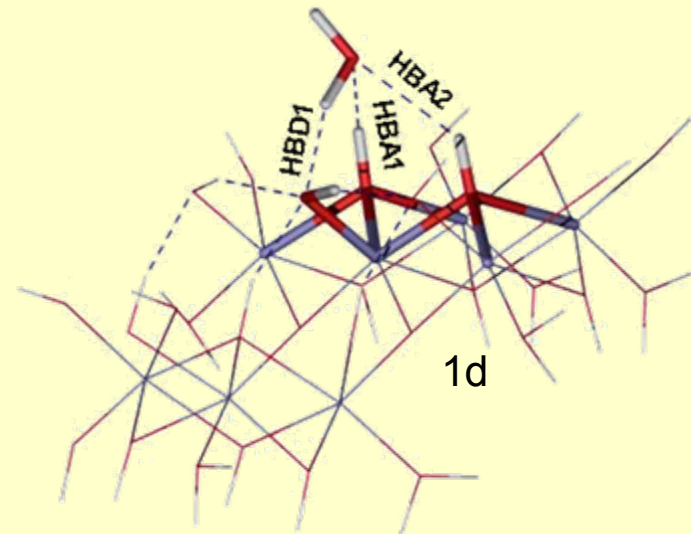
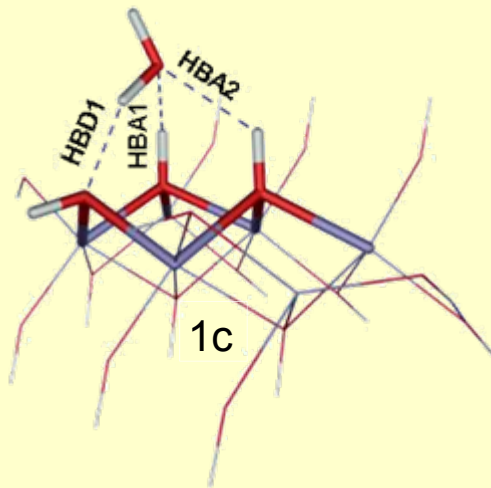
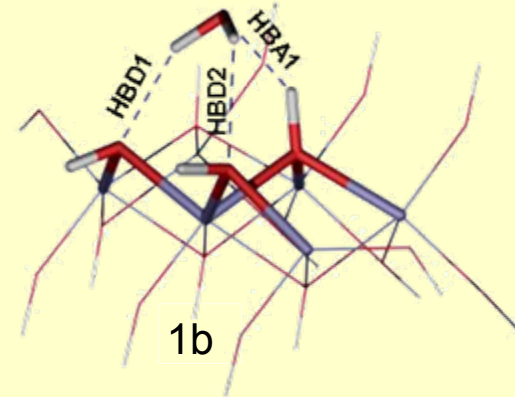
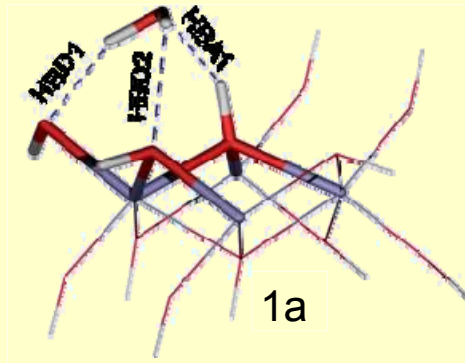




Geometrical parameters (in Å) of isolated iron clusters at low spin (LSPIN), high spin (HSPIN) and closed shell (CSHELL) using B3LYP/SVP approach

System	Method	R O ₁ -H	RO ₂ -H	RO ₃ -H	RO ₄ -H	RO ₅ -H	RO ₆ -H	RO ₇ -H	RO ₈ -H	RO ₉ -H
Fe ₄	LSPIN	0.969	0.971	0.968	0.970					
	HSPIN	0.969	0.971	0.970	0.965					
	CSHELL	0.973 (0.973)	0.980 (0.977)	0.969 (0.966)	0.966 (0.969)					
Fe ₆	LSPIN	0.984	0.971	0.968	0.967	0.969	0.968			
	HSPIN	0.988	0.972	0.966	0.966	0.967	0.969			
	CSHELL	1.001 (0.999)	0.972 (0.971)	0.969 (0.968)	0.977 (0.973)	0.969 (0.968)	0.979 (0.977)			
Fe ₈	LSPIN	0.969	0.969	0.970	0.987	0.977	0.972			
	HSPIN	0.967	0.967	0.968	0.987	0.977	0.971			
	CSHELL	0.981 (0.982)	0.977 (0.973)	0.969 (0.967)	0.969 (0.972)	0.977 (0.968)	0.969 (0.967)	0.988 (0.983)	0.975 (0.974)	1.003 (1.006)

^a values in parentheses are results obtained with the SVP+sp basis set



Hydrogen bond distances (Å) between goethite clusters and the water molecule using the B3LYP/SVP approach.

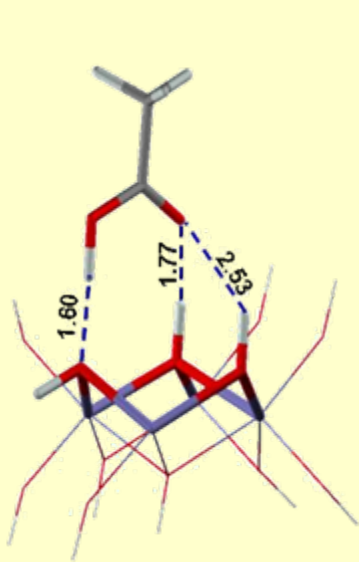
System	Distances		
Fe ₄ -H ₂ O (Fig. 1a)	HBA1	HBD1	HBD2
Low-Spin	1.70	1.78	2.44
High-Spin	1.70	1.68	2.53
Closed Shell ^a	1.63 (1.76)	1.79 (1.81)	2.43(2.41)
Fe ₆ -H ₂ O (Fig. 1b)			
Low-Spin	1.76	1.84	2.39
High-Spin	1.73	1.84	2.19
Closed Shell ^a	1.85 (1.99)	1.91 (1.97)	2.29 (2.39)
Fe ₆ -H ₂ O (Fig. 1c)	HBA1	HBA2	HBD1
Low-Spin	1.60	1.68	2.07
High-Spin	1.81	2.05	1.76
Closed Shell	1.84 (1.89)	2.19/(2.33)	1.76 (1.83)
Fe ₈ -H ₂ O (Fig. 1d)			
Low-Spin	1.92	2.39	1.71
High-Spin	1.95	2.08	1.71
Closed Shell ^a	1.96(1.98)	2.26(2.29)	1.70(1.73)

^a values in parentheses are results obtained with the SVP+sp basis set

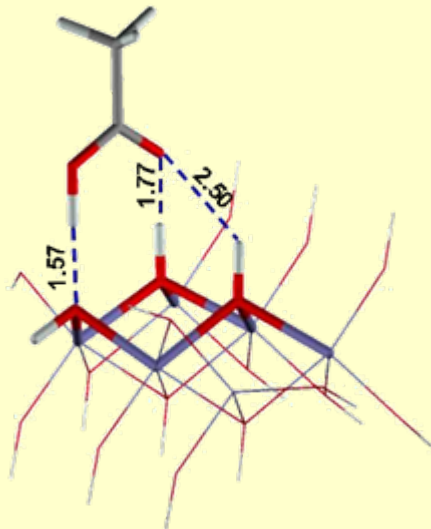
Interaction energies, ΔE , of the water molecule adsorbed on four different goethite clusters using the B3LYP/SVP approach. Energies are given in kcal/mol.

Fe ₄ -H ₂ O (Fig. 1a)		Fe ₆ -H ₂ O (Fig. 1c)	
Low-Spin	-16.4	Low-Spin	-21.3
High-Spin	-20.9	High-Spin	-24.6
Closed Shell ^a	-19.2(-16.5)	Closed Shell	-20.1(-16.5)
Fe ₆ -H ₂ O (Fig. 1b)		Fe ₈ -H ₂ O (Fig. 1d)	
Low-Spin	-18.3	Low-Spin	-16.8
High-Spin	-21.7	High-Spin	-17.8
Closed Shell ^a	-17.5(-13.2)	Closed Shell	-15.2(-13.1)

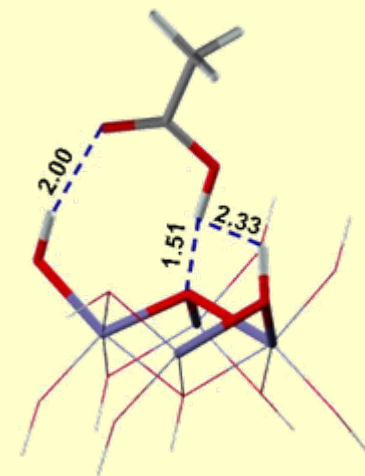
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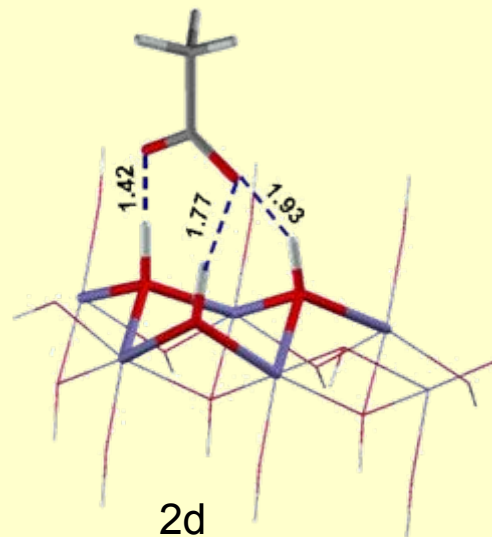
2a



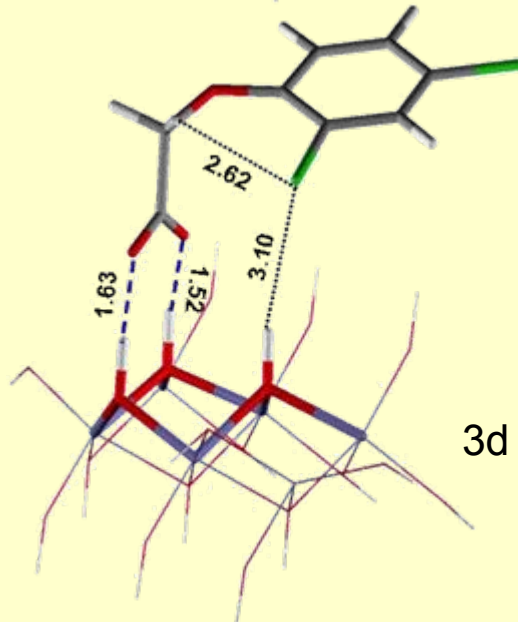
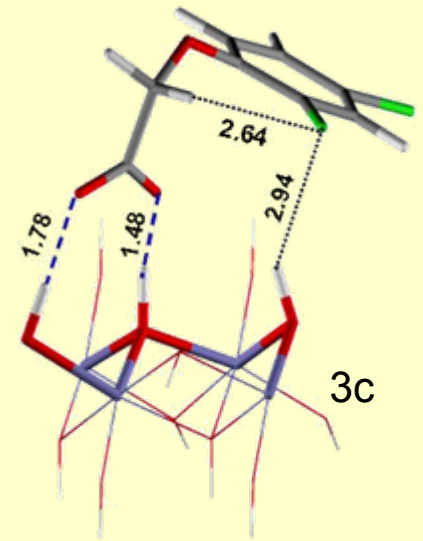
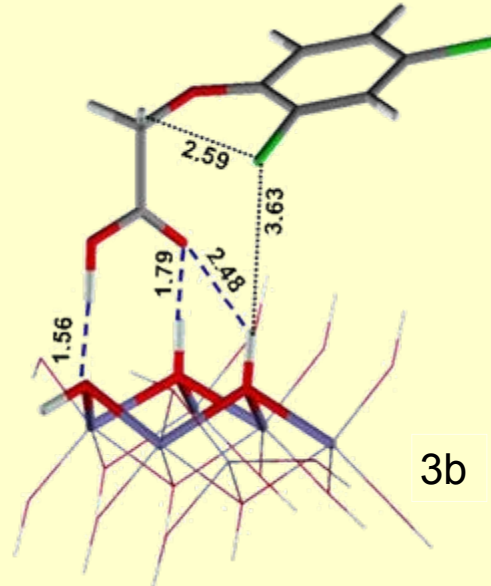
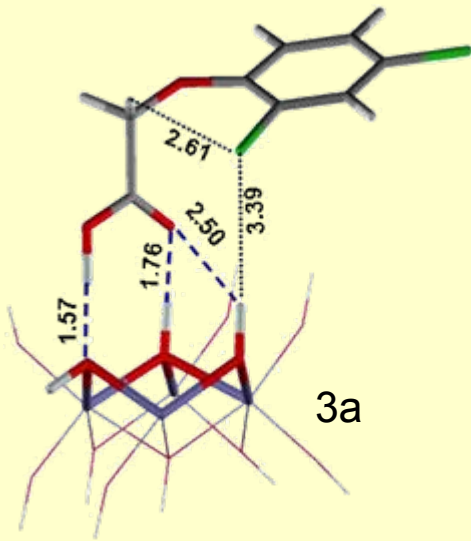
2b



2c



2d

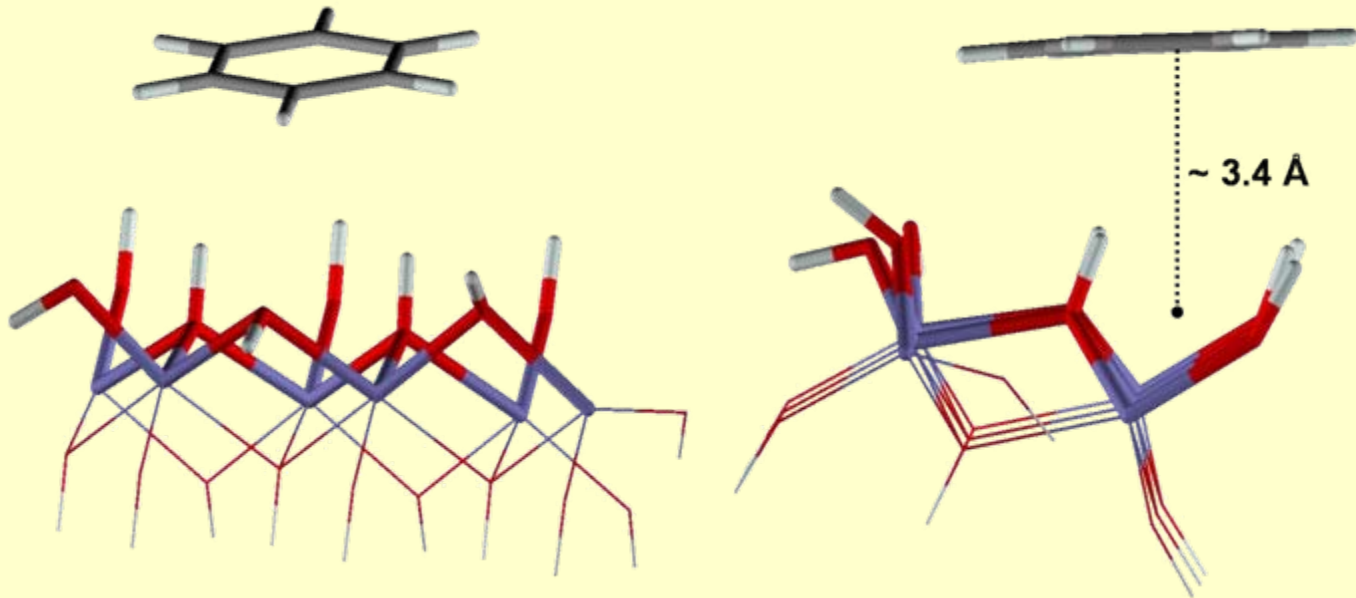


Interaction energies, ΔE , of acetic acid, acetate, 2,4-D, 2,4-D⁻ and benzene adsorbed on two goethite clusters using the closed shell B3LYP approach and two basis sets. Energies are given in kcal/mol.

System	Figure	ΔE (kcal/mol) (SVP basis)	ΔE (kcal/mol) (SVP+sp basis)
Fe ₄ -HAc	2a	-22.7	-25.3
Fe ₆ -HAc	2b	-23.7	-25.0
Fe ₄ -Ac ^{-a}	2c	-55.4	-43.4
Fe ₆ - Ac ⁻	2d	-58.3	-50.6
Fe ₄ -2,4-D	3a	-20.9	-21.1
Fe ₆ -2,4-D	3b	-23.9	-25.9
Fe ₄ -2,4-D ⁻	3c	-38.2	-32.1
Fe ₆ -2,4-D ⁻	3d	-37.4	-31.3
Fe ₆ - C ₆ H ₆	4	-2.6(-13.1/-15.4) ^b	-4.4

^a proton transfer from the goethite surface to the Ac⁻ anion

^b in parentheses single point /optimized MP2/SVP result





CONCLUSIONS

- Our investigations showed that the (110) goethite surface formed by three types of the hydroxyl groups offers a variety of possibilities for hydrogen bond formation with appropriate polar adsorbents.
- Two OH types, hydroxo- and μ -hydroxo, have sufficient flexibility for bending allowing them to act as proton acceptors while the third type, μ_3 -hydroxo, acts only as proton donor due to its more pronounced rigidity.
- Calculated interaction energies on different sites are ca. -20 kcal/mol for the water molecule, a number which is in line with the number and type of hydrogen bonds formed. Slightly larger interaction energies were observed for neutral acetic acid and 2,4-D in comparison to the goethite/water complexes.
- The aromatic ring actively participates in the interaction with the goethite surface groups. Interactions with the nonpolar, aromatic benzene molecule are much weaker. However, the estimated interaction energy range of -5 to -8 kcal/mol is still significant. This result rationalizes why goethite plays an important role for the retention of polyaromatic hydrocarbons in soils.



Acknowledgments



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