10.1071/EN21091_AC
Environmental Chemistry

Supplementary Material

Surface Chemistry of Bovine Serum Albumin with Hematite Nanoparticles and its Effect on Arsenate Adsorption

A. M. Eid[‡1], Shea Kraemer [‡1], and Hind A. Al-Abadleh[‡]*

[‡]Department of Chemistry and Biochemistry, Wilfrid Laurier University, Waterloo, ON, N2L 3C5, Canada

[1] These authors contributed equally to the work

Journal: Environmental Chemistry

Supplementary Data (11 pages)

Content

Table S1. Adsorption of different proteins and macromolecules on the surface of hematite and other iron oxides.

adsorbent	Protein	pH	Experimental setup	Model	Findings	Ref
Hematite NP (α-Fe_2O_3) (39, 68 nm size)	Bovine Serum Albumin (BSA)	5.7	ATR-FTIR under flow conditions	Modified kinetic two-state model for protein unfolding and refolding	The rate of BSA adsorption is dependant on three steps: 1-transport of proteins from the bulk solution to the near-surface region 2- adsorption/desorption of proteins onto/ from the surface 3- conformational changes/refolding of adsorbed proteins	(Liu *et al.* 2019)
Hematite NP (different exposed surface (001)&(104))	βglucosidase	5.7	ATR-FTIR under flow conditions	Kinetic Conc. /Time study: the ratio of concentrations of adsorbed molecules to the initially added	β-glucosidase had stronger interactions with hematite (001) face than hematite (104) face since the former has relatively higher surface density of hydroxyl groups. So, greater conformational change and less amount ofβ-glucosidase adsorbed on the (104) face.	(Zang *et al.* 2020)
α-hematite colloids	Humicacid (HA) and Fulvic acid (FA)	Range (7, 9.2, 11)	UV-VIS under batch with centrifugation	Langmuir isotherm	HA adsorbed to a greater extent than FA at the different pH ranges due to higher hydrophobicity than the FA	(Ko *et al.* 2005)
Hematite NP	human plasma	pH= 3.5-7	IR and Electrophoresis	Adsorption isotherm	Coulomb forces between the protein	(Koutsoukos *et al.* 1983)

(α-Fe_2O_3) (20-50 nm size)	albumin (HPA) and bovine pancreas ribonuclease (RNase)	for (HPA) and 7-10 for (RNase)	under patch with centrifugation		and the hematite were decisive with respect to adsorption of RNase, however for HPA other factors dominated the process such as the conformational changes on surface. This gives an idea on how each protein behaves differently on surface.	
Magnetite	BSA	7.4	FTIR under batch setup	Langmuir isotherm under pseudo second order kinetic model	1-BSA binds in a multi-layered fashion to the surface of the particles 2-BSA– BSA interactions are stronger than BSA–magnetite interactions. 3- protein corona formation around magnetite is favourable, but not strong	(Rahdar *et al.* 2019)

Table S2. Acid dissociation of inorganic arsenate and arsenite (Wang *et al.* 2016)

Species	Acid-base equilibria	pK_a
Arsenate	$H_3AsO_4 \rightleftharpoons H_2AsO_4^- + H^+$	2.20
As (V)	$H_2AsO_4^- \rightleftharpoons HAsO_4^{2-} + H^+$	6.97
	$HAsO_4^{2-} \rightleftharpoons AsO_4^{3-} + H^+$	11.53
Arsenite	$H_3AsO_3 \rightleftharpoons H_2AsO_3^- + H^+$	9.22
As (III)	$H_2AsO_3^- \rightleftharpoons HAsO_3^{2-} + H^+$	12.13
	$HAsO_3^{2-} \rightleftharpoons AsO_3^{3-} + H^+$	13.40

Table S3. Adsorption competition between As(III)/As(V) and macomolecules.

Arsenical	Competing macromolecule	Macro molecule Conc. (ppm)	Surface	Mode of testing	Adsorption model	Binding efficiency of As in presence of macro-molecules	Ref
As (V)	—	—	TiO_2	Batch adsorption on pre-coated TiO_2 with macromolecule	Langmuir adsorption isotherm	60%	(Ren *et al.* 2019)
	BSA	100				40%	
	Alginate					30%	
	SDBS					30%	
	FA					20%	
As (V)	HA	50	Goethite	Batch adsorption of HA/FA simultaneously with As (V) on the goethite surface	CD-MUSIC model	10 time increase of As(V) (aq) than in absence of HA.	(Weng *et al.* 2009)
	FA					100 time increase of As(V) (aq) than in absence of FA.	
As (III)	—	—	MGNS	Batch adsorption with two arrangements: 1- As (III)/ As (V) added after pre-equilibration of MGNS with macro-molecule solutions 2- MGNS added after pre-equilibration of As (III)/As (V) with macro-	Langmuir and Freundlich isotherms	qe =199 mg kg^{-1}	(Li *et al.* 2017)
	HA	40				qe1= 197 mg kg^{-1} qe2= 194 mg kg^{-1}	
	FA					qe1= 196 mg kg^{-1} qe2= 196 mg kg^{-1}	
As (V)	—	—				qe = 199 mg kg^{-1}	
	HA	40				qe1= 165 mg kg^{-1} qe2= 190 mg kg^{-1}	
	FA					qe1= 180 mg kg^{-1} qe2= 186 mg kg^{-1})	

				molecule solutions			

* Notes: BSA: Bovine Serum Albumin, SDBS: Sodium Dodecyl Benzene Sulphonate, HA: humic Acid, FA: Fulvic Acid, MGNS: Modified Granular Natural Siderite, CD-Music model: charge-distribution multi-site complexation model. qe: adsorption capacity (loading) at equilibrium in absence of NOM, qe1: adsorption capacity (loading) at equilibrium for arrangment1, qe2: adsorption capacity (loading) at equilibrium for arrangment2.

Table S4. Calculated partial charges for the simulate hematite particle in electron charge as unit charge.

Atom	Partial charge	Atom	Partial charge	Atom	Partial charge	Atom	Partial charge
Fe	0.861	Fe8	-0.119	O2	0.021	O10	-0.343
Fe1	-0.605	Fe9	-0.607	O3	0.019	O11	-0.566
Fe2	-0.123	Fe10	-0.608	O4	-0.568	O12	0.019
Fe3	-0.120	Fe11	-0.119	O5	-0.568	O13	-0.350
Fe4	-0.604	Fe12	-0.121	O6	-0.346	O14	-0.566
Fe5	-0.607	Fe13	-0.608	O7	0.019	O15	0.021
Fe6	-0.121	O	-0.351	O8	-0.568	O16	0.021
Fe7	0.864	O1	-0.351	O9	-0.344	O17	-0.564

Conformational analysis

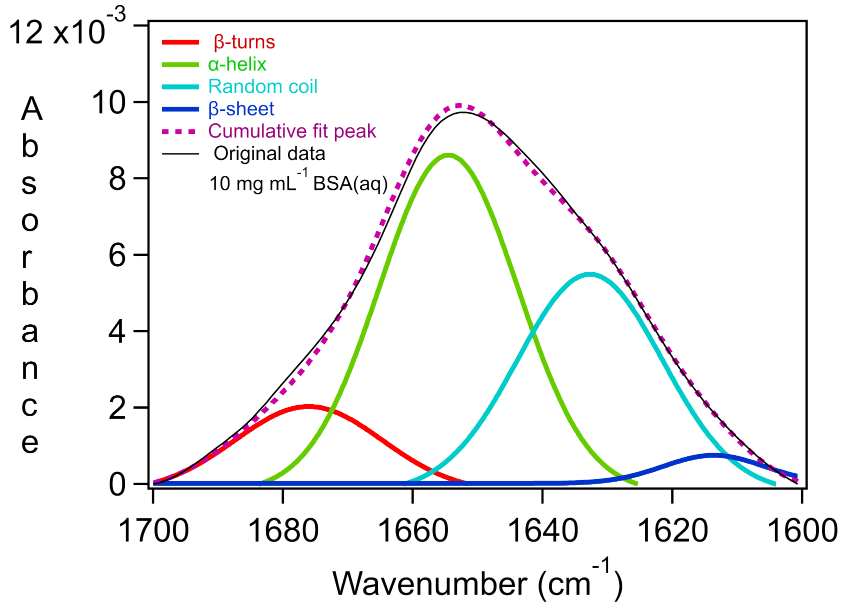

Figure S1. Original amide I band of adsorbed BSA [BSA(aq)] = 10 mg L^{-1} , the deconvoluted peaks representing the different secondary structure features. The dotted lines representing the cumulative fit peak to the original one with R^2= 0.998

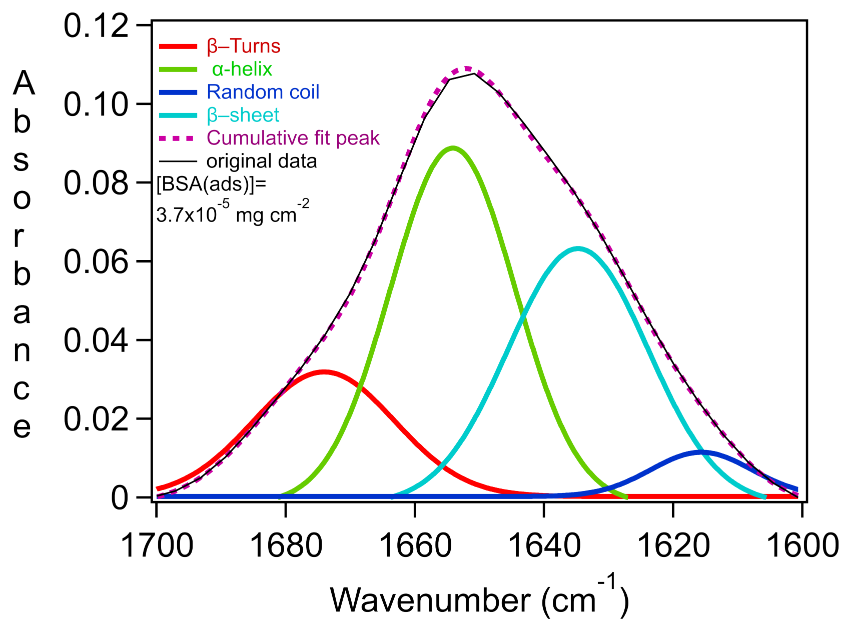

Figure S2. Original amide I band of adsorbed BSA $[BSA(ads)]_0 = 3.7\times 10^{-5}$ mg cm^{-2} on hematite surface and the deconvoluted peaks representing the different secondary structure features. The dotted lines representing the cumulative fit peak to the original one with R^2= 0.99986.

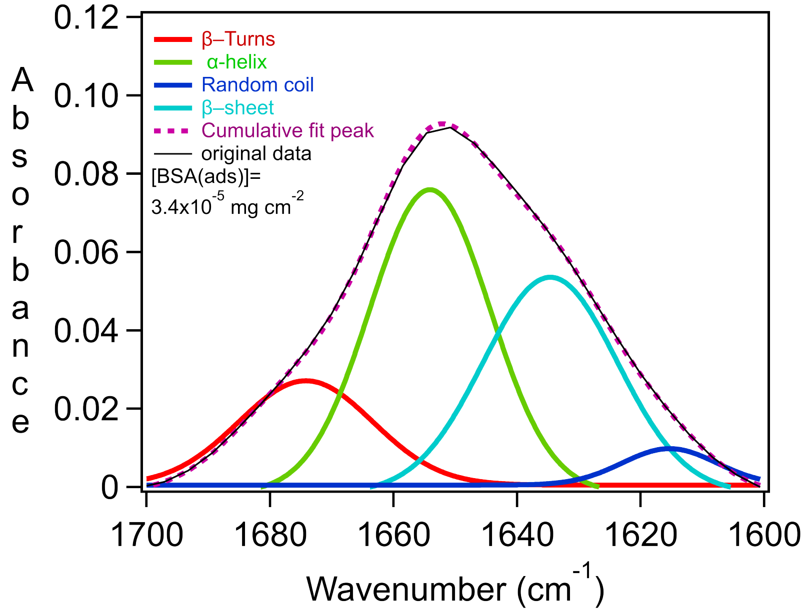

Figure S3. Original amide I band of adsorbed BSA $[BSA(ads)]_0 = 3.4\times 10^{-5}$ mg cm^{-2} on hematite surface and the deconvoluted peaks representing the different secondary structure features. The dotted lines representing the cumulative fit peak to the original one with R^2= 0.99988.

L-RMSD visualization

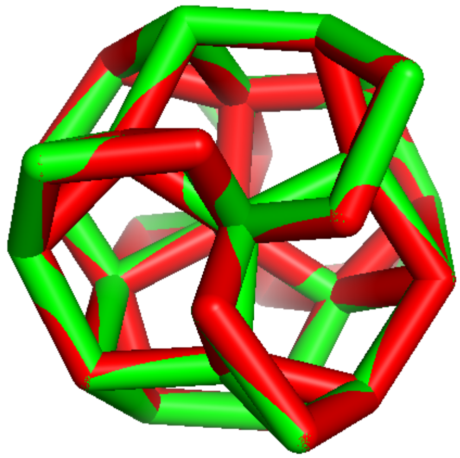

Figure S4. The superimposed structures of the native energetically minimized hematite (light green colored) with the docked one (red colored) for L-RMSD analysis

References

Ko I, Kim J-Y, Kim K-W (2005) Adsorption properties of soil humic and fulvic acids by hematite. *Chemical Speciation & Bioavailability* **17** (2), 41-48. doi:10.3184/095422905782774928

Koutsoukos P, Norde W, Lyklema J (1983) Protein adsorption on hematite (α-Fe2O3) surfaces. *Journal of colloid and interface science* **95** (2), 385-397. doi:10.1016/0021-9797(83)90198-4

Li F, Guo H, Zhou X, Zhao K, Shen J, Liu F, Wei C (2017) Impact of natural organic matter on arsenic removal by modified granular natural siderite: Evidence of ternary complex formation by HPSEC-UV-ICP-MS. *Chemosphere* **168**, 777-785. doi:10.1016/j.chemosphere.2016.10.135

Liu F, Li X, Sheng A, Shang J, Wang Z, Liu J (2019) Kinetics and Mechanisms of Protein Adsorption and Conformational Change on Hematite Particles. *Environ Sci Technol* **53** (17), 10157-10165. doi:10.1021/acs.est.9b02651

Rahdar S, Rahdar A, Ahmadi S, Trant JF (2019) Adsorption of bovine serum albumin (BSA) by bare magnetite nanoparticles with surface oxidative impurities that prevent aggregation. *Canadian Journal of Chemistry* **97** (8), 577-583. doi:10.1139/cjc-2019-0008

Ren M, Qu G, Li H, Ning P (2019) Influence of dissolved organic matter components on arsenate adsorption/desorption by TiO2. *J Hazard Mater* **378**, 120780. doi:10.1016/j.jhazmat.2019.120780

Wang Y, Sun L, Han T, Si Y, Wang R (2016) Arsenite and arsenate leaching and retention on iron (hydr) oxide-coated sand column. *Journal of soils and sediments* **16** (2), 486-496. doi:10.1007/s11368-015-1230-3

Weng L, Van Riemsdiik WH, Hiemstra T (2009) Effects of fulvic and humic acids on arsenate adsorption to goethite: experiments and modeling. *Environ Sci Technol* **43** (19), 7198-204. doi:10.1021/es9000196

Zang Y, Liu F, Li X, Sheng A, Zhai J, Liu J (2020) Adsorption kinetics, conformational change, and enzymatic activity of beta-glucosidase on hematite (alpha-Fe2O3) surfaces. *Colloids Surf B Biointerfaces* **193**, 111115. doi:10.1016/j.colsurfb.2020.111115