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Quantum Mechanical Modeling of Organic-Oxide Surface Complexation Reactions

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QUANTUM MECHANICAL MODELING OF ORGANIC- OXIDE SURFACE COMPLEXATION REACTIONS

Undergraduate Senior Thesis

DEPARTMENT OF CIVIL AND ENVIRONMENTAL ENGINEERING
UNIVERSITY OF CONNECTICUT

Abstract: *Recent advancements in agriculture, industry, and pharmaceutical formulations have increased the presence of organic contaminants in the environment. It is important and necessary to study and understand the processes which control the environmental fate and transformation of contaminants and improve removal and remediation techniques. The use of advanced quantum mechanical modeling is a promising technique to better understand the mechanisms of adsorption within the environment. Relative Gibbs free energy values of adsorption have been calculated using such modeling for selected organic acids sorption to iron oxides, revealing the thermodynamic favorability of each of the reactions, except one involving bidentate mononuclear iron oxide. Theoretical spectra were constructed and evaluated with previous IR spectra studies to confirm the appropriate reliance on the modeling to accurately predict adsorption mechanisms.*

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1 Introduction

Synthetic organic compounds have been introduced to the environment continually throughout history by human societies. Often organic chemicals have been introduced in an attempt to control organisms, such as weeds, pests, and pathogens [1]. A common organic compound used in pesticides is organochlorine, which has been found to highly contaminant surrounding soils where the pesticide is applied. As has been continually found, introducing synthetic chemicals into the environment rarely occurs without consequences. Even under highly contained conditions amounts of synthetic chemicals will be discharged to the environment unintentionally. Industrial organic pollutants, such as perfluorinated compounds and polybrominated diphenylethers, have been found to be one of the major sources of food contamination. The industrial organic pollutants mentioned here are classified as persistent organic pollutants, which means that they are resistant to degradation and highly susceptible to bioaccumulation, with long range transportation potential [1]. Along with the toxic characteristic of organic pollutants, this is why organic contamination is of such concern. Biocides have been found to harm organisms they were not meant to target and the dispersion of biocides can be wide spread [1]. Introduced organic chemicals contaminate water, air, and soil, thus will continue to be a relevant environmental problem. The drug industry and production of new contaminants continues to grow, producing more potential hazards in the environment. There are over 100,000 synthetic chemicals being used daily, most of them organic chemicals, with little indication of slowing down [1]. There has been an increase in organic contaminants in the environment due to organic compounds increased use in agriculture, industry, and pharmaceutical formulations as active ingredients [2]. It is important and necessary to study the

processes of organic pollutants that control transport and transformations in the environment. Understanding the processes will aid in improving removal and remediation techniques.

Physical, chemical, and biological processes act on chemicals in the environment to result in the fate of the compound. When organic compounds come into contact with certain compounds in the environment, depending on the organic compounds chemistry, they sorb to soils in a variety of ways. The organic compound sorption to soils is an important transfer processes to understand and predict the fate of the compounds. This sorption is an integral part of the movement, degradation, and bioavailability of contaminants. Understanding the sorption of contaminants not only outlines organic compounds environmental fate but also what possible dangerous or hazardous exposures could occur. In order to assess the environmental behavior of organic compounds requires knowledge of the molecular level of interactions. To understand this dynamic behavior models can be used which incorporate the occurrence of multiple processes at the same time.

Many different models have been used in order to estimate the Gibbs free energy of sorption onto environmentally relevant compounds such as iron oxides with varying degrees of accuracy. Sorption coefficients and isotherms have been relied upon, expanding on our knowledge of sorption processes [3]. The current models can be expanded to increase the understanding of sorption of contaminants in the environment. This expansion can provide a new rapid way to predict the behavior of contaminants in the environment, before such contaminants are even released. Coupling the advanced models which are being suggested in this paper with experimental results opens a broader range of research on environmental sorption to be investigated. To improve the models requires a better understanding of Gibbs free energy related to the sorption. Gibbs free energy is a function of both the nonbonding and bonding energies.

Quantum mechanics (QM) and the linear interaction energy (LIE) method have proven to be successful in other areas of science to accurately estimate bonding energies [2]. The LIE method along with molecular dynamic (MD) models offer knowledge on the driving forces of sorption. The LIE method has been found to be a robust and tractable method when used with organic compounds bound to aluminosilicate clay minerals [2]. Thus, this research is aimed at confirming the accuracy of the LIE method and QM models in predicting the bond energy of organic compounds with iron oxides.

The overall goal of this research is to reveal the advantages of quantum mechanics modeling in predicting sorption mechanisms in the environment, specifically for organic compounds. Incorporating the direct bonding interactions that occur in sorption in the models will extend the models used to predict sorption to include a new class of chemicals, such as the increasingly complex organic compounds being synthesized and released to the environment by growing industries. The advanced models used in this research enable us to predict the fate of newer chemicals before they are even developed, therefore an informed, conscious decision can be made on the efficacy of producing said chemical.

2 Methods

2.1 Quantum Mechanics

The research presented here was focusing on the use of quantum mechanics to predict bond energies. This bond energy prediction can be combined with predictions of nonbonding energies that will be gathered with molecular dynamic methods to overall predict Gibbs free energy of sorption (ΔG), equation (1).

$$\Delta G = f(E_{\text{binding}}, E_{\text{nonbinding}}) \quad (1)$$

The program used to make bonding energy predictions was Avogadro, which is a molecular builder. Within Avogadro, Gaussian 09 is the program that uses quantum mechanics to model the adsorption processes which were investigated [34]. Through this program scripts were written and submitted to a supercomputer for the specific compounds included.

Quantum mechanics is able to work with nano scale levels. The calculations completed utilized the quantum formula as show in equation (2), known as the Schrödinger equation.

(2)

Here E represents the energy we are concerned with, Ψ is the wave function, and \hat{H} is a math operator. The more detailed description of this equation can be seen in equation (3).

$$\hat{H}\Psi = [\hat{T} + \hat{V} + \hat{U}] \Psi = \left[\sum_i^N \left(-\frac{\hbar^2}{2m_i} \nabla_i^2 \right) + \sum_i^N V(\vec{r}_i) + \sum_{i < j}^N U(\vec{r}_i, \vec{r}_j) \right] \Psi = E\Psi \quad (3)$$

Here, this represents a N-electron system, \hat{T} is the kinetic energy, \hat{V} is the potential energy due to the external field, and \hat{U} is the electron-electron interaction energy. Using quantum mechanics enhances the description of dual particle and wave behavior and can accurately describe the interactions of energy and matter within various processes. The calculations are able to outline the behavior of atoms in chemical bonding, as this research was interested in the sorption of chemicals and binding energies.

2.2 Cluster Model

A cluster model approach was used and the investigated compounds were in a non-hydrated state. The specific modeling for this research utilized density functional theory (DFT), to investigate the electronic structure of adsorption processes. DFT is a method that is based on

computational quantum mechanics as have been discussed in this paper. The DFT equation is illustrated in equation (4).

$$X(k) = \sum_{n=0}^{N-1} x(n) e^{-\frac{j2\pi kn}{N}} \quad (4)$$

Where $X(k)$ is a complex number that represents the amplitude and phase of a sinusoidal component from the function $x(n)$ and the frequency is k cycles per N samples. Within DFT, the Kohn-Sham equations represent a fictitious local effective external potential within which the non-interacting particles move. This potential is denoted, $V_{KS}(r)$, and is called the Kohn-Sham potential (Equation 5-7).

$$\frac{\delta T_s[n]}{\delta n(r)} + V_{KS}(r) = \mu \quad (5)$$

$$V_{KS}(r) = \int dr' \frac{n(r')}{|r-r'|} + V_{XC}(r) + V_{ext}(r) \quad (6)$$

$$V_{XC}(r) = \frac{\delta E_{XC}[n]}{\delta n(r)} \quad (7)$$

Where $T_s[n]$ is the kinetic energy of the non-interacting gas with density $n(r)$, μ is the Lagrange multiplier, $V_{XC}(r)$ is the exchange-correlation potential, $V_{ext}(r)$ is the static external potential, and $E_{XC}[n]$ is the exchange-correlation energy per electron.

The properties of various systems, as being investigated within this research, through this theory are predicted using functionals, specifically for DFT the spatially dependent electron density. This method has proven to be very useful in computational chemistry, similar to the research completed here. With the DFT models, the models were used on molecular clusters. The functional used was ub3lyp for DFT calculations. The frequency calculation for the Gibbs free energy used geometry optimization with Cartesian coordinates. The nuclear positions in the models were be allowed to relax to minimum potential energy positions in order to complete

frequency calculations. The specific basis set used to calculate the aqueous Gibbs free energy were be scripted as follows: Fe LANL2DZ [35], [36], C, O, H 6-31+G* [37], [38]. The basis set is what determines the set of functions that will be combined in linear combinations which form the molecular orbitals. Table 1 shows a list of the commands used in the Gaussian 09 scripts submitted for each of the investigated compounds and a description of what each command is calling for. The hornet cluster run through the University of Connecticut was utilized to run these jobs, using the necessary sbatch scripts to run the Gaussian 09 calculations. Such models investigated as laid out in this paper allow for more accurate predictions of adsorption mechanisms and characteristics.

Table 1: Gaussian 09 script commands.

Command	Description
NProcShared=2	Use 2 processors for shared memory parallel execution on SMP (symmetric) multiprocessor computers.
Mem=1 GB	Sets amount of dynamic memory used to 1 GB 8-byte words. The default is 256 MB.
Chk=	Locates and names checkpoint file.
Ub3lyp	Hybrid functional used for DFT calculation (energy functional used in open shell systems). B-Becke exchange functional. Uses non-local correlation provided by LYP (Lee, Yang, and Parr) expression and VWN (Vosko, Wilk, and Nusair) functional III for local correlation (not functional V). LYP includes both local and non-local terms, VWN used to provide excess local correlation required.
Opt	Geometry optimization performed (frequency calculation for delta G).
Guess=core	Initial guess for Hartree-Fock wavefunction. Requests core Hamiltonian be diagonalized to form initial guess.
Scf=(xqc, maxcycles=512)	Quadratically convergent SCF procedure. Involves linear searches when far from convergence and Newton-Paphson steps when close. Xqc calls for a slower SCF with DIIS

	extrapolation, but is more reliable. The x in xqc adds an extra SCF=QC step in case the first order SCF does not converge. The maxcycles changes the maximum number of SCF cycles permitted to 512, the default is 128.
Gen	Allows a user-specified basis set to be used in a Gaussian calculation. It is used in the place of a basis set keyword or a density fitting basis set keyword. In this case, the basis set description must be provided as input (in a separate basis set input section). Used to specify alternate density fitting basis set.
Pseudo=read	Requests a model potential be substituted for the core electrons. Read pseudopotential data from input stream.
Scrf=(iefpcm, solvent=water)	Requests a calculation be performed in the presence of a solvent by placing the solute in a cavity within the solvent reaction field. The Polarizable Continuum Model (PCM) using the integral equation formalism variant (IEFPCM) creates solute cavity via set of overlapping spheres. The solvent here is specified as water
Freq	Computes force constants and the resulting vibrational frequencies. Intensities are also computed. By default, the force constants are determined analytically. Vibrational frequencies are computed by determining the second derivatives of the energy with respect to the Cartesian nuclear coordinates and then transforming to mass-weighted coordinates. (only valid at stationary point)
Fe 0 LANL2DZ	D95V on first row (Dunning/Huzinaga valence double-zeta), Los Alamos ECP plus DZ on Na-La, Hf-Bi (used for transition metals)
C 0 6-31+G* O 0 6-31+G* H 0 6-31+G*	Split-valence basis set of George Petersson, defined as part of Complete basis set, includes the diffuse function. A valence double-zeta polarized basis set, adds 6 d-type Cartesian-Gaussian polarization functions to the 6-31G set on each atom Li through Ca and 10 f-type Cartesian-Gaussian polarization functions on each atom Sc through Zn (all non-transition metal atoms)

2.3. Investigated Compounds

The following is a list of the compounds that have been studied in this research along with their known pKa values and Hammett constants, all for their sorption to iron oxide. The Hammett constant represents the energy relationship between reaction rates and equilibrium constants, specifically for meta- and para- substituents of benzoic acid.

Table 2: Compounds and corresponding pKa values.

Compounds	pKa values	Hammett Constant
Malonic Acid	2.83; 5.69	
Lactic Acid	3.86	
Phthalic Acid	2.89; 5.51	
para-hydroxybenzoic Acid	4.48; 9.32	-0.37
meta-hydroxybenzoic Acid	4.06; 9.92	+0.12
ortho-hydroxybenzoic Acid	2.97; 13.82	
Aminobenzoic Acid	2.501; 4.874	-0.66
Nitrobenzoic Acid	3.41	+0.778
Benzoate Acid	3.78	+0.45
Methoxybenzoic Acid	4.47	-0.268
Methylbenzoic Acid	4.36	-0.170
Bisulfide-benzoic Acid	4.05	+0.15

Adsorption of para-hydroxybenzoic acid to bidentate mononuclear iron oxide and bidentate binuclear iron oxide has been studied as well. For the purpose of this research the compounds that were tested were all organic compounds. The surface complexation of organic compounds on iron oxides was tested through cluster quantum mechanics models as described above. Benzoic acid, $C_7H_6O_2$, was the base of many of the organic compounds investigated. It is a contaminant of concern because of its wide use in the industrial synthesis of other organic substances, another reason why it was chosen as a focus in this research.

Malonic acid, $CH_2(COOH)_2$, is an organic acid that eventually can result in specialty polyesters. Malonic acid is used in many different manufacturing processes, especially within

electronics. It has also been known to be a useful building block chemical used for different compounds. Lactic acid, $C_2H_4OHCOOH$, is produced by animals, industry, and in medicines. With animals lactate is produced from pyruvate through fermentation which occurs with typical processes during metabolism and exercise. In industry the fermentation of lactic acid is from carbohydrates that are converted with lactic acid bacteria. Within medicine lactate is found in lactated Ringers solution and Hartmann's solution, normally used for fluid resuscitation necessary after excessive blood has been lost. Lactic acid is also used in pharmaceuticals in order to produce water soluble lactates. Additionally, cosmetics use lactic acid to adjust the acidity of products and for disinfection. Lactic acid can be found in food products, such as sour milk, and more recently is being used in detergents to remove soap scum and as an antibacterial agent. Thus it is clear lactic acid is a common organic acid found naturally and used in our society therefore is a concern for its fate in the environment. Phthalic acid, $C_6H_4(CO_2H)_2$, is closely associated with phthalic anhydride which is a commonly used commercial chemical. While the toxicity of phthalic acid is fairly low, with LD_{50} of 550 mg/kg, many of the phthalate esters more recently are being connected as endocrine disruptors. Such disruptions can cause cancer, birth defects, and similar developmental disorders, which is why we care about its environmental fate so it was investigated within this research.

P-Hydroxybenzoic acid, $C_7H_6O_3$, is found in Vitex and Hypericum plants as well as Spongiochloris spongiosa which is a freshwater green algae and Ganoderma lucidum which is a medicinal mushroom. P-Hydroxybenzoic acid is also found in foods such as Cocos nucifera, wine, vanilla, horse gram, Otaheite gooseberry, acai oil, cloudy olive oil, green-cracking russula, and can be found in humans when green tea infusion is consumed the acid is a catechins metabolite. In addition, P-Hydroxybenzoic acid is used as an antioxidant and is classified as an

irritant. The difference of position of the hydroxide on the aromatic hydrocarbon was investigated in this research to observe any influence this positioning had on the adsorption to iron oxide.

Benzoic acid with different substituents in addition to the hydroxide were tested. Of the variations of benzoic acids tested aminobenzoic acid, $C_7H_7NO_2$, was included. There are various food sources of aminobenzoic acid, such as liver, brewer's yeast, kidney, molasses, mushrooms, and whole grains. Aminobenzoic acid is also an intermediate for the folate produced by bacteria, plants, and fungi. It is also used in medicine, such as a drug for fibrotic skin disorders as well as claims that it can be used as a nutrient supplement which has been shown to fight fatigue, irritability, depression, weeping eczema, scleroderma, patchy pigment loss in skin, and premature grey hair. Aminobenzoic acid is sometimes used for its conversion to azo dyes and crosslinking agents. The most well-known use is for sunscreens acting as a UV filter. While aminobenzoic acid is not severely toxic, it is known to cause many allergic reactions.

Nitrobenzoic acid, $C_7H_5NO_4$, is known to be commercially important, having more than 1 million pounds produced in the U.S. per year and is suggested to have moderate toxicity, with long term effects on reproduction and development. Nitrobenzoic acid is approximately ten times more acidic than benzoic acid. It is known as a skin, eye, and respiratory irritant.

Substituents of methanol on benzoic acid were also tested. These included methoxybenzoic acid, also known as anisic acid, $C_8H_8O_3$, can be found naturally in anise. Methoxybenzoic acid has antiseptic properties and is used to prepare more complex organic compounds. Also tested was methylbenzoic acid, also known as toluic acid, $C_8H_8O_2$, is used in various industrial processes to oxidize p-xylene to terephthalic acid. Terephthalic acid is used to manufacture polyethylene terephthalate. All of the organic acids included in this research were

selected in order to better understand the fate of the organic acids in soils and how the acid may adsorb to iron oxides found in soils. This is important information to gather with such chemicals that are threats with contamination to the environment.

Figures 1-10 demonstrate the structures that were constructed using Avogadro. The hydroxybenzoic acid with the hydroxide in the meta and ortho positions are shown in Figure 1. The remaining figures show the benzoic acid with the various substitution group as well as malonic acid, lactic acid, and phthalic acid adsorbed to the given iron oxide. In the following figures the green atoms represent carbon, red represent oxygen, white represent hydrogen, orange represent iron, blue represent nitrogen, and yellow represent sulfur.

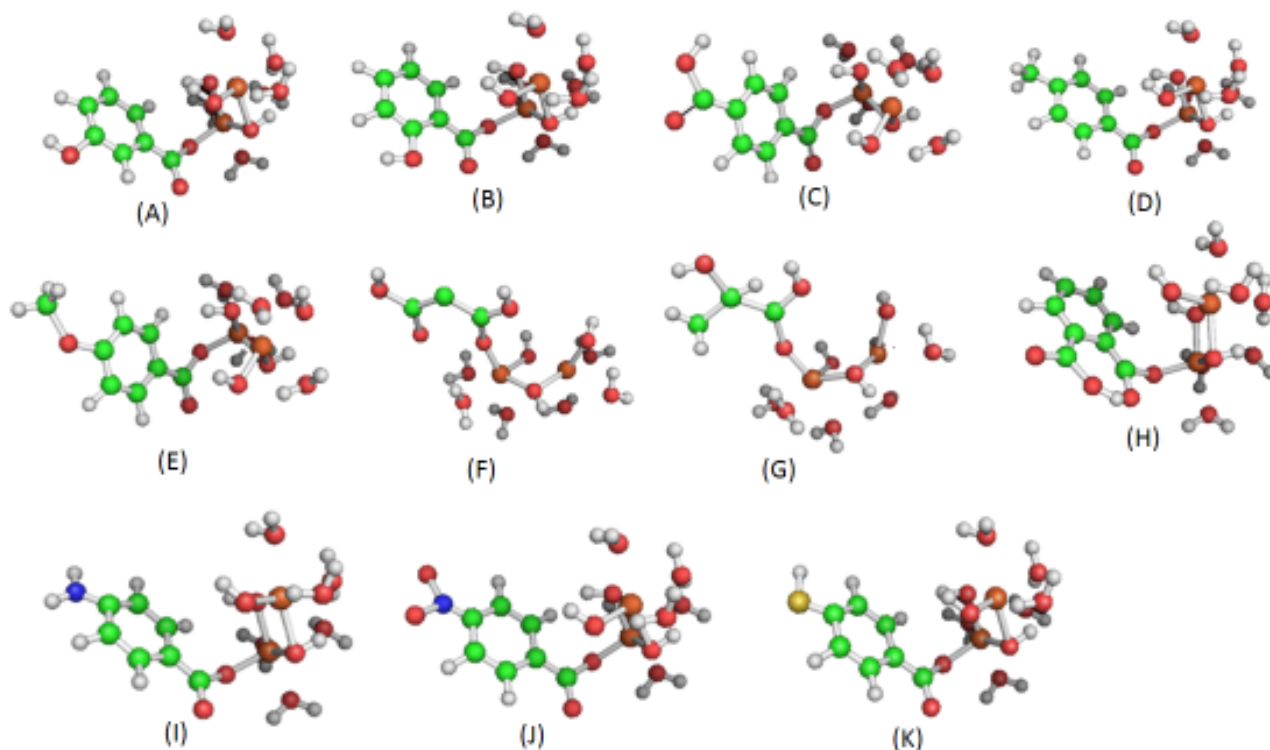


Figure 1. Adsorption of organic acids to iron oxide. The following are the organic acids: (A) meta-hydroxybenzoic acid; (B) ortho-hydroxybenzoic acid; (C) Carboxybenzoic acid; (D) Methylbenzoic acid; (E) Methoxybenzoic acid; (F) Malonic acid; (G) Lactic acid; (H) Phthalic acid; (I) Aminobenzoic acid; (J) Nitrobenzoic acid; (K) Bisulfide benzoic acid.

2.4. Gaussian 09 Calculations

The investigated molecules were constructed in Avogadro and the coordinates were retrieved from Gaussian 09. The compounds before and after the sorption to iron oxide were run through the program, as the data for the individual reactants and individual products is required to calculate the Gibbs free energy of sorption. The information needed from the output from the model is under Gaussian thermochemistry. The calculations that were used assume an ideal gas. Here the zero-point vibrational energy can be found, which is when there is 0 K quantum motion, as well as the Thermal correction to Energy, Enthalpy, and Gibbs free energy. The change in Gibbs free energy can be calculated by taking the sum of all the Gibbs free energy correction terms and the total electronic energy for the products minus the sum of all the Gibbs free energy correction terms plus the total electronic energy for the reactants.

$$H_{\text{corr}} = E_{\text{tot}} + k_b T \quad (8)$$

$$G_{\text{corr}} = H_{\text{corr}} - TS_{\text{tot}} \quad (9)$$

$$S_{\text{tot}} = S_t + S_r + S_v + S_e \quad (10)$$

$$\Delta_r G^\circ(298K) = \sum(\epsilon_0 + G_{\text{corr}})_{\text{products}} - \sum(\epsilon_0 + G_{\text{corr}})_{\text{reactants}} \quad (11)$$

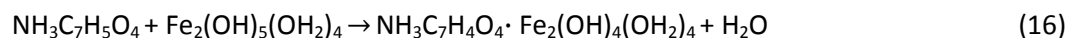
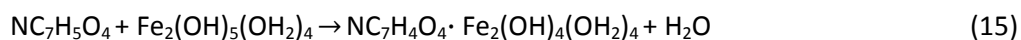
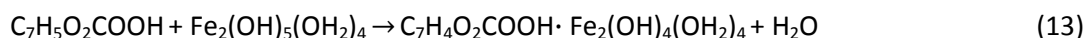
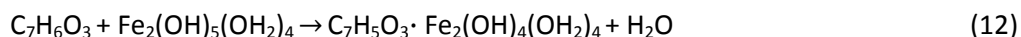
The change in Enthalpy can be calculated in a similar manner, replacing the Gibbs free energy correction terms with the Enthalpy correction terms [42]. The sign of the change in Gibbs free energy indicates the favorability of the reaction. A negative sign means the reaction is spontaneous, and thus favorable in the environment, being more likely to occur. The occurrence of the sorption's are very important to study in order to understand the fate of such contaminants in the environment.

Predicting the binding of the organic acids to iron oxides was completed through the methods described above. The results of the quantum mechanics models were compared to data from sorption isotherms and previous models for similar compounds to iron oxides. Theoretical spectra were created given the resulting peaks and corresponding locations determined by the model. A standard band width of 20 cm^{-1} was consistently used and graphs were constructed in excel. The infrared (IR) spectra data was drawn from previous studies with experimental results. This is how the accuracy of the models were evaluated.

3 Results and Discussion

In this research the change of Gibbs free energy of adsorption for the organic compounds listed in the methods section were calculated. The adsorption energies indicate the thermodynamic favorability of the adsorption reaction taking place in the given conditions. The output files from the Gaussian 09 quantum mechanics calculations provided the information to determine the energy values for the various structures adsorbed to iron oxide. The calculated values can be seen in Table 3.

The following equations (Equation 12 through 21) are the chemical reactions that were investigated:



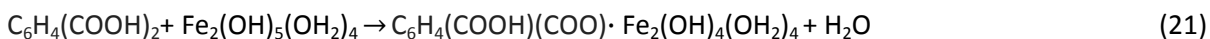
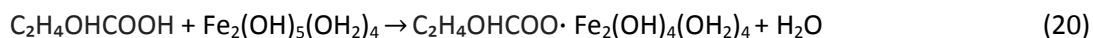
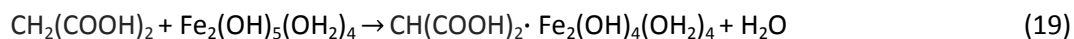
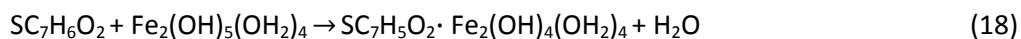


Table 3. Gibbs free energy of adsorption for organic compound sorption to iron oxides.

Compound	$\Delta_r G^\circ(298\text{K})$ (KJ/mol)	$\Delta_r H^\circ(298\text{K})$ (KJ/mol)
Para-hydroxybenzoic acid	-40.7038	-40.0609
Carboxybenzoic acid	-47.5986	-47.5227
Methylbenzoic acid	-42.3473	-41.9869
Meta- hydroxybenzoic acid	-41.6365	-41.391
Ortho- hydroxybenzoic acid	-40.9961	-40.7976
Nitrobenzoic acid	-53.2728	-53.3361
Aminobenzoic acid	-39.8923	-39.3759
Methoxybenzoic acid	-40.281	-39.9421
Bisulfide-benzoic acid	-45.8215	-45.6282
Malonic acid	-413.5957	-413.2736
Lactic acid	-42.0809	-42.2158
Phthalic acid	-57.5008	-57.1641
Para-hydroxybenzoic acid with bidentate binuclear iron oxide	-48.0664	-45.0541
Para-hydroxybenzoic acid with bidentate mononuclear iron oxide	125.2468	127.0777

Gibbs free energy values indicate that every organic compound that was investigated with iron oxide was thermodynamically favorable, given the negative change in Gibbs free energy of adsorption, with one exception. This one exception is the para-hydroxybenzoic acid adsorbed to bidentate mononuclear iron oxide. The positive Gibbs free energy of adsorption indicates that this reaction will not take place in the environment. The most thermodynamically favorable organic compound investigated was malonic acid. All the other organic compounds investigated

revealed closely related Gibbs free energy terms, thus the adsorption of such compounds to iron oxides in the environment is predicted to be very similar across all the organic compounds investigated, except for those as previously indicated.

Studies involving sorption of benzoic acids to soils, in which K values are obtained have been completed. From K values found for benzoic acid sorption to Danish soils, the calculated Gibbs free energy term of adsorption was around -15.13 KJ/mol [40]. This is lower in magnitude than the terms found from the models. However the models specifically involve iron oxide, and these findings agree with the claim that the adsorption of benzoic acids to soils is thermodynamically favorable. A different study on the adsorption of phthalic acids to soils found K values of adsorption which correspond to Gibbs free energy terms around -42.44 KJ/mol [41]. This is only slightly lower in magnitude than the predicted free energy terms for the phthalic acid. The experimental K values found in the previously mentioned studies indicate that the quantum mechanical model has properly predicted the favorability of adsorption for the organic compounds investigated. While the magnitude of adsorption predicted may be slightly high, this discrepancy is likely due to the specific investigation of adsorption to iron oxide rather than general adsorption to soils. Finding experimental K values for the investigated organic acids adsorption specifically to iron oxides could further confirm the accuracy of the model predictions.

Previous studies have found Gibbs free energy of sorption through similar means. Kubicki, et al, 2007 investigated the adsorption of phosphate onto goethite and found Gibbs free energy of sorption values ranging from -34 kJ/mol to -61 kJ/mol for diprotonated bidentate and unprotonated monodentate, respectively. Many of the organic compounds investigated in this research calculated values that fell within this range when sorbed to iron oxide. Kubicki also

investigated the adsorption of As(V) onto Fe(OH)₃ and found Gibbs free energy values over -140 kJ/mol, indicating its highly thermodynamically favorable [29]. However of all the compounds investigated in Kubicki's study, none showed to be as thermodynamically favorable as malonic acid was predicted to be adsorbing to iron oxide. Kubicki also found from the energy values that arsenate is more thermodynamically favorable than phosphate which is more thermodynamically favorable than carbonate in the adsorption to iron oxide. It was also indicated that the adsorption of sulfate to iron oxide is similar to that of phosphate [29]. This study reveals that the para-hydroxybenzoic acid with various substitutions of the hydroxyl are all thermodynamically favorable, with little preference between the substitutions. The nitro group substitution, then the carboxyl group substitution, and then the sulfide group substitution were the most thermodynamically favorable benzoic acid structures, in decreasing order. Aside from the bidentate mononuclear iron oxide complex investigated, the sorption of the benzoic acid with an amine group in the para position was the least thermodynamically favorable, although its adsorption energy value was still negative and is only least favorable by a small amount. Previous studies have indicated that carboxyl and hydroxyl functional groups on organic acids (specifically humic and fulvic acids) form stable complexes with metal cations, with Fe³⁺ being the highest [11]. The benzoic acid with carboxyl and hydroxyl groups investigated here agree with this in the form of complexes with iron oxides.

Positioning of the hydroxyl group on the benzoic acid had little influence on its adsorption to iron oxide. Previous studies suggested that weak aromatic acids adsorb more strongly when the structure had either carboxyl or phenolic functional groups in the ortho position [11]. This study found that the adsorption of benzoic acid with a hydroxyl group in the para, ortho, and meta position are all thermodynamically favorable, differing from previous

findings which indicate groups in the ortho position increase the favorability of adsorption. The same study also found that for natural organic matter adsorbing to iron oxides the typical Gibbs free energy value of adsorption is -35 kJ/mol, which is closely related to the values calculated for the organic compounds in this study.

A review completed by MacKay, et al. [3], using infrared studies concluded that para-substituted benzoic acids would have great bond strength to iron for compounds that had nonligand substitutes with high electron donating potential. It is suggested that such substitutes increase proton dissociation from hydroxyl groups [3]. However, if we take two of the substituent groups studied here, the nitro group, which is electron withdrawing, and the methyl group, which is electron donating, the structure with the nitro group is more thermodynamically favorable than the structure with the methyl group. This indicates the mechanisms of sorption is more related to cation exchange, as in this case it is expected that electron withdrawing substituents would increase sorption. The adsorption of organic compounds by cation exchange to soils is expected to be affected by the charge delocalization with heterocyclic rings, the proximity of charge groups, and the molecular orientation in the clay interlayer. The same study also indicated that the increase of a compounds size would increase the sorption by surface complexation [3]. The majority of the compounds in this study are of relatively similar size, thus this aspect has not been fully tested here. Previous studies have found, as mentioned, that the number, position, and type of anionic groups have an effect on sorption to iron oxides. Amine groups have been found to have little effect on complexation to metal oxides, as the results here agree as the amine group substituent had a lower negative Gibbs free energy value. Here the phthalic acid is expected to sorb similarly to other compounds with adjacent carboxyl groups [3].

A study of dimethylarsinic acid sorption to iron oxides revealed that like many of the organic compounds studied here, this sorption was thermodynamically favorable for both inner and outer sphere complex formations. Using the similar B3LYP/6-31+G models the structures with the most negative Gibbs free energy of adsorption values were the ones where electrostatics were important. Also the structures with one type of leaving groups, as coincides to the structures investigated here, had lower, thus more thermodynamically favorable, relative Gibbs free energies [10]. Many of the Gibbs free energies observed in the previous mentioned studied for the dimethylarsinic acid were lower than -100 kJ/mol, indicating that it has stronger sorption to iron oxides than most of the organic compounds studied here, aside from the malonic acid. A different study, using the LIE method found that there was an increase in sorption free energy to iron oxides with compounds with methyl substituents, in agreement with the findings here. It also stated that the sorption of free energy was relatively unchanged with the addition of substituents to an aromatic ring, and this is in agreement with the general pattern observed [2]. The study investigated various structures with a benzene ring and found all but one to be thermodynamically favorable (the one unfavorable was aminomethyl benzoic acid) which also agree with the general findings here.

Adsorption of different species of compounds to iron oxides have previously been studied. An analysis of the adsorption of hydroxide-chromate to different species of iron oxide (hematite) was conducted. This study found that the most thermodynamically favorable species for adsorption of outer-sphere chromate was the monodentate complexes [19]. A different study on the adsorption of arsenate to iron oxide found that the bidentate corner sharing species was most favorable [20]. The adsorption of para-hydroxybenzoic acid to bidentate mononuclear and binuclear iron oxide were investigated here. It was found, as previously mentioned, that the

bidentate mononuclear form was thermodynamically unfavorable, while the bidentate binuclear form was thermodynamically favorable, suggesting the dominance of this form. However, the form to which the bidentate binuclear converged contained unlikely geometry. In contradiction to the Gibbs free energy term, this indicates the bidentate binuclear form may not actually be more favorable. There are still many questions surrounding adsorption to iron oxide in the bidentate mononuclear and bidentate binuclear forms. A more focused, in depth study, could reveal important information about the mechanisms occurring.

Previous studies on adsorption to iron oxides found that maximum adsorption occurs at a pH near the pKa of the compound. While this is not strictly tested here the same study involving para-substituted benzoic acids found higher adsorption with higher pKa values [39]. Of the investigated compounds, the list of increasing pKa values is as follows: nitrobenzoic acid, benzoate acid, lactic acid, bisulfide-benzoic acid, methylbenzoic acid, methoxybenzoic acid, aminobenzoic acid, phthalic acid, malonic acid, para-hydroxybenzoic acid, meta-hydroxybenzoic acid, and ortho-hydroxybenzoic acid (Table 2). The Gibbs free energy terms the list of increasing adsorption of the compounds to iron oxides is as follows: aminobenzoic acid, methoxybenzoic acid, para-hydroxybenzoic acid, ortho-hydroxybenzoic acid, meta-hydroxybenzoic acid, lactic acid, methylbenzoic acid, bisulfide-benzoic acid, carboxybenzoic acid, nitrobenzoic acid, phthalic acid, and malonic acid (Table 3). These two lists reveal little correlation between the pKa values and strength of adsorption as indicated by the Gibbs free energy terms. This disagrees with previous findings, therefore other factors likely have a greater influence on the strength adsorption for these compounds to iron oxides.

Previous studies have also related Hammett constants of para- and meta- substituted benzoic acids to adsorption. The negative Hammett constants indicate electron donating

substituent groups and the positive Hammett constants indicate electron withdrawing groups (Table 2). The larger the magnitude of this constant, the greater effect the substituent has on adsorption [39]. In general, the electron withdrawing groups indicated greater adsorption than the electron donating groups. These electron withdrawing groups have higher electron density and in agreement with previous studies it would appear that higher electron density increases adsorption. The nitrobenzoic acid had the highest magnitude Hammett constant of the electron withdrawing groups and of all the para- and meta- substituted benzoic acids it had the greatest adsorption, further confirming previous findings.

Theoretical spectrum was completed for each of the adsorption reactions studied. Each of the spectra had peaks observed above 3000 cm^{-1} . This is expected to be due to the hydroxide functional groups, which are known to have strong adsorption bands around 3500 cm^{-1} . Figure 11 is the theoretical spectra for the adsorption of para-, ortho-, and meta-hydroxybenzoic acid to the iron oxide structure. Spectra for the same organic compounds as aqueous structures was also created (Fig 3). The major peaks for the aqueous structures are observed around 1750 cm^{-1} and $1200\text{-}1400\text{ cm}^{-1}$. While the larger peaks are observed around 1500 cm^{-1} and 1000 cm^{-1} for the adsorbed structures (Fig 2). This shift represents the aqueous structures have adsorbed as inner-sphere complexes with the iron oxide.

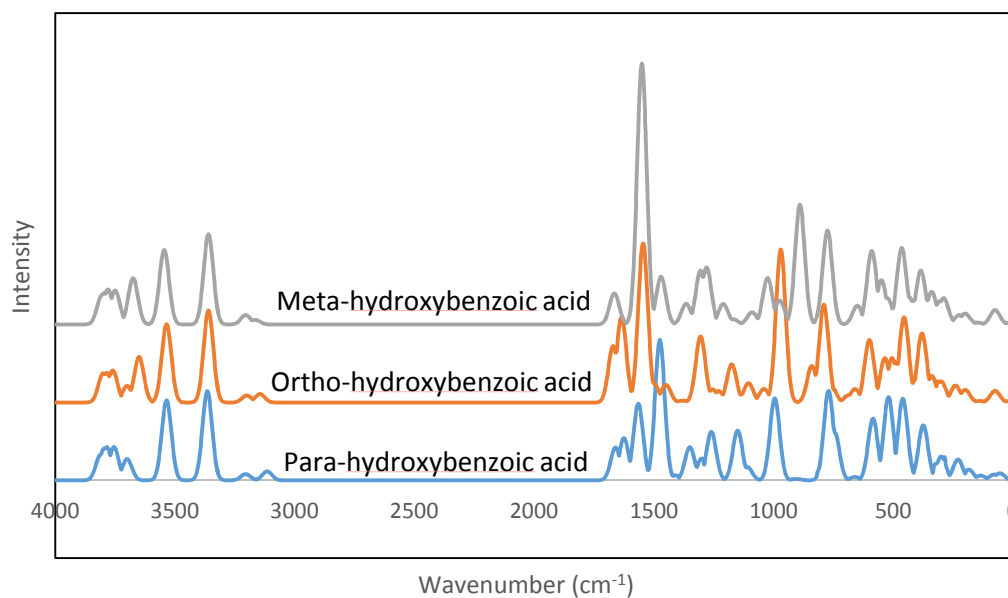


Figure 2. Theoretical spectra of hydroxybenzoic acids adsorbed to iron oxide.

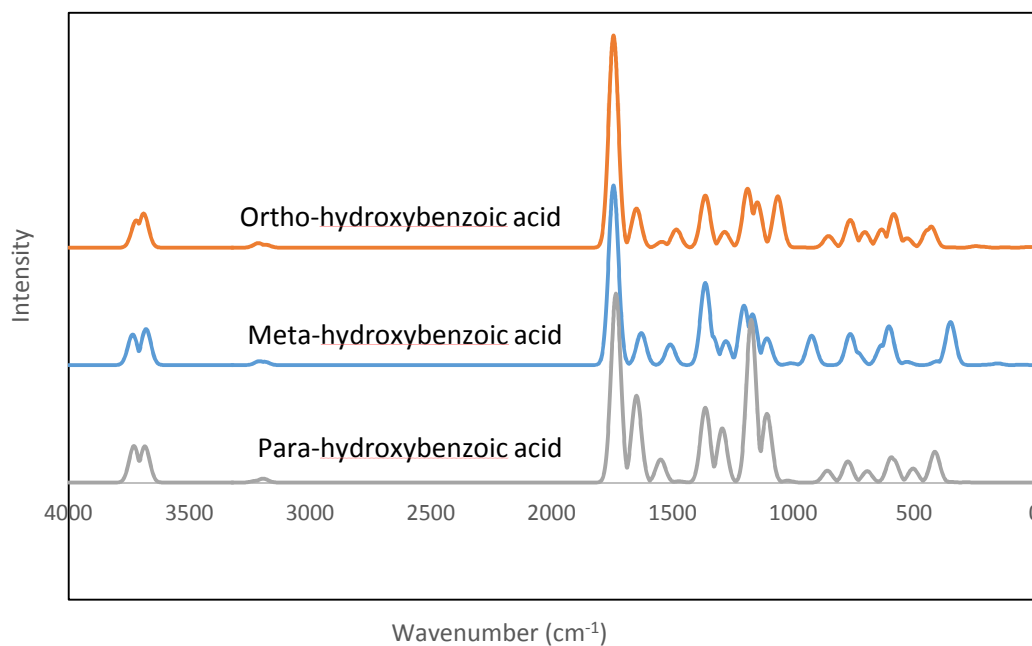


Figure 3. Theoretical spectra of aqueous hydroxybenzoic acids.

Theoretical spectrum for the benzoic acid with the investigated substituents as it adsorbs to iron oxide and the aqueous structures were constructed (Fig 4 & 5). Similar to the hydroxybenzoic acids, many of the aqueous structures had larger peaks around 1750 cm^{-1} as well

as $1200\text{-}1400\text{ cm}^{-1}$. This is expected given their similar nature, all being forms of benzoic acid. A shift in the peaks when iron oxide is introduced to lower wavenumbers indicates that the aqueous structures have adsorbed to the iron oxide, which agrees with the Gibbs free energy values of adsorption as discussed earlier. The carboxybenzoic acid, nitrobenzoic acid and bisulfide-benzoic acid displayed large peaks in the adsorbed compounds around 2550 cm^{-1} , 2900 cm^{-1} and 3000 cm^{-1} , respectively.

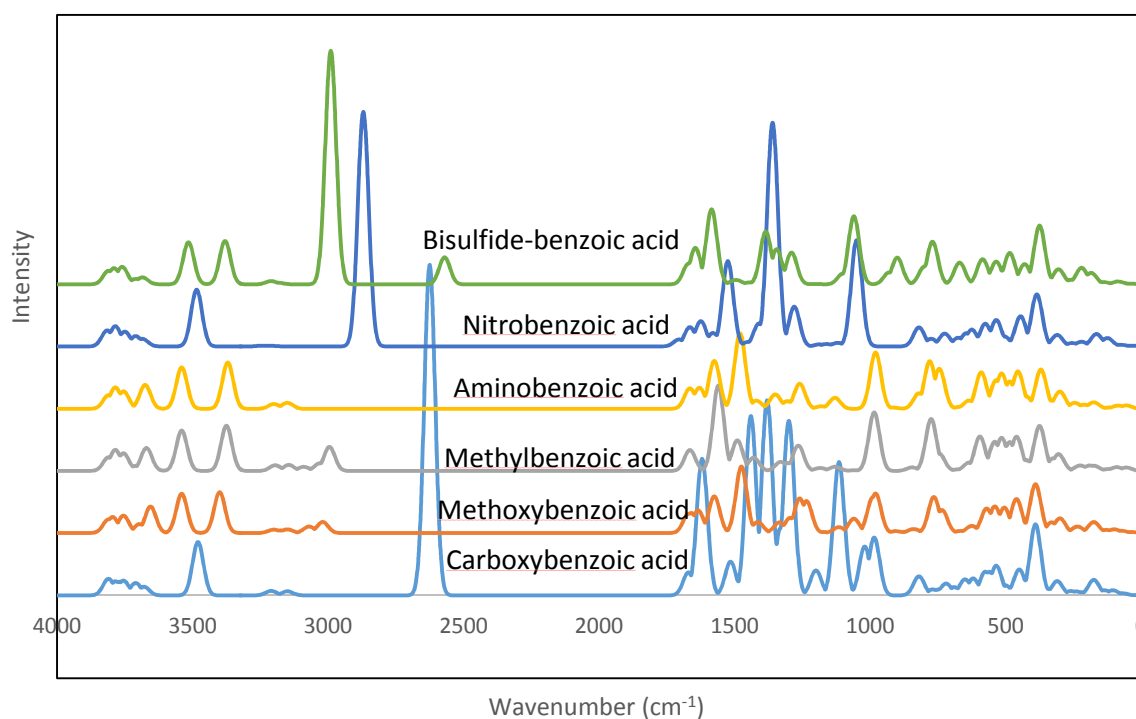


Figure 4. Theoretical spectra of benzoic acids, with various substituent groups, adsorbed to iron oxide.

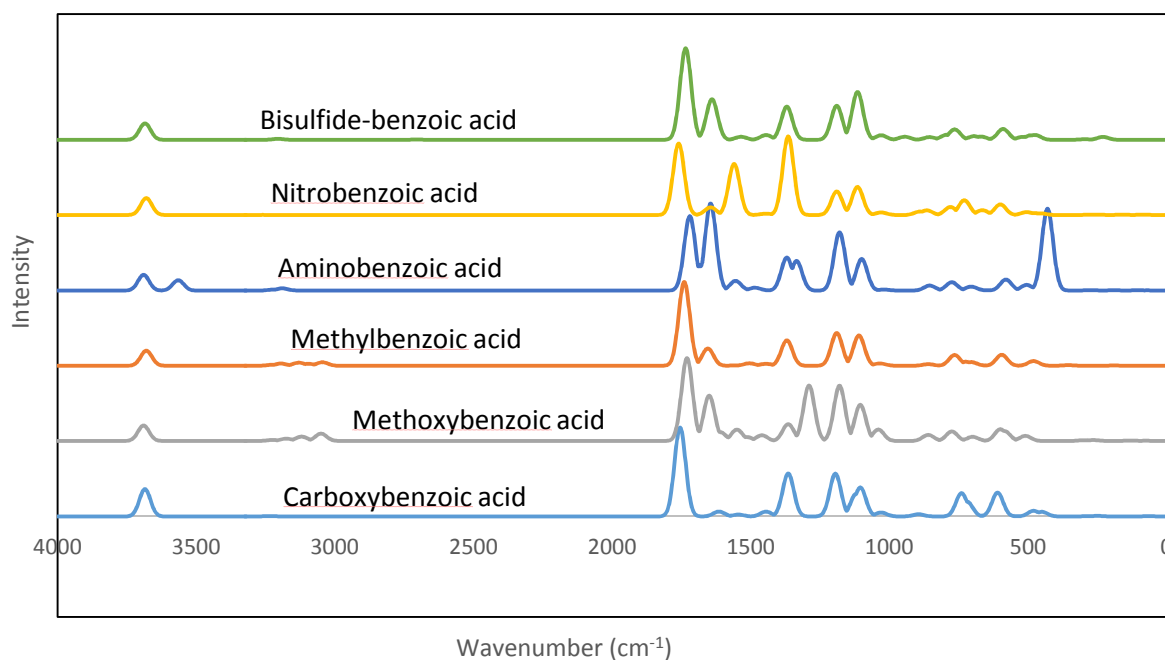


Figure 5. Theoretical spectra of aqueous benzoic acids, with various substituent groups.

Theoretical spectra representing the remaining organic acids studied in their adsorption to iron oxide and in aqueous form were also constructed (Fig 6 & 7). The malonic acid and lactic acid both displayed large peaks around 1750 cm^{-1} and 1450 cm^{-1} while the phthalic acid displayed a large peak around 1750 cm^{-1} in aqueous form. As with the previous structures upon the introduction of iron oxide, these peaks shifted down in wavenumber, indicating the successful adsorption. Peaks of the adsorbed phthalic acid and lactic acid were present around 2900 cm^{-1} and 2550 cm^{-1} , respectively.

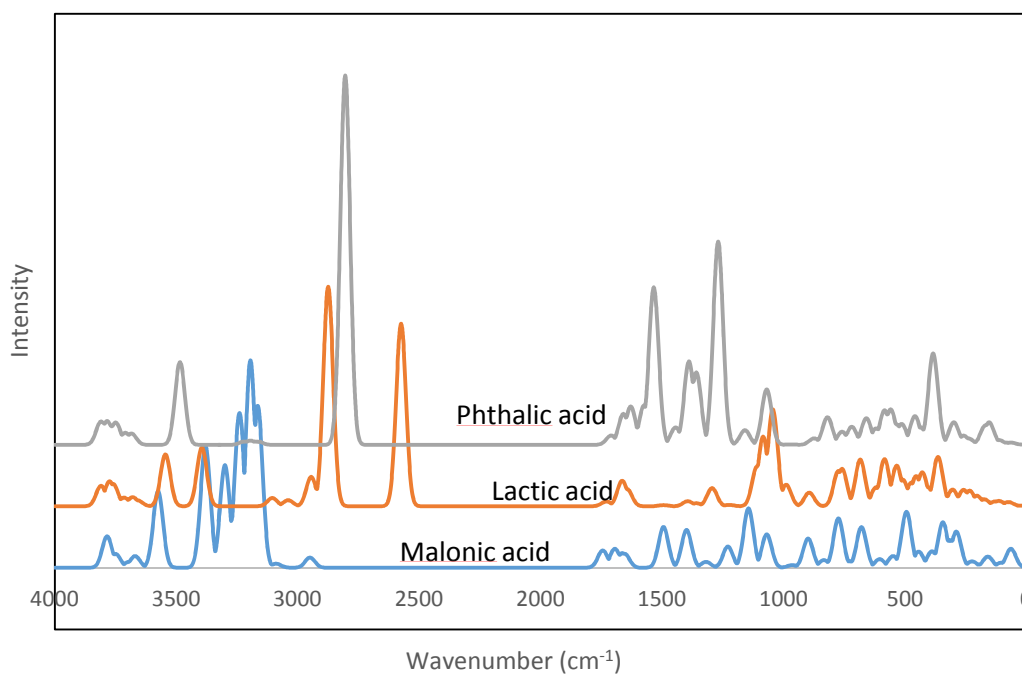


Figure 6. Theoretical spectra of indicated organic acids adsorbed to iron oxide.

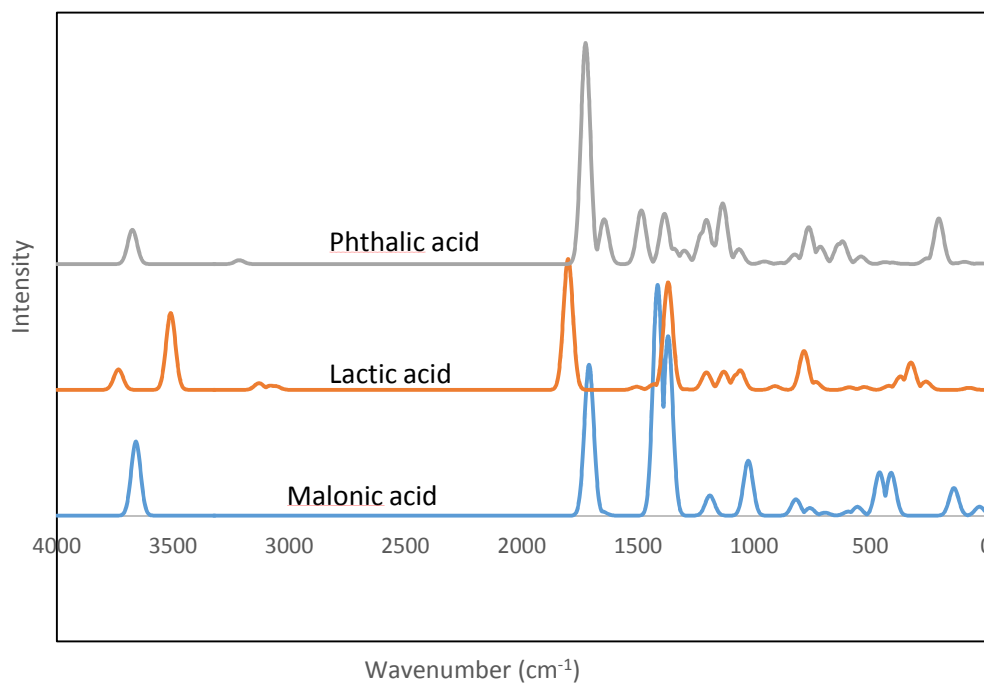


Figure 7. Theoretical spectra of indicated aqueous organic acids.

Theoretical spectra of para-hydroxybenzoic acid adsorbed to iron bidentate mononuclear iron oxide and bidentate binuclear iron oxide were constructed (Fig 8). The iron oxide formed as

bidentate mononuclear had major peaks displayed at 1500 cm^{-1} and 2500 cm^{-1} . For the bidentate binuclear form major peaks are displayed at 1500 cm^{-1} and 1050 cm^{-1} . The latter shows the shift as previously discussed to confirm the adsorption of the hydroxybenzoic acid to the iron oxide. However the absence of a peak around 1000 cm^{-1} in the former coincides with the observation from Gibbs free energy of adsorption values that the adsorption of hydroxybenzoic acid to the bidentate mononuclear form of iron oxide is unfavorable. Thus the bidentate binuclear form of iron oxide is more favorable.

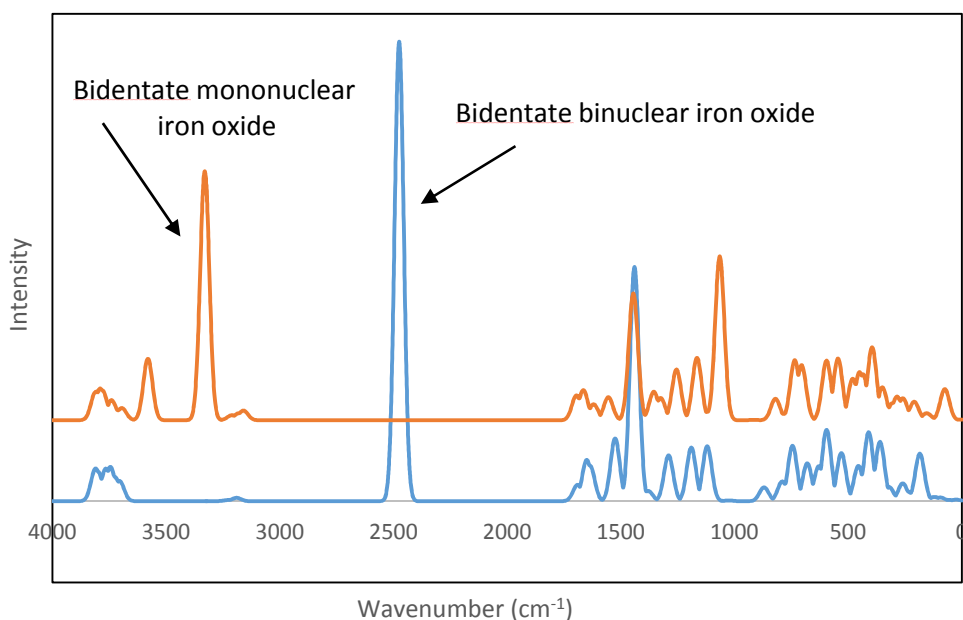


Figure 8. Theoretical spectra of para-hydroxybenzoic acid adsorbed to indicated forms of iron oxide.

The last theoretical spectrum is of the iron oxide to which the organic acids investigated were adsorbed (Fig 9). The peaks for the iron oxide are displayed around 1600 cm^{-1} and $450\text{-}650\text{ cm}^{-1}$ as well as the indicated hydroxide peaks around 3500 cm^{-1} .

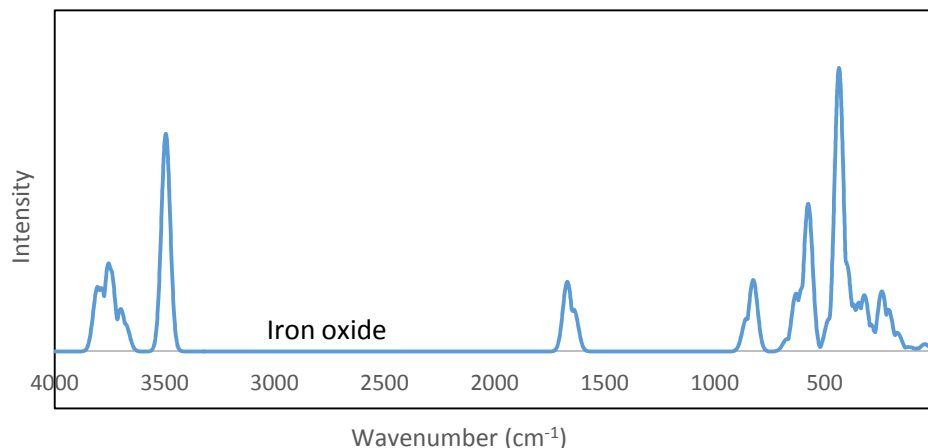


Figure 9. Theoretical spectra of iron oxide.

In a study of natural organic matter, various peaks in IR spectra have been associated to different bond stretching, bending, and deformation. Peaks at $2960/2925\text{ cm}^{-1}$ have been associated with C-H stretching of methyl groups; at 1730 cm^{-1} is associated with C=O stretching of carboxyl groups; at 1640 cm^{-1} indicates the stretching of quinones, for this study the benzene; at $1580\text{-}1620\text{ cm}^{-1}$ is associated with aromatic C=C double bonds; at $1460/1378\text{ cm}^{-1}$ indicates the deformation of C-H bond in the methyl groups; at $1285/1270\text{ cm}^{-1}$ is associated with OH stretching, C-O stretching, or OH deformation; and at $950\text{-}1125\text{ cm}^{-1}$ is an indication of C-O stretching of carbohydrates [11]. A similar study indicated that IR peaks at 1320 cm^{-1} and 1530 cm^{-1} indicated symmetric and asymmetric C-O bond stretching, respectively [29]. Lastly, a study specifically focused on adsorption of para substituted benzoic acids associated the various frequencies with bond activities. For methylbenzoic acid, bands at 1611 cm^{-1} was associated with the aromatic ring stretching; at 1182 cm^{-1} and 1118 cm^{-1} indicated C-H bending in the plane; at 1367 cm^{-1} represented C-H symmetric bending of the methyl group; at 1559 cm^{-1} and 1495 cm^{-1} represented asymmetric stretching of the carboxylate while at 1410 cm^{-1} and 1396 cm^{-1} represented this symmetric stretching. The peaks at 1559 cm^{-1} and 1410 cm^{-1} were associated

with adsorption through bridging mechanisms, thus the weaker outer-sphere physical sorption. While peaks at 1495 cm^{-1} and 1396 cm^{-1} were associated with adsorption through bidentate binding, thus stronger inner-sphere chemisorption [39]. The occurrence of both of the discussed adsorption mechanisms has been suggested for para substituted benzoic acids.

Adsorbed hydroxybenzoic acid presents peaks around 1500 cm^{-1} and $800\text{-}1000\text{ cm}^{-1}$ as well as around 500 cm^{-1} . This may be an indication of C-O bond stretching and possible C-H bond deformation as well as lower peaks around 1250 cm^{-1} may indicate OH bond stretching. It is possible the peaks around 1000 cm^{-1} are associated with the aromatic ring stretching. The peaks from $1500\text{-}1550\text{ cm}^{-1}$ specifically indicate the asymmetrical stretching of the carboxylate. Smaller peaks around 1400 cm^{-1} indicate this symmetrical stretching. In agreement with previous findings it would appear that both physical (bridging, outer-sphere) and chemical (bidentate binding, inner-sphere) mechanisms of adsorption are taking place. The observed peaks for carboxybenzoic acid, nitrobenzoic acid, and bisulfide-benzoic acid adsorption above 2500 cm^{-1} are likely due to C-H stretching. The substituted benzoic acids all displayed peaks around $1400\text{-}1500\text{ cm}^{-1}$ as well as 1000 cm^{-1} when adsorbed to iron oxide. This is an indication of C-H bond deformation and C-O bond stretching. Distinct peaks from $1400\text{-}1450\text{ cm}^{-1}$ and around 1550 cm^{-1} indicate the dual mechanisms of adsorption suspected of these para substituted benzoic acids. Adsorbed phthalic acid displays distinct peaks at 2900 cm^{-1} , 1550 cm^{-1} , and 1300 cm^{-1} . These indicate C-H stretching, possible stretching of aromatic C=C double bonds, and C-O bond stretching. The same separation of symmetric and asymmetric stretching vibrations is observed for phthalic acid, again confirming the dual mechanisms. Lactic acid has a more major peak around 1100 cm^{-1} which is indicative of C-O bond stretching. On the other hand for malonic acid the peak intensities for adsorption are generally smaller in comparison and located $500\text{-}1500\text{ cm}^{-1}$

¹ indicating possible OH stretching and/or deformation and C-O stretching. The malonic and lactic acid were the only investigated compounds not involving benzoic acid. The absence of the major peaks associated with the dual mechanisms, suggests one mechanism of adsorption, likely bidentate bridging, is much more dominant. The adsorption of para-hydroxybenzoic acid to bidentate binuclear iron oxide reveals spectra peaks at 1500 cm^{-1} and 1100 cm^{-1} , indicative of deformation of C-H bonds as well as C-O bond stretching. Along with the energy terms of adsorption it is suggested that bidentate binuclear iron oxide is the more dominant for adsorption with para-hydroxybenzoic acid. It should also be noted for all the studied compounds the absence of an observed band around 1700 cm^{-1} indicate the electron delocalization on the carboxylate group [39].

Shift of peaks between the aqueous and adsorbed structures as mentioned above indicate the presence of inner-sphere complexes. The larger shifts are what suggest the stronger inner-sphere complexes for adsorption. Outer-sphere complexes would be indicated by spectra that is similar to the aqueous structure, as with this adsorption the initial structure keeps its hydration, while for the inner-sphere complex through adsorption the initial structure is altered, as is the case with the compounds studied here. One study found that the shifts were correlated to the electronegativity of the substituent group, with para-substituted benzoic acids [39]. Another study on the adsorption of lactate to iron oxides indicated that low molecular weight organic acids produced peak shifts and/or splits associated with the carboxylate-metal ion interactions occurring when the inner-sphere complex forms [8]. This agrees with what has been observed in this research. The same study found that lactate adsorption formed mostly monodentate mononuclear complexes. Using a similar method of quantum mechanics modeling asymmetric and symmetric peaks for this adsorption were found at 1575 cm^{-1} and 1420 cm^{-1} , respectively

[8]. The lactic acid studied here had peaks at 1020 cm^{-1} and 2520 cm^{-1} , indicating that the acid has different mechanisms of adsorption to iron oxide than observed with lactate.

Various studies using IR spectra have been completed on the adsorption of relevant compounds to iron oxides. A study on dimethylarsinic acid found vibrational frequencies at $775\text{--}875\text{ cm}^{-1}$ when adsorbed to iron oxide [10]. Both arsenate and arsenite have been studied for their adsorption to iron hydroxides and one or two main broad peaks were found at $630\text{--}850\text{ cm}^{-1}$ [29]. Various forms of phosphate have been found to adsorb on iron oxides with IR peaks at $1000\text{--}1200\text{ cm}^{-1}$ [21]. Organophosphate were found to form monodentate complexes with iron hydroxide and showed frequency bands at 1150 cm^{-1} which is thought to be associated with the P=O double bonds [29]. Sulfate adsorbed to hydrated iron oxides and more specifically to hematite showed IR peaks at 1200 cm^{-1} when the samples were dehydrated [29]. The monodentate complexes studied of the sulfate compound revealed three distinct IR frequencies [22]. Lastly, an IR analysis of carbon dioxide adsorption to iron oxide found peaks at 1620 cm^{-1} , 1400 cm^{-1} , and 1220 cm^{-1} [23]. The use of quantum mechanical modeling of adsorption mechanisms has been found to provide accurate theoretical spectra when compared to observed IR analysis, however often the spectra is slightly shifted. Kubicki et al. [29], found that quantum mechanics calculations were within $100\text{--}200\text{ cm}^{-1}$ of observed absorbance. The spectra of methybenzoic acid had similar peaks at 775 cm^{-1} as observed with dimethylarsinic acid and had a shifted peak at 985 cm^{-1} , within the 200 cm^{-1} of observations from dimethylarsinic acid adsorption to iron oxide. Peaks for the adsorption of bisulfide-benzoic acid were predicted around 1050 cm^{-1} and 1600 cm^{-1} where the former is within the 200 cm^{-1} observed frequencies for adsorption of sulfate. The similarity between the model predictions and previous observations

of related adsorption occurrences confirm the appropriate use of such models to provide information on these adsorption mechanisms.

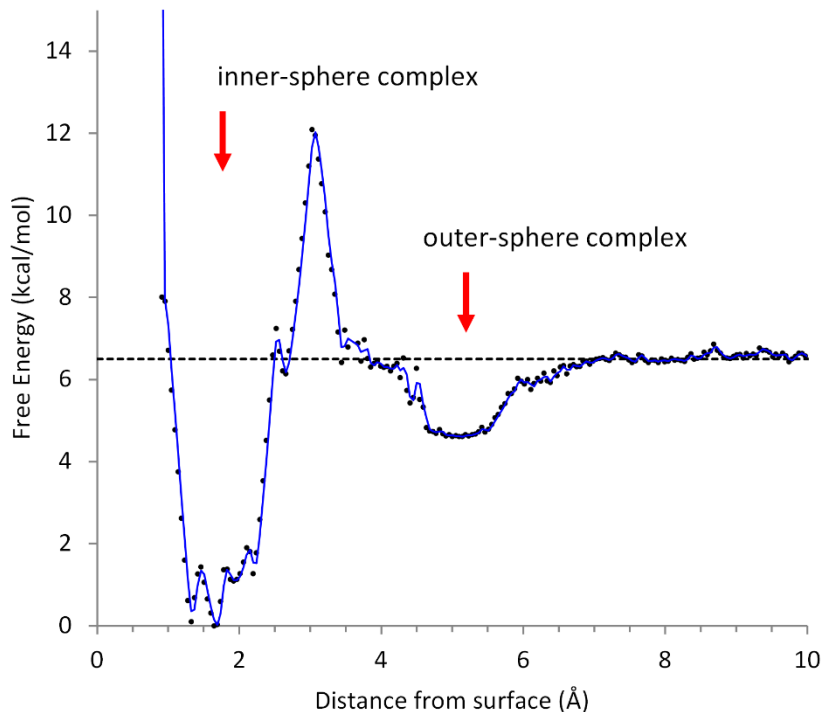


Figure 10. Complexes of adsorption of para-hydroxybenzoic acid to iron oxide related to the thermodynamic free energy and atomic distance from the surface (Chad Johnston, personal communication, April 29, 2015).

The prediction of inner-sphere and outer-sphere complexes are related to the free energy terms of adsorption (Fig 10). The inner-sphere complexes produce stronger sorption, thus the change in free energy is larger, while the outer-sphere complexes are weaker and the change in free energy is smaller. This relates to the quantum mechanical calculations that were completed in the models presented. The inner-sphere complexes also occur at closer atomic distances than the outer-sphere complexes. The change in Gibbs free energy of approximately 12 Kcal/mol (Fig 10), converts to 50.21 KJ/mol, which is slightly higher in magnitude than the prediction for para-hydroxybenzoic acid sorption to iron oxide from the quantum mechanical model. This shows that

quantum mechanical methods are useful to relate to molecular dynamic methods in prediction of adsorption. The use of quantum mechanics and molecular dynamics is of increasing interest in studies. A current problem is that molecular dynamics do not have any bonding terms. Utilizing the inner-sphere and outer-sphere complexes, which are based on charges and atomic properties of compounds, the quantum mechanical calculations presented can be related to molecular dynamic calculations. This will be very helpful, as the quantum mechanical models can be used to calibrate molecular dynamic simulations. Findings from quantum mechanical models, such as presented, become even more important and will help to improve the parameters of molecular dynamic simulations. The knowledge of adsorption of various compounds within the environment can be greatly expanded on this way.

4 Conclusion

Investigation of adsorption of the organic acids listed for this research through quantum mechanical modeling reveal the general thermodynamic favorability of the organic acids sorption to iron oxides. With the exception of para-hydroxybenzoic acid adsorption to bidentate mononuclear iron oxide, all the investigated organic compounds and their adsorption to iron oxide produced negative relative Gibbs energy terms of adsorption. The adsorption of malonic acid to iron oxide was the most thermodynamically favorable by a large margin. This information indicates that for the organic acids investigated, which consisted of many benzoic acids with various substituent groups as well as malonic acid and lactic acid, will in fact adsorb, as is described for each, to iron oxides in the environment.

Theoretical spectra produced for each adsorption reaction indicate the potential mechanisms of adsorption. The mechanisms of adsorption for the various forms of benzoic acid

studied involve both physical sorption with bridging, as well as chemisorption with bidentate binding. It is even possible these mechanisms of adsorption occur simultaneously. This is in agreement with previous studies utilizing IR spectra for similar organic acid sorption to iron oxides. When compared to spectra for the aqueous structures the shift in peak locations observed for all of the adsorbed species suggest the preferential inner-sphere complex formations for the adsorption process, as is expected for the organic acids. Understanding the adsorption mechanisms of potential contaminants is vital to creating remediation strategies. This understanding also helps to predict which contaminants are of most concern. The adsorption to iron oxides will influence a compounds fate in the environment. Using previous studies of observed IR spectra for similar compounds confirm the reliance on the quantum mechanical modeling methods used to predict actual adsorptions occurring in the environment. However, comparing to more IR spectra of the exact studied compounds presented here would be useful, to better confirm the accuracy of the modeling predictions for adsorption.

Use of modeling techniques similar to those presented here show great potential. The predictions made by the models on adsorption can be utilized to determine how contaminants of concern, such as the organic acids presented, will interact with the environment. The models allow the manipulation of various forms of compounds to see the influence on adsorption mechanisms. The information presented can be used to further extent the LIE method. The findings can be used to calibrate molecular dynamic simulations, which will likely be of great use in the future to study contaminants in the environment. Combining the quantum mechanical calculations with molecular dynamic simulations will be helpful to further investigate outer-sphere salvation interactions. The information presented in this research focuses on the bonding

energies of adsorption and by combining this with information on the non-bonding energy provides a greater scope of knowledge.

Limitations are present with the data provided. This study was focused on a specific group of compounds, only organic acids. This restricts the results to a specific group of compounds. It was even more specific, in that the main focus was on substituted benzoic acids. The findings are therefore somewhat limited to the organic acids. However, the methods used can be applied to other compounds of interest. This research can be expanded to include other organic acids as well as other nonorganic contaminants of concern. The accuracy of the model predictions can also be limited by the system size and level of required theory. However, the results can be relied upon to determine different structures. Model results should continue to be compared to experimental results to improve their reliability. The use of such models as presented allow for faster, high quality computations which reveal information concerning real systems.

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