



Teaching Adsorption Chemistry by Constructing Surface Complexation Models (SCM) in PHREEQC

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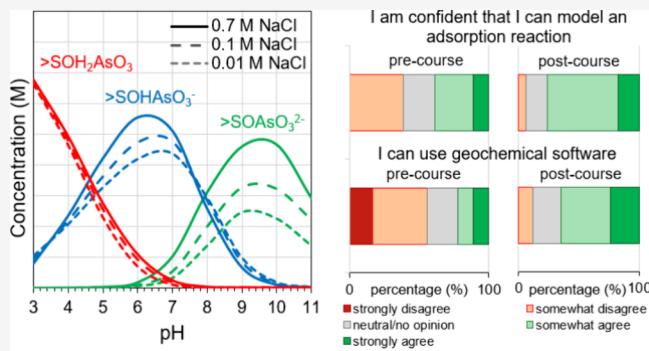
ABSTRACT: Adsorption modeling is important to understand and predict both how water contamination occurs, and how it might be prevented or remediated. Surface complexation models (SCM) help us understand adsorption under changing environmental conditions. This computational class introduces undergraduate students to adsorption and surface complexation and provides a foundation in geochemical modeling using freely available PHREEQC software from USGS. Practical capabilities are developed by (1) performing aqueous speciation reactions, (2) determining the surface charge of suspended metal oxide/mineral powders using potentiometric titration data, (3) calculating pH adsorption edges and adsorption isotherms, (4) applying PHREEQC to answer possible water treatment scenarios, and (5) using Visual Basic coding with loops to generate large data sets. This class is contextualized around arsenic contaminated groundwater and its treatment using iron oxide minerals, with hundreds of millions at risk worldwide (e.g., India, Bangladesh, Mexico). Participants report increases in their understanding of adsorption chemistry and confidence in the application of geochemical models to perform predictive SCM calculations.

KEYWORDS: Adsorption, Modeling, Second-Year Undergraduate, Research, Environmental Chemistry, Computer-Based Learning, Hands-On Learning, Colloids, Computational Chemistry, Surface Science, Geochemistry

INTRODUCTION

As a fundamental physical–chemical process, the adsorption of dissolved substances (adsorbates) onto solid surfaces (adsorbents) is an important topic for a broad range of disciplines, from earth science and environmental chemistry to chemical and civil engineering.^{1,2} In the natural environment, adsorption controls the groundwater mobility and attenuation of harmful geogenic contaminants (e.g., naturally occurring arsenic³ and uranium),⁴ anthropogenic contaminants (e.g., chromium from leather tanning and electroplating industries,⁵ or agricultural runoff including pesticides,⁶ phosphate, and nitrate fertilizers),⁷ and beneficial micronutrients for plants (e.g., zinc, iron, nickel, copper, manganese).⁸ The mineralogy of groundwater aquifers is often a critical control mechanism: where a particular rock or sediment forms strong chemical bonds with an adsorbate, that adsorbate is removed from the aqueous phase (attenuation), or at least its transport kinetics are slowed (a decrease in mobility).⁹

In the built environment, adsorption is an essential tool in the arsenal of civil engineers developing and maintaining safe drinking water systems. Fixed bed adsorption filters are employed to remove heavy metals,¹⁰ fertilizer runoff (phosphates and nitrates),¹¹ pesticides,¹² emerging contaminants such as PFAS “forever chemicals”,¹³ color compounds



including humic, fulvic and tannic acids,¹⁴ taste compounds such as hydrogen sulfide,¹⁵ and disinfection byproducts.¹⁶ Adsorption can recover valuable resources from wastewater effluents, e.g. gold from electronics waste¹⁷ and phosphate for fertilizer production.¹⁸ Ongoing research to enhance adsorption-based water treatment systems includes nanomaterial adsorbents with high adsorption capacities and tunable surface properties,¹⁹ magnetic materials that are easily recovered from treated water,²⁰ and multifunctional materials that introduce photocatalytic capabilities.²¹

We characterize adsorption systems using wet lab experiments to measure adsorption capacities and reaction rates. With limited time and resources, however, we can only study a finite number of experimental conditions. Computational modeling complements laboratory experiments by allowing new water compositions and new adsorbent material properties to be investigated,²² and modeling often generates new insights

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into the mechanisms that govern the chemical behavior observed experimentally.²³ However, undergraduate chemistry courses typically only discuss Langmuir and Freundlich adsorption isotherms; models that are valid for one set of experimental conditions only,²⁴ and cannot respond to changes in pH, ionic strength, or the addition of competitor adsorbates.²⁵

In contrast, surface complexation models (SCM) achieve sensitivity to changing experimental conditions by allowing the experimenter to describe as many reaction equilibria as are necessary to capture the key chemistry of the system.²⁴ Geochemical software packages contain libraries with hundreds of equilibrium constants already defined (adsorption, aqueous phase, gas phase, and precipitation reactions). By describing all relevant reactions, SCMs provide sensitivity to changes in water chemistry (pH, ionic strength, redox potential) and the adsorbent's physical properties (concentration, surface area, surface site density). The final model may contain dozens or hundreds of nonlinear equations, simultaneously solved using the Newton–Raphson method.²⁶

Despite being a fundamental process, adsorption is often missing from the teaching laboratory.^{1,27} When included, the classic approach is to adsorb a colored dye onto a powdered adsorbent, and analyze the concentration of adsorbate remaining in solution using UV-vis spectrophotometry or colorimetry,^{28–30} probably because optical detection is low-cost and widely available.^{31,32} Classes reported in the last two decades have included a wider variety of analytical methods: atomic absorption spectroscopy (AAS),³³ inductively coupled plasma emission spectroscopy (ICP-AES),¹ and attenuated total reflectance Fourier Transform infrared (ATR-FTIR) spectroscopy.³⁴ VanOursouw et al. (2023) measured the adsorption of perfluoroalkyl substances (PFAS) using ¹⁹F {¹H} NMR spectroscopy.³² In their experiment, the adsorbate is a high surface area metal–organic framework (MOF-808), introducing students to designer adsorbents for the removal of emerging contaminants. In some experiments, the adsorbent is first synthesized,^{1,35,32} offering opportunities for students to consider the physical and chemical properties that make an effective adsorbent. Students develop analytical chemistry skills, using background subtraction and external calibration curves.^{35,36} Data processing may develop Microsoft Excel skills, but is typically limited to fitting linearized Langmuir or Freundlich adsorption isotherm models to experimental data, using a linear regression (line of best fit).^{28–30,36} (We note that effective tutorials in nonlinear model fitting using Microsoft Excel are available for other topics.)³⁷

Despite the small variety of literature discussed above, we find no discussion of surface complexation modeling (SCM) in the teaching lab.³⁸ Potential benefits of supplementing wet chemistry experiments with SCM include (1) students work directly with adsorbent properties (surface area, site densities, surface functional groups), (2) students handle larger data sets, (3) opportunities to teach programming (e.g., Visual Basic in PHREEQC), (4) the chemistry of toxic substances is explored without risk, (5) access to a wet lab is not required. In the wet lab, students typically investigate a single set of experimental conditions only,³⁵ to avoid becoming “overwhelmed”.¹ In contrast, SCM software facilitates the investigation of how multiple independent variables interact, e.g. sweeping pH and ionic strength simultaneously (results may be plotted as heat maps or 3D graphs). In this article, we describe an experiment

on surface complexation modeling aimed for undergraduate students and above.

Learning Objectives

This experiment has been taught within undergraduate environmental chemistry and environmental engineering laboratory courses. The first aim of these courses was for students to understand the major geochemical reactions that explain the fate of elements in the environment, and the thermodynamics and kinetics that govern the observed reactivity. The second aim was to develop experimental skills, including data handling, analysis, and reporting. For the SCM experiment, the aims were (1) to understand adsorption and interface processes by building a surface complexation model, and (2) to apply geochemical modeling software in a research style. The objectives were to (i) define chemical problems in terms of equilibrium constants, (ii) construct a surface complexation model for the adsorption of arsenic onto goethite mineral surfaces, (iii) probe the sensitivity of this model with respect to water quality parameters (pH, ionic strength).

This experiment has also been taught during a workshop for early career researchers and water professionals. The overall aim was to provide a quantitative understanding of adsorption for water treatment systems, focusing on arsenic and fluoride contamination in the groundwater aquifers of central Mexico.³ The objectives were to (a) understand the chemistry that controls effective water treatment using adsorption; (b) identify potential adsorbent candidates based on their material properties; (c) use adsorption equilibrium equations to solve engineering challenges (e.g., predicting the lifetimes of groundwater treatment systems); (d) develop familiarity with geochemical modeling software (PHREEQC), quantitatively exploring the influence of experimental conditions on adsorption processes.

OVERVIEW OF THE EXPERIMENT

This experiment is designed for participants studying an undergraduate degree in environmental science, chemistry or similar, but with no prior knowledge of SCM or PHREEQC. It is expected that students understand chemical equilibrium equations and have been introduced to adsorption chemistry.

To date, this class has been implemented within undergraduate laboratory courses at the Department of Earth Science and Engineering, Imperial College London, UK (2019), and the Department of Civil and Environmental Engineering, Princeton University, US (2020). The 12-week course includes 11 other experiments (ten wet lab experiments,^{39,40} of which one covers adsorption isotherms,³⁵ and one modeling experiment using Density Functional Theory (DFT) calculations). At Imperial College London, adsorption equilibria had been introduced during a lecture course on Low Temperature Environmental Chemistry. The SCM class was also taught as the main component during a two-day workshop on adsorption at CIATEC in León, Mexico (2023). Here, the audience comprised 20 participants, both academic researchers and water utility professionals. The first day of the workshop covered the theory of adsorption, physical properties that make effective adsorbent materials, and factors that influence adsorption equilibria (such as surface charge and pH speciation). The first day also included a 2 h practical on fitting Langmuir and Freundlich adsorption isotherm models (both nonlinear and linearized fitting).⁴¹ The second day

focused on the SCM practical, followed by a 1 h discussion about how to better constrain adsorption models using advanced materials characterization methods.⁴²

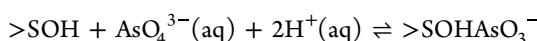
Four-hours teaching time is allotted for the class, with the first 45 min being a taught introduction to provide background theory. The practical provides graduated exposure,⁴³ with initially explicit instructions giving way to more creative coding later in the class. After distributing student handouts, the instructor and any teaching assistants should rotate around the room, initially to solve technical challenges (e.g., installation errors) and later to encourage students to think critically about the chemistry that explains their experimental observations. The instructor should bring the group together to review progress every 20 min, ensuring all students complete the experiment. Participants can collaborate and support one another with technical queries. A full lesson plan is provided within the *Supporting Information* (main DOC).

Several software packages performing SCM calculations are available (e.g., PHREEQC,⁴⁴ FITEQL,^{45,46} GeoSurf,⁴⁷ Visual MINTEQ,⁴⁸ Geochemist's Workbench).⁴⁹ This class uses PHREEQC, which is freely available, supported by an online forum, and can export to Microsoft Excel for further processing. The structure of code in this class is informed by the PHREEQC user manual (Example 8)⁵⁰ and modeling parameters are taken from Dixit and Hering.⁵¹

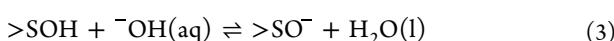
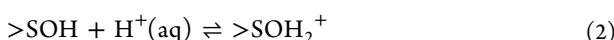
The case study for this class is arsenic adsorption onto goethite. Arsenic is a Category 1 carcinogen and naturally contaminated groundwaters are a health risk to over 100 million people worldwide.⁵² This includes communities in the Mexican state of Guanajuato³ where this class was taught in 2023. The commercial benchmark adsorbent for arsenic removal is a synthetic goethite mineral (FeOOH) named Bayoxide E33.⁵³ Interesting features of arsenic adsorption include different electrostatic effects between the adsorption of negative As(V) oxyanions (HAsO_4^{2-} , H_2AsO_4^-) and neutral As(III) (H_3AsO_3), as well as competition between As(V) and orthophosphate (PO_4^{3-}) for the same adsorption sites. This class can be easily tailored to different adsorbate–adsorbent systems by selecting different modeling parameters from the literature.

■ BACKGROUND INFORMATION AND RELEVANT THEORY

An overview of surface complexation modeling should be provided before the practical (*Supporting Information*, presentation PPT). Briefly, SCM allows us to simulate the influence of complex water chemistry on adsorption by using multiple reaction equilibria to build up a picture of the total system. For metal oxide adsorbents, adsorption occurs through chemical bonding between surface hydroxyl functional groups ($>\text{SOH}$) and dissolved adsorbates to form *surface complexes* (eq 1) ($>\text{S}$ denotes the solid surface). Surface complexes may be inner sphere, with a covalent bond between adsorbate and adsorbent, or outer sphere, where the adsorbate retains its solvation sphere and is held by electrostatic forces only. Surface hydroxyls can be protonated or deprotonated, causing pH-dependent surface charge, included within the SCM using appropriate equilibrium constants (eqs 2 and 3). Surface charge is neutralized by electrolyte counterions (e.g., Na^+ and Cl^-) and the resulting surface potential (Ψ , expressed in millivolts) is incorporated into adsorption equilibria, e.g. eq 4 (note that different SCMs calculate the activity of surface species within the mass action expression differently).²²



$$+ \text{H}_2\text{O(l)} \quad (1)$$



$$K = \frac{[>\text{SOHAsO}_3^-]}{[>\text{SOH}][\text{AsO}_4^{3-}][\text{H}^+]^2} \cdot \exp\left(\frac{F\Psi}{RT}\right) \quad (4)$$

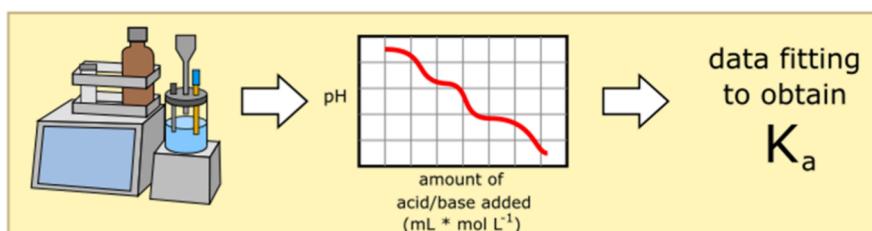
The modeler defines the adsorbent's concentration (g L^{-1}), its surface area ($\text{m}^2 \text{ g}^{-1}$), and how closely its surface hydroxyls are packed together (surface site density expressed as sites nm^{-2}). These parameters give the total concentration of surface hydroxyls (eq 5). Values for the capacitance of the electrical double layer (EDL) are needed to calculate Ψ in the constant capacitance (CCM), triple layer (TLM) and charge distribution multisite complexation (CD-MUSIC) models, but not for the diffuse double layer model (DDL) used in this class.

$$\begin{aligned} [>\text{SOH}] (\text{mol L}^{-1}) \\ = \text{adsorbent concentration} (\text{g L}^{-1}) \cdot \text{surface area} (\text{m}^2 \text{ g}^{-1}) \\ \cdot \text{site density (number of sites nm}^{-2}\text{)} \\ \cdot \text{conversion factor (10}^{18} \text{ nm}^2 \text{ m}^{-2}\text{)} \\ \div \text{Avogadro's number (6.023} \times 10^{23} \text{ mol}^{-1}\text{)} \end{aligned} \quad (5)$$

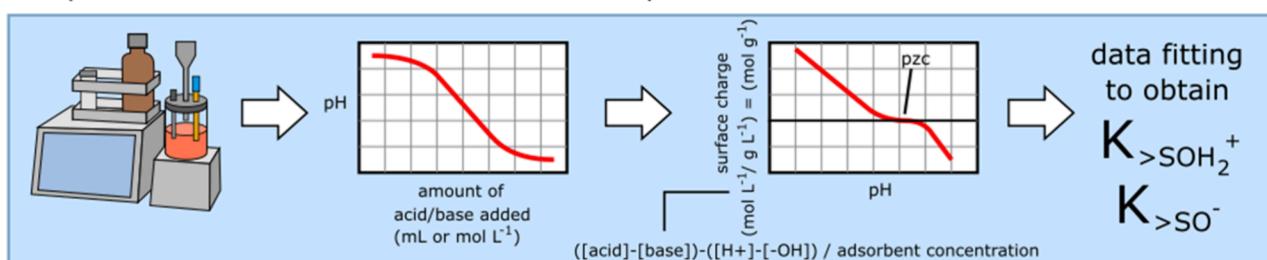
In SCM software, we define *master species* or *components*. These are the building blocks that allow us to construct all possible molecules, or *species*, in the system (italics denote software keywords). For instance, if we define surface master species $>\text{SOH}$ and solution master species H^+ , we can create the species $>\text{SOH}$ by using 1 $>\text{SOH}$ master species and 0 H^+ master species. We can also create the species $>\text{SOH}_2^+$ and $>\text{SO}^-$ by using 1 $>\text{SOH}$ master species and +1 or -1 H^+ master species, respectively. PHREEQC uses *keyword* blocks, which allow the user to (i) define master species; (ii) define each species and its $\log(K)$ equilibrium constant; (iii) define the composition of all solutions and surfaces in the system; and (iv) conduct different reactions using these solutions and surfaces (example PHREEQC code is provided in the *Supporting Information* model answers).

SCMs are only successful in predicting adsorption behavior when chemical and physical properties have been accurately characterized, and the instructor should use this opportunity to show students how modeling and lab work go hand-in-hand toward developing a comprehensive understanding of the underlying chemistry. First, for many reactions in the system (aqueous phase speciation, precipitation and dissolution, evaporation and condensation) experimentally determined equilibrium constants are often already available in the literature or software databases. Other parameters, such as surface complexation constants, are obtained by “fitting” the model to experimental data: varying a few parameters until the error between model and experiment reaches a minimum. Accurate characterization of the adsorbent material's surface is important (e.g., BET-specific surface area) as is identification of the surface complexes present (e.g., using X-ray Absorption Spectroscopy (XAS) and infrared spectroscopy).^{54,55} The point of zero charge (pzc or pH_{pzc}) denotes the pH at which the adsorbent surface is neutrally charged overall. High pzc materials are desirable for the removal of anions, and low pzc

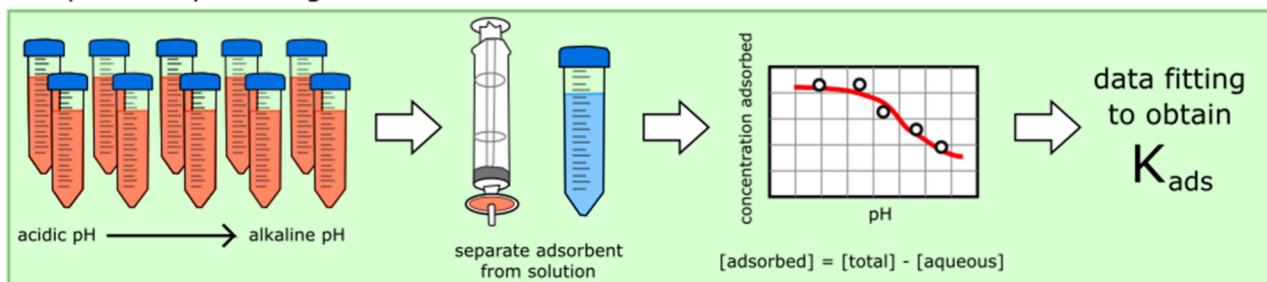
potentiometric titrations of adsorbate solutions



potentiometric titrations of adsorbent suspensions



pH adsorption edges



adsorption isotherms

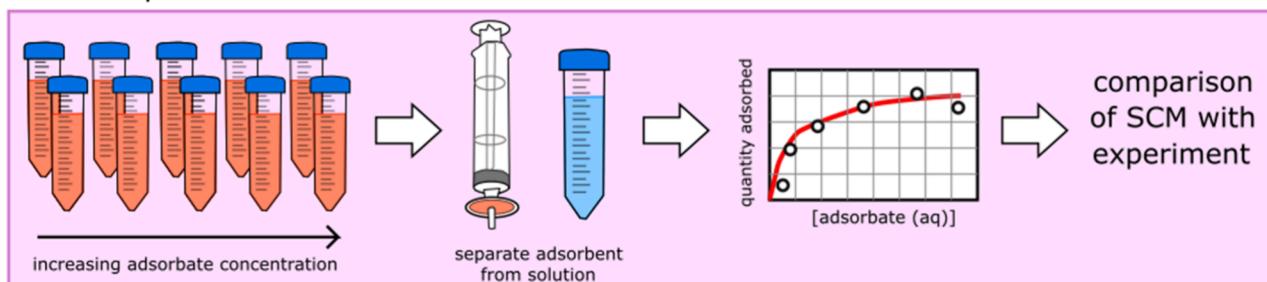


Figure 1. Depiction of a typical experimental workflow performed to construct and validate a surface complexation model.⁴²

materials for the removal of cations, due to electrostatic effects (eq 4). It may also be desirable to amend the pH of the influent water to optimize the electrostatic forces between the adsorbent material and charged adsorbates. The pzc is typically determined by potentiometric titration, but should be verified using the isoelectric point.⁵⁶ While the pzc refers to charge at the atomic surface, the isoelectric point refers to the pH at which the charge at the shear plane (zeta potential) is zero. At the isoelectric point, adsorbent particles may drop out of suspension, as van der Waals attractive forces overcome electrostatic repulsion.

EXPERIMENTAL PROCEDURE

The exercises in this class represent the typical workflow used to construct and validate an SCM ([Figure 1](#)).⁴² (1) Students calculate the pH-dependent speciation (protonation state) of

As(V) oxyanions. Acidity constants (K_a) are often obtained by fitting aqueous equilibrium models to potentiometric titration data. (2) Students simulate pH-dependent surface charge. Typically, equilibrium constants for surface hydroxyl protonation reactions and/or electrolyte adsorption (e.g., $K_{>\text{SOH}_2+}$ and $K_{>\text{SO}_4^-}$) are obtained by fitting models to potentiometric titrations of adsorbent suspensions. (3) Students simulate arsenic pH adsorption edges. Typically, surface complexation constants (K_{ads}) are obtained by fitting batch adsorption experiments across a wide pH range, given that (a) pH often shows a significant and easily measurable influence on the extent of adsorption, and (b) pH often influences both the protonation state and denticity of surface complexes. (4) Students simulate the adsorption isotherms that are used to validate SCMs (can the SCM predict unseen data?). In this class, students then investigate the influence of ionic strength

Table 1. Summary of Exercises

Exercise	Activity
(1) First PHREEQC calculation	<p>Students:</p> <ul style="list-style-type: none"> • Use SOLUTION_MASTER_SPECIES keyword to define aqueous H_2AsO_4^- as the component for building As(V) species. • Use SOLUTION_SPECIES to define As(V) species (H_3AsO_4, H_2AsO_4^-, HAsO_4^{2-}, AsO_4^{3-}) and give $\log(K)$ values for the formation of each (using components H_2AsO_4^- and H^+). • Use SOLUTION to define experimental conditions (pH, [NaCl], [total As(V)]). <p>Entire class:</p> <ul style="list-style-type: none"> • Reviews PHREEQC output data, focusing on relative abundances of different As(V) species. • Discusses the utility of additional output data (ionic strength, activity calculations, redox potential, charge balance).
(2) Aqueous pH speciation	<p>Students:</p> <ul style="list-style-type: none"> • Use SELECTED_OUTPUT to print As(V) speciation data to a text file. • Sweep pH (from 3 to 11) and plot results in Microsoft Excel. <p>Entire class:</p> <ul style="list-style-type: none"> • Discusses link between pH speciation and pK_a values.
(3) Surface charge calculations	<p>Students:</p> <ul style="list-style-type: none"> • Use SURFACE_MASTER_SPECIES and SURFACE_SPECIES to define the >SOH component, and >SO⁻, >SOH, and >SOH₂⁺ species (and respective $\log(K)$ values). • Use SURFACE to define adsorbent's mass (g L⁻¹), surface area (m² g⁻¹), and surface site density (sites nm⁻²). • Use EQUILIBRIUM_PHASES to prevent pH drift (otherwise occurring due to buffering capacity of >SOH groups). • Plot surface charge as a function of pH.
(4) pH adsorption edge	<p>Students:</p> <ul style="list-style-type: none"> • Define surface species for three potential As(V)-goethite surface complexes: >SOH₂AsO₃, >SOHAsO₃⁻, and >SOAsO₃²⁻. • Plot pH adsorption edges for each species plus total adsorbed As(V). <p>Entire class:</p> <ul style="list-style-type: none"> • Discusses contribution of surface charge to observed pH adsorption edge.
(5) Adsorption isotherm	<p>Students:</p> <ul style="list-style-type: none"> • Fix the pH to 7 and vary [As(V)] between 5 μM and 1 mM. • Plot [As(V) (ads)] as a function of [As(V) (aq)].
(6) Experiments	<p>Students</p> <ul style="list-style-type: none"> • Investigate the influence of ionic strength (0.01, 0.1, 0.7 M NaCl) on adsorption edges and adsorption isotherms. • Contrast As(III) adsorption behavior with As(V), considering different sensitivities to changes in pH and ionic strength. <p>Entire class:</p> <ul style="list-style-type: none"> • Discusses the application of USER_PUNCH keyword to automate sweeps of independent variables.

on As(V) adsorption, in the context of saline intrusion due to climate change and rising sea levels,⁵⁷ and compare the sensitivity of As(III) adsorption with As(V) adsorption, with respect to changes in pH and ionic strength.

Resources

Students are provided with (1) access to the lecture slides, (2) a lab script handout, (3) modeling parameters from Dixit and Hering,⁵¹ and (4) access to the model answers. All necessary resources are available in the [Supporting Information](#): main Word DOC, student handout DOC, instructor's presentation PPT, and model answers ZIP file. At least one computer between two students is required, but ideally each student will have their own. A recent version of PHREEQC⁵⁰ should be installed on each computer. For in-person teaching, display equipment such as a projector is useful to review progress collaboratively throughout the practical.

Exercises

The exercises in this class are summarized in [Table 1](#) and a full lesson plan is provided in the [Supporting Information](#), main DOC.

HAZARDS

Computing equipment must be used safely and in accordance with local standards, which may include laptop stands to raise display equipment to eye level, posture supporting chairs, and regular breaks to avoid eye strain.

RESULTS AND DISCUSSION

The major challenge in this class is minimizing time lost to nonchemistry challenges. Where students supply their own IT equipment, files may be installed in different hard drive locations and the local language may vary (e.g., Microsoft Excel function names may require translation). Students may fail to change the database from phreeqc.dat to llnl.dat and receive error messages. Typos are common, especially for chemical formulas, since PHREEQC requires the sign of the charge to be typed before the valency to avoid confusion between charge and stoichiometry. For instance, AsO_4^{3-} is written as AsO_4-3 .

In exercise 1 and 2, students generate the pH speciation of As(V) ([Figure 2](#)). Students are interested to learn how PHREEQC automatically outputs not just the pH speciation, but also ionic strength calculations, activity coefficients, redox potential and the charge balance. This exercise helps students reflect on equilibrium constants, pK_a values, and how the equilibrium expression $K_a = [\text{H}_{n-1}\text{AsO}_4^{n-4}][\text{H}^+]/[\text{H}_n\text{AsO}_4^{n-3}]$ is rearranged to $K_a/[\text{H}^+] = [\text{H}_{n-1}\text{AsO}_4^{n-4}]/[\text{H}_n\text{AsO}_4^{n-3}]$. Consequently, every time the pH increases by 1 unit, the ratio of HAsO_4^{2-} to H_2AsO_4^- increases by a factor of 10.

In exercise 3, students generate a surface charge profile for goethite (FeOOH) particles suspended in NaCl solution ([Figure 3](#)). The simple charge balance expressed in mol L⁻¹ is calculated by subtracting [SO_4^{2-}] from [SOH_2^+]. Students can use surface charge to predict how pH will influence the adsorption of charged metal contaminants, e.g., the enhanced

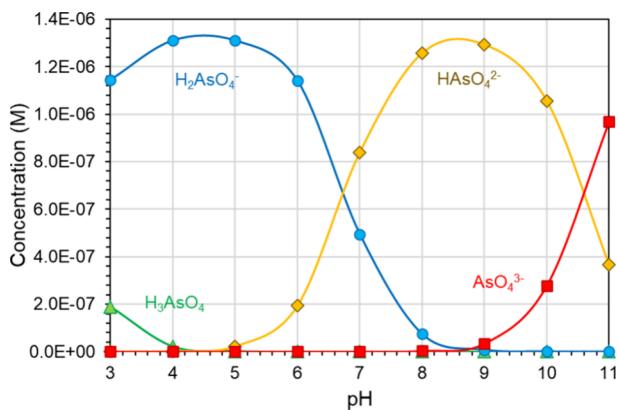


Figure 2. Aqueous speciation of As(V) as a function of pH. The experimental conditions were 1.3×10^{-6} M As(V) ($1.3 \mu\text{M}$ or $100 \mu\text{g L}^{-1}$) and 0.1 M NaCl.

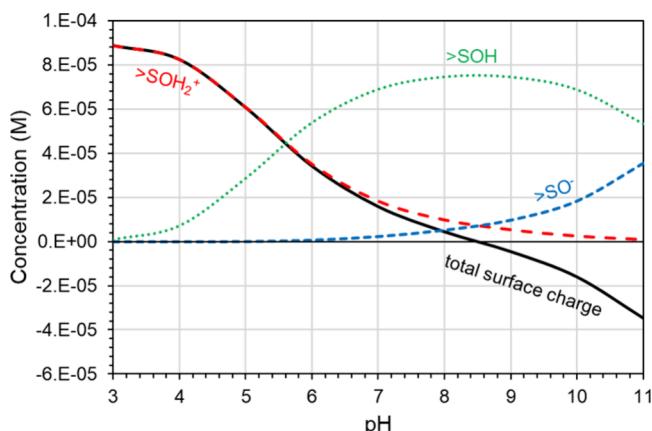
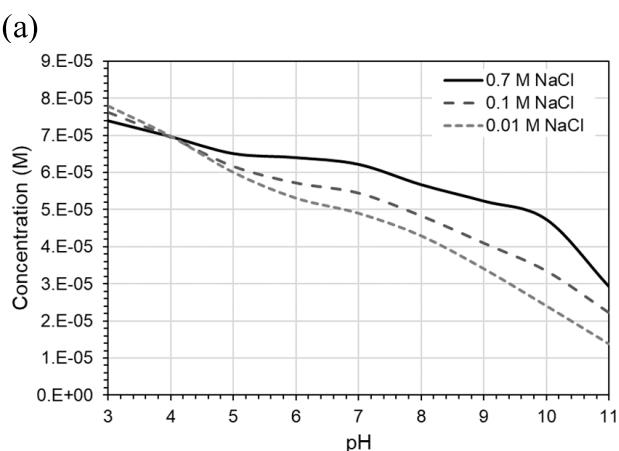


Figure 3. Influence of pH on the surface charge of goethite suspensions. The experimental conditions of the PHREEQC simulation were 0.5 g L^{-1} FeOOH with a surface area of $54 \text{ m}^2 \text{ g}^{-1}$ and $2.0 \text{ sites nm}^{-2}$, and 0.1 M NaCl as the electrolyte. The surface complexation constants are $\log(K) = 7.47$ for $>\text{SOH} + \text{H}^+ = >\text{SOH}_2^+$, and $\log(K) = -9.51$ for $>\text{SOH} = >\text{SO}^- + \text{H}^+$.



adsorption of AsO_4^{3-} arsenic anions at acidic pH with positive surface charge, versus the suppressed adsorption of Pb^{2+} lead cations. There are opportunities to discuss the electrical double layer (EDL) and how the EDL is not as sophisticated as the TLM, where we define additional surface complexation constants for specific adsorption of the electrolyte (e.g., formation of $>\text{SOH}_2^+ - \text{Cl}^-$ and $>\text{SO}^- - \text{Na}^+$). This exercise provides further opportunities to discuss potentiometric titrations (by which surface charge curves are obtained experimentally), how surface acidity constants are obtained by fitting the SCM to potentiometric titration data, and how we characterize the point of zero charge (pzc).

In exercise 4, students simulate a pH adsorption edge for the adsorption of As(V) onto goethite (Figure 4a). Students observe the changing distribution between neutral $>\text{SOH}_2\text{AsO}_3$ at acidic pH and deprotonated $>\text{SOHAsO}_3^-$ and $>\text{SOAsO}_3^{2-}$ surface complexes at neutral and alkaline pH respectively (Figure 4b). Students are reminded how accurate identification of the structure of surface complexes is challenging, with our understanding often updated according to the scientific method. Experimental approaches such as XAS, FTIR and zeta potential^{54,55} are complemented by modeling approaches including SCM and density functional theory (DFT) calculations.⁵⁸ Pertinently, more recent data indicates the preference for As(V) to form bidentate $(>\text{SO})_2\text{AsO}_2\text{H}$ and $(>\text{SO})_2\text{AsO}_2^-$ surface complexes, instead of monodentate complexes.⁵⁹

In exercise 5, students simulate an adsorption isotherm by fixing the pH and varying the concentration of As(V) added to the initial solution (Figure 5). Following these core exercises, students conduct experiments, first considering how ionic strength influences As(V) adsorption (with the context of saline intrusion into groundwater aquifers due to rising sea levels).⁵⁷ By considering the EDL as a “battery” or capacitor, able to store charge, students explain that the promotion of As(V) adsorption with increasing ionic strength (Figure 5) is due to the greater ability of electrolyte Na^+ cations to neutralize or screen the negative surface charge generated by formation of $>\text{SOHAsO}_3^-$ and $>\text{SOAsO}_3^{2-}$ (Figure 5).⁶⁰ Students identify how the formation of $>\text{SOAsO}_3^{2-}$ increases

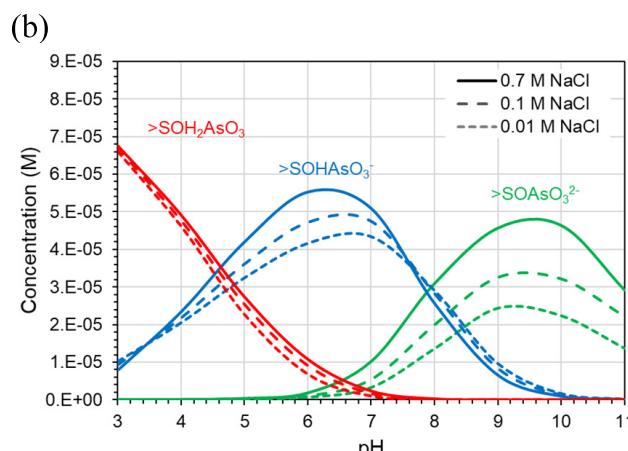


Figure 4. pH adsorption edges for the adsorption of As(V) onto goethite. (a) Students observe how above pH 4, total As(V) adsorption increases with increasing ionic strength due to the increased capacitance of the electrical double layer (EDL). (b) In the deconvolution of total As(V) adsorption into the constituent surface complex species, students learn how EDL capacitance is most important for strongly charged surface complexes (e.g., $>\text{SOAsO}_3^{2-}$). The experimental conditions of the PHREEQC simulation were 1.0×10^{-4} M As(V) ($100 \mu\text{M}$ or 7.5 mg L^{-1}), 0.5 g L^{-1} FeOOH ($54 \text{ m}^2 \text{ g}^{-1}$ and $2.0 \text{ sites nm}^{-2}$), and 0.01, 0.1, or 0.7 M NaCl as the electrolyte.

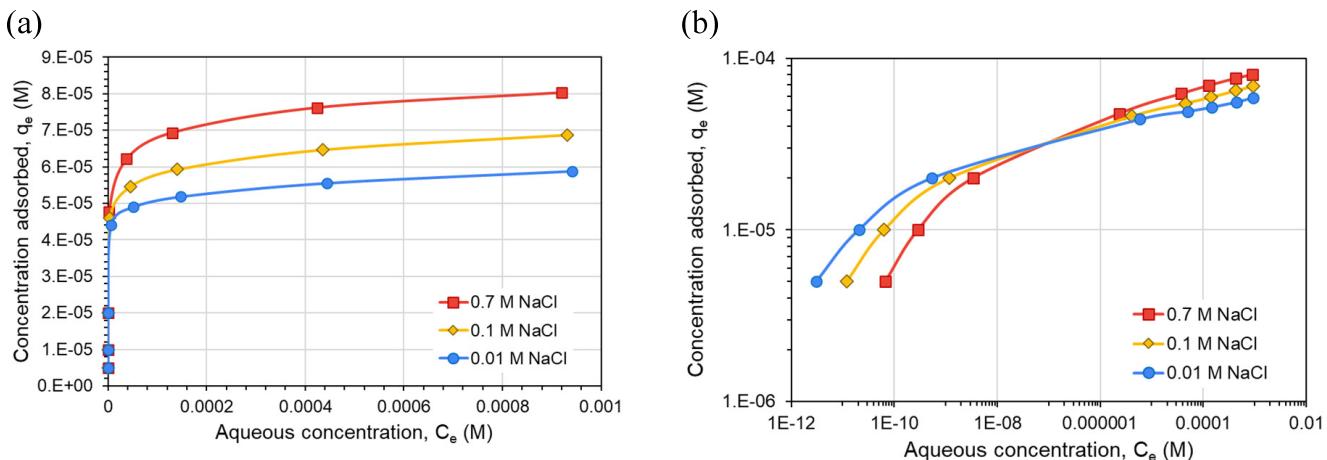


Figure 5. Adsorption isotherms showing the increasing capacity of goethite for the adsorption of As(V) with increasing ionic strength. The results are presented with (a) linearly scaling axes, and (b) logarithmic axes. The experimental conditions were pH 7 (fixed), 5.0×10^{-6} to 1.0×10^{-3} M total As(V) ($375 \mu\text{g L}^{-1}$ to 75 mg L^{-1}), 0.5 g L^{-1} FeOOH ($54 \text{ m}^2 \text{ g}^{-1}$, 2.0 sites nm^{-2}), and 0.01, 0.1, or 0.7 M NaCl.

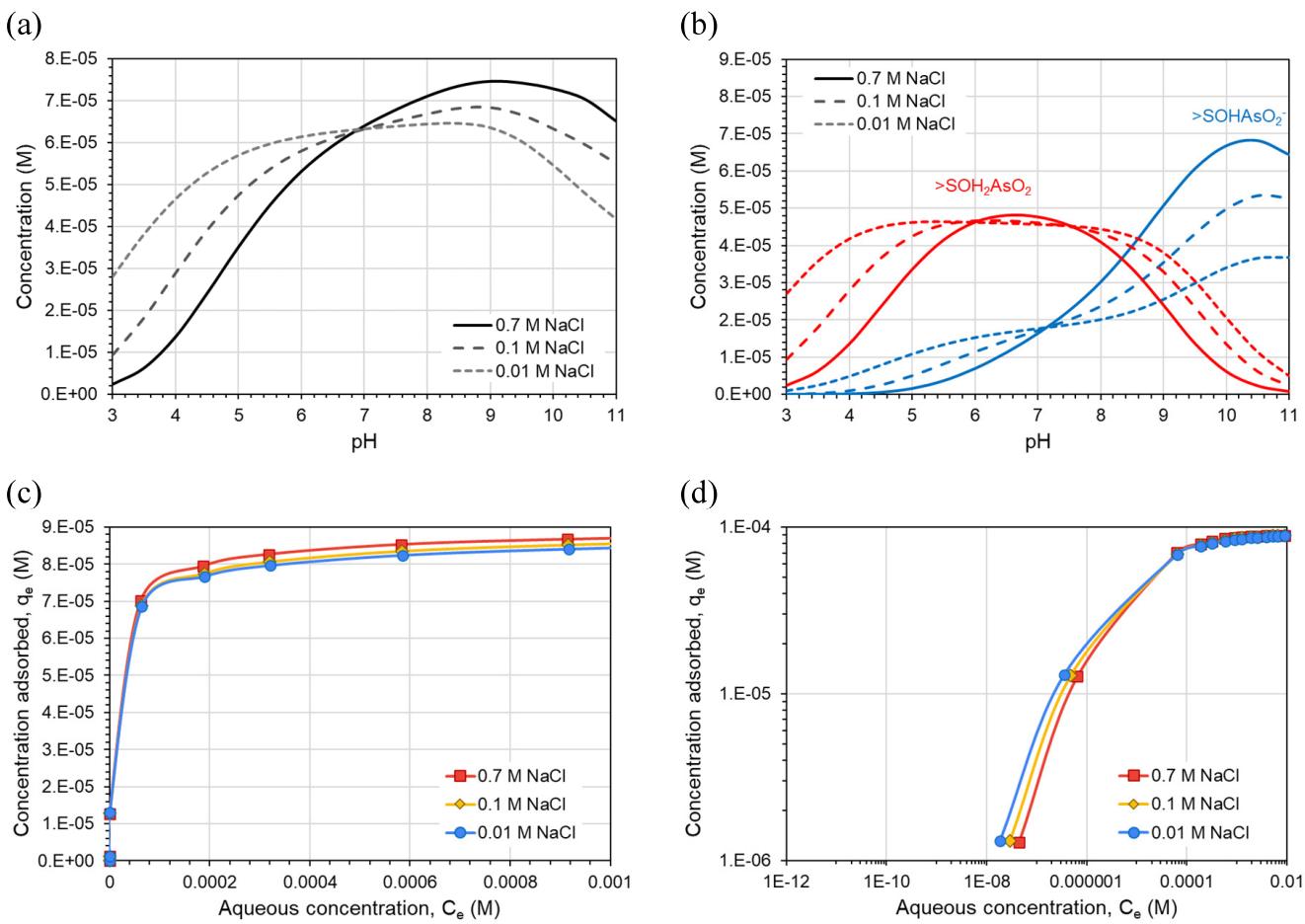


Figure 6. As(III) pH adsorption edges (a, b) and adsorption isotherms (c, d) calculated using PHREEQC. The experimental conditions were $100 \mu\text{M}$ As(III) (7.5 mg L^{-1}) for the pH adsorption edges, and 1.3×10^{-6} to 9.3×10^{-2} M total As(III) ($100 \mu\text{g L}^{-1}$ to 700 mg L^{-1}) for adsorption isotherms (fixed at pH 7), 0.5 g L^{-1} FeOOH ($54 \text{ m}^2 \text{ g}^{-1}$, 2.0 sites nm^{-2}), and 0.01, 0.1, or 0.7 M NaCl.

the most with ionic strength (-2 charge), while neutral $>\text{SOH}_2\text{AsO}_3$ is largely unchanged (Figure 4b).

Further experimental opportunities include an investigation of As(III) adsorption (Figure 6). While As(V) adsorption is greatest at acidic pH, neutral As(III) species (H_3AsO_3) tend to

form neutral $>\text{SOH}_2\text{AsO}_2$ complexes, unaffected by surface charge and prevalent at neutral pH (Figure 6a). Increasing ionic strength promotes the formation of negative $>\text{SOHAsO}_2^-$ surface complexes (Figure 6b). However, due to the prevalence of neutral As(III) surface complexes versus

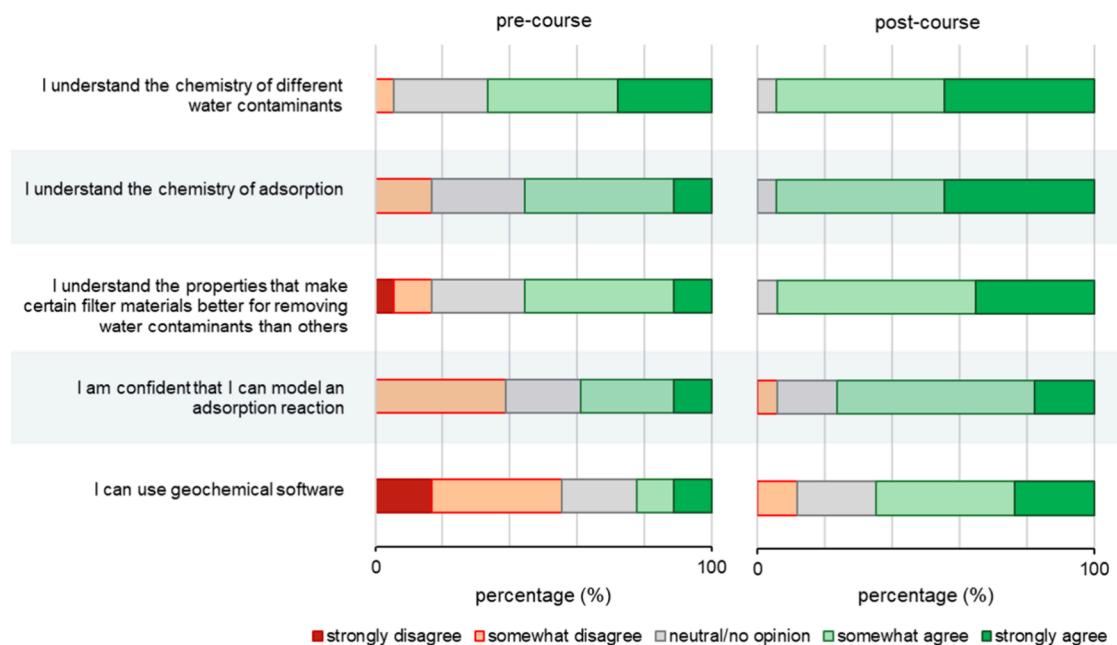


Figure 7. Results from precourse and postcourse surveys during the CIATEC workshop in Mexico, 2023. The sample size was $n = 18$ participants. Participants were asked to what extent they agreed with each statement.

negative As(V), ionic strength has significantly less influence on the adsorption isotherms simulated at pH 7 (Figure 6c).

Finally, to further highlight the data processing capabilities provided by computational models, we introduce the Visual Basic programming functionality within PHREEQC using the *USER_PUNCH* keyword. We highlight how running the simulation at integer pH values only (pH 4.0, 5.0, 6.0, etc.) and not the values in between (pH 4.1, 4.2, 4.3, etc.) produces low resolution curves (e.g., pictured in Figure 2). Students use Visual Basic loops to generate high resolution data sets, while maintaining a smaller and more easily managed code, and are typically impressed to learn how nested loops can conduct hundreds of simulations in one go, allowing us to investigate multiple independent variables simultaneously (e.g., to create 3D plots or heat maps).

LEARNING OUTCOMES

The undergraduate lab course aimed to develop experimental skills in the context of explaining the fate of elements in the environment, and students were assessed through their lab reports (~4,000 words per experiment). Lab report guidance and a marking rubric are available in the *Supporting Information* (main DOC). Using the British grading classification, in one cohort the majority of students were awarded a lower 2:1 (three of five students receiving 60–65%), with the remaining students awarded an upper 2:1 (65–70%) and a first (>70%) (discussed further in the *Supporting Information*, main DOC).

We reviewed lab reports to find evidence of learning outcomes, discussed fully in the *Supporting Information* (main DOC). In summary, students understood the difference between components and species in a geochemical model. Students compared the pH dependent protonation of adsorbent surface functional groups ($>\text{SOH}$) to the pH speciation of aqueous oxyanions, and could describe the diffuse double layer (DDL) model's representation of the electrical double layer (EDL) as a surface layer of adsorbate ions

surrounded by a diffuse layer of electrolyte counterions. Students described the increased adsorption of As(V) onto goethite at lower pH values using the electrostatic attraction of oxyanions to a positively charged surface, and contrasted this to weak pH dependence in the adsorption of neutral As(III). Students used their models to identify the concentration of initial arsenic at which treated water would fail to meet the World Health Organisation's $10 \mu\text{g L}^{-1}$ guideline limit. Understanding was limited around how increasing electrolyte concentrations increase the capacitance of the EDL and thus promote the formation of charged surface complexes. Discussion of additional literature was primarily focused around the role of phosphate as a competitor ion to As(V) adsorption.⁶¹

The two-day workshop for researchers and water professionals at CIATEC aimed to help participants understand adsorption quantitatively, and to solve engineering challenges around water treatment. Instead of a formal assessment, we assessed perceived learning outcomes using subjective surveys with a Likert scale (Figure 7). The workshop group comprised academics (e.g., PhD students with an interest in adsorbent materials) and water professionals (municipal drinking water supply managers). Before the workshop, most participants already somewhat or strongly agreed that they understood the chemistry of (i) water contaminants; (ii) adsorption; and (iii) the properties that make effective adsorbent materials. Despite this strong foundation, the proportion of participants who agreed with these three statements increased after the workshop by 28%, 39%, and 39% respectively. Before the workshop, only a minority of participants expressed confidence toward modeling adsorption reactions and using geochemical software (39% and 22%, respectively). After the workshop, the proportion of participants confident modeling adsorption reactions increased from 39% to 76% and the average Likert scale rating increased by 0.8 points (out of 4). The proportion of participants confident using geochemical software also increased from 22% to 65% and the Likert scale rating

increased by 1.2 points. The methodology and further analysis are provided in the [Supporting Information](#).

When taught to undergraduate students in 2020, the laboratory course was delivered remotely due to campus lockdowns in response to the COVID-19 pandemic. While wet laboratories were replaced with prerecorded videos, computational experiments proceeded with minimal changes thanks to video calling software. With free geochemical software available, modeling experiments might facilitate the teaching of adsorption chemistry where lab access is not available.

CONCLUSIONS

We present an experiment aiming to improve participants' understanding of adsorption, introduce the principles of surface complexation modeling, and introduce the use of geochemical software to solve environmental problems. Students successfully modeled arsenic adsorption with varying pH and ionic strength, and could explain their observations using an appropriate description of the chemistry. Academics and professionals became more confident modeling adsorption reactions using geochemical software.

The modeling experiment can be coupled with wet chemistry (as per the undergraduate courses),³⁵ or taught as a standalone class, if sufficient theory is provided (as per the workshop). An interesting application of this class might be the remote delivery of practical exercises when wet lab facilities are not available. While we focused the experiment around the use case of arsenic remediation via iron oxides, the experiment could be adapted to new adsorbate–adsorbent systems or other geochemical processes using modeling parameters from the literature.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available at <https://pubs.acs.org/doi/10.1021/acs.jchemed.3c01195>.

Modeling parameters, lesson plan, lab report guidance, marking rubric, and further analysis of learning outcomes([PDF](#), [DOCX](#))

Student handout for practical exercises ([PDF](#), [DOCX](#))

Presentation on surface complexation modeling ([ZIP](#))

Model answers for PHREEQC input and output files ([ZIP](#))

Model answer: As(V) (aq) pH speciation ([XLSX](#))

Model answer: Goethite surface acidity ([XLSX](#))

Model answer: Surface complexation ([XLSX](#))

Model answer: Influence of salinity ([XLSX](#))

Model answer: As(V) adsorption isotherm ([XLSX](#))

Model answer: Loops (pH adsorption edge) ([XLSX](#))

Model Answer: As(III) adsorption edge ([XLSX](#))

Precourse questionnaire ([PDF](#), [DOCX](#))

Postcourse questionnaires ([PDF](#), [DOCX](#))

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Notes

The authors declare no competing financial interest.

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