



Comment

Comment on Zhou et al. Adsorption Behaviors of Lanthanum (III) and Yttrium (III) Ions on Gibbsite. *Minerals* 2023, 13, 1530

Bahram Hosseini Monjezi  and Johannes Lützenkirchen * 

Institute for Nuclear Waste Disposal (INE), Karlsruhe Institute of Technology (KIT),
Hermann-von-Helmholtz-Platz 1, 76344 Eggenstein-Leopoldshafen, Germany; bahram.hosseini@kit.edu
* Correspondence: johannes.luetzenkirchen@kit.edu; Tel.: +49-721-608-2-4023

Abstract: We compare trends in experimental observations reported by Zhou et al. to relevant results from numerous previously published studies. Based on these comparisons, we question the reliability of the gibbsite titration data and consider the cation uptake curves to be incomplete and questionable as well. The adsorption edges in Zhou et al. are too flat compared to the typical adsorption edges reported in hundreds of studies. Finally, we are convinced that trends of cation adsorption with NaNO_3 content not only disagree with relevant, previously published results, but are even opposite to trends expected with increasing ionic strength, whenever such effects are observed. Finally, we discuss other inconsistencies in the experimental data.

Keywords: adsorption; gibbsite; lanthanides

The adsorption of inorganics on oxide-type surfaces is of relevance in many domains and has been the topic of various monographs [1,2]. Zhou et al. [3] present and discuss experimental results for the adsorption of La(III) and Y(III) on gibbsite, covering both kinetic data and steady state batch results. They systematically vary the ionic strength in the steady state adsorption study and observe that the corresponding uptake of both cations increases with the concentration of NaNO_3 . Titration data of their gibbsite samples are also included in the paper.

We are afraid that both the titration data and the steady-state uptake data are in conflict with a plethora of published data for oxide-type minerals in general. We first discuss the gibbsite titration data before turning to the cation adsorption results.

1. Potentiometric Titrations and Surface Charge. In Figure 3 of the original article, Zhou et al. [3] plot the pH values measured after the addition of a known volume of base (after stabilization of pH) vs. the total volume of base added at two different levels of NaNO_3 concentration. The lower salt level of 50 mM requires more addition of base than the 500 mM salt level; i.e., for otherwise identical conditions and in the absence of carbon dioxide as assured by an inert gas atmosphere (argon), in the titration experiments, according to Zhou et al., more proton release occurs from the suspension with less sodium nitrate. This contradicts the generally accepted trend, namely, the increase of proton-related surface charge density of oxide minerals with salt concentration for monovalent salts [1,4,5].

Figure 1 shows a comparison of results from various publications related to potentiometric titrations of gibbsite samples. The data are sometimes reported as pH values vs. volume added (A,B) or in terms of proton related surface charge density vs. pH (C,D). These literature data (B–D) all show that increasing ionic strength causes an increase in proton related surface charge density (in absolute values), in contrast to the data of Zhou et al. [3]. This is particularly clear in the comparison with the experimental results from the thesis of Barajas [6].

It is not clear what leads to the results in Figure 1A, and discussing the differences in the titration data at the low pH would be futile for the present authors in the absence of more information, such as data on the dissolution of gibbsite. Suffice it to say that at low



Citation: Hosseini Monjezi, B.; Lützenkirchen, J. Comment on Zhou et al. Adsorption Behaviors of Lanthanum (III) and Yttrium (III) Ions on Gibbsite. *Minerals* 2023, 13, 1530. *Minerals* 2024, 14, 1137. <https://doi.org/10.3390/min14111137>

Received: 23 May 2024

Accepted: 24 October 2024

Published: 11 November 2024



Copyright: © 2024 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (<https://creativecommons.org/licenses/by/4.0/>).

pH, the dissolution of gibbsite is extensive and needs to be accounted for when calculating relative charge density. Such dissolution (after a 72-h pre-equilibration at $\text{pH} \approx 3$) and subsequent precipitation (when increasing the pH) will affect the interpretation of the titration data of gibbsite. In Section 2.2 of the original paper, Zhou et al. discuss potential dissolution effects and justify pH restrictions in their uptake experiments partly by gibbsite dissolution effects [3], but this of course could also have been a reason to restrict the titration experiments to a similar pH range. As depicted in Figure 1B–D, literature data actually have such a restricted pH-range. The issue at lower pH levels are discussed elsewhere [7], where in particular data in the pH range of 3.1–4 are quoted to be subject to significant effects of dissolution, even for the very high solid content used in that work. The strong buffering slightly above pH 4 results in the pH hardly changing despite the addition of more than 1 mL NaOH. This can, for example, be the effect of neutralizing the protons from the initial acid addition or be due to reactions related to gibbsite dissolution/precipitation. Subsequently, the pH changes sharply from about 4.5–9.5 due to the addition of only 0.5 mL of titrant. We noticed that when plotting the data starting with pH 4.5, the volume of titrant added for the 500 mM salt level is higher than that for the 50 mM solution, which would agree with higher relative changes in surface charge in the former. The steep curve in this pH range also raises suspicion in particular since no blank titration curve is reported. A blank titration would allow for an estimation of whether the amount of gibbsite in the vessel was sufficient to obtain reliable data. Steep curves in acid–base titrations of oxides, as in Figure 1A, between pH 4.5 and 9 may be too close to the blanks (i.e., titrations in the absence of the solid). If blank and solid titration data are too close, evaluating the solid titration data becomes nearly impossible. The aim is to obtain much more proton reactivity from the surface than from solution reactions. An insufficient quantity of protons coming from (too little) surface area compared to the proton reactions in solution leads to a substantial increase in relative errors.

Besides the steep curves, the intersection point between two titration curves as a measure of the point of zero charge (pzc) is certainly not recommended. In such cases, the intersection point (cip) is not conclusive, and a third salt level is required to prove the intersection point is really a common one. However, even in the presence of specific adsorption, a common intersection can be obtained [8], and this makes it necessary to measure additional quantities like electrophoretic mobility, which, unlike acid–base titration, can yield absolute zero electrokinetic charge. If the corresponding pH (i.e., the isoelectric point (iep) at which the electrokinetic charge is zero) concurs with the cip, one can be reasonably sure that the pristine pzc of the solid has been determined. Ultimately, the pzc reported by Zhou et al. [3] would not be deemed sufficiently reliable to be included in compilations of pzcs [9,10], even if it falls within the expected range for gibbsite [10].

The leveling off in the pH measurements at added volumes above approximately 2 mL can again be related to dissolution and the formation of $\text{Al}(\text{OH})_4^-$ in solution or the required increased addition of NaOH to elevate the pH at such high levels.

To sum up, not only are the titration data in conflict overall with the common observations of many papers, but the pzc inferred from the titration data is not reliable.

2. Trivalent cation adsorption on gibbsite. The results from Figure 5 of the original paper [3], replotted in Figure 2A, summarize the observed effects of pH and ionic strength on the reported adsorption of Y^{3+} ions on gibbsite [3]. While the increase in Y-uptake on gibbsite under the given conditions with the elevation of pH values from 4 to 7 is expected, the reported results are unexpected since significant uptake of above 60% occurs at pH 4. In typical experiments of this kind [1], measurements at lower pH levels would be attempted to obtain the full adsorption edge (which the original authors state they avoided due to gibbsite dissolution). Similarly, higher pH, where in corresponding work 100% uptake can be achieved [1], was avoided due to potential $\text{Me}(\text{III})$ precipitation [3]. Solubility and aqueous speciation calculations could have helped to avoid some problems. With respect to speciation, the authors do not seem to clearly state if the uptake experiments were performed in the presence or absence of CO_2 . Carbon dioxide related species may affect the

speciation of the ions in solution and adsorb to oxide surfaces (as competitor or in ternary surface complexes).

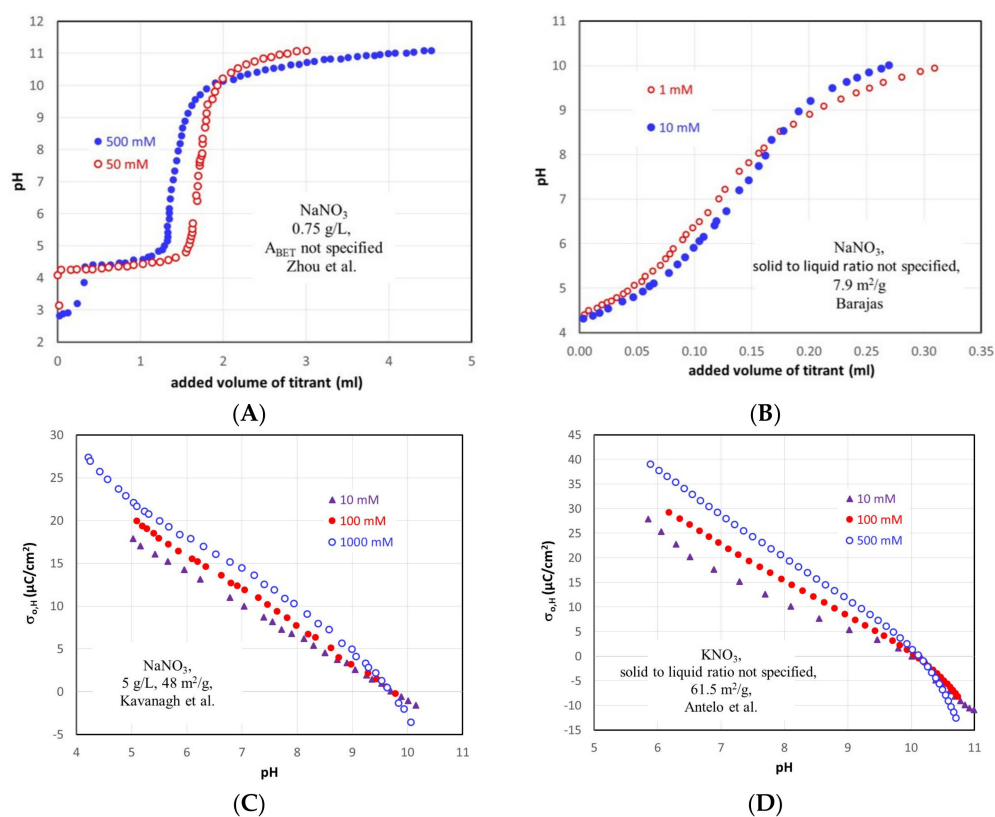


Figure 1. Results from potentiometric titrations of gibbsite plotted as either pH as a function of added volume of titrant (A,B) or as proton-related surface charge density ($\sigma_{o,H}$) as a function of pH (C,D). Data in A are from Zhou et al. [3], in B from Barajas [6], in C from Kavanagh [11], and in D from Antelo et al. [12].

In the uptake data (Figure 2A), the rise in the concentration of the background electrolyte in the solution (NaNO_3 , from 0.005 M to 0.5 M) increased uptake of Y^{3+} ions across the entire pH range. This contrasts with previous studies that report the inverse trend for a case in which an ionic strength effect is observed [13].

Zhou et al. [3] attribute the observed trend with NaNO_3 concentration to the compression of the electric double layer on the surface of gibbsite. They also cite corroborating work, but, it turns out that in the cited papers an increase in ionic strength leads rather to a decrease in ion adsorption.

To more clearly illustrate the problems, in Figure 2A we have replotted the data from Figure 5 of the paper by Zhou et al. [3]. For comparison, Figure 2B–D show literature data for trivalent cation adsorption on gibbsite [6,14,15]. Although different trivalent cations are involved, we can safely compare them to Y, because the behavior of the lanthanides (plus Yttrium and the trivalent actinides) is sufficiently similar in an aqueous system in pure solutions [16] and on surfaces [17]. In the literature data sets, uptake starts at around pH 4, exhibiting minimal to no adsorption at the lower pH, and proceeds to pH about 7 with 100% adsorption. All this is very different from the results shown in Figure 2A, where, already at pH 4, 50% adsorption is observed, and at pH 7 at most 90%. The uptake depends on the metal ion concentration to sorbent surface area ratio (see Figure 2B,D): at constant solid concentrations, an increased metal concentration pushes the adsorption edge to higher pH values. All this is well established [1,2,18] and can be simulated by surface complexation models of different complexities (including in the most advanced models molecular scale details).

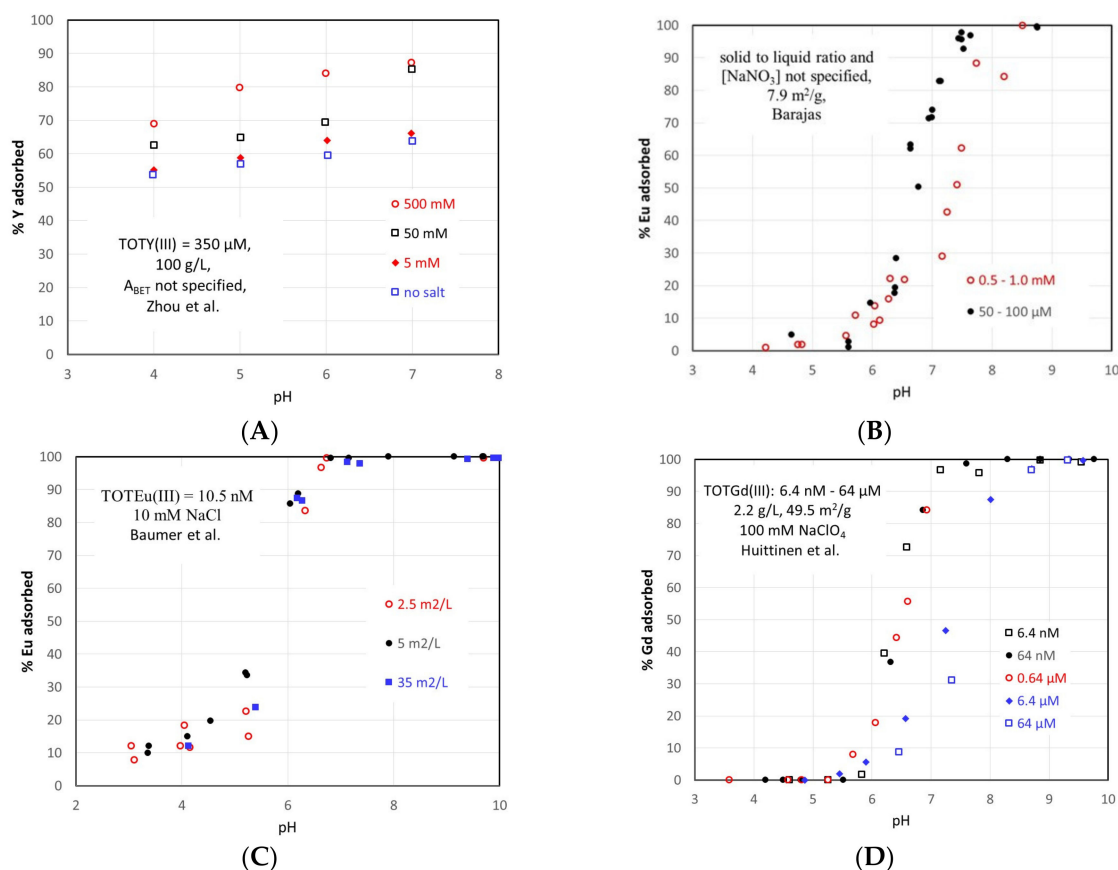


Figure 2. Results from batch adsorption experiments for trivalent lanthanide cation on gibbsite from the literature. Percentage adsorption as a function of pH. Data in (A) are from Zhou et al. [3], in (B) from Barajas [6], in (C) from Baumer et al. [14], and in (D) from Huittinen et al. [15].

Concerning the effects of salt content, Huittinen et al. also report that a variation of the background salt from NaClO_4 to NaCl (100 mM each) or from 10 mM NaCl to 100 mM NaCl does not shift the adsorption edge for a given Me(III) concentration at a constant gibbsite content [15], in contrast to the results in Figure 2A. So, in general, the literature data cited for directly comparable systems contradict the results in Figure 2A. These available sources are not referenced in the original paper by Zhou et al., maybe because they deal with nominally different trivalent cations.

Given the obvious problems in the reported results, it is permissible to discuss the origin of the discrepancies. One potential factor contributing to these differences may be the solid liquid separation technique employed by Zhou et al. [3]. They used a polyethersulfone (PES) membrane filter with a 450 nm pore size. Figure 2 of the original paper suggests that the gibbsite particles are rather large, so that the filter may have resulted in their complete solid–liquid separation. However, on the same figure, attached to the big ones, one may identify particles which are clearly smaller than the 450 nm and, thus, may have passed the filter. In such cases, it is advisable to measure the aluminum in the supernatant, which could be interesting regarding gibbsite solubility and important to check if particles can pass the filter [19]. Furthermore, the filter itself may adsorb Me(III) , so that the finally measured concentrations have been artificially lowered. This could result in an apparent increase in the observed uptake of Me(III) . The extent of such effects again depends on the precise details, i.e., how much volume is filtered (the higher the volume, the sooner the membrane is saturated with Me(III)). Blanks then help check potential losses of target ions on the filter. This may also vary depending on pH and salt level. To ensure the accuracy of results and mitigate potential artifacts, cross-checking the stock solution concentration and the filtrates (preferably centrifugates) for Me(III) and aluminum concentration by another

method (i.e., ICP-MS) could be a robust approach. In summary, the uptake data reported by Zhou et al. in their Figure 5 [3] appear questionable.

3. Data inconsistencies. In Section 3.4 of the original paper, significant differences in scales are observed in Figure 6, with the pseudo-first-order data plotted from 0–70 h and the pseudo-second-order data from 0–120 min. It is not clear why the original authors chose to cut data for the pseudo-second-order model. All the more so since in the experimental part they state that the models were both fitted to data up to 2 h. In the caption to Figure 6, the experimental conditions are not specified, such as Me(III) concentrations, gibbsite content, or salt concentration (if any). This is true for most of the figures but the information for the data in Figure 6 can be retrieved in Section 2.3.

In Section 3.4 it is also stated that the “initial” pH in the isotherm study was 7, but the uptake of cations on oxidic minerals releases protons [20–22]. Due to the extremely steep titration curve of gibbsite at pH 7 (see Figure 1A), the pH may significantly decrease with a total cation concentration of 350 μM . The pH should be constant for these experiments, but it is not clear at all whether the pH was kept constant and, if this was done, how it was achieved. One may also compare the uptake in the kinetic experiment to that of the steady state result at pH 7 in the absence of salt (Figure 5 and Figure 6 in the original paper, respectively). In the former, the ratio of La to Y adsorbed is about $0.32/0.2 = 1.6$, i.e., 1.02 after correction for molar masses (left part of Figure 5), and $0.31/0.15 = 2.1$, i.e., 1.32 after correction for molecular masses (right part of Figure 5), whereas in the latter case it is about $72/60 = 1.2$. In Figure 4, probably the same experimental results as in Figure 6 (left) are plotted, just in other units; the ratio in percentage uptake is quoted to be $70/65 = 1.08$.

The overall consistency of the data becomes questionable, particularly since we only found the applied equilibration time of 72 h for the isotherm, and it is unclear whether this timeframe is applicable to the pH-dependent study. The absence of the precise conditions in the figure captions makes it very awkward for reviewers and readers to compare the data. Clarity and precision in reporting experimental parameters are fundamental for enhancing the reproducibility and comprehensiveness of the experimental conditions and observations. The authors of the original paper could have plotted the data from the different sources (Figure 4 and Figure 5) for pH 7 and 350 μM total M(III), in the absence of salt for example, in the Figure reporting the isotherm at pH 7.

Section 3.5 of the original article treats the results from adsorption isotherm experiments at constant pH thermodynamically. Maximum uptake is presented in mg/L or ppm. However, for improved comparability across studies, moles per square meter is appropriate (gibbsite preparations exist with a wide range of specific surface areas [1]). The frequently used unit milligrams per gram (mg/g) to compare maximum uptake between different solids also falls short of the appropriate scale. Since adsorption is a surface process, surface area is the more appropriate basis on which to compare. For the solute adsorbed, molar units are preferable to mass-based units if one wants to compare uptake between different solutes. Zhou et al., in the same section, report Freundlich model fits, but in Figure 8 (right) and in Table 2, the units of the plotted quantities are not given, and those of the Freundlich-constant K_F are missing. The quantities in the logarithmic terms should be dimensionless, so the quantity given should be divided by the unit. Thus, the published parameters cannot be used for calculations without figuring out the correct units in Figure 8; e.g., by assuming the same units were used as in Figure 7. In that figure, it is not clear what the lines correspond to. In the case of Langmuir isotherms, the Q_{max} value appears lower than the one in Table 2.

On each graph or the associated captions, the precise conditions of the experiments should be given, which makes it easier, e.g., for referees to crosscheck data. The authors of the original paper have missed the opportunity to do such crosschecks by themselves, for example, by plotting the concomitant results from the pH-dependent data at pH 7 in the isotherm at pH 7. For the isotherm, total concentrations of 300 and 400 μM were used (amongst others) according to the information in the experimental part. The 350 μM concentration, which was not used in the isotherm study but in the pH-dependent mea-

surements, could have served as a cross-check. As already pointed out, the authors need to state whether carbon dioxide was excluded in the cation uptake experiments: CO₂ is recognized for its adsorption tendencies on mineral surfaces [23]; its capacity to form complexes with metal ions both in solution [16] and on surfaces [24] introduces further complexity. The presence of CO₂ potentially influences the speciation of dissolved ions; the potential formation of carbonate containing solid phases with metal ions is also possible and will directly impact the interpretation of the cation uptake results. Much of this can be evaluated beforehand by the appropriate speciation calculations.

Some remarks in the original paper may suggest that the final pH was not reported in all cases. The adsorption of cations releases protons into the solution and this changes the pH. Variations in pH directly impact the chemical behavior in the system (speciation of the cations, for example), and such processes can even lead to higher than expected uptake, as discussed elsewhere [25]. The pH-drifts depend on the conditions of the experiments and the properties of the components. Concerning the study of Zhou et al. [3], the combination of high metal ion concentrations and the steep titration curve suggest that this could have influenced the results. It could also explain why the uptake of Y decreases in the isotherm experiment, since a decrease in pH during the experiment would decrease metal ion uptake. However, the desorption process may be sluggish, and then the initial adsorption of metal ions at a given pH may persist, since the expected desorption may not occur rapidly enough during the experiment. This sluggish desorption could potentially contribute to the high uptake at low pH reported in the pH-dependent experiments, especially if the reported pH values represent the initial rather than the final conditions. Unfortunately, many options for speculation are available here.

4. Modelling. It can be discussed whether such data sets should be modelled using, e.g., a surface complexation model. This would make sure, for example, that data consistency is checked, since the authors would need to invest more into analyzing the data. Moreover, it would probably make hundreds of papers more useful, since the data could be used in comprehensive modelling efforts that lead to databases such as the work by Dzombak and co-workers [1,2,18].

5. The Materials and Methods section in the paper by Zhou et al. [3] lacks crucial pieces of information that should be included in any such publication. For instance, this section should have started with a detailed description of the materials used in the study, such as the source of the gibbsite sample, the rare earth ions (lanthanum and yttrium), and any specific chemicals used for the experiments. This would definitely provide essential information for replicating the study and understanding the experimental procedures. Most prominently, the specific surface area of the gibbsite is not reported. This value is necessary, for example, for the calculation of specific surface charge density to enable comparison of the results of the potentiometric titrations with previously published studies. Moreover, calculating the uptake of the trivalent cations (normalized to surface area) could further help to understand whether the reported results are within expected ranges. For accurate and comprehensive interpretation of the adsorption studies, it should be clearly stated whether the experiments were conducted in the presence or absence of carbon dioxide. Not only can CO₂ species can adsorb to oxides [23,26,27], they can also form complexes with the trivalent cations in solution [28], (see references therein). Additionally, in principle, they can interact at the surface of these minerals through ternary surface complexes [29]. Furthermore, carbonate may even compete for sites with strongly adsorbing anions like phosphate on oxide surfaces [30]. Ideally, one would find a description of the pH-calibration procedure, which can be done on the proton concentration scale, the activity (pH) scale, employing two or three buffers, or be carried out using more sophisticated methodologies. The purpose of the experimental methods and procedure sections is to report comprehensive details that would allow readers to redo the experiments. Therefore, the meticulous reporting of such information holds significant value.

In summary, a substantial amount of problematic issues in the paper by Zhou et al. [3], ranging from lack of information about experimental procedures to conflicting results

compared to previously published work was found. Previous literature (and we only cited a few of the studies dealing with adsorption of cations to gibbsite) is from our point of view not sufficiently considered. For example, besides the papers by Weerasoonya and co-workers [4,31–33] being of relevance, many others are. In particular, the book on adsorption on gibbsite by Karamalidis and Dzombak would have been a good source [1].

Author Contributions: All authors contributed equally. All authors have read and agreed to the published version of the manuscript.

Funding: This work was funded by the Federal Ministry for the Environment, Nature Conservation, Nuclear Safety and Consumer Protection (BMUV), grant number 02E12052C.

Conflicts of Interest: The authors declare no conflicts of interest.

References

1. Karamalidis, A.K.; Dzombak, D.A. *Surface Complexation Modeling: Gibbsite*; John Wiley & Sons: Hoboken, NJ, USA, 2011.
2. Dzombak, D.A.; Morel, F.M.M. *Surface Complexation Modeling: Hydrous Ferric Oxide*; Wiley: Hoboken, NJ, USA, 1990.
3. Zhou, Z.; Wan, Q.; Yu, W.; Nie, X.; Yang, S.; Yang, S.; Qin, Z. Adsorption Behaviors of Lanthanum (III) and Yttrium (III) Ions on Gibbsite. *Minerals* **2023**, *13*, 1530. [\[CrossRef\]](#)
4. Weerasooriya, R.; Dharmasena, B.; Aluthpatabendi, D. Copper–gibbsite interactions: An application of 1-pK surface complexation model. *Colloids Surf. A Physicochem. Eng. Asp.* **2000**, *170*, 65–77. [\[CrossRef\]](#)
5. Hiemstra, T.; Yong, H.; Van Riemsdijk, W.H. Interfacial Charging Phenomena of Aluminum (Hydr)oxides. *Langmuir* **1999**, *15*, 5942–5955. [\[CrossRef\]](#)
6. Barajas, C.L. *The Effect of Desferrioxamine B on Eu(III) Interactions with Gibbsite*; The Ohio State University: Columbus, OH, USA, 2002.
7. Rosenqvist, J.; Persson, P.; Sjöberg, S. Protonation and Charging of Nanosized Gibbsite (α -Al(OH)₃) Particles in Aqueous Suspension. *Langmuir* **2002**, *18*, 4598–4604. [\[CrossRef\]](#)
8. Lyklema, J. Points of zero charge in the presence of specific adsorption. *J. Colloid Interface Sci.* **1984**, *99*, 109–117. [\[CrossRef\]](#)
9. Kosmulski, M. *Surface Charging and Points of Zero Charge*; Taylor & Francis: Oxfordshire, UK, 2009; pp. 1–1065.
10. Kosmulski, M. *Chemical Properties of Material Surfaces*; CRC Press: Boca Raton, FL, USA, 2001.
11. Kavanagh, B.V.; Posner, A.M.; Quirk, J.P. Effect of polymer adsorption on the properties of the electrical double layer. *Faraday Discuss. Chem. Soc.* **1975**, *59*, 242–249. [\[CrossRef\]](#)
12. Antelo, J.; Fiol, S.; Mariño, S.; Arce, F.; Gondar, D.; López, R. Copper Adsorption on Humic Acid Coated Gibbsite: Comparison with Single Sorbent Systems. *Environ. Chem.* **2009**, *6*, 535–543. [\[CrossRef\]](#)
13. Hayes, K.F.; Leckie, J.O. Modeling ionic strength effects on cation adsorption at hydrous oxide/solution interfaces. *J. Colloid Interface Sci.* **1987**, *115*, 564–572. [\[CrossRef\]](#)
14. Baumer, T.; Kay, P.; Hixon, A.E. Comparison of europium and neptunium adsorption to aluminum (hydr)oxide minerals. *Chem. Geol.* **2017**, *464*, 84–90. [\[CrossRef\]](#)
15. Huittinen, N.; Rabung, T.; Lützenkirchen, J.; Mitchell, S.C.; Bickmore, B.R.; Lehto, J.; Geckeis, H. Sorption of Cm (III) and Gd (III) onto gibbsite, α -Al(OH)₃: A batch and TRLFS study. *J. Colloid Interface Sci.* **2009**, *332*, 158–164. [\[CrossRef\]](#)
16. Schijf, J.; Byrne, R.H. Speciation of yttrium and the rare earth elements in seawater: Review of a 20-year analytical journey. *Chem. Geol.* **2021**, *584*, 120479. [\[CrossRef\]](#)
17. Tertre, E.; Hofmann, A.; Berger, G. Rare earth element sorption by basaltic rock: Experimental data and modeling results using the “Generalised Composite approach”. *Geochim. Cosmochim. Acta* **2008**, *72*, 1043–1056. [\[CrossRef\]](#)
18. Mathur, S.S.; Dzombak, D.A. Chapter 16—Surface complexation modeling: Goethite. In *Interface Science and Technology*; Lützenkirchen, J., Ed.; Elsevier: Amsterdam, The Netherlands, 2006; Volume 11, pp. 443–468.
19. Honeyman, B.D.; Santschi, P.H. Coupling adsorption and particle aggregation: Laboratory studies of “colloidal pumping” using iron-59-labeled hematite. *Environ. Sci. Technol.* **1991**, *25*, 1739–1747. [\[CrossRef\]](#)
20. Gunneriusson, L.; Lövgren, L.; Sjöberg, S. Complexation of Pb (II) at the goethite (α -FeOOH)/water interface: The influence of chloride. *Geochim. Cosmochim. Acta* **1994**, *58*, 4973–4983. [\[CrossRef\]](#)
21. Gunneriusson, L. Composition and stability of Cd(II)-chloro and Cd(II)-hydroxo complexes at the goethite (ALPHA-FeOOH) water interface. *J. Colloid Interface Sci.* **1994**, *163*, 484–492. [\[CrossRef\]](#)
22. Lövgren, L.; Sjöberg, S.; Schindler, P.W. Acid/base reactions and Al (III) complexation at the surface of goethite. *Geochim. Cosmochim. Acta* **1990**, *54*, 1301–1306. [\[CrossRef\]](#)
23. Su, C.; Suarez, D.L. In Situ Infrared Speciation of Adsorbed Carbonate on Aluminum and Iron Oxides. *Clays Clay Miner.* **1997**, *45*, 814–825. [\[CrossRef\]](#)
24. Bargar, J.R.; Reitmeyer, R.; Lenhart, J.J.; Davis, J.A. Characterization of U (VI)-carbonato ternary complexes on hematite: EXAFS and electrophoretic mobility measurements. *Geochim. Cosmochim. Acta* **2000**, *64*, 2737–2749. [\[CrossRef\]](#)
25. Lützenkirchen, J. Evaluation of Experimental Procedures and Discussion of Two Different Modelling Approaches with Respect to Long-term Kinetics of Metal Cation Sorption onto (Hydr)oxide Surfaces. *Aquat. Geochem.* **2001**, *7*, 217–235. [\[CrossRef\]](#)

26. van Geen, A.; Robertson, A.P.; Leckie, J.O. Complexation of carbonate species at the goethite surface: Implications for adsorption of metal ions in natural waters. *Geochim. Cosmochim. Acta* **1994**, *58*, 2073–2086. [[CrossRef](#)]
27. Villalobos, M.; Leckie, J.O. Carbonate adsorption on goethite under closed and open CO₂ conditions. *Geochim. Cosmochim. Acta* **2000**, *64*, 3787–3802. [[CrossRef](#)]
28. Philippini, V.; Vercouter, T.; Vitorge, P. Evidence of Different Stoichiometries for the Limiting Carbonate Complexes across the Lanthanide (III) Series. *J. Solut. Chem.* **2010**, *39*, 747–769. [[CrossRef](#)]
29. Villalobos, M.; Trotz, M.A.; Leckie, J.O. Surface Complexation Modeling of Carbonate Effects on the Adsorption of Cr (VI), Pb (II), and U (VI) on Goethite. *Environ. Sci. Technol.* **2001**, *35*, 3849–3856. [[CrossRef](#)] [[PubMed](#)]
30. Mendez, J.C.; Hiemstra, T. Carbonate Adsorption to Ferrihydrite: Competitive Interaction with Phosphate for Use in Soil Systems. *Acs Earth Space Chem.* **2019**, *3*, 129–141. [[CrossRef](#)]
31. Weerasooriya, R.; Seneviratne, W.; Kathirarachchi, H.A.; Tobschall, H.J. Thermodynamic assessment of Hg (II)-gibbsite interactions. *J. Colloid Interface Sci.* **2006**, *301*, 452–460. [[CrossRef](#)] [[PubMed](#)]
32. Weerasooriya, R.; Wijesekara, H.K.D.K.; Bandara, A. Surface complexation modeling of cadmium adsorption on gibbsite. *Colloids Surf. A Physicochem. Eng. Asp.* **2002**, *207*, 13–24. [[CrossRef](#)]
33. Weerasooriya, R.; Aluthpatabendi, D.; Tobschall, H.J. Charge distribution multi-site complexation (CD-MUSIC) modeling of Pb(II) adsorption on gibbsite. *Colloids Surf. A Physicochem. Eng. Asp.* **2001**, *189*, 131–144. [[CrossRef](#)]

Disclaimer/Publisher’s Note: The statements, opinions and data contained in all publications are solely those of the individual author(s) and contributor(s) and not of MDPI and/or the editor(s). MDPI and/or the editor(s) disclaim responsibility for any injury to people or property resulting from any ideas, methods, instructions or products referred to in the content.