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PhreeFit: A powerful tool to find the globally optimal parameters of surface complexation models

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Surface complexation models (SCMs) are used to predict the adsorption of solutes to solids based on reaction thermodynamics. By incorporating the speciation of elements, surface electrical properties of sorbents, and structures of adsorbed species on the surface, SCMs provide superior representations of the mechanisms of solute adsorption compared to empirical adsorption models. For this reason, SCMs are powerful tools for investigating the bioavailability of elements, the reactivity of surfaces, and the fate of elements when being transported across changing aqueous environments. However, existing SCM optimization programs often fail to converge because they do not find the global optimum solution, which represents the best mathematical solution for parameters such as proton and metal binding constants or corresponding surface site concentrations. Furthermore, they also lack universality in optimizing any of the SCM parameters and unfortunately do not have user-friendly interfaces. In this study, which uses the IPHREEQC library, the performance of the most popular global optimization algorithms used to estimate global optimum SCM parameters were applied to five experimental proton and metal adsorption data sets, involving nonelectrostatic, generalized diffuse double layer, constant capacitance, and charge-distribution multisite complexation models. The global optimization algorithms achieved overall better fits than existing fitting programs, including FITEQL, ProtoFit, MINFIT, and ECOSAT-FIT. Indeed, the algorithms accurately estimated various parameters such as intrinsic equilibrium constants, site densities, capacitances, and charge distribution coefficients, as well as solutions with multiple ionic strengths. Of the tested algorithms, the differential evolution algorithm converged to solutions with the shortest time, had the highest stability in reproducing a good fit in all the tested examples, and was not restricted by the quality of the initial guesses and the number of fitted parameters. Further tests on metal adsorption to biochar, minerals, and mineral-microbe aggregates showed consistently superior results to existing programs in convergence and finding optimal parameters. Based on these tests, we developed a program named “PhreeFit” with an open-source license. This easy-to-use tool promises to facilitate the construction of SCMs and hence enrich the broader use of SCM approaches within the scientific community.