Cation Competition in Soil Materials: Adsorption Equilibria and Transport

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Abstract

Binding of major cations to subsurface natural porous media plays an important role in issues related to degradation of physical structure of the porous media. These major cations are also known to compete with strongly binding cations for sorbing onto the porous media. As a result, an accurate description of cation competition is required to be able to quantitatively predict fate and transport of contaminants in natural porous media. The primary objectives of this study were (i) to measure competitive adsorption of major cations, Ca$^{2+}$, Mg$^{2+}$, and Na$^+$ and a trace metal cation, Cd$^{2+}$ to a natural soil material using simple batch techniques, (ii) to test the ability of simple (one-site) and complex (multi-site) phenomenological adsorption models to comprehensively describe adsorption data that span over several orders of magnitude in concentrations, and (iii) to measure multicomponent transport of Ca$^{2+}$ and Na$^+$ in soil columns and to compare experimental results with predictions obtained from the above mentioned adsorption models.

Competitive adsorption experiments were performed in laboratory batch experiments using a flow-through reactor technique in all possible binary combinations and selected ternary and quaternary combinations. Typically, soluble cation concentrations used for measuring adsorption isotherms spanned over at least four orders of magnitude. It was found that adsorption of the major cations to the soil material displayed specific preference in the following order: Ca$^{2+} >$Mg$^{2+} >$Na$^+$. This behavior as seen in binary adsorption systems was also clearly visible in ternary cases. In addition, exchange ratios between the mono- and divalent cations were usually less than two. Cadmium showed a strong dependence not only on the concentration of the electrolyte in the background, but also on the type of the electrolyte on the background. Calcium cation displayed the strongest competition to Cd$^{2+}$ adsorption followed by Mg$^{2+}$ and Na$^+$ in that order. These patterns were mainly observed in binary adsorption systems and were verified in several ternary and one quaternary adsorption systems. Adsorption of Cd$^{2+}$ was not accompanied by a proportionate release of cations present on the soil matrix indicating the specific adsorption mechanisms occurred.

It was found that one-site exchange (Gaines-Thomas, Vanselow, Gapon, and Černík conventions) and adsorption (competitive Langmuir) isotherms did not completely describe the experimental adsorption data in most cases. In
order to provide a better description of the adsorption data, an approach where
adsorption was assumed to occur at multiple adsorption sites was required.
This approach consistently provided a better description of the experimental
adsorption data. In cases where exchange ratios were less than two, a model
based on the combination of exchange sites that followed one-to-one and one-
to-two stoichiometry were required. Multi-site adsorption models based on a
combination of exchange isotherms provided similar fits of the adsorption data
regardless of the exchange convention used to construct the model. Multi-site
models based on competitive Langmuir isotherms provided the best description
of adsorption data as exchange isotherms are just limited cases of competitive
Langmuir isotherms.

The models constructed, both one-site and multi-site variations, were cou-
pled with a transport code IMPACT, a mixing-cell model, to predict transport
of Ca\(^{2+}\) and Na\(^{+}\) in laboratory soil columns. All predictions of transport were
based on exchange models constructed with Gaines-Thomas or Černík conven-
tions. As expected, one-site models were only moderately successful in predict-
ing all experimental breakthrough curves. Multi-site models were more suc-
cessful with the predictions. As multi-site exchange models (Gaines-Thomas
and Černík) gave a similar description of the adsorption data, they gave similar
predictions of the cations transport as well. Overall, models constructed with
exchange sites of mixed stoichiometry gave the best prediction of the break-
through curves. Local chemical equilibrium was assumed in all cases; based on
the predictions of transport, the assumption was good.

In conclusion, to accurately predict multicomponent transport two things
were essential. Firstly, high quality adsorption data that has been measured
over a large range of concentrations. Secondly, an adsorption model that could
describe the entire adsorption data well. Based on these two aspects one should
be able to provide an accurate prediction of cation transport. This modeling
approach may be extended for prediction of cation transport in larger and more
complex systems in field-scale with reasonable accuracy.
Zusammenfassung


Die experimentellen Daten konnten in den meisten Fällen weder mit one-site-Austauschisothermen (Gaines-Thomas-, Vanselow-, Gapon- und Černik-Konventionen) noch mit kompetitiven Langmuir-Adsorptionsisothermen komplett beschrieben werden. Für eine bessere Beschreibung der Daten war eine Näherung nötig, in der eine Adsorption an multiplen Adsorptionsplätzen ange-
