



Modeling Adsorption Kinetics of Magnesium and Phosphate Ions on Goethite by Empirical Equations

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Received: 07-11-2015

Accepted: 15-02-2016

Introduction: Natural environments, including soils and sediments, are open and complex systems in which physico-chemical reactions are in semi equilibrium state. In these systems, bioavailability of plant nutrients, like phosphate, is influenced by environmental conditions and concentrations of other ions such as calcium and magnesium. Magnesium is a dominant cation in irrigation water and in the soil solution of calcareous soils. Recent evidences show relative increase in the concentration of magnesium in irrigation water. Because of the importance of chemical kinetics in controlling concentrations of these ions in the soil solution and for understanding their effects of adsorption kinetics of magnesium and phosphate ions, in this research, adsorption kinetics of these two ions on goethite is investigated as function of time and pH in single ion and binary ion systems. The experimental data are described by using the adsorption kinetics equations. These data are of the great importance in better understanding adsorption interactions and ion adsorption mechanism. With respect to the importance of these interactions from both economical and environmental point of view, in this research, the kinetics and thermodynamics of phosphate and Mg^{2+} adsorption interactions were investigated as function of pH on soil model mineral goethite in both single and binary ion systems.

Materials and Methods: Kinetics experiments were performed in the presence of 0.2 mM magnesium and 0.4 mM phosphate in 0.1 M NaCl background solution and 3 g L⁻¹ goethite concentration as function of pH and time (1, 5, 14, 24, 48, 72 and 168 h) in single ion and binary ion systems. After reaction time, the suspensions were centrifuged and a sample of supernatant was taken for measuring ions equilibrium concentrations. Phosphate concentration was measured calorimetrically with the ammonium molybdate blue method by spectrophotometer (Jenway-6505 UV/Vis). Magnesium concentration was determined by atomic absorption spectrophotometer (AA-670 Shimadzu AA/FE). The amounts of adsorbed ions were calculated from the difference of the initial and the equilibrium concentrations. The experimental data were described by using the several widely-used kinetic models. Models performance was evaluated based on their ability to describe experimental data and obtained values for coefficient of determination (R^2) and standard error of the estimate (SE).

Results and Discussion: The results demonstrate that phosphate and magnesium adsorption on goethite reached equilibrium within the 24 h equilibration time. The equilibration time is, however, pH-dependent. No systematic differences are observed among time-dependent adsorption isotherms for phosphate at $pH < pH_{PZC}$ and for magnesium at $pH > pH_{PZC}$. It seems that the effect of pH on kinetics of phosphate and magnesium adsorption is related to the mineral surface charge, which influences electrostatic interactions between the ions and the surface charges. Thus electrostatic attractive and repulsive forces dominantly control the reaction. The equilibration time for phosphate and magnesium adsorption on goethite was calculated to be ≤ 1 h when electrostatic forces are attractive and approximately 24 h when electrostatic forces are repulsive. In binary ion systems, phosphate and magnesium enhanced the amount and accelerated the adsorption rate of each other. Adsorption of phosphate could reverse electrostatic forces from repulsive to attractive for the adsorption of magnesium and vice versa. Also, because of the smaller ionic radius of magnesium (0.065 nm) in comparison with phosphate (0.22 nm), reduction in equilibration time of magnesium adsorption in the presence of phosphate could be partly diffusion-controlled. Fitting different kinetic models on experimental data showed that pseudo-second order model can successfully describe phosphate and magnesium adsorption data in both single and binary ion systems with highest determination coefficient ($R^2 \sim 0.99$) and lowest standard error of the estimate ($SE < 0.01$). The experimental data could also be described reasonably well by diffusion-controlled kinetics models, i.e. Elovich and parabolic diffusion models. The latter equations had less agreement with the data, i.e. their coefficient of determination was in the range of 0.7-0.9. This might suggest that adsorption of phosphate and magnesium on goethite, at least in diluted suspensions, is chemical-controlled and diffusion is not the dominant rate-limiting factor.

Conclusions: Equilibration time for phosphate and magnesium adsorption on goethite is pH-dependent. Adsorption of magnesium is significantly faster in the presence of an oxyanion like phosphate, and vice versa.

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This effect is related to the change in electrostatic potential at the mineral surface upon phosphate adsorption. Description of experimental data by various kinetic models indicated that the pseudo-second order model can successfully describe phosphate and magnesium adsorption data in both single and binary ion systems.

Keywords: Adsorption, Electrostatic, Kinetic, Magnesium, Phosphate

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