An indicator dye-sorption method for measuring the surface pH of natural soil minerals

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The surface acidity of natural soil minerals is an interesting aspect of surface structure, which plays an important role in the soil acidification. The acid strength can be defined by the surface or microenvironment pH, and usually indicated by the pH of the suspension. However, the pH of the suspension is influenced by mineral concentration, solubility and particle size, so it can not accurately represent the pH in the real microenvironment of mineral surfaces. Fortunately, some dyes, so-called “indicator” ($InH \leftrightarrow In^- + H^+$), adsorbed on the mineral surface, can be protonated and deprotonated when reacting with their surface acid or base groups, and the ionization degree of the dyes were consisitent with that in aqueous solution at the same pH values. The purpose of this study is to establish a more feasible method for determining the mineral surface pH by measuring the adsorbed pH indicators with a diffuse-reflectance spectroscopy. In this study, high purity nanoscale kaolin, alumina, silica, and titanium oxide were used as mineral samples, and six dyes (thymol blue, methyl orange, bromocresol green, bromocresol purple, neutral red, and phenol red) with measuring pH range of 1.2-9.6 were used as pH indicators. Each sample was colored by a small amount of the indicators with appropriate concentration, and dried at 60 °C. Their diffuse-reflectance spectra were collected in an UV-visible spectrophotometer with an integrated sphere. The mineral surface pH values could be calculated based on the acid-base (In^-/InH^+) peak ratios of adsorbed indicator compared with the aqueous indicator, which representing the same degree of dye ionization. The results showed that the concentrations of indicators (2 mg ml^{-1}) were appropriate for coloring minerals. The calculated pH values of kaolin, silica, titanium oxide, and alumina were successfully obtained as 4.95, 4.46, 6.07, and 8.03, respectively. This study provides a approach for determining the surface pH of minerals, which may be very helpful for understanding the surface acid-base reactions and potentially developing a more robust method for evaluating the soil acidification.

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