Soil Adsorption Phenomena and the Langmuir Equation

Harter and Baker (1977) have proposed that the concentration of the desorbed ionic species in solution will alter the reaction of the newly adsorbed species with the surface in such a way that it will cause the commonly observed curvilinearity of the linear transformation of the Langmuir isotherm. This, of course, results in an under-estimate of the calculated adsorption maximum which invariably follows the use of the simple Langmuir equation (Gunary, 1970). They apparently assume that the theoretical basis for this claim is self-evident as their only support is to test the goodness-of-fit of a modified and rather more complex form of the Langmuir isotherm. This involves the determination of the concentration of the desorbed ion in solution.

Unfortunately, the application of their equation to some Zn adsorption data appeared to give predicted adsorption values with the same shortcomings as the traditional Langmuir isotherm, namely a marked underestimate of the adsorption maximum. In two of seven soils in which they compared their modified equation with the traditional Langmuir equation, the latter actually gave a better estimate of the maximum, and their modified equation was superior in only two of the seven soils. In spite of the necessity to make a number of questionable assumptions in the use of their equation, the wide scatter of points in their plotted data, and their admission that "the lack of agreement between observed and calculated adsorption at high adsorption may indicate two adsorption mechanisms", the authors surprisingly conclude "that the reported curvilinear relationship of C/x vs. C plots... can be due to the neglect of the effect of desorbed ions".

Although Harter and Baker deal with the development of the Langmuir equation, they fail to mention the two fundamental assumptions that Langmuir made when he derived his equation: uniformity of adsorption energy over the entire surface, and the absence of interactions between the adsorbate molecules. In a system as complex as soil, it seems unreasonable to assume that all adsorbing components will have the same bonding energy for any particular species. It is more likely that there will be a range of bonding energies which, in the simplest model, comprise a population of sites with high bonding energy, and another population of sites with low bonding energy (Holford and Mattingly, 1975). It seems to have been overlooked that Langmuir himself proposed an extended form of his simple equation to describe this situation.

It follows that the curvilinear phenomenon is simply caused by the fact that Langmuir's first assumption does not apply, and one must postulate the occurrence of a nonuniform adsorption energy in soils. In this circumstance the Langmuir isotherm to linear form will produce a curve because adsorption occurs simultaneously on all surfaces in direct proportion to the bonding energy and frequency of the unoccupied sites. The attempt by Harter (1968) and others (Syers et al., 1973) to resolve the curve into two straight lines is not valid because this procedure assumes that adsorption on the low energy sites occurs after adsorption on the high energy sites.

The four parameters of the Langmuir "two-surface" equation may be calculated by the method of least squares, the method of numerical optimization for the bonding energy terms. Using this procedure, Holford et al. (1974) obtained near-perfect fits to phosphate adsorption isotherm data for soils from Britain and Australia. Subsequently they demonstrated the significance of the Langmuir parameters, particularly those of the high-energy sites, in controlling...