

NITRATE ADSORPTION MODEL FOR GEORGIA VARIABLE CHARGE SUBSOILS

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Abstract. Nitrate adsorption in subsoil affects nitrate leaching, which in turn can affect water quality. A model to describe the adsorption of nitrate in acidic variable charge subsoils in Georgia and other tropical and subtropical areas is proposed. In the first step, a portion of the effective charge that vanishes as a result of the overlapping of oppositely charged diffuse layers on different colloids, termed “the mutually neutralized charge”, σ_M , is established. The “newly developed charge”, σ_N , is developed during the second step, in response to ionic strength increase in subsoil solution. The reestablishment of these two components of the effective charge causes “salt adsorption”. The last step is “ionic exchange” with the corresponding effective charge component σ_{EX} . The separation of “temporarily effective” ($\sigma_M + \sigma_N$) from “permanently effective” (σ_{EX}) portions of the effective charge is very crucial when displacement and transport of ions like NO_3^- are considered, in order to understand that these ions are only temporarily adsorbed and can be immediately leached out by rain.

INTRODUCTION

Salt adsorption (Thomas, 1960; Wada, 1984; Marcano-Martinez and McBride, 1989; Alva et al., 1991; Bolan et al., 1993; Bellini et al., 1996; Pearse and Sumner, 1997; Qafoku, 1998) is a relatively new concept related to simultaneous cation and anion adsorption with no net release of other ions into the soil solution. While some proposed mechanisms have been advanced, no unified and clear explanation of the phenomenon has been established.

The objective of this study was: (1) to develop a model to explain salt adsorption and describe indifferent ion adsorption in acidic variable charge subsoils and (2) to provide experimental evidence to support the model.

THE MODEL

Sposito (1984) proposed the following equation for the net total particle charge (σ_p):

$$\sigma_p = \sigma_0 + \sigma_H + \sigma_{IN} + \sigma_{OS} \quad (1)$$

where σ_0 , σ_H , σ_{IN} , and σ_{OS} , are permanent structural charge, the net proton charge, inner-sphere complex charge, and outer-sphere complex charge, respectively. A more precise algebraic formulation of this equation is:

$$(\pm)\sigma_p = (-)\sigma_0 + (\pm)\sigma_H + (\pm)\sigma_{IN} + (\pm)\sigma_{OS} \quad (2)$$

where the sign of the net total particle charge depends on the sign of the sum in the right hand side of the equation (2). The net total particle charge is balanced by the diffuse-ion swarm charge (σ_D) (Sposito, 1989):

$$(\pm)\sigma_p = (\pm)\sigma_D \quad (3)$$

where σ_D is equal in magnitude and opposite in sign to σ_p . The net total particle charge equation may be written as:

$$(\pm)\sigma_D + (\pm)\sigma_{OS} = (-)\sigma_0 + (\pm)\sigma_H + (\pm)\sigma_{IN} \quad (4)$$

based on the fact that the total net surface charge results from isomorphic substitution and specifically adsorbed ions (Hunter, 1981). The ions that form outer sphere complexes with the surface reactive groups have at least one water molecule between them and the solid surface; the bonding is coulombic, long range (Langmuir, 1979) and they can be exchanged with indifferent ions in the soil liquid phase; so they may be considered as ions in the liquid layer most adjacent to the colloidal surface. The ions that are adsorbed by inner-sphere forces form “extensions” of the colloidal solid phase. Therefore, equation (4) separates the charge in the solid from that in the liquid phase near the colloidal particle. The last can be defined as the effective surface charge ($\sigma_{EFFECTIVE}$).

The surface charge in acidic variable charge subsoils is caused by the protonation and deprotonation reactions of hydroxyl groups on the surfaces of the colloids. When in contact with the subsoil solution or with an indifferent electrolyte at pH values 4 to 6 commonly found in these subsoils (Qafoku, 1998), the variable charge on a given soil constituent may be net uncharged, net negatively, or net positively charged (Chorover and Sposito, 1995). The mineralogy of these subsoils was found to be dominated by kaolinite, gibbsite, goethite, and hematite (Qafoku, 1998). Kaolinite’s point of zero charge (PZC) is between 2.8 and 2.9, while that of Al and Fe oxides is between 8 and 9 (Goldberg, 1996). As a result, kaolinite particles have

surface net negative charge and Fe and Al oxides have a net positive charge at pH 4 to 6. Assuming no permanent charge minerals are present and no inner-sphere complexes are formed, the net total particle charge equation (Sposito, 1989) for kaolinite and Al or Fe oxides particles can be written as:

$$\sigma_{O^-} = \sigma_{OS^+} + \sigma_{D^+} \quad \text{kaolinite} \quad (5)$$

$$\sigma_{H^+} = \sigma_{OS^-} + \sigma_{D^-} \quad \text{Fe/Al oxides} \quad (6)$$

where σ_{O^-} is the net proton charge on kaolinite surfaces generated from OH groups that have lost their protons, and σ_{H^+} is the net proton charge on Al and Fe oxides surfaces generated from OH groups which gain one proton. These equations show that effective charge is a direct function of subsoil pH. The right hand sides represent the effective surface charge ($\sigma_{EFFECTIVE}$). In other words, they represent cation exchange capacity (CEC) and anion exchange capacity (AEC) in subsoil. The variable charge subsoil is at PZNC when $(\sigma_{O^-}) + (\sigma_{H^+}) = 0$ or $(\sigma_{OS^+} + \sigma_{D^+}) + (\sigma_{OS^-} + \sigma_{D^-}) = 0$ and CEC equals AEC.

Variable charge soils have extremely low soil solution concentration (Gillman and Bell, 1978; Seaman et al., 1995; Qafoku, 1998) and leaching promotes the release of ions from the double layers into soil solution. Oppositely charged double layers on different colloids expand and overlap one another. At this moment, negatively charged silicates and positively charged sesquioxides mutually neutralize their particle charges. Under such conditions, the ions in the diffuse double layers of both colloids are no longer required to balance the respective particle charges, so that they are free to be leached and leave the system. This causes the double layer thickness to further increase with even greater mutual neutralization of the particle charge on the surfaces of oppositely charged particles and greater release of diffuse layer ions. The magnitude of the effective charge, expressed as the total amount of ions adsorbed, decreases and tends towards zero. Under extreme conditions, the outer-sphere and diffuse layer charges will be zero corresponding to the "isoelectric state" (Mattson, 1931). As a further development of the two step model proposed by Katou et al., 1996 to describe the anion adsorption, the following three step adsorption reaction is proposed to describe the adsorption of the ions of an indifferent electrolyte in contact with a highly weathered acidic variable charge subsoil.

Assume that the oppositely charged double layers are overlapping so that some of particle positive and negative charges on oppositely charged colloidal surfaces are neutralized by this direct interaction. On addition of electrolyte, these mutually neutralized charges now take up cations and anions in equivalent amounts essentially screening the surface charges from each other. The double layer thickness decreases until there is no longer any overlap. This reestablishes a portion of the effective charge measurable as exchangeable ions and can be termed "the

mutually neutralized charge (σ_M)", which measures the magnitude of the overlap between oppositely charged colloids. During this process the screening ions in the added electrolyte are completely depleted from the soil solution. With further addition of electrolyte, soil solution concentration begins to increase and previously uncharged sites on oppositely charged colloids now develop more positive and negative charges. This component of effective charge may be termed "the newly developed charge (σ_N)". σ_N is expressed as exchangeable ions needed to balance the new charge developed on variable charge surfaces when ionic strength is increased. The addition of indifferent ions into the solution drives the potential determining ions (pdi), H^+ and OH^- , onto the surface (Hunter, 1993). As indifferent electrolyte concentration increases, the potential falls off more rapidly at the surface, and the change in surface potential as a function of the distance from the surface is higher (Hunter, 1993). To keep the potential the same, one must increase the surface charge so that the amount of work to be done in bringing a new charge up to the surface remains the same (Hunter, 1993). Therefore, the charge is increased by the pdi adsorbed on the surfaces. The sum ($\sigma_M + \sigma_N$) is defined as the salt adsorption capacity of the soil (σ_{SA}).

When the salt adsorption capacity of the soil is satisfied and the concentration of the added electrolyte continues to build up in the soil solution, those ions originally present in the double layer at maximum overlap are now exchanged by the added ions and appear in the soil solution in stoichiometric amounts. This is the "ionic exchange" step and the corresponding effective charge component is the "ionic exchange or counterion charge (σ_{EX})". Hence, when pH is constant, the effective surface charge ($\sigma_{EFFECTIVE}$) may be written as:

$$\sigma_{EFFECTIVE} = \sigma_M + \sigma_N + \sigma_{EX} \quad (7)$$

Even though it is difficult to measure the contributions of σ_M and σ_N , the first term can be approximated from the electrical conductivity (EC) breakthrough curves obtained in leaching experiments (Qafoku, 1998). If one measures the ECEC or EAEC, that is the sum of all cations or anions adsorbed on the subsoils surfaces σ_{EX^+} or σ_{EX^-} , one can find an approximation for σ_N using equation (7). This can be measured when subsoil is near the PZSE where σ_N^+ equals σ_N^- . From what was presented above it is clear that when an electrolyte is added to soil, σ_{SA} ($\sigma_M + \sigma_N$) tends to zero while σ_{EX} increases toward $\sigma_{EFFECTIVE}$. With different methods proposed to measure CEC and AEC in soils, much higher concentrations of indifferent ion electrolytes than the native concentration of the soil solution are used (Gillman and Sumpter, 1986; Zelazny et al., 1996). They measure, in fact, the effective charge at a specific concentration or soil solution ionic strength. However, the effective charge in variable charge subsoils has three components (equation 7), two of

them being direct functions of the soil solution ionic strength. The total amount of the cations (or anions) adsorbed as outer sphere complexes and in diffuse layers on the colloids in the native acidic variable charge subsoils σ_{EX} , is the "real" effective charge in these subsoils. The indifferent ions temporarily used to satisfy the salt adsorption capacity of the subsoils can be "displaced" when the soil is leached out, because the compression/expansion of the diffuse layers is a reversible process. This phenomenon appears to be one of the unique chemical characteristics in variable charge soil systems. Therefore, equations (5) and (6) do not hold true because particle charges are greater or equal to the sums of cations and anions adsorbed in outer-sphere and in the diffuse layer.

EVIDENCE FROM THE LITERATURE TO SUPPORT THE MODEL

Salt adsorption is more frequently observed in soils with a low or very low soil solution concentration (Wada, 1984; Pearse, 1994; Qafoku, 1998) and the magnitude of this effect depends strongly on the initial ionic strength in soil or subsoil solution (Wada, 1984; Pearse, 1994; Qafoku, 1998). Thomas (1960) reported that the concentration of salts in the soil solution remained rather low even when salt was added because the soil acted both as a cation-exchanger and as a salt-sorber. This indicates that salt adsorption is not a simple stoichiometric ionic exchange reaction. Allophanic soils from Japan sorbed significant quantities of Na^+ and Cl^- , but neither aluminum hydroxide nor silica alone exhibited any salt sorption behavior (Wada, 1984). This is the strongest evidence that salt adsorption occurs only when two oppositely charged solid phases are present.

Some of the arguments presented in the study by Qafoku (1998) that support the model, are the following:

1. Salt adsorption is a common phenomenon in variable charge subsoils. The σ_M magnitudes, however, vary considerably with pH and electrolyte concentration of the subsoil solutions. This phenomenon is not a simple stoichiometric exchange reaction, because both, cations and anions of the added salt disappear from the subsoil solution. It is not either an exchange reaction between the ions of the added electrolyte and H^+ and OH^- adsorbed on outer sphere sites and diffuse layers on the subsoil colloids, because no exchange reactions with other ions were observed during the salt adsorption phase.

2. During the salt adsorption phase, the ionic strength of the subsoil solution does not change because the ions of the input solution are adsorbed with no net release of other ions into subsoil solution; therefore, no new charged sites can be generated in this phase, and only σ_M is satisfied. However,

charged sites can be generated when the concentration of the input solution starts to build up in solution when there is no more overlap. Therefore, three chemical phenomena are possible, namely salt adsorption (σ_M), new charge generation (σ_N), and stoichiometric exchange reactions (σ_{EX}).

3. Salt adsorption occurred only in subsoils where both, kaolinite and Al/Fe oxides were present in appreciable amounts and in colloidal suspension of mixtures of kaolin with synthetic goethite, and not in colloidal suspensions of only kaolin or goethite. This phenomenon occurs only when two types of oppositely charged colloids, kaolinite and goethite, are present.

4. Salt adsorption occurred when subsoils were treated with very dilute electrolyte solutions that do not promote the formation of inner-sphere complexes. Thus, it is caused by the adsorption of ions in the respective diffuse layers of oppositely charged colloids.

5. In some subsoils, large differences between ECEC (σ_{EX}) at native ionic strength and pH, and CEC ($\sigma_{EFFECTIVE}$) at native soil pH but measured in a much more concentrated subsoil solution were observed. The amount of charge created as a result of the increase in ionic strength σ_N , appears not to be sufficient to account for the enormous salt adsorption capacity this subsoil manifests. This supports the idea that a third component (σ_M) should be introduced in the effective charge formula ($\sigma_{EFFECTIVE} = \sigma_M + \sigma_N + \sigma_{EX}$).

6. Salt adsorption was found to be a reversible phenomenon because the adsorbed salt is "displaced" immediately after the subsoil is leached with a more dilute solution or distilled water, and $\sigma_{EFFECTIVE}$ tends towards σ_{EX} . The separation of "non-effective" ($\sigma_M + \sigma_N$) from "effective" (σ_{EX}) portions of the effective charge is very crucial when movement of ions like NO_3^- is considered. They can be leached out by rain.

7. At low concentrations and native pH, an L-type NO_3^- isotherm was observed in some subsoils. In these subsoils NO_3^- adsorption is not a linear function of NO_3^- concentration in the subsoil solution. Therefore, another term σ_M , besides σ_N , is needed to reinforce the dependence of NO_3^- adsorption to the electrolyte concentration in the subsoil solution.

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