Decisive Factors of Clay Dispersion in Alluvial Soils of the Nile River Delta – A Study on Surface Charge Properties

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Abstract: Clay dispersion in soils can result in reduced water infiltration and increased surface runoff. In order to improve the understanding of the decisive factors of clay dispersion of soil clays in alluvial soils of the Nile River Delta, the surface charge of the clay fraction of a typical Fluvisol was determined on its dispersion properties in dependence of pH, organic matter content, Na and Ca concentration. The surface charge was quantified by combining the electrokinetic signal of a Particle Charge Detector (PCD) with polyelectrolyte titration. The results revealed that at low pH the surface charge of both clay soil samples (original clay and the organic matter removed clay soil) had low negative values, which is due to the protonation of variable charge. With increasing pH, where deprotonation of functional groups occurs, the surface charge becomes more negative. This is most pronounced for the sample after organic matter removal. Here, surfaces of the clay minerals are not covered with organic matter and negatively charged silicate layers are detected better. On the other hand, this might be also due to the increase of the specific surface area due to the H_2O_2 treatment.

Key words: Surface charge · particle charge detector · clay dispersion · alluvial soils

INTRODUCTION

In the Nile Delta, fluvisols are the most common soil type. Fluvisols are relatively young soils developed on recently deposited stratified material, mainly fluviatile but also lacustrine, or marine sediments and on some of the coastal plains. The carbonate content is usually less than 4%. Organic matter content decreases irregularly with depth (although it remains above 0.35 % in the upper 1.25 m) and the soils contain sulfides in the Gr horizon. Generally fluvisols exhibit little horizonation, except for a weakly developed A-horizon and peaty horizons. They are the most intensively farmed soils in Egypt and have a high development potential due to the ease of irrigation and their ability to be double-cropped.

The delta ecosystem no longer receives a yearly input of sediments and nutrients from upstream due to the High Dam impact. Consequently, the soils of the floodplains are poor and large amounts of fertilizers are applied to the land each year. Run-off of fertilizers and dumping of wastewater and sewage sludge is leading to the accumulation of trace elements and salts in the

sediments of the delta [1]. Fertilizers, along with salt-water intrusion, have also caused the upper delta to become more saline. In the Nile Delta, salinity may continue to increase by the infiltration of seawaters as the delta face erodes and as erosion opens the existing lagoons to the sea. Rising sea levels of a half-meter due to changing global climatic conditions would be inundating the Nile River Estuary [2].

With high Na saturation of the exchange sites, Alluvisols of the Nile River Delta undergo degradation when used for agriculture. By irrigation clay leaching might be very intensive and often leads to subsoil compaction and pan formation, secondary salinization and gleying. Also the water erosion potential might increase. There are also potential wind erosion problems in silt-rich areas if the topsoil is allowed to dry out. Flocculation and dispersion of the clay affects many properties of the soil. Clay dispersion can result in surface crushing. As a consequence water infiltration might be reduced, which can increase surface runoff and erosion and as a result the fertility of the top soil will be reduced. Clay colloids that remain suspend in surface

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runoff or in water infiltrating into the soil can also enhance the translocation of adsorbed contaminants.

Beneath the different methods for characterizing the charge properties of particles the technique of the Particle Charge Detector (PCD) was selected. Here, the electrokinetic signal of the PCD is combined with polyelectrolyte titration, which allows the quantification of surface charge. Usually, surface charge of clay minerals is determined by using three different approaches: Ion adsorption, potentiometric titration and Electrokinetic's technique. Ion adsorption is time consuming. Potentiometric titration overestimates the surface charges. And the surface charge calculated by using electrokinetic's technique is also approximated due to the defect in the double layer theories and their assumptions.

The determination of clay dispersion characteristics, including surface charge properties is important to evaluate an appropriate soil management system. The dispersion characteristics are governed by many factors [3]. Therefore the effect of organic matter, pH, electrolyte concentration on surface charge and dispersion of typical soil clay fractions from the Nile River Delta was determined.

MATERIALS AND METHODS

Sample origin, preparation and characteristics: The A-horizon of a typical Fluvisol, the characteristic soil prevalent in the Nile River Delta, was sampled from the A-horizon in the agricultural road, close to Tanta city. The air dried sample was 2 mm sieved. The clay fraction (<2 μm) was separated by sedimentation/decantation after shaking and ultrasonic treatment (20 s) without further pretreatment. For comparison surface charge properties were also determined for the clay fraction where the organic matter was removed by wet oxidation (H_2O_2). The suspensions were flocculated with NaCl and washed until salt-free. The electrical conductivity of the suspensions was between 0.6 and 0.9 dSm^{-1}. The clay fractions were dried at 70°C and afterwards gently pounded in a mortar. The degree of dispersion of the dried sample was determined by electron microscopy (Fei, Quanta 200). According to X-ray diffraction and FT-IR-spectroscopy, the clay fraction contains of high amounts of smectite and also kaolinite. Traces of quartz were detected. The specific surface area, determined by N_2-adsorption (Quantasorb, Quantachrome), is 31 $m^2\ g^{-1}$ for the original clay and 46 $m^2\ g^{-1}$ for the one where organic matter was removed.

Quantification of surface charge: A particle charge detector (Mütek, PCD 03) was used by employing a titration with charge compensating polyelectrolytes [4]. This method is already well established for the determination of metal complexation capacities of aquatic humic substances [5], surface charge properties of soil clay fractions [6] and latex particles [7]. The endpoint of titration was at zero potential. For negative surface charge the cationic polyelectrolyte poly-DADMAC (poly-Dially-dimethyl-ammonium chloride) and for positive surface charge the anionic polyelectrolyte PES-Na (Sodium-Polyethylen-sulfonate) was used. For each titration 20 mg of the sample was mixed with 10 ml of distilled water, which was adjusted with 0.1 N HCl and 0.1 N NaOH to pH 5, 8 and 10. For the determination of surface charge at different Na- and Ca-concentrations (0-10 mmol L^{-1}) the chloridic salts were used. The pH of these solutions was adjusted to pH 5, 8, and 10. After dispersion by an ultrasonic treatment for 15 seconds, the sample was transferred into the titration cell. In a separate experiment, the Na- and Ca-concentration in the "equilibrium solutions" were determined by flame photometer (Cole Parmer 2655-10) and atomic adsorption spectroscopy (Perkin Elmer PE 3300), respectively.

Determination of the dispersion degree: For the determination of the dispersion properties at different ionic strength a determination in test tubes according to Lagaly *et al.*[8] was performed. Ten ml of clay suspension (20 mg clay fraction, 10 ml solution) was put in the test tube and dispersed by ultrasonic treatment for 15 seconds. After 2 hours, 2 ml of the suspension were sampled from the surface and the transmission was determined using UV-visible spectrophotometer (Varian Cary 50 scan) at 600 nm wavelength.

Microstructure of individual and aggregated particles: The microstructure of the particles as affected by Na- and Ca-saturation was determined by using an environmental scanning electron microscope (Fei, Quanta 200). Suspensions of Na- and Ca-saturated clay fraction were prepared on glass slides, air dried and sputtered with Au.

RESULTS AND DISCUSSION

Effect of pH on surface charge and clay dispersion: At pH 3 the surface charge of both samples has low negative values (Fig.1), which is due to the protonation of variable charge. With increasing pH, where deprotonation of functional groups occurs, the surface charge becomes
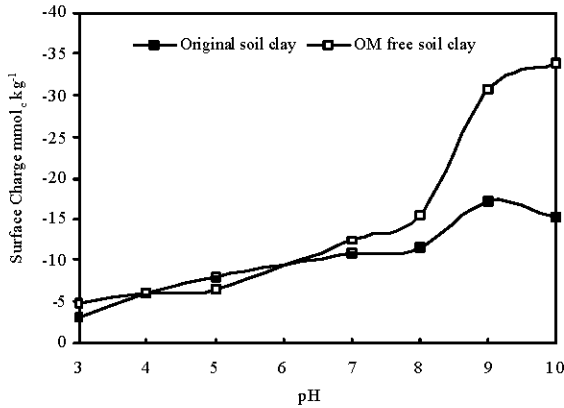
Fig. 1: Surface charge of the <2 μm fraction at pH 3, 4, 5, 7, 8, 9 and 10 before and after OM removal. Na-saturation of the exchange sites. The surface charge was determined in duplicate
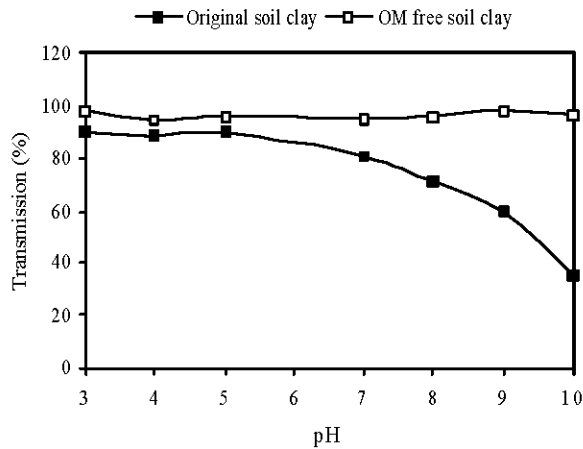

Fig. 2: Effect of pH on clay dispersion (measure: transmission) of the original sample and after OM removal
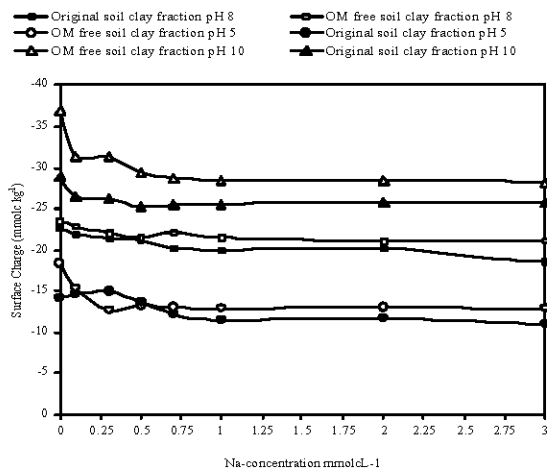

Fig.3: Surface charge as a function of Na-concentration at pH 5, 8 and 10 of the suspension of the original clay fraction and after OM removal
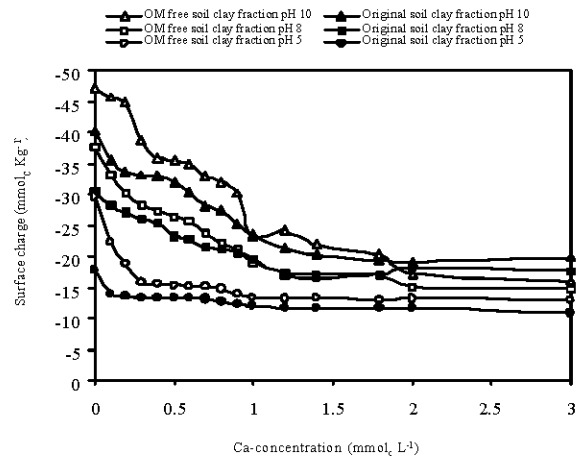

Fig. 4: Surface charge as a function of Ca-concentration at pH 5, 8 and 10 of the suspension of the original clay fraction and after OM removal.
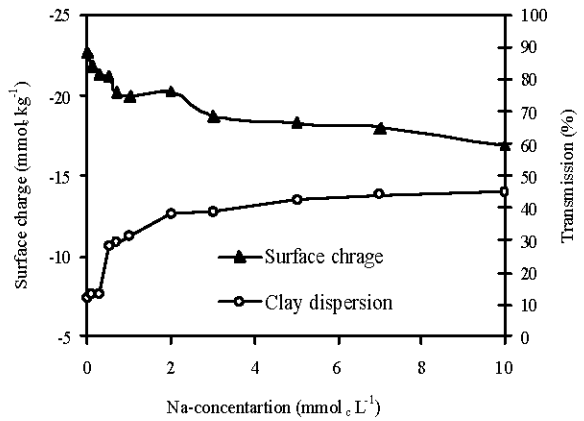

Fig. 5: Surface charge and clay dispersion as a function of Na-concentration for the original clay. Determinations at pH 8.
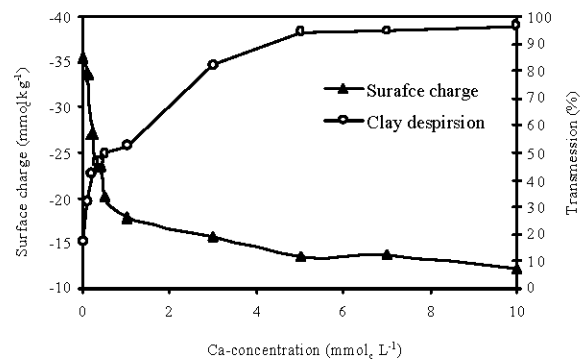

Fig. 6: Surface charge and clay dispersion as a function of Ca-concentration for the original clay. Determinations at pH 8.
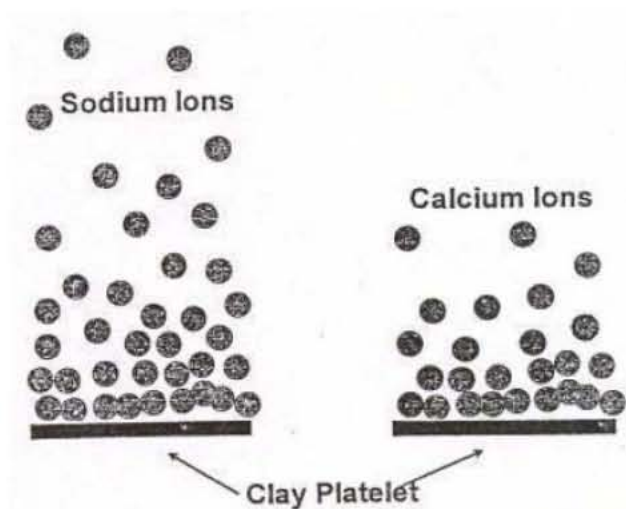
Fig. 7: Behavior of sodium and calcium ions attached to a clay platelet. (Source: [20])
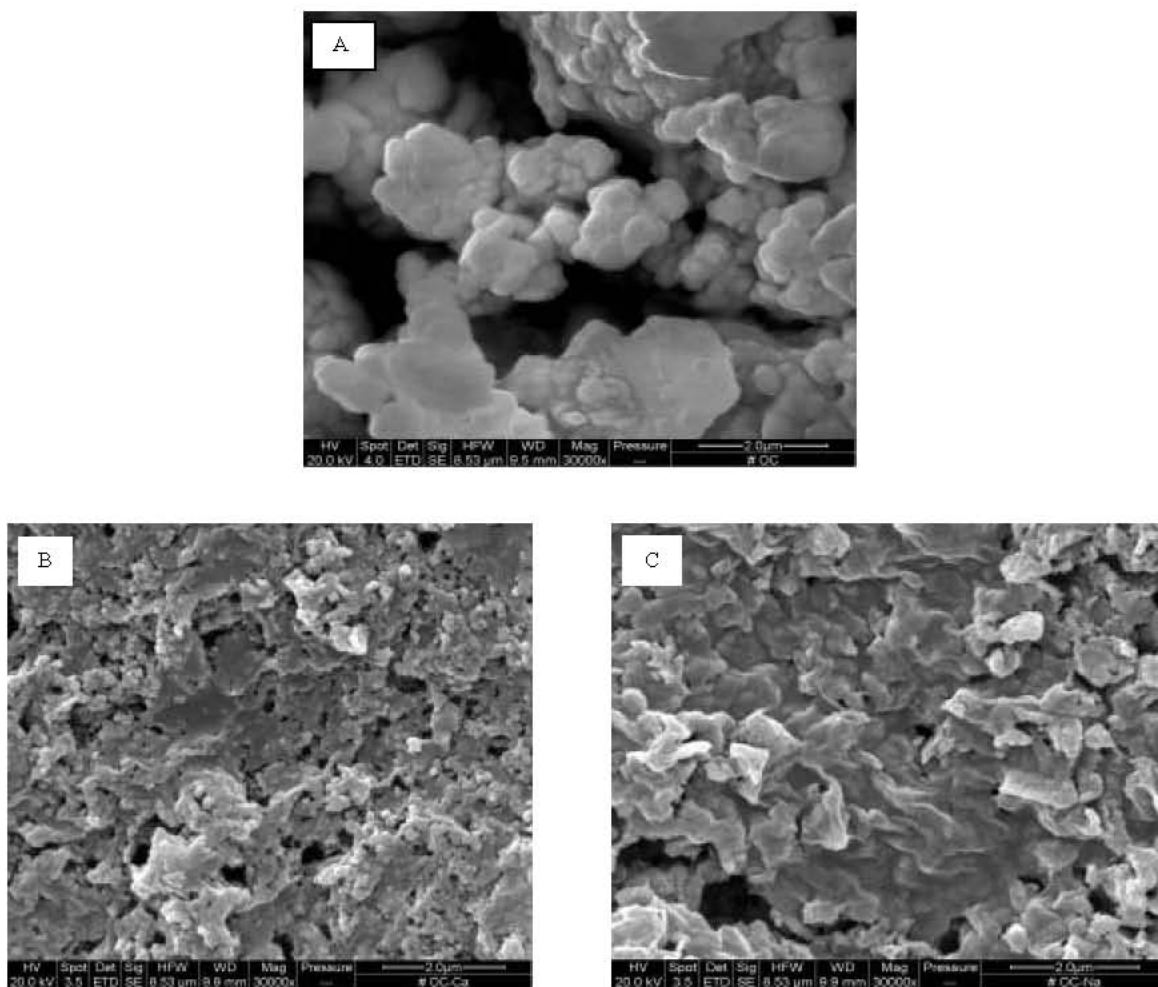

Fig. 8: Back scattered electron image of the clay fraction, original clay (A #OC) original clay with calcium (B #OC-Ca) and original clay with sodium (C #OC-Na) prepared at 0.4 mmol L^{-1} Ca and Na-concentrations

more negative i.e., dissociation of functional groups at pH>5 increases the number of negatively charged sites [9, 10]. This is most pronounced for the sample after removal of organic matter. Here, surfaces of the clay minerals are not covered with organic matter and negatively charged silicate layers are detected better. On the other hand, this might be also due to the increase of the specific surface area due to the H_2O_2 treatment. Also, increasing pH leads to make the charge on the edges of clay layers become more negative, that means this soil clay fraction is pH dependent charge.

Role of organic matter (OM): OM contributes mostly to an increase in the variable-charge; functional groups (e.g. carboxylic acids) of OM are believed to be one of the main contributors to provide negatively charged sites [10]. While charge development in OM is predominantly negative, as it is provided by functional groups (mainly carboxylic and phenolic acids), positive charge can occur through the protonation of amino groups but this is considered to be relatively small [11]. The results showed that the surface charges increased in soil clay fractions after organic matter removal by H_2O_2 suggesting that the permanent charges of the clay had been partially blocked by OM [10].

Dependency of Na- and Ca-concentration on surface charge: The data of PCD showed that at low Na^+ and Ca^{2+} concentrations the charges increased as Na ions made the double layer more diffused comparing with Ca ions (Fig. 3 and 4). By increasing Na^+ and Ca^{2+} concentrations, this part of charges decreased due to the effect of salt concentration in reducing the electrokinetic potential of the Double Layer. At low pH, there is a replacement of adsorbed ions (Na^+ and Ca^{2+}) by H^+ which has two effects: one is to increase the concentration of Na^+ and Ca^{2+} in the solution and thus to increase the electrical conductivity of the suspension and the other is to increase the concentration of H^+ on the surface. However, H^+ ions on the clay surface may slowly penetrate into lattice [12]. This attack by protons causes the clay to decompose and releases cations such as Al^{3+} and Mg^{2+}. The presence of di-or trivalent cations in the electric double layer can reduce the net negative charge due to the inner sphere complexation of these ions with clay surfaces [13]. At high pH, OH^- ions interact with the edges of the clay particles making them neutral or negatively charged. Laboratory studies have shown that the rate of dissolution of silicate minerals increases with increasing pH above 8 [14]. In spite of increasing EC at high pHs,

the clay dispersed because of the development of strong negative charge.

Effect of Ca- and Na-concentration on clay dispersion: Sodium ions have a single positive charge and therefore their clay-binding ability is poor. In a dispersive soil with a large exchangeable sodium percent ESP and small concentrations of water soluble salts, the weak bonding of the clay particles by sodium ions can be broken. As water enters between the clay particles it hydrates the sodium ions. This in turn forces the plates away from the ions and lowers the attractive force between the clay particles and the ions. The plates may move far enough apart for attraction forces to be overcome. The result is dispersion (Fig. 5) soil clay dispersion is the primary physical process associated with high sodium concentrations [15-22].

Calcium ions have a double positive charge and therefore their clay-binding ability is good. In addition calcium is not as strongly hydrated as sodium; therefore, the calcium ions are held closer to the surface with consequently greater attraction, the result is flocculation or aggregation (Fig. 6). This combination of conditions does not cause the disruption to soil structure that sodium does [22, 23]. Figure 7 illustrates this difference in physical arrangement of sodium and calcium molecules on the clay surface. Basically, attractive forces which bind clay particles together are disrupted when too many sodium ions get between the clay particles. When such separation occurs, repulsive forces begin to dominate and the soil disperses [18-22, 24, 25].

Microstructure in dependence of Ca and Na-concentration: Scanning electron microscopy (Fig. 8) of original clay (A) original clay with calcium (B) and original clay with sodium (C) shows the difference between aggregation and dispersion to be present and is related to the treatment given. The aggregation is obvious in the Ca treated sample, while dispersion is pronounced in Na treated sample in addition to large surface undulations, but these are due to the shrinkage of the clay as it dried and not due to aggregation.

CONCLUSIONS

This study clearly shows that pH primarily affects dispersion and flocculation of clay by changing the amount of surface negative charge on clay particles i.e., the clay dispersion and flocculation were related to the net negative charge on clay particles. In general, while

increasing pH increase the negative charge, increasing electrolyte concentration at constant pH induces charge reduction, probably because there are more cations were tend to be specifically adsorbed in the Stern layer.

The present study has clearly demonstrated that surface charge of clay particles is the common factor affecting clay dispersion under different conditions of pH, ionic strength and cation type.

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