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ARTICLE

Aspects of colloid and interface in the engineering science of soil and water with emphasis on the flocculation behavior of model particles

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Abstract

Dynamic aspects of colloidal dispersion form a critical basis of the engineering science of soil and water quality when the relation between microscopic physicochemical and hydrodynamic conditions and macroscopic hydrological transport phenomena is considered. Examples in the paddy and environment can be found in the transportation and diffusion of pollution in the discharge of irrigation water. In this review, I focus on this validity with emphasis on the fact that the majority of colloidal materials in the soil and water environment are apt to flocculate. That is, the mechanical unit of transportation is a floc rather than individual fine matter: fragments of clay particles, insoluble metal oxides and any other natural organic matter, such as protein, polysaccharide and humic substances. On the surface of colloidal materials present in soil and aquatic environments, it is known that many chemical substances, nutrients, agrochemicals and pollutants are concentrated by adsorption or sorption. In addition, such adsorption and sorption behavior will alter the nature of the colloidal surface to induce different types of colloidal flocculation and complexation, which will result in differences in the transport phenomena in the aquatic and soil environments. Therefore, the analysis of flocculation dynamics in relation to adsorption of chemical substances onto colloidal particles is a key factor in comprehensive management of soil and water environments. For this purpose, we have carried out a study of flocculation by choosing four clay minerals: allophane, imogolite, montmorillonite and kaolinite. The choice was rather arbitrary but has been established to cover mostly different shapes and surface properties. Comparison with results obtained for a colloidal system composed of monodispersed spheres and polymeric flocculants is found to clarify the validity of the framework of analysis. The strategy is very useful to accumulate characteristic data and has opened the way to further analysis of the complex system of soil and aquatic environments.

Keywords Model colloid · Soil and water · Clay · Floc · Natural organic matter (NOM)

Introduction

Owing to the increasing social interest in environmental issues, interfacial phenomena and the behavior of colloidal particles in soil and water have attracted much attention (Adachi and Iwata 2003; Wilkinson and Lead 2004). From the early stage of soil science, the colloidal component of soil has been considered to bear the original source of the unique nature of soil (Baver 1984; Rose 1966). The smallest components of solid particles with a size less than 2 μm are called soil colloids. They are fine fragments of clay minerals, metal hydroxide and organic substances such as proteins, polysaccharides and humic substances. Usually, they associate with each other to form complex aggregates in soil. Although it is not always easy to characterize chemical identity, they are believed to be the origin of the unique properties of soil. Analysis based on physical chemistry in relation to mechanics is critically important in this stage. Such necessity and philosophy can be found in soil physics texts published in the end of the 1960s by Japanese scientists (Yamazaki 1969, 1971). In those days, under the policy of the government, there was a strong and urgent interest in establishing systematic knowledge to construct agricultural infrastructure for stable food production. Colloidal material, and mainly clay

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colloid, in soil is recognized to reduce the permeability of water and also to influence the state of water, which is critically important in the material aspect of soil for agriculture and construction work. Many studies are reported in these respects leading to the field of soil engineering. Physical properties of soil are discussed, in terms of soil moisture, soil tilth, traffic compaction and soil sticking. Soil consistency values are remarkably affected by the presence of soil colloids. The state and presence of water in soil has been discussed in terms of transport phenomena and thermodynamics (Sudo et al. 1963). With relation to such historical reasons for its development, soil physics in Japan can be regarded as a basic science of land consolidation and land reclamation. Yamasaki's school produced many fruitful results of research on both the engineering and scientific aspects of soil in Japan, which features abundant volcanic ash soil including Kanto loam (Tsutsumi et al. 1983; Iwata et al. 1994).

However, the motivation for interest in soil colloids is shifting from the aspect of soil mechanics to the aspect of hydrological transportation and/or the ecological fate of chemical substances reflecting the social interest of environmental issues. A considerable amount of suspension load of water quality from paddy fields can be observed from place to place at the period of puddling and transplanting. This load can be reduced by the application of calcium salt (Akae 1992). Kobayashi et al. reported a strong correlation of the runoff properties of SS, TN and TP in agricultural areas in Iwate Prefecture and that the load will be increased by an increase in rainfall (Kobayashi et al. 2011). They also discussed the flocculation behavior of the sampled suspension, which can be interpreted in line with DLVO theory (Verwey and Overbeek 1948). Makino et al. repoted that the suspension load will be significantly reduced by flocculation (Makino et al. 2011). This analysis clearly explained the reason for Akae's result. In addition to subsurface water, Suzuki et al. pointed out that discharge through cracks in soil generated in a field will be a serious source of SS. The discharged SS has abundant phosphate and agricultural chemicals (Suzuki et al. 2005). Such transportation of suspension in groundwater can also be controlled by the flocculation behavior (Yamashita and Adachi 2004).

During the last two decades, Makino et al. have engaged in several projects regarding pollution problems in relation to paddy farming. Basically, their works can be separated into two categories. One is soil remediation: an effort to remove contaminants from polluted soil by washing (Makino et al. 2007; Zhang et al. 2013). This idea is applied to reduce the amount of cadmium, arsenic and radioactive cesium. The other countermeasure is to reduce the discharge of pollutants by artificial immobilization (Makino 2014; Makino et al. 2015). Usually, inorganic or organic flocculants were applied. A mixture of oppositely charged polyelectrolytes called polyion complex was urgently applied in the Chernobyl accident zone to prevent wind and water erosion (Zezin et al. 2015). Basically, forming soil aggregate by flocculation can be regarded as the same idea.

Through these efforts, it has become clear that the flocculation behavior and resulting properties of soil colloidal aggregate are the most significant items to be further investigated from the viewpoint of controlling the transportation of chemical substances in the field. In many applications, the motivations to start the study of soil colloid are different in the beginning; however, there must be common points that should be further investigated in the long run. We may recognize, however, that colloidal systems found in actual soil and water are apparently very different to each other and are usually very complicated. They are composed of various chemical species of inorganic and organic substances. They are non-homogeneous, polydispersed, porous and anisotropic in shape. The system is not equilibrium and is affected by water flow. Our strategy to cope with this complex situation is, firstly, to clarify the behavior of a model system made of monodispersed spheres. This choice

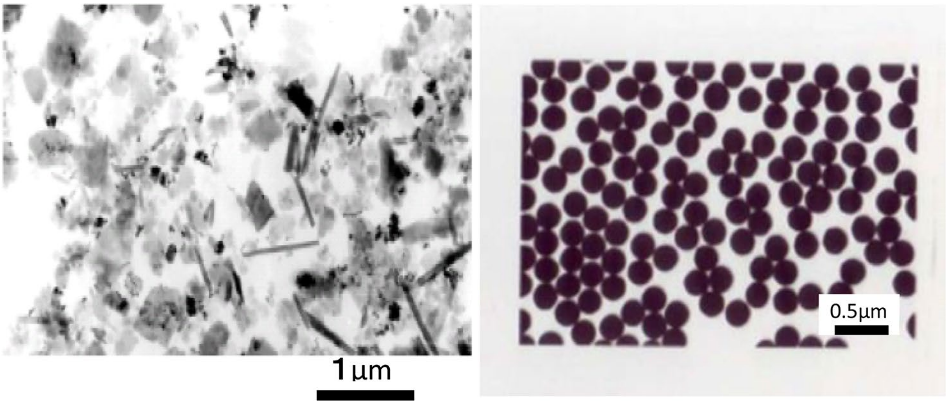

Fig. 1 Typical sample of soil colloid (Okinawa Kunigami merge, left). Colloidal spheres made of polystyrene latex (right)

of model colloid was originally carried out in the domain of colloid science to check the validity of theoretical predictions (Zezin et al. 2015; Boodt et al. 1984). As demonstrated in Fig. 1, a big gap between actual soil colloid and model colloid is apparently obvious. The approach is very slow in the beginning, but the veil of the complex system of soil has been removed step by step. That is, an analysis of flocculation of monodispersed spherical colloid can be regarded as the starting point of a long research trip on the basis of the knowledge of colloid and interface science. As the second step, we have tested the validity of the result of the first step for the case of typical colloid encountered in practice. For this, we have selected the dispersion of four clay minerals, e.g., the dispersion of allophane, imogolite, kaolinite and montmorillonite. Recently, such an approach has turned out to be a very useful measure to accumulate the fragments of knowledge in a more systematic way in relation to the word of colloid and interface science. In this short review, I shall introduce some typical examples which have been encountered in our activity in the last three decades.

Usage of monodispersed spheres

Structure and strength of flocs

As described in previous texts (Adachi 1995; Adachi et al. 2012), experimental results obtained using monodispersed colloidal spheres were found to be powerful to describe the geometrical structure of flocs. In this context, the applicability of the fractal concept mainly developed by numerical analysis was confirmed in our first study. We reproduced the numerical result by our table-tennis-ball simulation introducing the new concept of the degree of freedom at the contact between colliding clusters. The concept of the degree of freedom is related to the strength of flocs. It was obviously demonstrated by experimentally formed flocs. As indicated in Fig. 2, flocs formed in rapid coagulation (under high ionic strength) are very dendritic in shape. On the other hand, rounded and dense morphology was confirmed for flocs produced under slow coagulation in the turbulent mixing operation. The validity of the usage of model colloid was also confirmed for the refined expression on the strength of a floc in the turbulent flow (Kobayashi et al. 1999). Later this result turned out to be very effective to describe the rheology of flocculated suspension (Kobayashi et al. 2000). Another finding was confirmed in the successful description of the sedimentation of a floc (Adachi 2016). Further analysis on the permeability of a settling floc and extending applicability to the problem of hindering sedimentation has been tested along these lines.

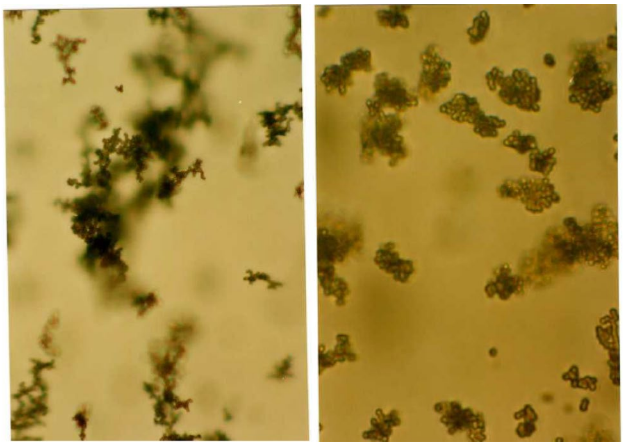

Fig. 2 Flocs made of polystyrene latex particles of 0.804 μm in diameter coagulated in electrolyte solution. Left: Salt-induced rapid coagulation under Brownian motion. Right: Flocculation induced in a turbulent mixing in slow (low electrolyte concentration) coagulation (Adachi et al. 2012)

Kinetics of flocculation in a flow field (Adachi et al. 1994; Feng et al. 2015)

In addition to the application of the fractal concept, the usage of monodispersed suspension was found to be very suitable for the qualitative analysis of the kinetics of flocculation. The idea had been originally tested for the analysis of the stability of colloidal suspension. However, more valuable results were confirmed in the kinetic analysis of flocculation in the flow field. Unstable suspension exposed in a system far from equilibrium is a situation when colloidal suspension is treated by flocculant. Upon the mixture of soil colloid and flocculant at the occasion of puddling, the system will be placed in a very chaotic condition of turbulent mixing. The system has been regarded as notoriously difficult to be characterized, but the application of monodispersed colloid has opened the way for the quantitative analysis of the rate of flocculation. That is, under the condition of rapid coagulation where all collision will successfully lead to the formation of flocs, the rate of coagulation is equivalent to the rate of collision between colloidal particles, which is a function of the rate of energy dissipation per unit mass of the turbulent flow. After the characterization of the hydrodynamic condition of mixing in terms of the rate of collision of monodispersed spheres,

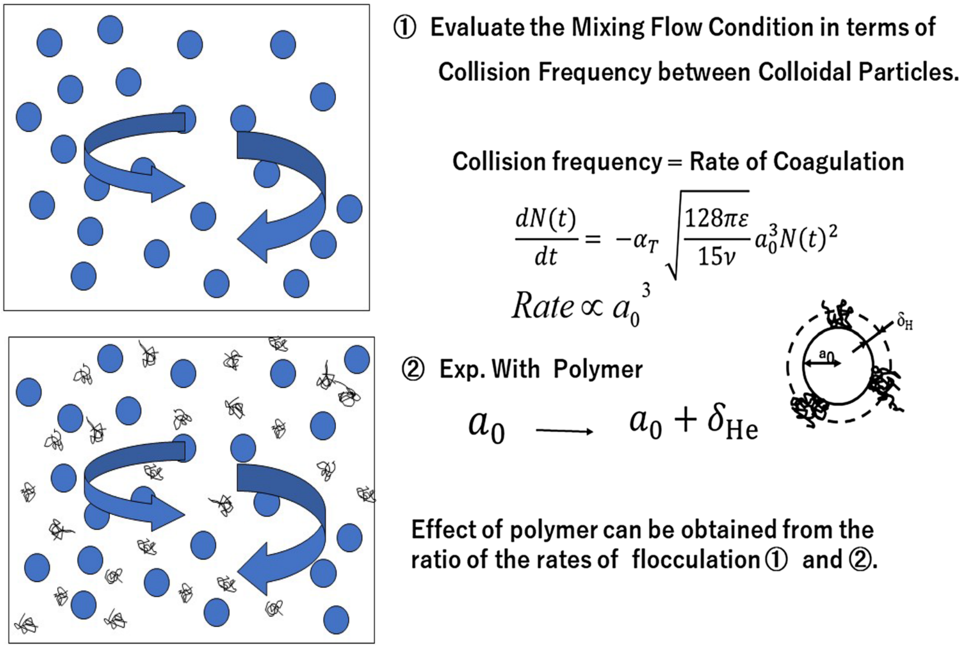

Fig. 3 The idea of the normalizing method of mixing in terms of the rate of coagulation under high ionic strength such that the rate of coagulation is equivalent to the rate of collision between colloidal particles. After normalizing the mixing condition, the effect of polymer flocculant can be evaluated just by comparing the rate of flocculation. The effect is detected as an increase in collision radius. $N(t)$, a_0, ε, ν and δ_{He} denote number concentration of colloidal particles, radius of primary particles, rate of energy dissipation in the mixing flow per mass, kinematic viscosity and effective layer thickness of adsorbed polymer layer, respectively

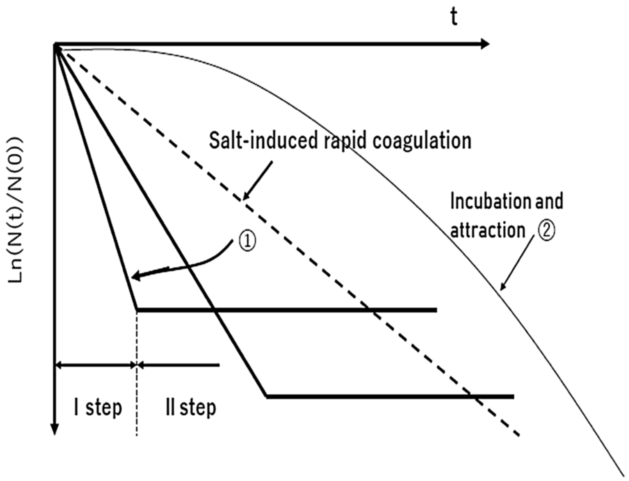

Fig. 4 Progress of flocculation compared with that of salt-induced rapid coagulation indicated by the dotted line (1). Typical result in the case of excess dosage of flocculant (2). In the case of charge neutralization. Flocculation is enhanced after the initial incubation time

further analysis of a system with a chemically different condition can be analyzed by normalizing the mixing method in terms of the collision process (Fig. 3). Since the rate of coagulation in a flow field is a strong function of the size of colloidal particles, this idea has been confirmed to identify the effect of macromolecules that are solving in water. The same situation can be imagined when polymer flocculants are applied to soil colloid. Analysis of the effect of humic substances can be done in this regime. The typical progress of flocculation obtained along with this principle is illustrated in Figs. 4 and 5.

Analysis of flocculation with selected clay colloids

Structure and electrophoresis of allophane aggregates

The unit of allophane is a nano-ball with a diameter of about 5 nm. It is usually contained in volcanic ash soil forming aggregate as indicated in Fig. 6. The aggregates were confirmed as a typical example of a fractal (Adachi and Karube1999). The charging property is also important when flocculation and coagulation behavior are considered (Adachi et al. 2005). It was very surprising that the results of electrokinetic measurement are more or less the same even though aggregates are obviously different in size and shape. This result motivated the theoretical investigation of the mobility of fractal aggregate (Adachi 2016).

Role of imogolite deposition

Together with allophane, fibrous imogolite is known to characterize volcanic ash soil. As demonstrated in Fig. 7, the unique shape is obvious. It is not difficult to imagine that such a unique shape will be an origin of uniqueness of the soil. In addition to shape, our measurement of mobility through a sand column demonstrates the unique nature of flocculation behavior near neutral pH (Shimura et al. 2012). The reason is not yet clear.

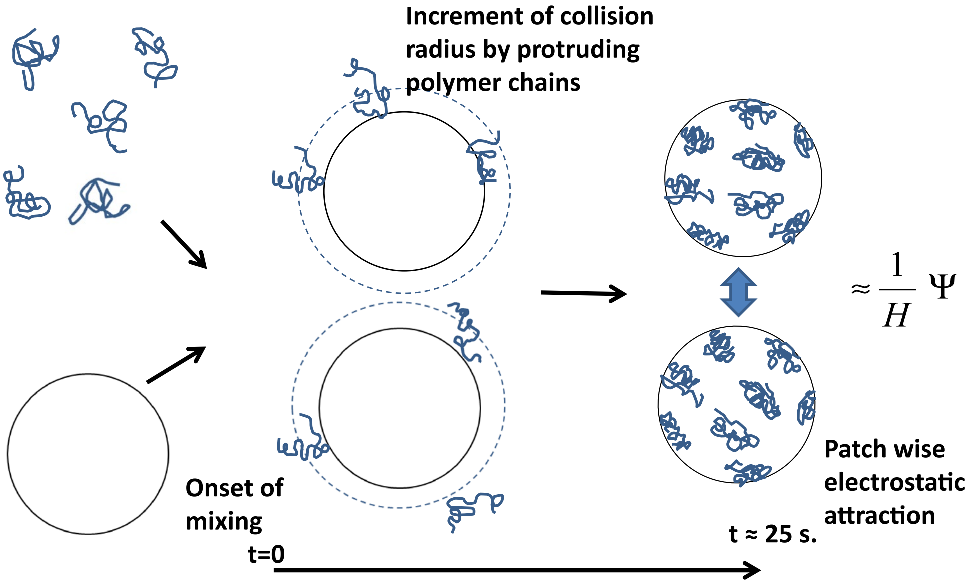

Fig. 5 Progress summarizing the story of flocculation with adsorbing polyelectrolyte. It was found to take about 25 s for patch-wise electrostatic attraction setting in. Ψ denotes the potential of attractive force between two particles with gap distance of H

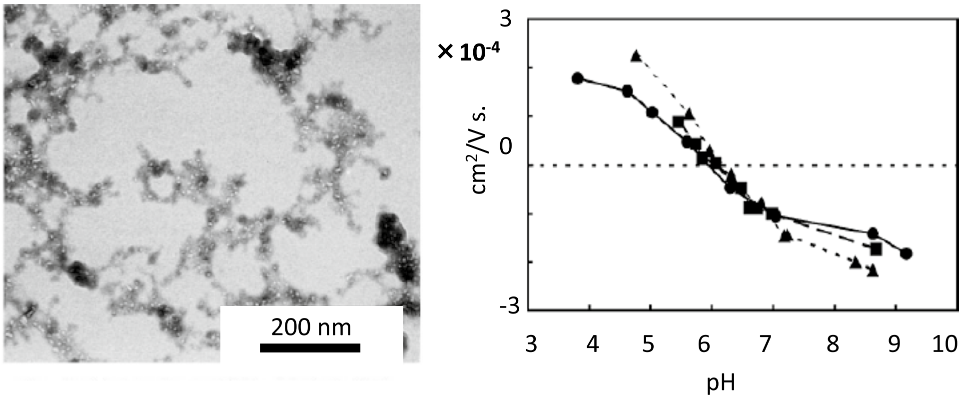

Fig. 6 TEM photograph of allophane aggregate (left) and their electrophoretic mobilities (right) (Adachi et al. 2005)

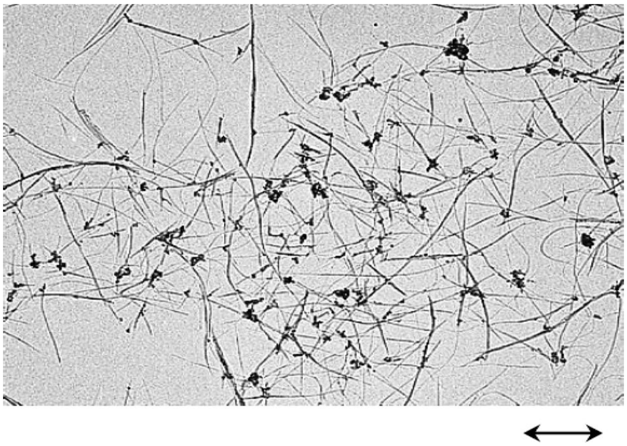

Fig. 7 TEM photograph of imogolite fiber. Allophane aggregates are also present. Bar indicates 200 µm (Shimura et al. 2012)

Sediment gel collapse of flocculated montmorillonite suspension

Montmorillonite is one of the most studied clays (Van Olphen 1977). The unit is a very thin sheet with a thickness of 1 nm and an aspect ratio of a few hundred. In addition, it is known to flocculate easily by the addition of salt forming very big aggregate. That is, when the concentration of ions changes, macroscopic behavior also changes in accordance with the coagulation behavior. One typical example of such macroscopic behavior is hindering sedimentation. We focused on the sedimentation of the semi-dilute regime illustrated in Fig. 8. We have found an important index of flocculation time, t_f, which is the waiting time for gel collapse. The very interesting result was confirmed that the value of t_f is a function of pH and ionic

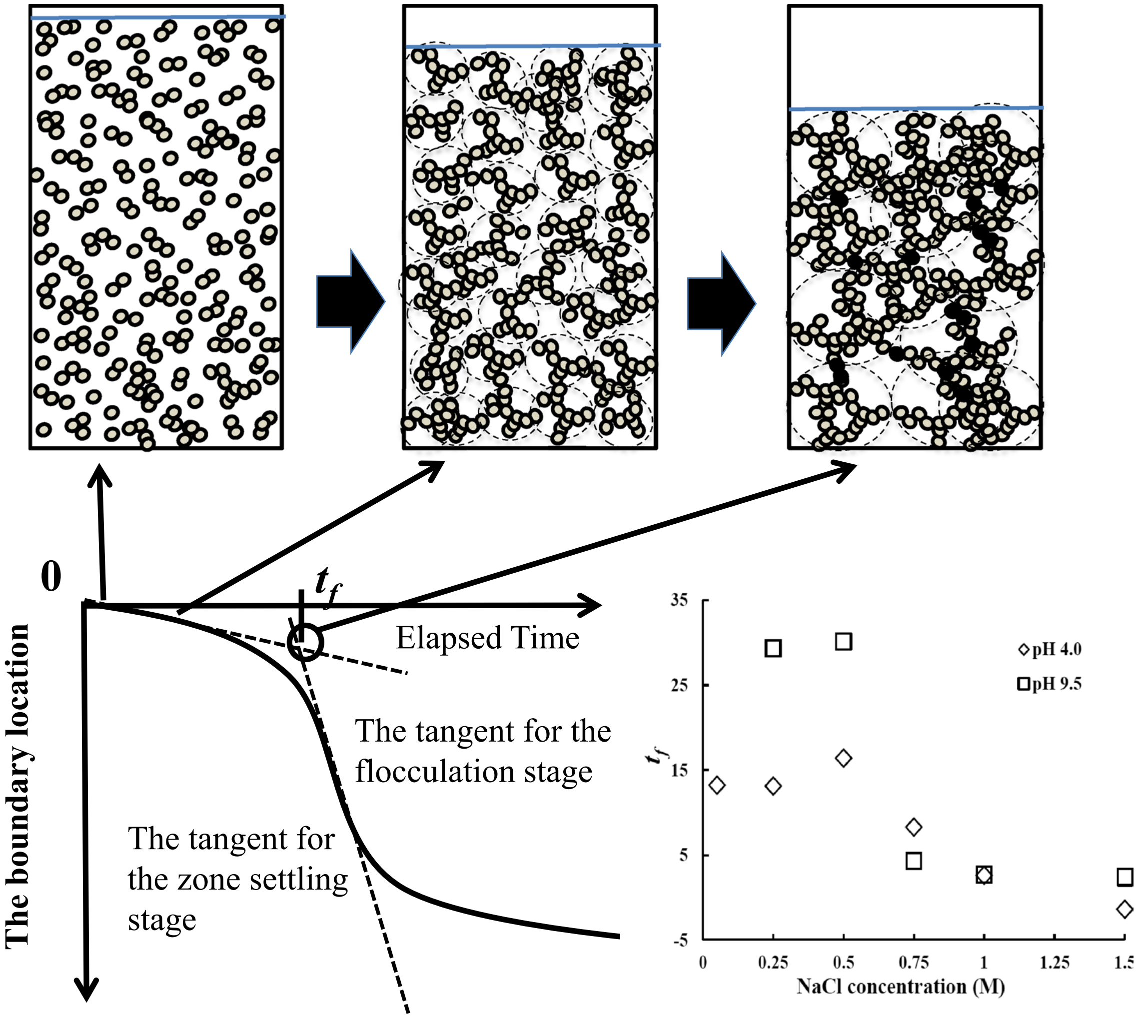

Fig. 8 Sedimentation behavior of montmorillonite suspension in the semi-dilute regime (Wu and Adachi 2018)

strength. This behavior was found to be interpreted from the microscopic interaction between clay sheets (Wu and Adachi 2018; Tombácz and Szekeres 2004).

Sedimentation of a single kaolinite floc

The dispersion of kaolinite is used as an index of turbidity of water. The flocculation behavior of kaolinite has been studied in relation to water treatment. As indicated in Fig. 9, evidence of insoluble aluminum oxide was confirmed. The presence corresponds to the formation of big flocs that is not found in the solution with NaCl (Kuroda et al. 2003). The surface properties of kaolinite are probably somewhat different from those of the other three clays. With kaolinite, the adhesive force will result in only small flocs with a diameter of few tenths of a micron. This size is also a frequently encountered size of flocs in real soil and water (Makino et al. 2011).

Conclusions

A historical review of soil engineering and environmental soil for farming activity confirms the necessity of the study of soil colloid with respect to flocculation. Applicative trials for the flocculation of model colloid and clays confirm the validity of the framework of study and demonstrate considerable potential. Systematic and continued research activity in the future will elucidate various aspects of soil colloid.

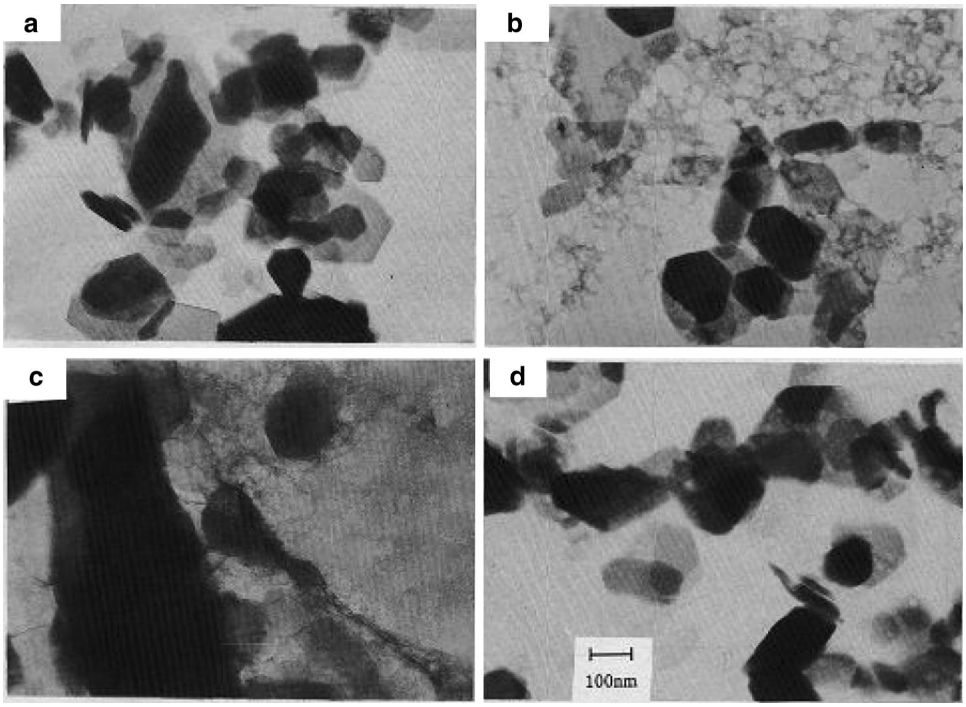

Fig. 9 TEM photographs of kaolinite flocs taken for different pH. **a** pH = 3.7, **b** pH = 4.6, **c** pH = 6.7, **d** pH = 11.3 (Adachi et al. 1999)

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