Effect of Monomeric Silicic Acid ($H_4SiO_4^{0}$) on Dispersion of a Kaolinitic Soil Clay: A dynamic Light Scattering Study

Dam Thi Ngoc Than, Phung Thi Mai Phuong, Nguyen Ngoc Minh[*]

Faculty of Environmental Sciences, VNU University of Science, 334 Nguyen Trai, Hanoi, Vietnam

Abstract: Clay loss is the process happening frequently in the slopy hill area without the cover of vegetation. In this study, the effect of monosilic acid (MSA) on dispersion of a kaolinitic soil clay in the hilly land of Phu Tho tea trees was considered under the influence of different pH values and concentrations by the improved dynamic light scattering method. Adsorption of MSA on clay was characterized by zeta potential (ζ) and batch adsorption isotherm in a pH range of 2 to 12. At a MSA concentration range within 0 and 35 mg L^{-1}, it was found that MSA was absorbed onto exchange sites, lowered the ζ, prohibited formation of card-house structure and finally counteracted the flocculation of clay. The most effective concentration of MSA was 5 mg L^{-1} at the pH range of 3.5 to 5 and electrolyte background of 0.01 mol_c L^{-1}. Out of this pH range or at higher electrolyte backgrounds, clay suspension is more strongly favored or prohibited; the effect of MSA was usually hidden. Due to an ubiquitous presence in soils, it is highlighted that the impact of MSA on clay loss cannot be ignored regarding soil conservation. Fluctuated changes in adsorption and flocculation of Fe-removed clay samples for MSA have not allowed to define the role of Fe in conjunction with the relation between MSA and clay dispersibility. It should be stressed that MSA has been distributed all over assorted soil, so MSA's impact should be considered in protecting soil.

Keywords: Monomeric silicic acid, adsorption, kaolinitic soil, dispersion.

1. Introduction

Under the effect of the surface runoff and the slope, clay loss is a serious problem in mountainous area and bare soil, especially when dispersion state is favored. The interaction between negative electrolytes (e.g. anions, humus substances) in soil solution with 1:1 clay minerals, e.g., kaolinite can facilitate dispersion [1]. However, effects of neutralized

electrolytes such as dissolved silicic acid, the most common compound of the soil solution, on clay dispersion have not been clarified yet.

Silicon is well known as the second most abundant element in Earth's Crust. The dissolved Si can be derived from the dissolution of primary and secondary minerals [2] and its concentration in soil solution reported by Karathanasis is up to 2 mMol L^{-1} [3]. The dissolved Si occurs mainly in the molecular form of uncharged monomeric silicic acid (MSA, $H_4SiO_4^{0}$) in the soil solution [2], at the present soil pH values, and it can be

_____
[*]Corresponding author. Tel.: 84-1263307088
Email: minhnn@vnu.edu.vn

immobilized by adsorption on Al and Fe oxides and clay minerals e.g. kaolinite. At acidic conditions, positively-charged edge sites of this clay might favor the formation of edge-to-face structures, so-called "card house", which facilitates coagulation. MSA can be adsorbed onto the edges of clay particles and blocks functional groups which results in (possibly) interrupting "card-house" formation and facilitating dispersion state. However, the effect of the sorbed MSA on clay dispersion has not been well studied.

In the present work, clay fraction was separated from a typical kaolinitic soil in highly weathered area of the Red river basin, Vietnam for examining dispersion experiments. Dynamic light scattering developed from studies of [4] with minor adjustment has been utilized to investigate the dispersion state of clay fraction under the effect of MSA as a function of both pH and ionic strength. The comparison between original clay fraction and removed Fe oxides-clay was used to identify the role of coated-Fe oxides. ζ and batch adsorption isotherm were also investigated to provide more information on the adsorption of MSA on clay fractions.

2. Materials and methods

2.1. Sample description

The study area located in the center of the Red River basin with hundreds of years on tea cultivation. Soil sample was selected from a soil series collected from a hilly area of Phu Tho province, taken from the surface horizon (0 – 30 cm depth) of a Ferralic Acrisols on the top of a hill ($105^o15'47"$ E; $21^o26'16"$ N). The sample was air-dried and passed through a 2-mm sieve. Soil pH value (determined using 0.2 M KCl (w/v = 1:2.5) is 4.7 representing for highly weathered soil. Particle-size distribution was determined by sedimentation and decantation. Organic-C was quantified by Walkley-Black method, whereas total Fe was analysed by PIXE (Particle Induced X-Ray Emission) method, using proton beam of Tandem accelerator (5SDH-2 Pelletron

accelerator system, manufactured by National Electrostatics Corporation, USA). The results showed that soil texture is clay loam (sand: 22%, silt: 39%, clay: 39%) with a cation-exchange-capacity (CEC) of 45.3 $mmol_c$ kg^{-1}. The organic-C content was 1.6%, which is typical for ferralic acrisols in Northern Vietnam. An amount of ca. 2.8% of total Fe indicates that Fe could dominate on the soil surface matrix. XRD analysis of the clay fraction (pretreated with Mg, Mg and ethylene glycol, K, and K and heating at 550^oC respectively) by a Bruker X-ray diffractometer AXS D5005 with oriented samples on glass slides has shown that the clay fraction (<2 µm) is completely dominated by kaolinite.

The clay fraction was separated from soil sample. The suspension was flocculated with NaCl, centrifuged, washed until salt-free, and freeze-dried. The obtained clay sample was used for the dynamic light scattering and adsorption experiments.

2.2. Determination of dynamic light scattering

MSA solutions ($H_4SiO_4^0$) were prepared from pure silica gel (Fisher Scientific Company, USA) by dissolution with distilled water at 80^oC. Then, the obtained bulk solution was diluted to targeted concentrations between 2.5 and 25 mg L^{-1}. An appropriate addition of NaCl (pure salt) and 0.01 N HCl was used to generate an electrolyte background of 0.01 mol_c L^{-1} and adjusted pH to targeted values. In preliminary experiments, the weak effects of MSA at lower (< 0.005 mol_c L^{-1}) or higher electrolyte backgrounds (> 0.05 mol_c L^{-1}) were found, since it were not include in this paper.

The volume of 10-ml-prepared MSA solution containing 2.5 mg clay was treated in an ultrasonic bath for 30 s to maximize particle dispersion. A subsample (3 mL) was then quickly transferred into a glass cuvette, and the transmittance (T %) is monitored every 60 s for 90 minutes using a spectrophotometer (L-VIS-400, Labnics Company, Fremont, CA, USA) at a wavelength of 600 nm.
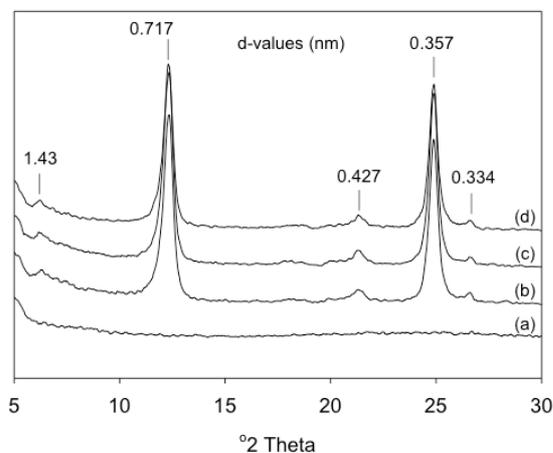
Fig. 1. X-ray diffraction patterns of the clay fractions (<2 μm) with different pretreatments: a) Mg saturation and Glycerol, b) Mg saturation, c) K saturation, and d) K saturation and 500°C heat treatment.

2.3. Batch adsorption experiments

For establishing adsorption isotherms, each 100 mg of the clay fraction or Fe-removed clay was mixed with 20 mL of MSA solutions (prepared from the pure silica gel as mentioned in section 2.2) with the concentrations of 10, 20, 30 and 40 mg L^{-1}. Samples were shaken for 1 h in polycarbonate centrifuge tubes and kept standing for 24 h. The supernatant was separated by centrifugation and decantation. The remained MSA in solution was quantified by the molybdenum blue method. Adsorption isotherms of MSA were found to be non-linear resulting in large coefficients of determination for Freundlich isotherms ($R^2 \sim 0.9$). Freundlich isotherms are based on the equation:

$$Q_s = K_F C_e^{\beta} \qquad (1)$$

where Q_s and C_e denote the amount of MSA sorbed (mg kg^{-1}) under equilibrium conditions and the concentration in the equilibrium solution (mg L^{-1}), respectively. K_F represents an affinity constant (L^{β} $mg^{1-\beta}$ kg^{-1}) and is numerically equivalent to the amount of MSA sorbed in mg Kg^{-1} at a solution concentration of 1 mg L^{-1}. The regression constant β describes the non-linearity of the isotherm and provides

information about the relative saturation of the adsorption sites. Freundlich constants (K_F and β) and standard errors were calculated from the linear form of the Freundlich equation:

$$\ln Q_s = \ln K_F + \ln C_e \qquad (2)$$

Kinetic adsorption experiments were prepared by mixing 400 mg of the original clay fraction with 100 mL of a 40 mg L^{-1} MSA solution. Gentle shaking was kept in 24 hours and in every hour 5 mL of the suspension was sampled and used for Si determination.

2.4. Electrophoretic mobility examination

For ζ determination of the clay suspension under the presence of MSA and different pH values, aqueous MSA solutions containing 5 to 25 mg L^{-1} were prepared. The electrolyte background of 0.01 mol_c L^{-1}, and pH values (pH 2-12) were adjusted by a proper amount of NaCl and a suitable addition of 0.01 N HCl or 0.01 N NaOH. Each 10 mL of suspension containing 2.5 mg of the clay fraction was used to determined ζ by a particle charge detector (PCD 05, Mütek, Germany).

3. Results and discussion

3.1. Evaluation of dynamic light scattering

The flocculation rate of the clay fractions in the presence of MSA at different pH values was shown in Fig. 2. There are no obvious differences between transmission curves revealed that Si might not have such an effect on clay dispersion at pH 3.0. Obtained transmission values are very close together and started rising after 30 minutes that confirmed a flocculation of the clay fraction. At pH 3.5 and 4.5, the increases of transmission values were observed at different time periods. It is suggested that the presence of MSA resulted in delays in flocculation. As the curves representing for MSA at 5 mg L^{-1} appeared below the other curves, it means that this concentration is the most effective in favoring dispersion at pH range of 3.5 to 4.5. At pH 5.0,

the increases of transmission were only observed for the experiment at a concentration of 2.5 mg L^{-1} and for the clay sample in distilled water, whereas transmission values were maintained at around 25% for other higher concentrations. For the Fe-removed clay fraction, we found fluctuated trends of the transmission (data not shown).
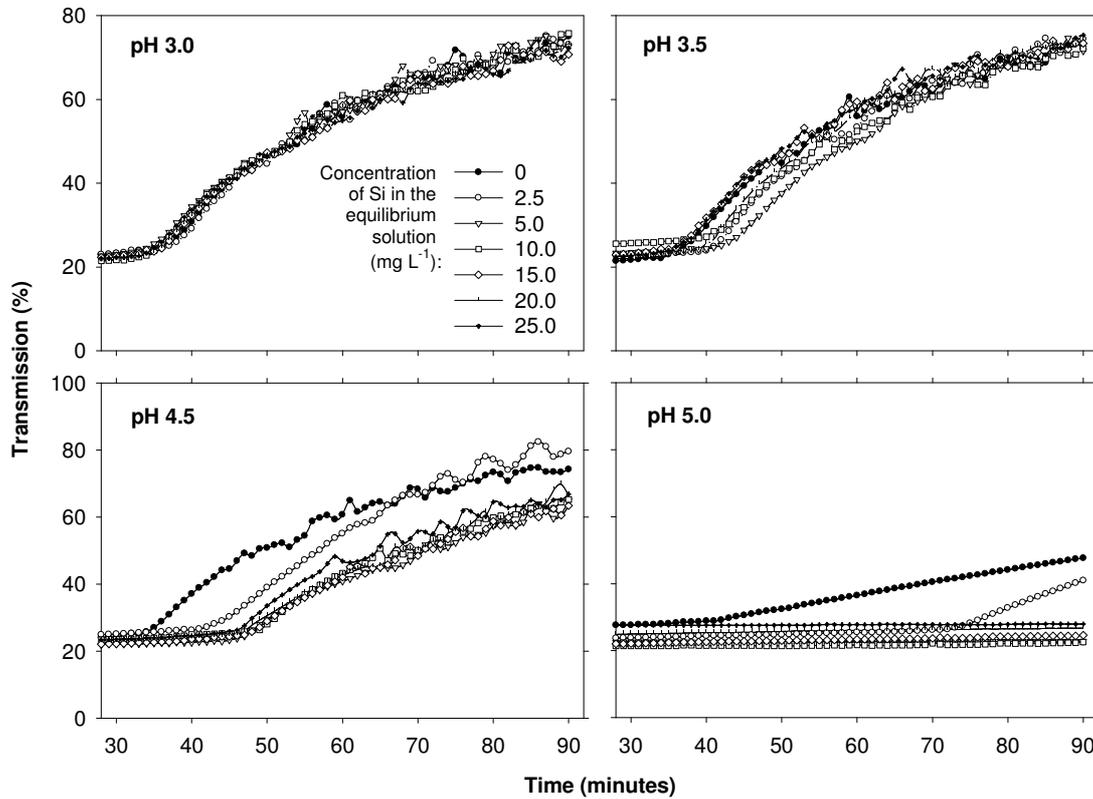
Fig. 2. Transmission (T%) of the clay suspension under the presence of MSA as a function of time at the electrolyte background of 0.01 mol_c L^{-1} and pH values of 3.0, 3.5, 4.5 and 5.0.
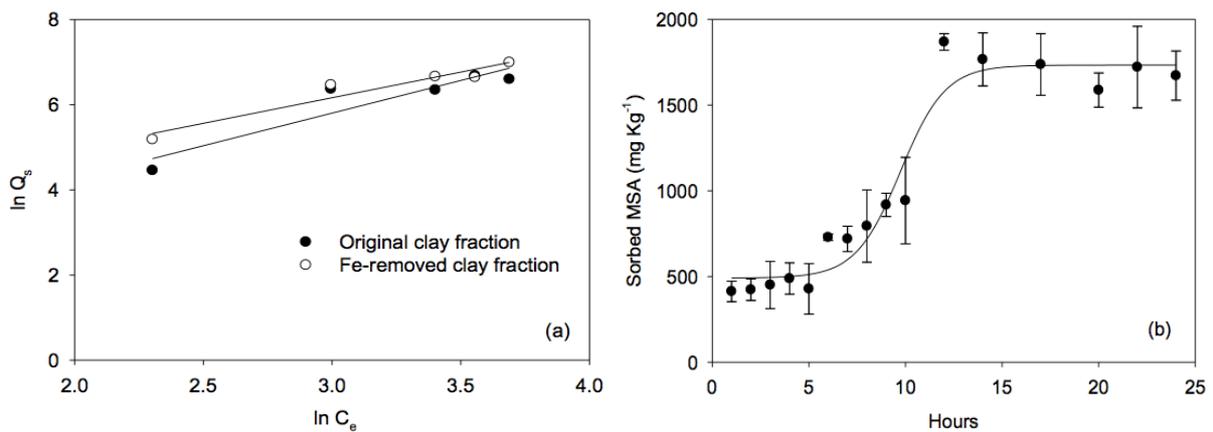
Fig. 3. Adsorption of MSA fitted with the Freundlich form (a) and adsorption kinetic (b).

It is thought that clay react with MSA involves in serving as exchange sites functioned by Si-OH or/and Fe-OH groups of the clay particle. In the study pH range of 3 to 5, MSA mostly presented in the soil solution with uncharged form of $H_4SiO_4^0$, but some of MSA molecular was changed to negatively charged form, $MSA^{(-)}$ ($H_3SiO_4^-$). Since, it is most probable that deprotonated $MSA^{(-)}$ associated with protonated hydroxyl groups on edge surface of clay fraction [5].

3.2. Adsorption isotherm of MSA

In general, there was an increasing trend of sorbed amounts along with MSA concentrations and time sequence in the clay suspensions (Fig. 3). The linear relationship of lnQ_s versus lnC_e from Eq. (2) reveals that the adsorption isotherms for MSA fit well to the Freundlich equation (Fig. 3a). From the linear form larger distances between the fits of the adsorption isotherms were found for the original clay fraction and Fe-removed clay fraction emphasizing that MSA was sorbed more strongly on the clay fraction of which Fe was previously removed by dithionite treatment. The sorbed amounts lnQ_s are 4.46 - 6.60 and 5.19 - 7.00 for the original clay fraction and Fe-removed clay fraction, respectively. The steeper slope of the adsorption isotherm resulted in higher K_F values for the original clay fraction in comparison with the Fe-removed clay fraction. For the sample under investigation the highest K_F-values for the original clay fraction and Fe-removed clay fraction are 3.33 and 12.84, correspondingly. For both samples, β values of the Freundlich equation were >1, suggesting an increasing energy of sorption with increasing saturation of the exchange sites (Karathanasis, 1999). Adsorption kinetic of MSA on clay fraction was shown in Fig. 3b. Increase of sorbed amount of MSA was found within 12 h, and after that there is no increase of adsorption indicated a saturation of MSA binding on clay particles.

3.4. Electrophoresis

A decrease of ζ with an increase of the pH of the clay suspension was a general trend as shown in Fig. 4 Negative ζ of the clay fraction was mostly observed even at low pH values. Major decreases in ζ occurred at pH < 5, whereas minor changes in ζ were observed at pH > 5. In general, it can be seen that the higher MSA concentration, the more negative surface charge of the clay fraction was obtained. At pH > 5, increase in distance between ζ curves suggests a stronger effect of MSA on ζ. For the Fe-removed clay fraction, a similar trend in which decrease of ζ along with increase of pH was obtained. However, the effect of MSA on ζ changes for this sample was not clearly recognized.

In soils, clay itself with specific properties of charge can be a first important factor that decides whether it is affected by MSA. The reaction of anions with clay particles results in a lower ζ and enhances repulsive force between clay particles that favors dispersion state of clay in suspension [1].

The results of dispersibility from dynamic light scattering showed a high sensitivity on pH and ionic strength while MSA seems to play a minor role. As revealed in Fig. 3, MSA showed the most obvious effect at pH range of 3.5 and 4.5, and blurred effect at out of this pH range. At pH < 3.5, protonation might result in a strong reverse of charges at edge surface, since it created card-house structure and flocculation occurred. In this case, it is likely that binding forces between edge and basal surface of particles to make card-house structure is so strong that MSA cannot break them to favor clay dispersion (as shown in Fig. 3). At pH > 5, a change of the positively-charged edge sites to negative contributed more negative charges for clay surface resulting in an increase of repulsion forces between clay particles which in turn would definitely facilitate dispersion. MSA can still be sorbed onto clays at pH > 5 as deduced from Fig. 4, but its role on clay dispersion was not really specified.
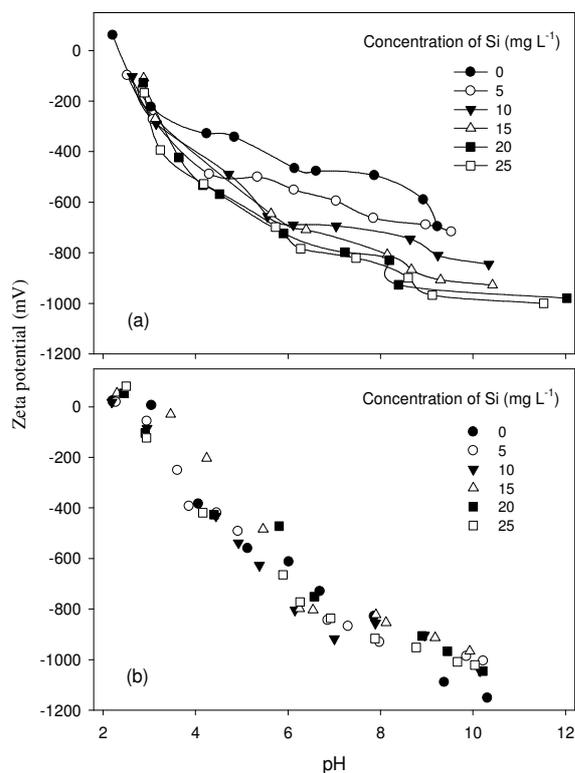
Fig. 4. Zeta potential of the original clay fraction (a) and Fe-removed clay fraction (b) at the electrolyte backgrounds of 0.01 mol_c L^{-1} as a function of pH.

Besides pH, it is also important to note about ionic strength as a factor to blur out the effect of MSA. The most visual effect of MSA was observed at the electrolyte background of 0.01 mol_c L^{-1}, whereas no apparent effect of MSA was found at the electrolyte backgrounds < 0.005 mol_c L^{-1} or > 0.05 mol_c L^{-1}. Dispite showing effect in narow range of pH and ionic strength, MSA can still be warned as an enhancing factor for clay dispersibility in a certain extent for acidic and variable charge soils in the tropical regions.

In kaolinitic soils, precipitation of Fe might result in a partial- or whole covering of the clay surface. As MSA can sorb onto surface Fe-OH groups through ligand exchange to form silicate bi-dendate innersphere complex [5], it infers that Fe can play as a mutual role to drive colloidal properties of the clay fraction through enhancing adsorption of MSA. However, there

are no apparent trends for MSA to affect adsorption and dispersion of the Fe-removed clay fraction. This suggests that there is still lack of understanding to clarify the role of Fe regarding clay colloidal properties under the effect of MSA.

4. Conclusion

MSA generally showed an enhancing effect for dispersibility at a wide concentration range of clay suspensions, since MSA adsorbed onto exchange sites, lowered the ζ, prohibited formation of card-house structure and finally counteract flocculation of the clay. MSA showed its most obvious effect on clay dispersion at slightly acidic and low ionic strength. It implies that the effect of MSA can be hidden in certain conditions (e.g. strong acidic or alkali) where flocculation or dispersion of clay is strongly favored. Despite the fact that MSA played a role as an enhancer of clay dispersibility in a "narrow window" of its concentration, pH and ionic strength, it is still valuable to highlight MSA's impact regarding soil stability due to the ubiquitous presence in soils. Fe was thought to play a certain role as a bridge to link MSA with clay surface through ligand exchange reactions, however, results from experiments conducted for the Fe-removed clay sample were not sufficient to make a concrete conclusion. It suggests that dispersion of clays as function of Fe should be considered for future works.

References

[1] Nguyen, N.M., Dultz, S., Tran, T.T.T., Bui, T.K.A., Effect of anions on dispersion of a kaolinitic soil clay: A combined study of dynamic light scattering and test tube experiments. Geoderma, (2013) 209.

[2] Iler, R.K., The Chemistry of Silica. Wiley-Interscience, New York (1979).

[3] Karathanasis, A.D., Mineral equilibria in environmental soil systems, in: Soil Mineralogy

with environmental applications. Soil Science Society of America (2002) 109.

[4] Kretzschmar, R., Holthoff, H., Sticher, H., Influence of pH and Humic Acid on Coagulation Kinetics of Kaolinite: A Dynamic Light Scattering Study. Journal of Colloid and Interface Science 202 (1998) 95.

[5] Hiemstra, T., Barnett, M.O., van Riemsdijk, W.H., Interaction of silicic acid with goethite. J. Colloid. Interf. Sci. 310, (2007) 8.

Ảnh hưởng của axit mono silicic tới khả năng phân tán của khoáng sét kaolinit trong đất: Thí nghiệm tán xạ ánh sáng

Đàm Thị Ngọc Thân, Phùng Thị Mai Phương, Nguyễn Ngọc Minh

Khoa Môi trường, Trường Đại học Khoa học Tự nhiên, ĐHQGHN, 334 Nguyễn Trãi, Hà Nội, Việt Nam

Tóm tắt: Mất sét là quá trình xảy ra thường xuyên ở khu vực đồi núi dốc không thảm thực vật che phủ. Trong nghiên cứu này, ảnh hưởng của axit mono silicic (MSA) tới khả năng phân tán của đất giàu khoáng sét kaolinit khu vực đồi núi trồng chè Phú Thọ được xem xét dưới ảnh hưởng của pH ở các mức nồng độ khác nhau bằng phương pháp tán xạ ánh sáng cải biên để phù hợp với việc sử dụng trên máy quang phổ khả kiến. Khả năng hấp phụ được đặc trưng bởi thế điện động (ζ) xác định trên máy PCD 05 (PCD 05, Mütek, CHLB Đức) và đường hấp phụ đẳng nhiệt trong khoảng pH dao động từ 2 đến 12. Trong khoảng nồng độ của dung dịch MSA từ 0 đến 35 mg L^{-1}, axit silicic có thể hấp phụ lên các vị trí trao đổi của khoáng sét, làm giảm thế từ đó ngăn cản sự hình thành cấu trúc card-house, thúc đẩy sự phân tán của khoáng sét Ảnh hưởng của MSA thể hiện rõ nhất ở nồng độ 5 mg L^{-1} và trong khoảng pH từ 3,5 đến 5, nền điện ly 0.01 mol$_c$ L^{-1}. Ngoài khoảng pH này hoặc ở nền điện ly cao hơn, huyền phù có xu hướng tụ keo nhanh hoặc phân tán mạnh, do đó ảnh hưởng của MSA tới khả năng phân tán của khoáng sét không rõ ràng. Cần nhấn mạnh rằng MSA phân bố rộng khắp trong các loại đất, do đó, ảnh hưởng của MSA cần được xem xét trong bảo vệ đất.

Từ khóa: Axit mono silicic, hấp phụ, kaolinit, keo tán.