シプロフロキサシン存在下での Na モンモリロナイトの帯電と凝集
Charging and aggregation of Na-montmorillonite in the existence of ciprofloxacin

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Abstract

The effect of a typical antibiotic ciprofloxacin on the charging and aggregation of Na-montmorillonite was studied. The results of electrophoretic mobility (EPM) and hydrodynamic diameters, critical coagulation concentration (CCC), critical coagulation ionic strength (CCIS), surface charge density, and stability ratio confirmed that the aggregation of Na-montmorillonite can be affected by the change in charge due to the adsorption of ciprofloxacin.
Keywords： clay, dynamic light scattering, electrophoresis, antibiotic

1. Introduction

Antibiotics typically flow from wastewater to surface water and then to soil [1]. Most antibiotics can be retained in soil due to their strong adsorption ability on clays and have a strong impact on soil microorganisms. Antibiotics can make impact on the human health and environment even at the low doses [2].

Ciprofloxacin is widely used as an antibiotic in people and animals and thus remains in the natural environment. Ciprofloxacin can be easily adsorbed on the soil and co-transported with the soil particles from the wastewater to surface water, because the soil colloidal particles have large specific surface area and affect the transport of the antibiotics in soil and water.

Among soil colloidal particles, a typical clay montmorillonite usually works as effective adsorbent for pollutants in the water and soil due to the large specific surface area and the constant negative surface charge. Previous works showed that montmorillonite can adsorb ciprofloxacin and facilitate its transport in sand. Transport of colloidal particles is often affected by the dispersion-aggregation and surface charge of the particles. Nevertheless, the effect of ciprofloxacin on the aggregation-dispersion and charging have not been studied.

In this context, we have decided to study the charging and aggregation of montmorillonite in the presence of ciprofloxacin. The dynamic and electrophoretic light scattering experiments were carried out for the montmorillonite with/without ciprofloxacin under different salt concentrations and pH conditions.

2. Materials and Methods

2.1 Na-montmorillonite and ciprofloxacin

Na-montmorillonite dispersion was prepared from “Kunipia-F” powder (Kunimine Industry Co. Ltd.). The refining technique was adopted from Tsujimoto *et al.* [3]. Ciprofloxacin hydrochloride monohydrate (M_w: 367.8 g/mol) was purchased from Tokyo Chemical Industry.

2. 2 Experimental methods

In the experiment, the hydrodynamic diameters and electrophoretic mobility of montmorillonite were measured as a function of the concentration of ciprofloxacin. The electrophoretic mobility and the diameter were measured by zetasizer nano (Malvern) using electrophoretic and dynamic light scattering methods. NaCl, NaOH, and HCl solutions were used to adjust the electrolyte concentration and pH.

3. Results and discussion

Figure 1 shows the electrophoretic mobility

(EPM) of montmorillonite in the presence of ciprofloxacin under the pH 4 ± 0.1. As the concentration of ciprofloxacin was increased, the EPM of the montmorillonite increased. The EPM of montmorillonite was reversed from the negative to the positive. When the concentration of ciprofloxacin was between 0.0815 mM and 0.1087 mM, the EPM showed the charge reversal. The results showed that the electric double layer of montmorillonite was compressed as the concentration of ciprofloxacin increased. The positive and negative charges of ciprofloxacin and montmorillonite were effectively cancelled at the isoelectric point.

The particle sizes of montmorillonite were measured to verify the aggregation at different ciprofloxacin and salt concentrations under various pH conditions. Figure 2 shows that the hydrodynamic diameter of montmorillonite increased with increasing ciprofloxacin and salt concentrations. The size of montmorillonite at the low concentration is around 170 nm to 200 nm. The particle size increases with increasing concentration, indicating that the montmorillonite aggregates with increasing electrolyte concentration. The higher salt concentration was required to induce the aggregation at pH 10 compared to the case at pH 4. This result is probably due to the disappearance of the effect of edge (+) / face (-) attraction at pH 10. The lower concentration of ciprofloxacin for aggregation was observed because of the charge neutralization by the high ability of adsorption of ciprofloxacin on montmorillonite as indicated in Fig. 1.

4. Conclusion

The aggregation and charging of montmorillonite with ciprofloxacin were studied by measuring the electrophoretic mobility and hydrodynamic diameter. The adsorption of ciprofloxacin on the montmorillonite significantly affects the aggregation of montmorillonite. The adsorption of ciprofloxacin on montmorillonite changes the surface charging property to make the montmorillonite aggregate with each other.

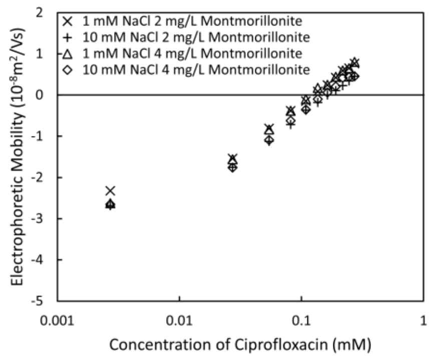

Figure 1. Electrophoretic mobility of montmorillonite against ciprofloxacin concentration at different NaCl concentrations and pH 4.

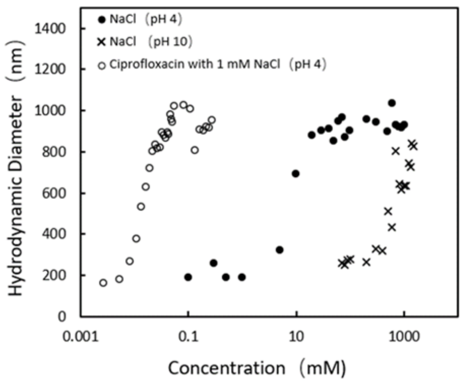

Figure 2. Hydrodynamic diameter of montmorillonite at 4 mg/L as a function of concentration of NaCl or ciprofloxacin at pH 4.0 and 10.0. The data shows hydrodynamic dimeter of montmorillonite adsorbed with the ciprofloxacin in 1 mM NaCl compared with that without ciprofloxacin.

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