シプロフロキサシン存在下における各種粘土の帯電挙動

Charging of various clays in Presence of Ciprofloxacin

Chuanzi ZENG[1], Motoyoshi KOBAYASHI[2*] ([1] Graduate School of Science and Technology and [2] Institute of Life and Environmental Sciences, University of Tsukuba, kobayashi.moto.fp@u.tsukuba.ac.jp)

Abstract

One of typical antibiotics ciprofloxacin bears positive charge and negative charge under different pH and can adsorb various soil particles. Such adsorption may affect the charging and aggregation-dispersion of clay and colloidal particles, which are important phenomena in soil and water environments. This study was performed to examine the effect of ciprofloxacin on the charging of various clays particles.

Keywords： clays, electrophoresis, antibiotic

1. Introduction

Antibiotics have been widely used in human, plant and animal medical supplies and growth promotion [1]. Antibiotics typically flow from wastewater to surface water and then to soil. Most antibiotics can be retained in soil due to their strong adsorption ability on clays and have a strong impact on soil microorganisms [2].

Ciprofloxacin (CPFX) is one of the widely used antibiotics. The ionic property of CPFX varies with pH and thus the interaction with soil changes as well. CPFX does not migrate in sand, but can be co-transported with clays [3]. According to Derjaguin-Landau-Verwey-Overbeek (DLVO) theory, the colloidal particles are dispersed in the solution when the repulsive force is larger than the attractive force. With increasing the concentration of ions and/or decreasing the magnitude of surface potential, the attractive force will dominate and result in aggregation. CPFX adsorption may affect the charging of clay particles, and thus the study on the charging of clays particles with CPFX is important. Nevertheless, such studies have not been performed as far as we know. Thus, we have decided to study the effect of CPFX on the charging and aggregation of various clays material.

In this study, we employed three different clay particles, namely, montmorillonite, allophane, and halloysite. The three types of clays materials have their own structure and charging ability. The surface charging of these clays was investigated by using electrophoretic light scattering with and without CPFX.

2. Experimental methods

The electrophoretic mobility was used to study the charging of three clay particles. The electrophoretic mobility of allophane, montmorillonite, and halloysite in the absence and presence of ciprofloxacin was measured as a function of NaCl concentration.

2.1. Materials

Ciprofloxacin hydrochloride monohydrate (molecular mass: 367.8 g/mol) was purchased from Tokyo Chemical Industry(Tokyo, Japan). Chemical formula of ciprofloxacin is $C_{17}H_{18}FN_3O_3{\cdot}H_2O$. In the experiment, NaCl solutions were used to control the salt concentration of suspension. NaOH solution and HCl solution were used to control pH. Aqueous Na-montmorillonite dispersion was prepared from “Kunipia-F” powder (Kunimine Industry Co. Ltd.). The refining technique was adopted from Tsujimoto et al. [4]. The purified sample of allophane used in this investigation was taken from Kitakami pumice in Iwate, Japan [5]. Halloysite was purchased from Sigma-Aldrich and subjected to H_2O_2 treatment, NaCl saturation, and dialysis against deionized water before use. Allophane and halloysite are abundant in the fine clay fraction of the pumice particle. The suspension pH was measured by a pH meter (HM-30R, TOA-DKK).

2.2. Electrophoretic mobility

To examine the effect of the adsorption of ciprofloxacin on the charging of clays, the electrophoretic mobility of the clays in the absence and presence of ciprofloxacin was measured. The electrophoretic light scattering has been used to evaluate the charging behaviors of colloidal particles. In this experiment, the concentration of allophane was adjusted to 6 mg/L, the concentration of halloysite was 10 mg/L, and the concentration of montmorillonite was 2 mg/L. The EPM of the three types of clays at various concentrations of NaCl and ciprofloxacin under different pH conditions was measured by Zetasizer Nano (Malvern Panalytical Ltd, Malvern, UK). The EPM of the clays at each condition was recorded 3 times and the average values were calculated.

3. Results and discussion

Figure 1 indicates the EPM of three clays as a function of NaCl concentration. The magnitude of EPM of allophane decreased with increasing NaCl concentration. In contrast, halloysite had constant negative EPM even when electrolyte concentration increased. A slight effect of the NaCl content on the EPM of montmorillonite is visible.

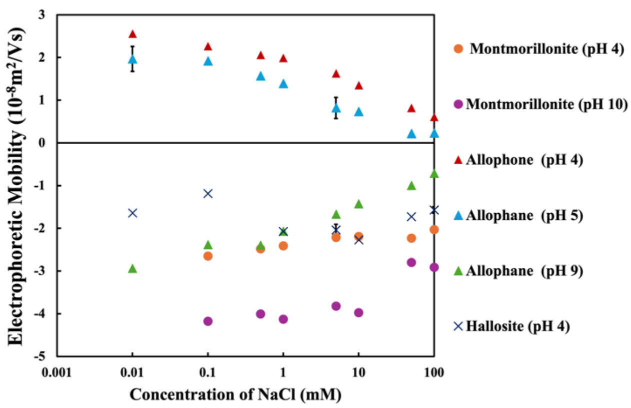

Figure 1. Electrophoretic mobility of allophane, halloysite and montmorillonite under different NaCl concentrations and pH conditions.

Figure 2 shows that the EPM of allophane, montmorillonite, and halloysite changed with ciprofloxacin concentration. The tested pH were 4, 6, and 10 for montmorillonite, 4 for halloysite and 4, 5, and 9 for allophane. When ciprofloxacin concentration increased in a low pH condition, the EPM of allophane increased in comparison to the salt concentration (Figure 1). At high pH, the magnitude of EPM of allophane decreased with increasing the concentration of ciprofloxacin. At low pH, positively charged ciprofloxacin is adsorbed on the negatively charged part of allophane. Greater EPM is associated with higher charges. The magnitude of EPM of montmorillonite and halloysite decreased with increasing the concentration of ciprofloxacin under low pH condition. These trends on montmorillonite and halloysite can be explained as follows: the decrease in the absolute value of EPM is due to the adsorption of oppositely charged ciprofloxacin and the reduced magnitude of charge density. In an alkaline condition, the EPM was constant negative, showing the negative charge of montmorillonite irrespective of ciprofloxacin concentration. Both ciprofloxacin and montmorillonite under alkaline condition have negative charge that causes strong repulsion between them. The repulsion between ciprofloxacin and montmorillonite at high pH prevents the adsorption and thus the EPM was more or less constant. Both montmorillonite and halloysite had an isoelectric point (IEP) with charge reversal at acid condition. The values of EPM of montmorillonite and halloysite became zero because there was no net charge to drive their movement in an electric field. After the IEP, the EPM of halloysite and montmorillonite increased with increasing ciprofloxacin concentration.

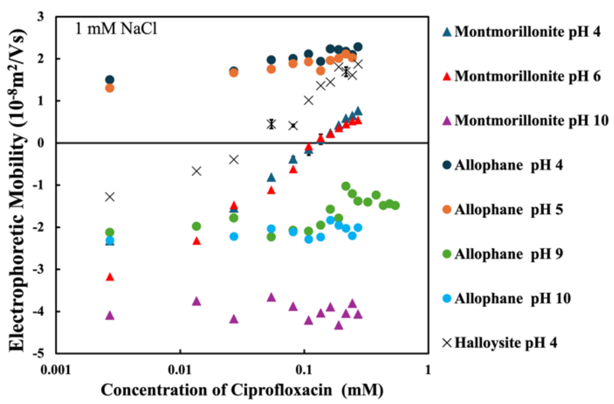

Figure 2. Electrophoretic mobility of allophane, montmorillonite and halloysite with ciprofloxacin at different NaCl concentration and pH condition.

4. Conclusion

Compared to the concentration of salt, ciprofloxacin has less effect on the EPM of allophane but affects the EPM of montmorillonite and halloysite. The findings of different effect of ciprofloxacin on the EPM of three different clays deserve more investigation and discussion.

References

[1] S. Thiele-Bruhn, 2003, doi: 10.1002/jpln.200390023.

[2] E. M. Golet et al., Anal. Chem., 2002, doi: 10.1021/ac025762m.

[3] S. B. Roy and D. A. Dzombak, 1997, doi: 10.1021/es9600643.

[4] Y. Tsujimoto et al., 2014, doi:10.1016/j.colsurfa.2012.11.005.

[5] Takeshita C et al., 2019,. https://doi.org/10.1016/j.colsurfa.2019.05.054