

Adsorption and Desorption Behavior of Ammonium Ion on Expandable Illite

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The adsorption and desorption behavior of ammonium ion on the treated natural expandable illite was investigated. The natural non-expandable illite (HS) was treated with dodecylamine hydrochloride solution, and the obtained HS (Alkyl-HS) after alkylammonium ion exchange. The alkylammonium ion in Alkyl-HS exchanged with Na^+ , and consequently the Na-exchanged HS (Na-HS) swelled due to formation of water layer in interlayer spaces. The sodium ion in Na-HS can be exchanged with ammonium ion. In the adsorption experiment, the intensity of $d_{(001)}$ -spacing of Na-HS (i.e. 12 Å) decreased with an increase in initial NH_4^+ concentration. The increase in the diffraction peak at 10 Å with higher initial ammonium ion concentration indicates ammonium ion exchanged with the Na ion in the interlayer spaces. The maximum ammonium ion adsorption capacity of Na-HS was determined to be 0.37 mmol/g. Desorption experiments in ammonium-exchanged Na-HS (NH_4 -HS) was carried out by immersing in 0.5M CaCl_2 aqueous solution. The concentrations of ammonium ion after filtering the solids attained a constant value after five repetitions of CaCl_2 treatments. Total concentration of desorbed ammonium ion was 50% of the maximum ammonium ion adsorption capacity of Na-HS. These results indicate that 50% of the maximum adsorbed ammonium ion is fixed in the interlayer spaces of the treated HS.

Key words: Adsorption, Desorption, Ammonium ion, Expandable-Illite, Alkylammonium

1. INTRODUCTION

Removal of harmful elements from wastewater is important to preserve a clean environment. Ammonium ion has been touted as the main cause of eutrophication in rivers and lakes. A process that can significantly reduce the quantity of ammonium ion levels in wastewaters is necessary.

The mica layer is composed of two opposing tetrahedral sheets with an octahedral sheet in between forming a "TOT" layer (Figure 1)[1]. The negatively-charged TOT layers are compensated and bonded together by positively charged interlayer cations in the interlayer sites (Figure 1)[1]. Ammonium ion has fixed in the interlayer of some natural mica instead of potassium (e.g. tobelite) [1-3]. The interlayer cation (e.g. K^+ and NH_4^+) in natural micas are generally non-exchangeable. An exception, however, is the exchange of alkylammonium ion with interlayer cations in some natural mica [4-9]. The exchanged alkylammonium ion can in turn be further exchanged with other inorganic cations (e.g. Na^+ , Ca^{2+} and Mg^{2+}) [5, 9]. This treated natural mica achieves expandability and high cation exchange capacity. So far, no adsorption and desorption experiments with ammonium ion has been performed using this treatment procedure. The treated natural mica which can fix the ammonium ion in the interlayer can be used as an environmental purification material for reducing and removing ammonium ion in water systems.

The goals of this study are (1) to determine the maximum ammonium ion adsorption capacity of the treated expandable illite, and (2) to assess the stability of adsorbed ammonium ion in treated expandable illite.

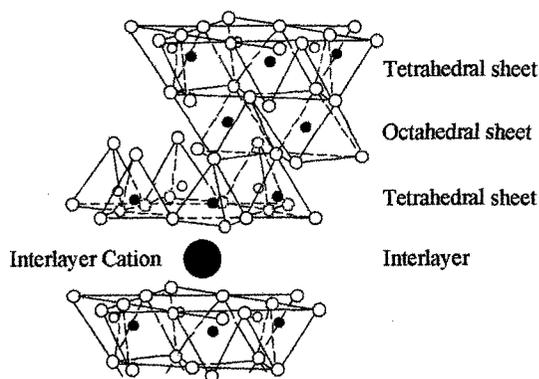


Figure 1 Illustration of mica mineral structure.

2. EXPERIMENTAL

2.1 Material

Refined non-expandable illite (HS; Hikawa Industry Co. Ltd.) from a hydrothermal illite deposit in Shimane Prefecture, Japan was used. The sample consists mainly of non-expandable illite with kaolinite as the only impurity (Figure 2). The chemical formula of HS as determined by X-ray fluorescence (XRF) analysis is as

follows:

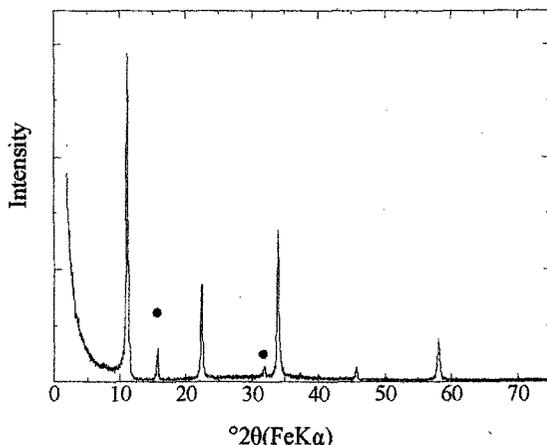


Figure 2 The XRD pattern of HS with kaolinite as impurity. ●; Kaolinite.

2.2 Pretreatments

The alkylammonium ion exchange was carried out following the previous study [9]. The 1-2 μm fractions of HS (10 g) were treated at 70°C for 3 days with 0.1M dodecylamine hydrochloride aqueous solution (1 L). After treatment, the sample was washed 5 times with 50% ethanol and 2 times with pure ethanol until the sample was chloride-free (as indicated by the AgNO_3 test). The obtained sample (Alkyl-HS) was then oven-dried at 60°C.

The 1 g of Alkyl-HS was further treated with 1M NaCl aqueous solutions more than twice. Each treatment was carried out at 25°C for 1 day. After treatment, the sample was washed 5 times with 80% ethanol until the sample was chloride-free. The dried sample (Na-HS) was used for the ammonium ion adsorption experiment.

To obtain ammonium exchanged Na-HS ($\text{NH}_4\text{-HS}$) for the following desorption experiment, the Na-HS was treated with 1M NH_4Cl aqueous solutions with similar procedure for Na exchange treatment.

2.3 Adsorption and desorption experiments

In the ammonium adsorption experiment, 30 mL of each solution containing different proportions of NH_4Cl (10^{-4} to $4 \times 10^{-3}\text{M}$) was added to 0.1 g of Na-HS in sealed polypropylene tubes. The tubes were shaken by an end-over-end shaker (TOWA LABO RKVSD 0101) at 25°C for 24h. The mixture was separated by centrifugation at 15000 rpm for 15 min and then filtered with a 0.2 μm membrane filter.

In the ammonium desorption experiments, 30 mL of 0.5M CaCl_2 solution was added to 0.1 g of $\text{NH}_4\text{-HS}$ in sealed polypropylene tubes. The tubes were shaken by an end-over-end shaker at 25°C for 24h. The mixture was separated by centrifugation at 15000 rpm for 15 min. The separated solid was further treated over five repetitions of the same treatment. The solutions after each separation was filtered with a 0.2 μm membrane filter.

The ammonium concentration of the filtered solutions was determined using an ammonium ion specific electrode (TOA Electronics Ae-235). It has an analytical

error of 10%. X-ray diffraction (XRD) analyses were performed on the separated solids after the adsorption and desorption experiments (Rigaku; RINT2100S).

3. RESULTS AND DISCUSSION

3.1 Cation-exchange experiments

The XRD patterns of untreated, Alkyl-, Na- and $\text{NH}_4\text{-HS}$ are shown in Figure 3. The 10 Å-basal spacing of untreated HS changed to 23 Å after alkylammonium ion exchange. The 23 Å-basal spacing of Alkyl-HS could be related to the formation of "pseudotrimolecular layer" structure of alkylammonium ion in the interlayer. A weak reflection at 10 Å indicating the non-reacted HS was observed. Yokoyama et al. [9] concluded that particles corresponding to the 10 Å $d_{(001)}$ -spacing after the alkylammonium ion exchange has a relatively high layer charge (e.g. 1.0 esu/half unit cell) which is impossible to intercalate alkylammonium ion.

After sodium ion exchange, the 23 Å-basal spacing of the Alkyl-HS disappeared, and the 12 Å-basal spacing that indicates Na-HS emerged. These indicate that almost all of alkylammonium ion in the interlayer was exchanged with sodium ion. The $d_{(001)}$ -spacing of Na-HS further depend on the relative humidity (RH) [9]. The 10 Å-basal spacing is observed under 60% RH [9]. While, the two faces of 10 Å and 12 Å-basal spacing were observed at over 60% RH [9]. The observed 10 Å reflection in the XRD pattern after sodium ion exchange corresponds to Na-HS and non-reacted HS. The change from 12 Å to 10 Å after ammonium ion exchange with Na-HS shows sodium ion in the interlayer has exchanged with the ammonium ion.

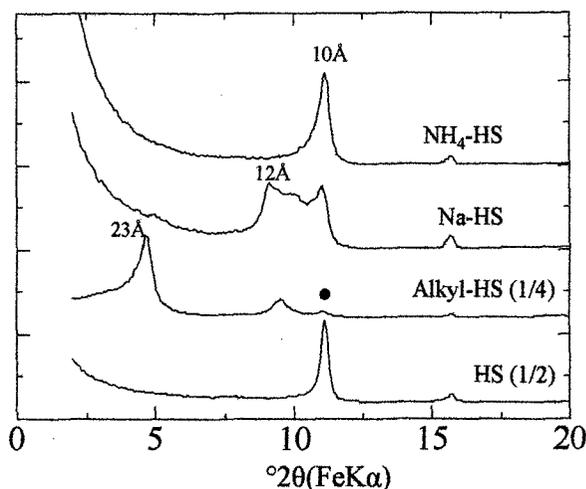


Figure 3 The XRD patterns of untreated, Alkyl-, Na- and $\text{NH}_4\text{-HS}$. The number in the parentheses indicated reduction of full scale intensity. ●; non-reactive particle.

3.2 Adsorption experiment

Figure 4 shows the adsorption isotherm of ammonium ion in Na-HS corresponding to a Langmuir isotherm. The amount of adsorbed ammonium ion on Na-HS increased with higher initial ammonium ion concentration in the reacting solution, and almost attained a constant concentration of 2.3mM of ammonium ion. The maximum ammonium ion adsorption capacity of Na-HS is 0.37 mmol/g.

The XRD patterns after the adsorption experiment are

shown in Figure 5. The intensity of the $d_{(001)}$ -spacing in Na-HS (i.e. 12 Å) decreased with higher initial NH_4^+ concentration. Consequently, the diffraction peak at 10 Å increased indicating that sodium ions in the interlayer were exchanged by ammonium ions.

The $d_{(001)}$ -spacing of sheet silicate depend on its hydration state, which is controlled by the layer charge density, nature of interlayer cation and activity of water [9-15]. In the present study, the change of $d_{(001)}$ -spacing after ammonium adsorption results from ammonium ions exchange with the interlayer cation (i.e. Na^+) considering all other factors were held constant.

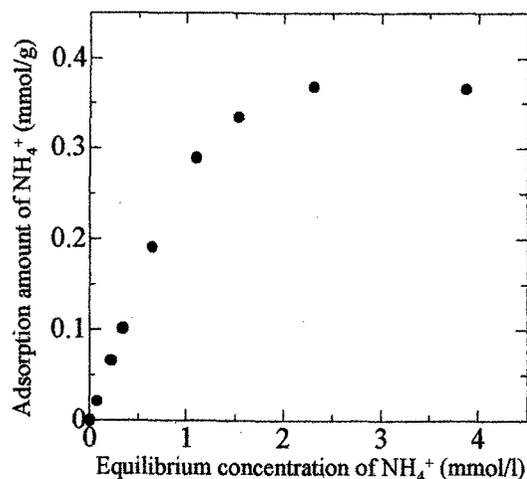


Figure 4 Adsorption isotherm of ammonium ion on Na-HS. The maximum ammonium adsorption capacity was 0.37 mmol/g.

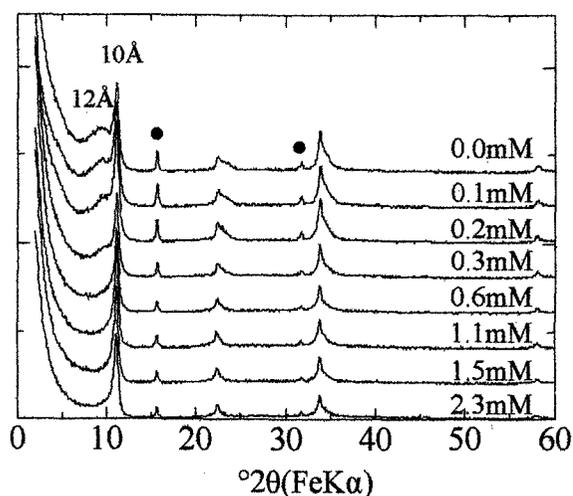


Figure 5 The XRD patterns of HS after ammonium adsorption experiment. •, Kaolinite

3.3 Desorption experiment

The relationship between total concentrations of desorbed ammonium ion and number of treatment times with CaCl_2 aqueous solution is shown Figure 6. The concentration of desorbed ammonium ion after the treatment increased with the number of treatment times with CaCl_2 aqueous solution. Total concentration of desorbed ammonium ion is 50% of the maximum ammonium ion adsorption capacity of Na-HS.

The XRD patterns after desorption experiment are shown in Figure 7. After the CaCl_2 treatments, the 15 Å and 25 Å reflections were observed. The 15 Å and 25 Å reflections correspond to the Ca-HS and regular type interstratified structure of Ca-HS and NH_4 -HS, respectively.

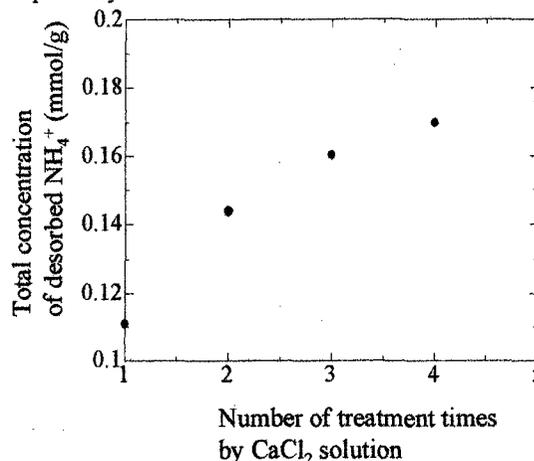


Figure 6 The relationship between number of treatment by CaCl_2 solution and total concentration of desorbed ammonium ion.

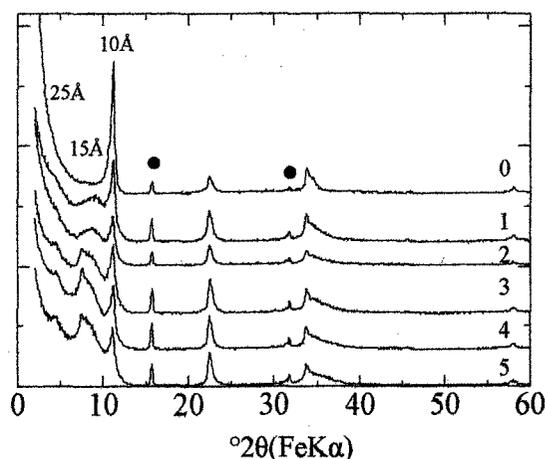


Figure 7 The XRD patterns of HS after ammonium desorption experiment. The number indicates the treatment times with CaCl_2 solution. •; Kaolinite

Although a higher ionic strength of CaCl_2 aqueous solution was used for the desorption experiment, 50% of the adsorbed ammonium ion remained. This suggests that the ammonium ions are fixed in the interlayer spaces of the HS. The desorption behavior of ammonium ion can be related to the high layer charge of HS, and nature of the ammonium ion. The fixation of ammonium ions is useful for application in the reduction or removal of ammonium in water systems. Furthermore, the Ca-HS after ammonium desorption experiments will be reused for ammonium removal since exchanged Ca into interlayer of HS can exchange with ammonium ion.

4. CONCLUSION

The interlayer cation (i.e. K^+) of non-expandable illite was exchanged with alkylammonium ion, and

subsequently with Na^+ . After the ion exchange, non-expandable illite achieved expandability and cation exchangeability.

The maximum ammonium adsorption capacity of Na-HS was 0.37 mmol/g. The $d_{(001)}$ -spacing of Na-HS (i.e. 12 Å) decreased after the adsorption experiment. Consequently, the 10 Å $d_{(001)}$ -spacing of NH_4 -HS was increased due to interlayer cation exchange (i.e. Na^+ to NH_4^+).

Half of the maximum adsorbed ammonium ion on HS is fixed in the interlayer of HS, even after repeated treatment with a high ionic strength solution (i.e. CaCl_2). The interstratified structure of Ca-HS and NH_4 -HS was observed after the desorption experiments.

These results indicate the treated illite is an exquisite material for fixing ammonium ion compared to other cation exchangeable materials (i.e. smectite and zeolite). The treated illite in the present study will be useful as an environmental purification material for removal of ammonium ion in water systems.

ACKNOWLEDGEMENTS

The authors are grateful to Mr. T. Ito of Hikawa Industry Co Ltd. for providing the necessary experimental samples used in the present study. We also wish to thank Drs. T. Watanabe and T. Oba in Joetsu University of Education for helpful discussion. The authors express their utmost gratitude to Chelo S. Pascua (Kanazawa University) for polishing up the manuscript.

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(Received December 24, 2004; Accepted March 19, 2005)