

Environmental Purification Materials: Removal of Ammonium and Phosphate Ions in Water System

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The environmental-purification materials for removal of ammonium and phosphate ions in wastewater were investigated. For removal of ammonium ion, the Korean natural zeolite, mordenite and clinoptilolite with illite and feldspar, was modified at alkali hydrothermal condition with 1.0 mol/l NaOH solution at 100°C under autogeneous pressure for 17 hours to improve the effectiveness of adsorption capacity for ammonium ion. The reaction product was mainly phillipsite and its adsorption capacity for ammonium ion was higher than that for starting material. The ammonium adsorption capacity was 1.14 mmol/g in 10 mmol/l NH₄Cl, which was slightly higher than published data for other natural zeolites. For removal of phosphate ion, andosol from Shimane Prefecture, Japan was examined. The andosol was nonallophanic soil, and consisted mainly of quartz, feldspar with trace of vermiculite and hornblende, and organic matter. The phosphate adsorption capacity of andosol was 0.20 mmol/g, which was comparable with published adsorption values on other clays.

Key words: ammonium, andosol, hydrothermal treatment, natural zeolite, phosphate

1. INTRODUCTION

Removal of harmful elements from wastewater is important to preserve clean environment. Especially, ammonium and phosphate ions are main factors of eutrophication in rivers and lakes. Therefore a process to further reduce the quantity of ammonium and phosphate levels is needed.

Clinoptilolite and mordenite are the main minerals of the natural zeolite found in abundance in many locations [1-2]. They have high cation exchange capacity (CEC), ion adsorption, and especially high ammonium ion selective properties. They were widely used as low cost ion-exchangers and especially used for the removal of ammonium ions in wastewater treatment [3-6]. The improvement of effectiveness of ammonium removal has also been described [4-6]. But the increasing levels of ammonium adsorption were small.

The most effective minerals for phosphate adsorption are boehmite, gibbsite, and kaolinite [7-9]. The andosols is also known as Al-bearing material in many locations in Japan [10-11]. The andosols are mainly classified into nonallophanic and allophanic andosol. Dissimilarities between these andosols are reported by Shoji et al.[11]. Major clays and main active Al in allophanic andosols were allophane and imogolite, and these in nonallophanic andosol were 2:1 type layer silicates and Al-hums, respectively [10]. They have high phosphate adsorption capacity [12-13] and are considered for good candidate for the removal of phosphate ion form wastewater.

In the present study, Korean natural zeolite, mordenite and clinoptilolite with traces of illite and

feldspar were hydrothermally treated with 1.0 mol/l NaOH solution at 100°C for 17 hours. The amount of adsorbed ammonium ions on hydrothermally treated zeolites was compared with that of untreated zeolites and published natural zeolites.

For removal of phosphate ion, the phosphate adsorption behavior of andosol from Shimane, Japan was investigated. The results were compared with published adsorption values for various clays and clay minerals.

2. EXPERIMENTAL

2.1 Materials

Natural zeolite from Pohang, Southeast Korea, was used for ammonium adsorption. It was ground and milled to below 100 μm particle size before use.

Two gram of the natural zeolite and 30 mL of 1.0 mol/l NaOH solution were placed into a Teflon cup fitted in a stainless steel pressure vessel. After heating at 100°C in an oven for 17 hours, the vessel was cooled in water. The products were filtered and washed with distilled water for several times to remove excess cations.

Andosol from Shimane Prefecture, Japan, was used for phosphate adsorption. It was sieved to below 50 μm particle size and heated at 60°C in an oven for 1 day before use.

2.2 Characterization

Mineral identification of the samples was carried out by the powder X-ray diffraction (XRD) method with

CuK α radiation (RIGAKU RINT 2200). The morphology was characterized by the scanning electron microscopy (SEM) (JSM-5800LV). Specific surface area was measured by the multi-point BET method using a Beckman Coulter SA3100 instrument with N₂ gas as an adsorbate. The chemical composition was determined by Inductively coupled plasma spectroscopy (ICP) (SEIKO-SPS4000) for Si, Al, Fe, Na, K, Ca, and Mg, Multiphase Analyzer (LECO RC-412) for H₂O, and Carbon/Sulfur Determinator for C (LECO CS-444LS).

2.3 Adsorption

For ammonium adsorption experiments, 30mL of each solution containing different proportions of NH₄Cl (0.1-10.0 mmol/l) was added to 0.1 g of air-dried samples in stoppered polypropylene tubes. The tubes were shaken by an end-over-end shaker (TOWA LABO RKVSD10101) at room temperature for 17 hours. The mixture was separated by centrifugation at 15000 rpm for 15 min and then filtered. The ammonium concentration was determined using an ammonium ion-specific electrode (TOA Electronics Ae-235).

For the phosphate adsorption experiments, 30mL of each solution containing different proportions of phosphoric acid solution (0.01 to 1 mmol/l) was added to 0.1 g of andosol contained in stoppered polypropylene tubes. The tubes were shaken at 25°C for 24 hours and then the mixture was separated by centrifugation and filtration. Phosphate concentrations of filtrated solution were determined by ICP. Adsorption amounts of phosphate were calculated from the loss of phosphate between separated solution and initial solution. The pH values were measured by pH meters (Toa Dempa Kogyo HM-60V). After the adsorption experiments, XRD using CuK α radiation was used to examine the structural change.

3. RESULTS AND DISCUSSION

3.1 Ammonium adsorption on untreated and treated Korean natural zeolites

Figure 1 shows the XRD patterns of the untreated and treated samples. The zeolites consisted mainly of mordenite and clinoptilolite with feldspar and illite as impurities (Figure. 1a). After the hydrothermal treatment phillipsite was identified as the main phase, but clinoptilolite, mordenite and impurities (feldspar and illite) did not disappear (Figure. 1b).

Figure 2 shows the SEM images of the untreated and treated samples. In the untreated sample clinoptilolite of submicron in size was coffin-shape similar to heulandite (Figure 2a(c)), and mordenite was fibrous and ranged from 0.05 to 0.1 μ m in diameters and 3 to 5 μ m in length (Figure 2a(m)). In the hydrothermal products, phillipsite showed rosettes like intergrowth of crystals, with diameter of about 10 μ m (Figure. 2b). These morphologies were concordant with previous studies [6, 16].

Figure 3 shows the adsorption isotherms of ammonium ion on untreated and treated samples. The products after hydrothermal treatment showed adsorption amount for ammonium ion twofold higher than untreated samples in high ammonium concentration. The ammonium adsorption capacity was 1.14 mmol/g in 10 mmol/l NH₄Cl.

The increase in the amount of adsorbed ammonium ions on hydrothermal product is related to higher number of exchange sites in phillipsite framework in comparison to mordenite and clinoptilolite lattices. Theoretical CEC for anhydrous and Na⁺-form of phillipsite is 4.7 meq/g, which is nearly twofold higher for mordenite and clinoptilolite (2.6 meq/g) [15].

The ammonium adsorption capacity of the treated samples was compared with other published data on natural zeolites in Table 1. The results indicate that the treated samples have similar but slightly higher exchange properties than other published data on natural zeolites.

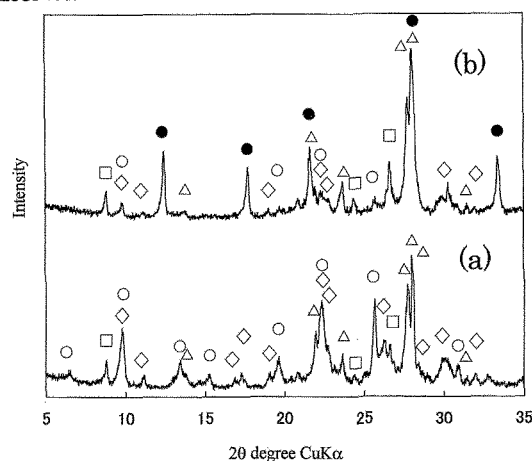


Figure 1. X-ray diffraction patterns of (a) natural zeolite and (b) the product after the hydrothermal treatment in 1.0 mol/l NaOH at 100°C.

○: mordenite. ◇: clinoptilolite. □: illite. △: feldspar. ●: phillipsite.

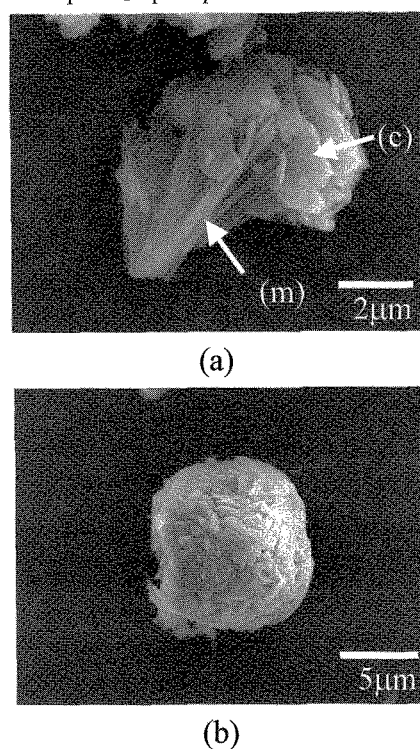


Figure 2. SEM images of (a) untreated zeolite, ((c) clinoptilolite and (m) mordenite), and (b) phillipsite treated with 1.0 mol/l NaOH solution at 100°C.

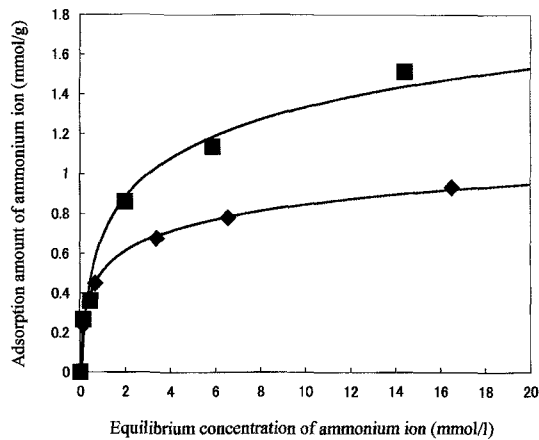


Figure 3. Adsorption isotherm of ammonium ion on natural zeolite and the product after the hydrothermal treatment in 1.0 mol/l NaOH at 100°C.

◆: untreated natural zeolite. ■: product after treatment in 1.0 mol/l NaOH solution at 100°C.

Table 1. Adsorption capacities of various zeolites in 10 mmol/l (NH_4^+).

Zeolite Origin	NH_4^+ Adsorption Capacity meq (NH_4^+)/g	Reference
Hydrothermal product	1.14	(1)
Natural clinoptilolite and mordenite (Pohang, Southeast Korea)	0.78	(1)
Natural clinoptilolite (Shimane, Japan)	1.09	(2)
Natural mordenite (Shimane, Japan)	0.98	(2)
Natural clinoptilolite (Akita, Japan)	1.31	(3)
Natural clinoptilolite (Mount Gipps, Australia)	0.75	(3)

(1)= This study. (2)= Watanabe et al. (2003) [6].

(3)= Watanabe et al. (2003) [14].

3.2 Phosphate adsorption on andosol

Table 2 shows chemical composition of andosol determined by ICP analysis and Multiphase Analyzer and Carbon/Sulfur Determinator. Si/Al ratio of the sample was 2.77. The total amounts of cations in the andosol is about 8 wt%. The amount of carbon in organic matter and H_2O was 4.6 and 8 wt% respectively. Specific surface area measured by the multi-point BET method was $10.0 \text{ m}^2/\text{g}$

Table 2. Chemical composition of andosol (wt.%).

Si	Al	Fe	Na	K	Ca	Mg	C	H_2O	Si/Al
24.9	9.00	2.06	1.84	1.91	1.53	0.39	4.60	8.00	2.77

Figure 4 shows the XRD pattern of andosol. The andosol was consisted mainly of quartz and feldspar with trace of vermiculite (2:1 type layer silicates), and hornblende but no contents of allophane. This indicates the andosol was nonallophanic.

Figure 5 shows the adsorption isotherms of phosphate ion on the andosol. The maximum phosphate adsorption capacity is 0.2 mmol/g . The phosphate adsorption

capacity of the andosol was compared with other published data on various clays and minerals in Table 3. Phosphate adsorption capacity of nonallophanic andosol used in the present study was greater than those on the oxisols, imogolite, gibbsite and halloysite [9,13]. But it was small compared with those of allophane and soil clay [13-14].

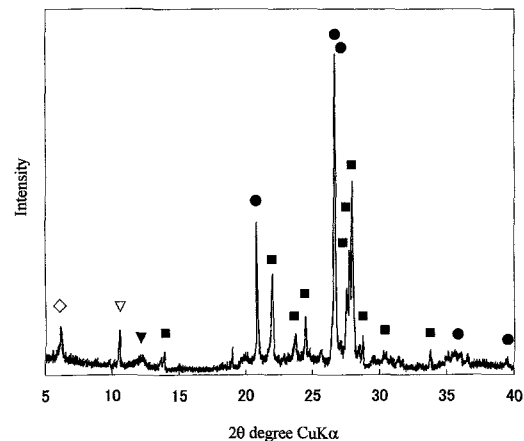


Figure 4. X-ray diffraction pattern of andosol.

●: quartz. ■: feldspar. ▼: kaolinite.

▽: hornblende. ◇: vermiculite.

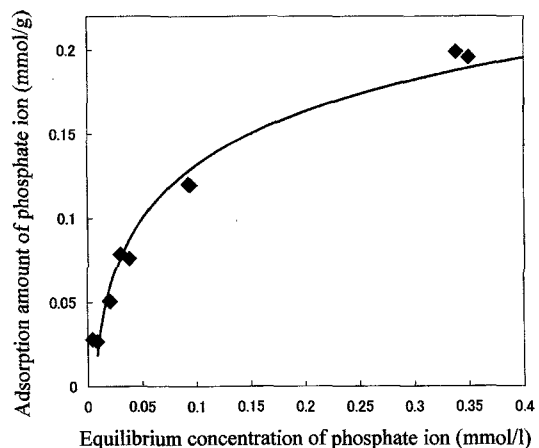


Figure 5. Adsorption isotherm of phosphate ion on andosol.

Table 3. Phosphate maximum adsorption capacities of various clays and clay minerals.

Clay Origin	Maximum phosphate maximum adsorption capacity mmol(P)/g	Reference
Andosol (Shimane, Japan)	0.20	(1)
Oxisols (Brazil)	0.07-0.16	(2)
Soil clay (Egmond, New Zealand)	0.35	(3)
Allophane (Rhyolitic tephra)	0.27	(4)
Allophane (Andesitic tephra)	0.25	(4)
Imogolite	0.10	(4)
Gibbsite	0.05	(4)
Halloysite (Te Puke)	0.01	(4)

(1)= This study. (2)= Fontes et al. (1996) [9].

(3)= Clark et al. (1984) [12]. (4)= Theng et al. (1984)

[13].

4. CONCLUSION

The Korean natural zeolite was changed into phillipsite by the hydrothermal treatment in 1.0 mol/l NaOH solution at 100°C for 17 hours. The hydrothermal product showed better adsorption behavior for ammonium ion than untreated zeolite. The ammonium adsorption capacity was 1.14mmol/g in 10 mmol/l NH₄Cl, which was slightly higher than published data for other natural zeolites.

Andosol from Shimane Prefecture, Japan was nonallophanic andosol consisted mainly of quartz and feldspar with trace of vermiculite, hornblende and organic matter. The phosphate adsorption capacity of andosol was 0.20 mmol/g. The adsorption capacity of andosol was comparable with those of other published data on various clays.

These data suggest that the materials examined in the present study will be useful as environmental-purification materials for removal of ammonium and phosphate ion in water system.

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