PHYSICAL CHARACTERISTIC IMPROVEMENT OF BENTONITE BY PILLARING METHOD FOR ORGANIC COMPOUND REMOVAL

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ABSTRACT

The improvement of physical characteristic of bentonite to develop new adsorbent for organic compound removal by cation exchange properties of bentonite was investigated. Raw bentonites were pillared with tetraethyl ammonium chloride, TEA, equivalent to 0.75, 1.00, 1.25, 1.50, 1.75, and 2.00 times of bentonite CEC so that the pillared clay became more organophilic. The result showed that more surface area could be enhanced by pillaring method. After pillaring, bentonite’s Langmuir surface and micropore areas increased 26.27% or 145.12 m$^2$/g and 70.17% or 40.78 m$^2$/g, respectively. Considering the 1-day and 2-day aging time for pillaring, it’s found that BET, Langmuir surface areas and micropore area were not affected. Additionally, after replacing cation with TEA, CEC of bentonite was decreased from 67.5 meq/100 g to 37.3 meq/100 g with 44.7%. From this reason, it may imply that the pillared bentonite became higher organophilic or hydrophobic, which could be further applied for organic compound adsorption.

Key Words : Bentonite, Pillaring, Cation exchange capacity

INTRODUCTION

Pillared bentonites are modified adsorbents that are synthesized by exchanging inorganic cations with organic cations. The bentonite surface becomes hydrophobic and, in turn, organophilic. Organic cations possessing ling-chain alkyl groups are particularly able to impart the hydrophobic quality to the mineral surface. Such pillared bentonite complexes are able to sorb molecules which themselves are hydrophobic by what has been called hydrophobic bonding.$^{1,2}$ Gitipour et al.$^3$ investigated the clay-aromatic interactions with a view to the use of bentonite clay for binding benzene, toluene, ethylbenzene, and o-xylene (BTEX compounds) in contaminated soils. The modified (organophillic) bentonites are prepared by replacing the exchangeable inorganic cations present in bentonite particles with a quaternary ammonium salt. The findings of his study reveal that organophillic bentonite can act as a successful adsorbent for removing the aromatic organics from contaminated soil.$^4$ Accordingly, pillared bentonite or organobentonite could be enhanced their properties to develop new adsorbents for organic compound removal from contaminated soil or water.$^5,6,7$

Objectives

The purpose of this study was to investigate the characteristics of bentonite after developed by pillaring technique. The exchanging of tetraethylammonium chloride onto the bentonite surface was investigated as the surface areas by BET method and compared to the unpillared bentonite.
Additionally, the aging times of pillaring stage were studied to the effect on pillared bentonite characteristics.

**MATERIAL AND METHODS**

Seven adsorbents were used in this study; unmodified bentonite and six pillared bentonite synthesized with tetraethylammonium chloride. The bentonite used as the raw clay was composed primarily of sodium bentonite (from American Colloidal Company). The cation exchange capacity (CEC) of starting bentonite was 67.5 meq/100 g. Tetraethylammonium chloride \([\text{Tea}^+\text{Cl}^-]\) was purchased from Sigma-Aldrich Chemie Company and was used as the pillaring agent.

The pillared bentonite was prepared by exchanging the naturally occurring organic cations on the surface of commercial bentonite with tetraethylammonium chloride, TEA, at the following percentages of the bentonite’s CEC: TEA cations at 75, 100, 125, 150, and 200%. The quantity of organic cation added to the clay was determined as Equation 1.

\[
f = \frac{M_{\text{cation}}}{\text{CEC} \cdot M_{\text{clay}} \cdot \text{GMW}_{\text{cation}} \cdot X}
\]

Where \(f\) = fraction cation exchange capacity satisfied by organic cation, \(M_{\text{cation}}\) = mass organic cation required to achieve required fraction of CEC (mass), CEC = cation exchange capacity of clay (equivalents/mass), \(M_{\text{clay}}\) = mass clay (mass), \(\text{GMW}_{\text{cation}}\) = gram molecular weight of organic cation (mass/mol), and \(X\) = moles of charge per equivalent = 1 mol/eq for the cations used in this study (mol/equivalent).\(^8^9\)

Ten grams of the starting bentonite sample were suspended in deionized water and stirred continuously for 16 hours.\(^10\) Then, the suspended clay was recovered by centrifugation at 6,000 rpm for 5 min. The mass of organic cation or pillaring agent, tetraethylammonium chloride, necessary to achieve the desired fraction of CEC was dissolved into deionized water. After that, the pillaring agent solution was added over the raw bentonite while stirred vigorously. The resulting suspension was kept at 80 °C for 3 hours and at room temperature for 24 to 48 hours. After equilibrium, the surface water was removed and the bentonite solid was repeatedly rinsed with deionized water at 80 °C to remove unattached organic cations until the wash water conductivity was lower than 20 µS/cm. Afterwards, samples were investigated the BET, Langmuir surface areas and micropore area by BET/ASAP 2000\(^11\) and remained cation exchange capacity.\(^12^13\)

**RESULTS AND DISCUSSION**

The cation exchange capacity of bentonite was reduced from 67.5 to 37.3 meq/100 g bentonite after pillaring by tetraethylammonium chloride at 44.7% and given in Table 1. This is consistent with literature data that clay CEC reduced after pillaring.\(^14^15\)

<table>
<thead>
<tr>
<th>Table 1: Cation exchange capacity of bentonite after pillaring</th>
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<tr>
<td>Samples</td>
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<td>CEC (meq/100g)</td>
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Surface areas of bentonite were developed after pillaring, but it’s not different between fractions of CEC conditions. BET surface areas were ranged from 103.64-109.91 m²/g or averaged 106.50 m²/g. Whereas Langmuir surface area of bentonite were generated to the range of 140.25-150.35 m²/g with average 145.12 m²/g or increasing 26.27% (Fig. 1). Similarly, micropore areas were increased by ranging between 36.13 - 44.64 m²/g with average 40.78 m²/g and increasing 70.17%.

Consider to N₂ Adsorption by isotherm at 77 K, Fig. 2 revealed that pillaring bentonite with TEA equivalent to 0.75 – 2.00 stepwise times the CEC was increased from raw bentonite but it’s not different between CEC fraction factors.

After aging the bentonite sample with TEA for 2-days, it’s found that not only BET and Langmuir surface areas were not quite different from 1-day aging time but also micropore area characterized in the same practice (Fig. 3).
Fig. 3: BET, Langmuir surface areas and micropore area of pillared bentonite with various aging times

CONCLUSION

Bentonite can be developed their surface areas even BET and Langmuir surface areas and micropore area by pillaring with tetraethylammonium chloride, TEA, equivalent to 0.75, 1.00, 1.25, 1.50, 1.75, and 2.00 times of CEC. Nevertheless, their surface areas were not obvious different between times of bentonite CEC. Additionally, longer pillaring aging time does not contribute their surface areas. Bentonite became higher organophilic or hydrophobic characterization which further applies for organic compound removal from contaminated soil and water.

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REFERENCES

7. Changchaivong S., Adsorption of polycyclic aromatic hydrocarbons from synthetic wastewater by organoclays,