REMOVAL OF PHENOLS FROM AQUEOUS SOLUTION WITH ORGANICALLY MODIFIED BENTONITE

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Abstract: Bentonite was organically modified by using ammonium cations such as hexadecyltrimethylammonium(HDTMA), dodecyltrimethylammonium(DDTMA) and tetramethylammonium(TMA) to enhance removal capacity of organic contaminants dissolved in aqueous solution. This modification produced a change of the surface property of bentonite from hydrophilic to organophilic. The individual adsorption of three ammonium cations was performed in a batch reactor to investigate their uptake behavior on bentonite surfaces at 25°C. Among the three ammonium cations, HDTMA showed the strongest adsorption in terms of monolayer capacity and adsorptive strength. These adsorption isotherms were well represented by the Langmuir and the Redlich-Peterson(R&P) models. The removal of toxic organic contaminants such as 2-chlorophenol, aniline, and benzyl alcohol was subsequently achieved by incorporating the modified bentonite. The sorption capacity of the modified bentonite for the organic contaminants was significantly enhanced.

Key Words: adsorption, organic contaminants, organo-bentonite, sorption capacity, wastewater

INTRODUCTION

Various chemical materials and energy sources are discharged to the environment as an industrial waste. This unsuitable discharge plays a large part in water and soil pollution. Especially, rapidly increasing industrial wastewater and the growth of usage of organic detergents and agricultural chemicals are accelerating the water pollution. Therefore, the removal of organic contaminants from wastewater has been extensively researched by using various physicochemical and biological techniques. Among these researches, the removal of organic contaminants by means of adsorption using organically modified clay has drawn much attention¹⁻³. This modification of natural clay is achieved by fixing a quaternary ammonium cations such as hexadecyltrimethylammonium(HDTMA), dodecyltrimethylammonium (DDTMA), and tetramethylammonium (TMA) on the inorganic clay surface through ion exchange reaction. These quaternary ammonium cations used in this modification are cationic surfactants which have carbon chains comprised of over 10 carbon atoms. Bentonite has a large specific surface area and a high cation exchange capacity(CEC). The major interactions between the surfactants and the support are adsorption, intercalation and ion exchange.

Many investigators have studied the adsorption of organic contaminants onto organo-clays⁴⁻⁸. The liquid and gas phase adsorption of aromatic compounds such as benzene, toluene, p-xylene, ethylbenzene, o-xylene, o-dichlorobenzene, 1,2,3-trichlorobenzene and lindane by ex-
changed smectite with tetramethylammonium (TMA) have been studied by Lee et al.\textsuperscript{4,5}. They observed that the adsorption capacity of aromatic compounds on TMA-smectite was considerably enhanced, and the adsorption affinity of relatively large molecules such as o-xylene and 1,2,3-trichlorobenzene was less than other solutes due to molecular sieve effect caused by water molecules. Lee et al. also conducted the adsorption of benzene, toluene and ethylbenzene on A-horizon and Bt-horizon soils treated with nonyltrimethylammonium(NTMA), dodecyltrimethylammonium, and hexadecyltrimethylammonium, which have different alkyl chain lengths. In this study, they emphasized that organic cations acted as partition media, and hence adsorbents with more organic carbon content should have a larger partition coefficient. Cadena\textsuperscript{6} has experimented the adsorption of benzene, toluene and o-xylene on TMA-bentonite in variable pH conditions. According to his results, pH did not affect the adsorption of the organics on TMA-bentonite and benzene was sorbed selectively in the interlamellar space. Smith et al.\textsuperscript{7,8} have studied the adsorption of tetrachloromethane on the clay that is modified by ten quaternary ammonium cations. They found that the adsorption isotherms of trichloromethane on organo-clays modified with long-chain ammonium cations such as dodecyltrimethylammonium, tetradeccyltrimethylammonium(TDTMA), and hexadecyltrimethylammonium showed linear isotherms and noncompetitive adsorption behaviors. So, solute sorption to long-chain sorbed clay is characterized by partition mechanism. However, the adsorption isotherms of trichloromethane on organo-clays treated with short-chain ammonium cations such as tetramethylammonium, tetraethylammonium, benzyltrimethylammonium, and benzylytrimethylammonium show nonlinear isotherms and competitive adsorption behaviors. They reconfirmed these phenomena through the adsorption of a solute on organo-clay modified with dual long- and short-chain cations. Therefore, they suggested the use of this dual organo-clay to the removal of organic contaminants from water of either low or high solute concentration. The typical applications of organo-clay in environmental fields are a filter system for separating organic contaminants from waste water, solidification of organic wastes and contaminated soil, fuel spill control, and liner system for fuel storage tanks\textsuperscript{9}.

**MATERIALS AND METHODS**

**Modification of Bentonite**

Bentonite was obtained at Gampo area (Kyungpook, Korea) and its particle size is 15 μm on an average. The CEC of this bentonite was 94 meq/100 g-clay, measured by a Rhoades' method\textsuperscript{10}. The cationic surfactants of HDTMA (25 wt% in water solution), DDTMA(99+%), and TMA(99+%) were used as an organic modifier, which were purchased from Aldrich Chemical Company. First, solutions of each surfactant were prepared at varying concentrations. Each 20 ml surfactant solution was placed into a 50 ml flask containing 0.5 g natural bentonite, and then shaken on an orbit shaker for 24 hours at 25°C and 250 rpm. After 24 hours, the suspensions were centrifuged for 20 minutes at 10000 rpm. Equilibrium concentration was determined such that the supernatant of each solution was analyzed by TOC analyzer (Total organic carbon analyzer, TOC-5000, SHIMADZU).

The modification of natural bentonite was performed by using both dry and wet processes. The procedures for both methods are presented below.

Wet process : Natural bentonite was added to a 2 L batch reactor containing surfactant solution and then stirred by mechanical stirrer at 250 rpm for 24 hours. Modified bentonite was dried in an oven at 60°C after decanting the supernatant solution off.

Dry process : Natural bentonite was added to a bumpyer mixer, and along with addition predetermined volume of HDTMA stock solution for modifying bentonite.
The modified bentonite was dried in an oven at 60°C.

**Adsorption of Organic Pollutants**

2-chlorophenol (99+%), aniline (99+%), and benzyl alcohol (99+%) were purchased from Aldrich and used without further purification. Adsorption isotherms were determined by contacting aqueous solutions of pollutants with modified bentonite in a batch reactor. Solutions of each pollutant were prepared with the concentrations of 50, 100, 200, 300, 500, 750, 1000, 1500, 2000, 3000, 4000, and 5000 ppm. Each of 20 ml solutions were transferred to 50 ml flasks containing 0.5 g bentonite separately modified by HDTMA, DDTMA and TMA. The flasks were then shaken on an orbit shaker at 25°C for 24 hours. After agitation, the suspensions were centrifuged for 20 minutes at 10000 rpm. The equilibrium concentration of each supernatant suspensions was determined at the maximum wavelength of UV using a 8452 diode array UV-visible spectrophotometer, Hewlett-Packard.

Bi-solute systems were prepared by incorporating two aromatic compounds into a solution, respectively. Three bi-solute systems of 2-chlorophenol/aniline, aniline/benzyl alcohol, benzyl alcohol/2-chlorophenol were prepared. Bi-solute adsorption experiments were carried out by following the same procedures as described for single component adsorption experiments. Equilibrium concentrations were also determined using a UV analysis which correlated absorbency at different wavelengths to the concentrations of multiple pollutants involved.

**Adsorption Models Used**

The adsorption isotherms frequently employed for single-component systems are the 2-parameter Langmuir (10) and the 3-parameter Redlich-Peterson (R&P) (11) models that obey the thermodynamic boundary condition of the Henry's law over an infinitely dilute concentration range. The Langmuir and the R&P models for liquid phase adsorption are written respectively as follows.

\[ q_e = \frac{q_m b C_e}{1 + b C_e} \]  
\[ q_e = \frac{\alpha C_e}{1 + \frac{\alpha}{\beta} C_e^{1-\gamma}} \]

In these equations, \( C_e \) is the equilibrium solute concentration in the solution phase and \( q_e \) is the adsorbed equilibrium concentration of solute per unit weight of adsorbent. \( q_m \) and \( b \) in the Langmuir model represent monolayer adsorption capacity and a constant related to adsorption equilibrium constant respectively, and \( \alpha \), \( \beta \), and \( \gamma \) in the R&P model are empirical constants.

The Ideal Adsorbed Solution Theory (IAST) (12) model was used to analyze multi-component competitive adsorption behaviors in this study. The IAST model is based on the equivalence of spreading pressure in a mixture under equilibrium. The spreading pressure can be evaluated using the Gibbs isotherm as the following:

\[ \pi = \frac{RT}{A} \int_0^{q_e^*} \frac{d \log C_e}{d \log q_e} dq_e \]

The equivalence of spreading pressure in a mixture is

\[ \pi_1 = \pi_2 = \pi_3 = \ldots = \pi_n \]

Other equations for the calculation of IAST model are:

\[ C_{m,i} = Z_i \cdot C_{e,i} \]
\[ \sum_{i=1}^{n} Z_i = 1 \]
\[ q_{e,i} = f(C_{e,i}) \]
\[ \frac{1}{q_{e,i}} = \sum_{i=1}^{n} \frac{Z_i}{q_{e,i}} \]
\[ q_{m,i} = Z_i \cdot q_{e,i} \]
\[ q_{m,i} = \frac{C_{m,i}}{M} \]

Here, \( C_{m,i} \) and \( q_{m,i} \) denote equilibrium concentrations in the liquid phase and on the
adsorbed phase of a solute \( i \) in a mixture, respectively. \( z_i \) is a mole fraction of solute \( i \), while \( C^*_{e,i} \) and \( q^*_{e,i} \) are equilibrium concentrations in the liquid phase and on the solid phase of solute \( i \) in single component adsorption, respectively. \( q_{e,i} \) is the total amount adsorbed from the mixture. \( C_{m,i}^0 \) is the initial concentration of solute \( i \), and \( M \) is a weight of adsorbent per unit volume. There are \( 5n+1 \) equations in total, while \( C_{m,i} \), \( q_{m,i} \), \( C^*_{e,i} \), \( q^*_{e,i} \), \( z_i \) and \( q_{e,i} \) comprise a set of \( 5n+1 \) unknowns. Therefore, we can predict multi-component adsorption equilibrium by solving these equations simultaneously.

RESULTS AND DISCUSSION

Modification of Bentonite

In the modification of bentonite with organic cations, various interactions are possible between clay and surfactants. The most important interactions are adsorption, intercalation, and cation exchange. The most stable bonding is due to ion exchange between quaternary ammonium cations and inorganic cations on the surface of bentonite clay. Results of this experiment are described as adsorption isotherms in Figure 1. The maximum uptakes of HDTMA and DDTMA were above 130% of their CECs, while that of TMA was 90% of its CEC. Adsorption of surfactants (HDTMA and DDTMA) beyond the 100% of the CEC is probably due to hydrophobic interactions among the surfactant hydrocarbon tails.

Three surfactants were adsorbed at the 60% of CEC. At wet process, after surfactant solutions were added to bentonite, the supernatant was decanted off. The wet clay was dried and grounded by a pug mill. At dry process, after modified clay had been taken out from an intensive mixer, it was dried and grounded by the same method. Organobentonites are produced by the exchange of organic cations with inorganic cations on the internal and external surfaces of bentonite. The surfaces of resulting organobentonite are organophilic. As a result, organobentonites become powerful sorbents for organic pollutants compared with a natural bentonite. Compared modification effect by both wet and dry process, adsorption property was turn out to be very similar. It presented in Figure 2.
Adsorption of Organic Pollutants

The adsorption of 2-chlorophenol onto organically modified bentonites is presented in Figure 3. The adsorption data were represented employing the 2-parameter Langmuir and 3-parameter R&P models.

Although the 3-parameter R&P model showed a little better fit to adsorption data than the 2-parameter Langmuir model, both models were in a good agreement with the actual data shown in Tables 1 and 2 by the correlation coefficients.

The organophilic property of the modified bentonites enhanced a sorption capacity for organic phenol contaminants. Adsorption affinities of 2-chlorophenol for the modified bentonites were differently determined because of possible different physical adsorption factors. These factors would be caused partly by a Van der Waals force between surfactants' alkyl chains and adsorbate and partly by an electrical affinity between head groups of surfactants and functional group of adsorbate. Figure 3 shows isotherm data for 2-chlorophenol sorption to HDTMA, DDTMA, and TMA modified bentonite from aqueous solution. Sorption to HDTMA and DDTMA modified bentonite is characterized by relatively strong solute uptake, while sorption to TMA modified bentonite is much weaker. The adsorption of aniline onto organically modified bentonites is presented in Figure 4.

Table 1. Langmuir parameters of 2-chlorophenol on the surfactants coated bentonite

<table>
<thead>
<tr>
<th></th>
<th>q_m</th>
<th>b</th>
<th>A=q_m b</th>
<th>Correlation coefficient</th>
</tr>
</thead>
<tbody>
<tr>
<td>HDTMA coated</td>
<td>121.24846</td>
<td>0.00248</td>
<td>0.30070</td>
<td>0.9994</td>
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<tr>
<td>bentonite</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>DDTMA coated</td>
<td>113.75093</td>
<td>0.00129</td>
<td>0.14674</td>
<td>0.9986</td>
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<tr>
<td>bentonite</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>TMA coated</td>
<td>66.44066</td>
<td>0.00015</td>
<td>0.00997</td>
<td>0.9861</td>
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<tr>
<td>bentonite</td>
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</tbody>
</table>

Table 2. R&P parameters of 2-chlorophenol on the surfactants coated bentonite

<table>
<thead>
<tr>
<th></th>
<th>α</th>
<th>β</th>
<th>γ</th>
<th>Correlation Coefficient</th>
</tr>
</thead>
<tbody>
<tr>
<td>HDTMA coated</td>
<td>0.32038</td>
<td>84.2781</td>
<td>0.04690</td>
<td>0.9992</td>
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<tr>
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<tr>
<td>DDTMA coated</td>
<td>0.13440</td>
<td>258.575</td>
<td>-0.10262</td>
<td>0.9987</td>
</tr>
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<td></td>
<td></td>
</tr>
<tr>
<td>TMA coated</td>
<td>0.00938</td>
<td>750.553</td>
<td>-0.27877</td>
<td>0.9867</td>
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<td>bentonite</td>
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</tr>
</tbody>
</table>

Figure 3. Adsorption isotherm of 2-chlorophenol onto modified bentonite.

Figure 4. Adsorption isotherm of aniline onto modified bentonite.
Adsorption of aniline for each bentonites were different from 2-chlorophenol. It is not generally monolayer adsorption behavior; that is, influenced by partition with adsorption. It showed linear behavior at low equilibrium concentration but exhibited Langmuir adsorption behavior at high equilibrium concentration. Adsorption of benzyl alcohol was much less than those of 2-chlorophenol and aniline as shown in Figure 5. It seems that benzyl alcohol underwent steric hindrance related to the shape of the molecule.

Binary competitive adsorption experiments on HDTMA-bentonite were performed using the three binary systems, 2-chlorophenol/aniline, aniline/benzyl alcohol, and benzyl alcohol/
2-chlorophenol. Figures 6, 7, and 8 show the competitive adsorption behaviors of each binary system along with the graphical prediction of the IAST model. In view of these figures, IAST model provided favorable prediction for the binary competitive adsorption on modified clays. The order of adsorption affinities of the organic solutes for the HDTMA-bentonite remained the same as that observed from single component adsorption experiments.

CONCLUSIONS

Hydrophilic bentonite was modified into organophilic clay by the ion exchange of quaternary ammonium cations (HDTMA, DDTMA, and TMA) for inorganic cations. The maximum uptakes of HDTMA and DDTMA were above 130% of their CECs, while that of TMA was 90% of its CEC. Adsorption of surfactants (HDTMA and DDTMA) beyond the 100% of the CEC is probably due to hydrophobic interactions among the surfactant hydrocarbon tails. This is stable and irreversible adsorption at an exchange of less than 80% of CEC. Therefore, experiments proceeded modifying 60% of CEC that might build stable fixation on bentonite surface. The organophilic properties of the modified bentonites enhanced a sorption capacity for organic contaminants. Adsorption affinities of organopollutants for modified bentonites were differently determined possibly because of different physical adsorption factors. Adsorption of 2-chlorophenol, aniline and benzyl alcohol from dilute aqueous solutions by organophilic clays occur through Van der Waals force at the organophilic sites and electrostatic bond force.

Both Langmuir and R&P models were in good agreement with the actual data. A 3-parameter R&P model showed a little better fit to adsorption data than the 2-parameter Langmuir model. Quaternary ammonium cations with a long-alkyl chain functional group cause a greater adsorption than short chain cations. Bentonites modified by both wet and dry processes have yielded a similar capacity. Adsorption results have shown that the adsorption affinity of 2-chlorophenol is largest, followed by aniline and benzyl alcohol. IAST model also showed good prediction in competitive adsorption systems on organophilic modified bentonites.

ACKNOWLEDGMENT

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REFERENCES

