Characterization and adsorption of phenol by organophilic clays

Authors: C.L. Vieira José, M.M.G. Ramos Vianna; F.R. Valenzuela Díaz; P.M. Büchler

PhD student at Chemical Engineering Department, Polytechnic School, University of São Paulo, São Paulo, Brazil, e-mail: carmen.jose@poli.usp.br

Department Mettalurgical and Materials Engineering, Polytechnic School, University of São Paulo, São Paulo, Brazil.

Chemical Engineering Department, Polytechnic School, University of São Paulo, São Paulo, Brazil.

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Abstract

Nowadays, increasing concern about pollution of groundwater by organic chemicals led to research on the use of various adsorbents. They can be applied to provide a barrier to the escape of organic contaminants from storage tanks and stabilization lagoons.

This study investigated, experimentally, the adsorption of phenol by six organoclays, using phenol in aqueous solution. This is the way that wastewater is discharged.

The organoclays were prepared with two different clays, a bentonite from the Brazilian State of Paraíba (SVC), sodium exchanged in laboratory and a Wyoming, bentonite (SWy) with three Brazilian quaternary ammonium salts. The cations exchanged were dialkyl dimethyl with the alkyls groups dodecyl (DADM), distearyl dimethyl (DSDM) and octadecyl trimethyl (ODTM). Through this technique the hydrophilic character is transformed into hydrophobic.

Adsorption of phenol followed the order of ODTM-SVC > DADM-SVC > DSDM-SVC > DADM-SWy > DSDM-SWy > ODTM-SWy.

Isotherms for DSDM-SVC, DSDM-SWy, DADM-SVC, DADMA-SWy, ODTM-SVC and ODTM-SWy followed a convex up pattern.

The equilibrium curves obtained are well represented by the Freundlich isotherm model. The adsorption data showed that the prepared materials were effective to adsorb phenol, being the Brazilian clay the most efficient of the three materials.

1. Introduction

Phenols are considered priority pollutants since they are harmful to organisms at low concentrations. Six organoclays were evaluated as adsorbents of water phenol.

Organoclays are effective sorbents for a variety of aqueous organic compounds including many common groundwater contaminants. Organoclays are formed when inorganic interlayer cations such as Ca$^{2+}$ and Na$^+$ in clay minerals are replaced by organic cations.

Due to the isomorphous substitution in the aluminosilicate layers, smectite clay minerals usually have a net negative charge, which is balanced by alkali metal and alkaline-earth-metal cations such as Na$^+$ and Ca$^{2+}$. The strong hydration of these inorganic cations creates a hydrophilic environment on the surface and in the interlayer region of the smectite clay. The substitution of Na$^+$ or Ca$^{2+}$ with quaternary ammonium cations of the form [(CH$_3$)$_3$NR]$^+$ or [(CH$_3$)$_2$NRR']$^+$ at the exchangeable sites...
result in organoclays with organophilic properties that can act as sorbents, for contaminants hydrocarbons\(^3,4,5\).

Organoclays formed with quaternary ammonium salts such as trimethylphenylammonium (TMPA) or hexadecyltrimethylammonium (HDTMA), from smectite were effective sorbents for phenol and chlorophenols compared to unmodified smectite. Sorption of phenol was maximized when TMPA-clay was utilized as the sorbent\(^3\).

In this paper we studied six organoclays. One organo-clay was commercial and the others were prepared using a bentonite from the Brazilian State of Paraíba, sodium exchanged in laboratory and a Wyoming bentonite with three Brazilian quaternary ammonium salt. The commercial salts useds were dialkyl dimethyl ammonium chloride with the alkyl group such as dodecyl (DADMA), distearyl dimethyl ammonium chloride (DSDMA) and octadecyl trimethyl ammonium chloride (ODTMA).

2. Materials and Methods

The smectite from Wyoming (SWy) was obtained from the Sigma Chemicals. The smectite clay from the Brazilian State of Paraíba (SVC) was sodium exchanged in laboratory in the manner previously described by Valenzuela Díaz (2001). The salt was obtained from Clarient Divisão Surfactantes. The clays have a Na\(^+\) cation exchangeable cation and a cation-exchange capacity (CEC) of ~ 100 cmol.kg\(^{-1}\) (centimoles of charge kg\(^{-1}\)). The Na-clays were dispersed by mixing with water, and these clays were settled overnight. The clays supernatant were removed and mixed with an aqueous solution of quaternary ammonium salt in the amount of about 100 meq ABDMA per 100 g of the clays and stirred for 20 minutes. The ABDMA-smectite complexes were vacuum filtered and washed with distilled water until free of Cl\(^-\), and stored at room temperature.

Basal spacings were determined by X-ray diffraction (XRD) analysis. X-ray diffraction patterns were recorded using CuK\(\alpha\) radiation (\(\lambda= 1,5416 \text{ Å}\)) and a Philips XPERT-MPD X-ray diffractometer, in steps of 0,02°2\(\theta\), at 1,0s/step.

Adsorption isotherms were determined using the batch equilibration technique. The initial concentrations for phenol were prepared in the range 200 to 800 mg/L. Glass tubes (35 mL) containing 500 mg of organoclays and 25 mL of phenol aqueous solutions were closed and mixed. Every batch stood by 24 hours at 33 °C. Preliminary kinetic investigations indicated that sorption equilibrium was reached at less than 20 hr. After reaching equilibrium, the aqueous phase was separated by centrifugation at 3000 rpm for 60 min at room temperature using a BIO-ENG, type BE-4004. A 10 mL portion of the supernatant was analyzed by total organic carbon method (TOC) with Shimadzu type TOC-5000 A, in order to measure concentration of phenol equilibrium. The amounts of phenol adsorbed were calculated by the differences between the initial and equilibrium concentrations. Isotherms were obtained by plotting the amounts adsorbed against the equilibrium concentration in solution. All experiments were carried out in duplicate and each point on the isotherm is the average of two experiments.

The swelling capacity of organophilic clays in toluene, ethanol and soybean oil and Diesel were measured, as described before by Valenzuela Díaz (2001)\(^6\).

3. Results and Discussion

Table-1 show the swelling and basal spacing for the organoclays. High values for the swelling in toluene, Diesel and ethanol were observed, showing the organophilicity of the clays.
Table 1: Swelling and Basal Spacing.

<table>
<thead>
<tr>
<th>Organoclay</th>
<th>d-Spacing d(001) (Å)</th>
<th>Swelling without mixing (mL/g)</th>
<th>Swelling with mixing (mL/g)</th>
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<tbody>
<tr>
<td></td>
<td></td>
<td>Diesel</td>
<td>toluene</td>
</tr>
<tr>
<td>DSDM-SWy</td>
<td>32.07</td>
<td>15</td>
<td>16</td>
</tr>
<tr>
<td>DSDM-SVC</td>
<td>37.61</td>
<td>10</td>
<td>9</td>
</tr>
<tr>
<td>DADM-SWy</td>
<td>32.07</td>
<td>9</td>
<td>14</td>
</tr>
<tr>
<td>DADM-SVC</td>
<td>30.20</td>
<td>9</td>
<td>12</td>
</tr>
<tr>
<td>ODTM-SWy</td>
<td>36.61</td>
<td>9</td>
<td>11</td>
</tr>
<tr>
<td>ODTM-SVC</td>
<td>39.40</td>
<td>8</td>
<td>10</td>
</tr>
</tbody>
</table>

The DSDM-SWy and DSDM-SVC had low swelling in ethanol and soybean oil (without and with mixing), middle swelling in Diesel and toluene (both without mixing). The DSDM-SWy and DSDM-SVC had high swelling in Diesel and toluene (both with mixing).

The DADM-SWy had low swelling in ethanol (without and with mixing) and soybean oil (without mixing). The DADM-SWy middle swelling in Diesel, toluene (both without mixing) and soybean oil (with mixing). The DADM-SWy had high swelling in Diesel and toluene (both with mixing).

The DADM-SVC had low swelling in ethanol and soybean oil (without and with mixing), middle swelling in Diesel and toluene (both without and with mixing).

The ODTM-SWy and ODTM-SVC had low swelling in ethanol and soybean oil (without and with mixing), middle swelling in Diesel and toluene (both without mixing). The ODTM-SWy and ODTM-SVC had high swelling in Diesel and toluene (both with mixing).

The interlayer spacing followed the order of DTM-SVC > DSDM-SVC > ODTM-SWy > DADM-SVC and DSDM-SWy > DADM-SVC. The interlayer of smectite had a pronounced effect on the adsorption of organic compounds that was showed in figure 1.

Adsorption of phenol followed the order of ODTM-SVC > DADM-SVC > DSDM-SVC > DADM-SWy > DSDM-SWy > ODTM-SWy.

The data were fitted to Freundlich model resulting in greater correlation of the data ($R^2$). The Freundlich equation can be expressed as follows:

\[ y = K_f C_e^{n_f} \]

where $K_f$ (L.mg$^{-1}$) and $n_f$ (dimensionless) are constants related to sorbate binding capacity and a conditional index that describes the shape of the isotherm, respectively. The results of fitting models to phenol sorption on organoclays are listed in table 2. The $n_f$ values were greater than 1 for six organoclays. Freundlich fitting with $n_f > 1$ would indicate conformity of the data to multilayer formation at the adsorbent surfaces. Such observation could also be attributed to the molecular interactions between the sorbate species and subsequent aggregation in the pattern of surface monolayer. Such mechanistic paths could be the possible attributes to the conformity of our data with Freundlich fitting. The $n_f$ values that are greater than 1 represent sorption results having convex up curvatures.
Figure 1 - Adsorption isotherms and Freundlich equation for organoclays smectite Verde Clara (SVC) and smectite from Wyoming (SWy). Fig. 1(a) with cation exchange distearyl dimethyl (DSDM), Fig. 1(b) with cation exchange dialkyl dimethyl (DADM) and Fig. 1(c) with cation exchange octadecyl trimethyl (ODTM).
Isotherms for DSDM-SVC, DSDM-SWy, DADM-SVC, DADM-SWy, ODTM-SVC and ODTM-SWy followed a convex up pattern. Banat (2000) used natural bentonite to adsorb phenol. He concluded that its adsorptive capacity was limited (of an order of magnitude of 1 mg/g).

Validation of the models for adsorption of phenol by organoclays was confirmed by testing the \( R^2 \) (correlation coefficient).

<table>
<thead>
<tr>
<th>Table 2: Model parameters for phenol adsorption by organoclays.</th>
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<tbody>
<tr>
<td><strong>Organoclays</strong></td>
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<tr>
<td></td>
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<tr>
<td>DSDM-SWy</td>
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<tr>
<td>DSDM-SVC</td>
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<td>DADM-SWy</td>
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<td>DADM-SVC</td>
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<td>ODTM-SWy</td>
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<td>ODTM-SVC</td>
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</table>

4. Conclusions

The interlayer formed by exchange of inorganic cations with organic cations works as pillars in order to provide interlayer surface available for contaminant adsorption. The DSDM-SVC, DSDM-SWy, DADM-SVC, DADM-SWy, ODTM-SVC and ODTM-SWy sorption curves for phenol showed in figure 1, indicate that the organoclays could be used as liners and waste disposal reservoirs. The adsorption data showed that the prepared materials were effective to adsorb the phenol, being the Brazilian clay the most efficient of the six materials.

The Freundlich isotherms were found to be applicable for the adsorption equilibrium data.

Acknowledgments

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References