Adsorption of Phenol by HDTMA-modified Organoclay

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Abstract
Naturally occurring clay materials can be modified organically by quaternary ammonium cations resulting into clay products commonly known as organoclays. Such organic modification alters the nature of clay from hydrophilic to hydrophobic, imparting enhanced interaction of the clay products towards hydrophobic pollutants in the environment. These materials can also be used to remediate ionisable organic contaminants such as phenol. The present study presents the adsorption of phenol by hexadecyl trimethyl ammonium (HDTMA) modified bentonite in aqueous medium. It was found that modification of bentonite by HDTMA hugely improved the adsorption of phenol as compared to the unmodified bentonite. Adsorption kinetics and isotherms were also studied.

Key words
Organoclay, adsorption, phenol, Freundlich isotherm, bentonite, hydrophobicity.

Introduction
Natural materials such as clays are profitably effective to immobilise toxic environmental contaminants due to their inexpensive availability, environmental stability and high adsorptive and ion exchange properties. Additionally, clay materials can potentially be modified using a variety of chemical/physical treatment to achieve the desired surface properties for best immobilisation performance of specific compounds. For example, most natural aluminosilicate clays are highly hydrophilic, and consequently show very low adsorption for hydrophobic organic contaminants. However when surfaces of these materials are modified by introducing long chain organic compounds, high sorption of organic contaminants can be achieved (Boyd et al. 1988; Xi et al. 2004; 2005; Xu and Zhu 2009). Ionisable organic contaminants such as phenol can also be adsorbed by organoclays (Zhu et al. 2000). Objective of the present study is to determine the adsorption capacity of organically modified Witheroo bentonite for phenol.

Materials and method
Organoclay HW2CEC was prepared by modifying Witheroo bentonite with cationic surfactant, hexadecyl trimethyl ammonium (HDTMA) in hydrothermal cation exchange reaction (Frost et al. 2008). Surfactant loading was adjusted as twice the CEC of the clay. Kinetic experiment was carried out to standardise the equilibration time for phenol sorption onto the organoclay at 23°C and at initial pH 4.8. Also phenol adsorption isotherm was established.

Results and discussion
Phenol was chosen in this study as a model compound representing a wide range of phenolic organic contaminants existing in the environment. The kinetic experiment showed that sorption of phenol by the organoclay reached the peak after 6 hours of equilibration. The data were fitted into different kinetic models. It was found that the kinetics obeyed pseudo-second order kinetic model ($R^2 = 0.9983$).

<table>
<thead>
<tr>
<th>Clay materials</th>
<th>Phenol removal from 100 ppm phenol solution (mg/g)</th>
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<tbody>
<tr>
<td>Witheroo bentonite</td>
<td>0.19</td>
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<tr>
<td>HW2CEC</td>
<td>11.76</td>
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</tbody>
</table>

The sorption isotherm indicated that for all initial equilibrium concentrations, HW2CEC adsorbed significant amount of phenol. Removal capacity of phenol by the clay improved to huge extent due to organic modification by HDTMA. When modified, HDTMA actually imparts hydrophobicity to the natural bentonite which is otherwise inherently hydrophilic due to isomorphous substitution in the layered silicate sheets. As a result, HW2CEC organoclay adsorbs more phenol than its unmodified natural species. The adsorption is better explained by the Freundlich isothermal model ($R^2 = 0.986$).
Conclusion
It is concluded that the organoclay prepared can remove phenol more efficiently than the unmodified natural clay. The adsorption process obeyed Freundlich isothermal model and the kinetics were best explained by the pseudo-second order model. This organoclay has potential to be used for waste water treatment for phenol.

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References
