Adsorption and Stabilization of Phenol by Modified Local Clay

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ABSTRACT: Phenol is a common pollutant that was listed by US Environmental Protection Agency (EPA) among the priority pollutants. Classical methods employed for phenol removal are either costly or limited to large-scale applications such as biological and thermal decomposition methods. In this study, adsorption of phenol by a type of clay that is extracted from a local soil called Khoweldi was investigated. The X-Ray diffraction revealed that the studied clay is mainly muscovite. The study showed that the local clay could be used as matrix for long-term storage of organic pollutants. Phenol adsorption isotherms conducted on natural and modified clay with Hexadecyltrimethylammonium (HDTMA) revealed that HDTMA enhanced the adsorption capacity of the clay for phenol. To prevent the migration of the adsorbed pollutants into the environment, encapsulation of the modified clay by organosilane was found to be very effective.

Key words: Phenol, Adsorption, Clay, Encapsulation, Solidification, Stabilization

INTRODUCTION

Clay minerals are effective in adsorbing both organic and inorganic pollutants. This is due to their large specific surface area and high ion exchange capacity. Understanding of the interaction between pollutants and the surface of the clay is essential for environmental solution design. The recent studies which were concerned with the development of new procedures for the immobilization of pollutants in aqueous media and soil showed that modified clays exhibit high affinity for a specific class of pollutants (Srinivasan et al., 1989; Jaynes and Boyd, 1991; Wibulswas et al., 1999; Shen, 2002). Abuzaid et al., 2000 reported that the Khoweldi soil, which can be found in the city of Qatif, Eastern Province of Saudi Arabia, showed to have good sorption capabilities for phenol. Accordingly, an economic liner designs can be achieved by using this soil, particularly, when modified using hexadecyltrimethy lammonium (HDTMA) to enhance its sorptive capacity for pollutants. The sorptive capacity of Khoweldi soil is expected to be improved if the clay proportion is increased by separating quartz (Abuzaid et al., 1989).

Phenols are considered as priority pollutants by US EPA and European Union (EU). They can be found in aquatic environments as biodegradation products of humic substances, lignins and tannins or as derivatives of plastics, dye industries and pulp processing (Bruzzoniti et al., 2000). Their adsorption by clays and soils has been studied extensively. Lawrence et al. (1998) studied the sorption of phenol and 2-, 3- and 4-chlorophenol from water by tetramethylammonium (TMA)-clay and tetramethylphosphonium (TMP)-clay. They showed that the (TMP)-clay was better sorbent than the (TMA)-clay. Furthermore, the TMP clay was selective within the chlorinated phenols studied, where phenol and 4-chlorophenol were effectively sorbed, while 2- and 3-chlorophenol were not sorbed. Irene (1996) showed that the use of quaternary ammonium modified clays as presolidification adsorbent produced a successful solidification and stabilization process in the treatment of soils contaminated with phenol. Shen (2002) reported that, under appropriate conditions, a removal of more than 90 per cent of phenol from water could be achieved by the use of dispersed bentonite to the phenol contaminated water followed by the addition of benzyltrimethylammonium bromide (BTMA) ions as a flocculant. The use of clay in phenol adsorption was also investigated by Wang and Lin (2003), Arellano-Cárdenas et al. (2005), Richards and Bouazza (2007), Roperts et al. (2007), Boufatita et al. (2007) and Froehner et al. (2009).

Song et al. (2001) reported that encapsulation of montmorillonite with organosilanes resulted in a hydrophobic coating that acts like a “cage” around the clay particles to limit diffusion of organic species previously adsorbed. The molecules of organosilanes...
are probably adsorbed to the outer surfaces and bound to the edges of the clay via condensation with edge-OH groups. The carbon and oxygen K-edge NEXAFS spectroscopy of the modified montmorillonite surfaces showed that surface coatings on the outside of the clay particles exist. This method was applied by Wasserman et al. (1998) to isolate hazardous metallic cations and to reduce their leach ability from storage media and from substrates containing toxic cations. There are many other ways to remove phenol from environment that will not be discussed in the present work (Dabhade et al., 2009; Agarry and Solomon, 2008; Samarghandi, et al., 2007).

Based on the above discussion, the main objectives of this study are to investigate the adsorptive capacity, for phenol, of the local clay after being separated from the local soil called Khoheldi and to study the effect of encapsulation of the clay with organosilane on the migration of pollutants to the environment, after being exposed to vigorous shaking.

**MATERIALS & METHODS**

In order to separate the clay part, 20 g of the Khoheldi soil was dispersed for one hour by stirring in 1 liter of distilled water at pH 9. The obtained suspension was then left to settle for 24 hours. The upper part of the liquid was filtrated with Whatman no. 42 filter paper and the residue was dried in the oven at 105 °C and then grinded to fine powder. The modification process consists of altering the surface polarity of the clay minerals via treatment with cationic surfactants such as hexadecyltrimethylammonium bromide (HDTMA), Jaynes and Boyd, 1991; and Wibulswas et al., 1999). Modified clay was prepared based on the cationic exchange capacity (CEC), which was measured as 60 meq/100 g. Fourteen (14) grams of the separated clay were mixed with 4.6 grams of HDTMA in 280 mL distilled water and were shacked at 270 rpm for one day. The mixture was then filtered using Whatman no. 44 filter paper. The residue was dried in an oven at 105 °C and was then grinded.

X-Ray diffraction (Cu-Ka) was performed using JEOL JDX 3530 X-Ray diffractometer. The sample was in powder form and its diffraction was compared with the standard diffraction pattern for different phases established by the International Center for Diffraction Data. The result showed that the separated clay was mainly muscovite with less than 1 per cent quartz impurity. A small amount of the sample was spread on adhesive conductive aluminum tape attached to a sample holder and examined with the scanning electron microscope JEOL 5800LV. The analysis was performed at a resolution of 40 Å, depth of penetration of electron beam of 5 Å and detection limit of 0.2 per cent. Energy Dispersive Spectrometry (EDS) analysis was performed at different spots and the percentages of the elements present were semi-quantitatively determined and corrected.

An amount of separated clay varying between 200 and 1000 grams was added to 25 mL of phenol solution having a concentration of 25 to 100 mg/L. The batch equilibration technique was used to determine the adsorption isotherms of phenol on modified and natural clay samples. All samples were sealed in Erlenmeyer conical flasks (50 mL) and oscillated at 165 rpm at room temperature for a period of 42h. Phase separation was then performed using centrifugation and filtration processes and separated samples were stored at 4 °C for further treatment before GC analysis. The adsorbed quantities of phenol were determined according to the balance equation 1

\[
q = \frac{V(C_0 - C_e)}{m}
\]

Where q is the sorbed phenol concentration (mg/g), V is the volume of phenol solution (L), m is the mass of adsorber (g) and C0 and Ce are initial and equilibrium phenol concentration (mg/L), respectively. The solid part that represents the polluted clay was dried at 105°C and reserved for further investigation (encapsulation with organosilane). The stabilization of pollutants is considered as an essential step in order to prevent their migration from clay as a result of leaching, evaporation or hydration. In the current investigation, contaminated clay was dried and encapsulated by organosilane. The clay was then treated by butyltrichlorosilane to make it hydrophobic. Samples of polluted clay with different amounts of adsorbed phenol were well mixed together and then grinded to obtain homogeneous polluted media with an average concentration of phenol of 1.63 and 1.5 mg/g in modified and natural clay samples, respectively. The encapsulation of the polluted clay was obtained by reacting the clay with organosilane in methylene chloride solvent. The reaction was performed at a weight ratio of 1:1:30 for polluted clay: silane: solvent in a closed system for 2-3 days. After that, the encapsulated clay samples were rinsed with a solvent several times in order to remove free silanes, and then air dried. Samples of 0.3g of modified and natural clay were dispersed in water at different environmental stresses. Both encapsulated and non-encapsulated samples were dispersed for 42 hours in aqueous solution with pH values of 3,5,7,9 and 11 to simulate extreme environmental conditions. After phase separation by centrifugation and filtration, the...
concentration of leached phenol was determined by gas chromatography (GC). Extraction of phenol was performed using liquid-liquid extraction as described in EPA method 3510C. Water samples were adjusted to a total volume of 100 mL and extracted three times with 15 mL of methylene chloride using separatory funnels. The pH of the samples was adjusted to less than 2 using sulfuric acid. Separatory funnels were sealed and vigorously shaken for 5 minutes using mechanical shaker with immediate and periodic venting to release excess pressure. The organic layer was then allowed to separate from the water phase for 10 minutes. Concentration of extracted samples was performed using the Kuderna-Danish Techniques, where methylene chloride was exchanged by iso-propanol. EPA method 604 was followed for examining the samples for phenol. Samples were analyzed by Agilent 6890 N Gas chromatograph using capillary column HP-5 [length of 30 m, I.D. of 0.32 mm and film 0.25 µm (5%- phenyl methyl polysiloxane)]. All standards and samples were prepared in HPLC grade glass distilled 2-propanol. FID detector in splitless mode was used to analyze the samples. The analysis was performed at an initial temperature of 80°C, a holding time of 1.5 minute and final temperature of 200°C at the rate of 10°C/minute. Nitrogen gas was used as the carrier gas at a rate of 4 mL/minute. The minimum detection limit of the applied method is 0.14 mg/L, while the minimum concentration that can be detected by the instrument is 100 mg/L.

RESULTS & DISCUSSION

Results of the X-ray diffraction analysis for modified and unmodified clay are shown in Fig. 1. The figure clearly shows that the d spacing of clay increased from 10.27 Å to 12.67 Å, which could be attributed to the HDTMA modification. It is worth to mention that atomic adsorption examinations conducted on the filtrate obtained after modification of the clays revealed that 57.35% of Ca, 10.11% of Mg and 3.71% of K have been displaced by HDTMA cations, which corresponds to 70 per cent of cation exchange capacity (CEC) of the clay. Furthermore, Table 1 shows the XRF results of all elements presents in the natural clay sample. Figure 2 shows the adsorption isotherm of phenol onto natural and modified clay samples. The isotherm can be modeled by using either Freundlich or Langmuir models as shown in Fig. 3. The sums of squares of deviations (SSD) for Freundlich and Langmuir models were 1.02 and 3.58, respectively, which resulted in using Freundlich model to describe the adsorption behavior of the clay for phenol. According Freundlich model:

\[ q = K C_e^n \]  

the linearized form of equation (2) is:

\[ \log(q) = \log(K) + n \log(C_e) \]  

where n is Freundlich constant, and K is the adsorption coefficient. Both n and K can be determined from Fig. 4, which is a log-log scale graph of Freundlich model. Table 2 shows the values of n and K that were determined from Fig. 4. The results in the table clearly demonstrate that the HDTMA modification resulted in improving the adsorption capacity of the clay for phenol. Furthermore, it can be deduced from the values Freundlich constants (1.33 and 1.82 for natural and
modified clay, respectively) that the adsorption bonds were weak in the both case but it was weaker in the case of the natural clay. Therefore, the predominant adsorption mechanism of phenol on surface clay is anticipated to be physical rather than chemical. The leachability is an important criterion to classify landfills. In this study, leachability testing was performed to measure the immobilization of pollutant within the clay. Figure 5 shows the leaching of phenol from different types of clays. The results showed that encapsulation was very efficient with natural clay since no phenol was found to migrate from the clay to the water after 24 hours of vigorous shaking.

![Sorption isotherm of phenol on natural and modified clay](image1)

**Fig. 2.** Sorption isotherm of phenol on natural and modified clay.

![Comparison between Freundlich and Langmuir models in the case of modified clay](image2)

**Fig. 3.** Comparison between Freundlich and Langmuir models in the case of modified clay.

<table>
<thead>
<tr>
<th>Element</th>
<th>Si</th>
<th>Al</th>
<th>Mg</th>
<th>Fe</th>
<th>K</th>
<th>Ca</th>
<th>C</th>
<th>O</th>
</tr>
</thead>
<tbody>
<tr>
<td>Weight%</td>
<td>23.34</td>
<td>7.02</td>
<td>1.91</td>
<td>8.86</td>
<td>4.07</td>
<td>0.78</td>
<td>3.19</td>
<td>50.83</td>
</tr>
<tr>
<td>Atomic%</td>
<td>16.98</td>
<td>5.32</td>
<td>1.61</td>
<td>3.24</td>
<td>5.32</td>
<td>0.4</td>
<td>5.42</td>
<td>64.91</td>
</tr>
</tbody>
</table>

**Table 1.** Elements in natural clay as determined using XRF analysis.
Fig. 4. Log(q) vs. log(Ce) adsorbing phenol by natural and modified clay.

Fig. 5. The leachability data for phenol in encapsulated and non-encapsulated clay.

Table 2. Gas Chromatography conditions

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<table>
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<tr>
<td>Total flow</td>
<td>97.5 mL/min</td>
</tr>
<tr>
<td>Head column pressure</td>
<td>117.41 kPa</td>
</tr>
<tr>
<td>Injector temperature</td>
<td>280°C</td>
</tr>
<tr>
<td>Oven program</td>
<td>80°C (1.5 min)+10°C/min, 200°C (1 min)</td>
</tr>
</tbody>
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Table 3: Freundlich isotherm constant for the adsorption of phenol onto both clays.

<table>
<thead>
<tr>
<th>Type of clay</th>
<th>Freundlich Constant (n)</th>
<th>Adsorption Coefficient (K)</th>
<th>Correlation Coefficient (R²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Natural Clay</td>
<td>1.82</td>
<td>2.28 \times 10^{-1}</td>
<td>0.97</td>
</tr>
<tr>
<td>Modified clay with HDTMA</td>
<td>1.33</td>
<td>0.024</td>
<td>0.97</td>
</tr>
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</table>
CONCLUSION

In conclusion, the results revealed that phenol was adsorbed from aqueous solution on clay samples that were modified with a cationic surfactant. Analysis of data obtained from the isotherms revealed that the presence of the HDTMA surfactant enhanced the adsorption capacity of the clays for phenolic compounds. The Freundlich model was found to best fit data obtained from the isotherm investigation and calculated constants revealed that adsorption mechanism was physical rather than chemical. The encapsulation of the clay by organosilane was found to be very effective in preventing the migration of phenol back to the environment in contact.

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REFERENCES


