Investigation of Titania Addition into Tar Sands for Removal of Phenol from Aqueous Solutions

Lua’y Zeatoun,† Munjed Al-Sharif and Abeer Al-Bsoul

Department of Chemical Engineering and Department of Civil Engineering, Jordan University of Science and Technology, P.O. Box 3030, Irbid 22110, Jordan

Tar sands were found to remove significant amounts of phenol from aqueous solution in the presence of titania; about 70% at an initial concentration of 10 ppm. Batch sorption experiments showed that phenol uptake was increased with either an increase in initial phenol concentration, percentage of titania in the sorbent or pre-activation temperature. On the other hand, the presence of soft ions such as sodium, Na⁺, or potassium, K⁺, or the increase of solution temperature suppressed the uptake of phenol. Physical pre-activation of the tar sands influenced the adsorption process positively. The sorption process appears to be exothermic and relatively fast; the equilibrium isotherm data were well represented by either Langmuir or Freundlich models.

Key words: tar sands, phenol, adsorption, activation, titania

Introduction

Water pollution by phenols is a serious environmental concern. Phenol compounds are similar in structure to herbicides and insecticides and known to be highly toxic and resistant to natural biodegradation (Rengaraj et al. 2002). Their presence in water supplies causes bad taste and odour, even at low concentrations. The maximum permissible limit for phenol concentration in drinking water has been set to 0.002 mg/L by regulation of the World Health Organization (1984). According to the U.S. Environmental Protection Agency, phenols constitute the eleventh top priority of the 126 chemicals which have been designated as priority pollutants. Therefore, it is necessary to eliminate phenols from wastewater before it is discharged.

Adsorption onto activated carbons is the typical wastewater treatment method (Bertoncini et al. 2003; Chang 1999; Kindzierski et al. 1992), due to the carbon’s high specific surface area, ample pore size and reasonably high mechanical strength. On the other hand, the cost of activated carbons is high and they require an additional step of adsorbent regeneration during which the pollutants are transferred to a vapor or organic phase. For these reasons, low-cost, naturally occurring materials have been investigated as replacement materials for the removal of phenols. Among these materials are waste tires (Ariyadejwanich et al. 2003), organophilic clays (Jose et al. 2003), organobentonites (Lin and Cheng 2000), palm seeds (Rengaraj et al. 2002), oak shells (Al Asheh et al. 2003) and coconut husks (Vinod and Anirudhan 2002).

Tar sands available in Jordan are mainly composed of sand grains, clay and heavy oils known as bitumen that can contain as high as 10% of the tar sand. Jordanian tar sands have been used successfully as an adsorbent for removal of copper and cadmium from aqueous solutions (Zeatoun and Yousef 2004; Zeatoun et al. 2004). Yet, experimental results showed that tar sands do not have a high affinity for phenol adsorption (Zeatoun et al. 2004). Titanium dioxide (TiO₂, titania) is a white pigment with wide-ranging commercial applications such as in coatings, fillers and catalysts (Pratsinis et al. 2000; Thayer 1998). Fetterolf et al. (2003) have utilized titania for adsorption of methylene blue and acid blue 40, while Takahashi et al. (2003) have used titania modified by various heat treatments for complex-dye adsorption. We anticipate that titania addition to the tar sands will improve phenol uptake; tar sands will serve as a support for the titania.

The objective of this research is to evaluate the use of locally available tar sands with titania addition for the removal of phenols from aqueous solutions. The amount of solute uptake of the tar sands will be investigated at different adsorption conditions, varying the initial solute and sorbent concentrations, pre-activation conditions and temperature.

Materials and Methods

Preparation of Adsorbent

Tar sands rocks were obtained from Wadi Isal in Jordan. They were crushed and sieved down to a particle size between 0.21 and 0.50 mm. Titania powder (Ti-Pure R-100) was supplied by DuPont (2003) with an average
particle size of 0.32 µm. The basis for the added amount of titania was weight percentage from the tar sands; titania percentages were varied between 1 and 4%. In addition, experiments using pure titania, i.e., without tar sands, were conducted. For some experiments, prior to sorption testing, physical pre-activation was accomplished by heating the tar sands between 450 to 700ºC. It was hoped that the activation would remove volatile components and thus possibly increase the surface area of adsorption.

**Batch Experiments**

Phenol solutions were prepared using deionized water and initial concentrations ranging between 10 to 100 ppm. Batch sorption tests were conducted by adding a known amount of the tar sands/titania mixture or pure titania to a bottle containing 10 mL of a phenol solution. The tar sands concentration was 5 mg/mL and initial pH value of the phenol solutions was 7.0. The sample bottles agitated in a temperature-controlled water bath shaker (Kottermann, Germany) to vary the temperature between 25 and 45ºC. Samples were withdrawn at different time intervals to study the kinetics of the adsorption process. In other experiments, the samples were left for 24 h to reach equilibrium. The suspensions were then centrifuged to separate the tar sands and titania from the solutions, then the filtrate collected and analyzed.

**Phenol Analysis**

The residual phenol concentrations were determined using a spectrophotometer 9423-UVG-1002E (Helios Gamma Company) following the method of Gales and Booth (1976). This method is based on the spectrophotometric analysis of the produced colour from the reaction of phenol with 4-aminoantipyrine. Buffer and potassium ferricyanide solution were added to the reaction mixture to adjust the pH and to give the desired colour. Two replicates per sample were averaged.

The difference between the initial concentration of phenol (C_0; ppm) and the equilibrium concentration of phenol (C_e; mg/L) was used to compute the equilibrium solid-phase concentration or the uptake of phenol (q_e; mg/g) by a mass of the adsorbent. The mass of adsorbent was calculated as the sum of the mass of the tar sands (W; g) and the mass of the titania added as 100 W m, where m is the mass percentage of titania based on the weight of tar sands (g titania/100 g tar sands). Therefore, the equilibrium uptake is as follows (equation 1):

$$q_e = \frac{0.01(C_0 - C_e)}{W + 100 \ W \ m}$$

Equation 1 was used to also compute the uptake of phenol at any time (q; mg/g) by replacing C_e with the concentration of phenol at any time (C; mg/L).

**Theory**

**Adsorption Isotherms**

Langmuir and Freundlich isotherms describe the relationship between the liquid phase concentration and surface concentration of the adsorbate at equilibrium. Both the Langmuir and Freundlich models were fit to the experimental data and then used to determine the adsorption capacity of the adsorbent. The Langmuir isotherm can be represented by equation 2:

$$q_e = \frac{K_L a_l C_e}{1 + a_l C_e}$$

The linearized equation of Langmuir is represented as follows (equation 3):

$$\frac{1}{q_e} = \frac{1}{K_L} + \frac{1}{K_L a_l} \frac{1}{C_e}$$

where K_L is the Langmuir constant related to the maximum adsorption capacity (mg/g) and a_l is the other Langmuir parameter related to the energy of adsorption (L/mg). The linearized Langmuir equation is plotted as $\frac{1}{q_e}$ versus $\frac{1}{C_e}$. In this form the slope of the line, $\frac{1}{K_L a_l}$, together with the intercept, $\frac{1}{K_L}$, can be used to determine the isotherm constant, a_l.

The Freundlich model was also used to predict the observed phenomena as given by equation 4:

$$q_e = K_F C_e^n$$

where n and K_F are constants. Equation 4 may be linearized via a logarithmic plot as follows (equation 5):

$$\ln q_e = \ln K_F + \frac{1}{n} \ln C_e$$

**Results and Discussion**

**Influence of Contact Time**

The effect of contact time on phenol adsorption by tar sands (2% titania added, activation at 700ºC prior to testing) was investigated using initial phenol concentrations of 10 and 100 ppm; the sorption test temperature was 25ºC, with 5 mg/mL of activated tar sands and particle diameter between 0.21 and 0.50 mm. Figure 1 shows a relatively fast rate of phenol removal by the adsorbent, indicating that adsorption of phenol is mainly at the surface of the sorbent. Equilibrium is approached in about 15 min, yet to ensure achievement of adsorption equilibrium, samples were left in the shaker for 24 h.

It was noticed that equilibrium phenol concentrations remain unchanged after one day, indicating that phenol was not degraded by the sorbents used in the study. It was

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*Phenol Removal using Titania and Tar Sands*
also observed that an increase in the initial phenol concentration (see Fig. 1) resulted in an increase in the adsorption of phenol. This is consistent with an increase in the mass transfer driving force (concentration difference of phenol between the bulk of fluid and the adsorbent surface), which allows more phenol molecules to reach the adsorbent surface from the bulk of the solution.

These kinetic results can be used to verify if intraparticle diffusion is the rate-limiting step for phenol adsorption onto the sorbent. The intraparticle diffusion model is used: \( q = k_p t^{0.5} \) (Weber and Morris 1963), where \( k_p \) is the intraparticle diffusion rate constant. Weber and Morris (1963) suggested that intraparticle diffusion will play a role in the sorption process if a plot of adsorbate uptake versus the square root of time displays a linear relationship. Additionally, the intraparticle diffusion would be the rate-controlling step if a line fit to the data intercepts the origin. Figure 2 shows that the phenol adsorption uptake rate on titania tar sands displays the appropriate linear relationship but the line fit does not pass through the origin. This indicates that intraparticle diffusion was involved in the sorption process but was not the only rate-limiting mechanism (Banat and Al Asheh 2001; Calace et al. 2002).

**Influence of Pure Titania Concentration**

The effect of pure titania concentration on the removal rate of phenol from aqueous solution was investigated at 25°C, with initial phenol concentrations of 10, 20, 80 and 100 ppm. The concentration of titania sorbent was varied from 5 to 40 mg/mL at constant initial phenol concentration. The amount of phenol removed from solution was dependent on the titania concentration. Upon increasing the titania concentration, the resulting equilibrium concentration of phenol decreased and the removal percentage of phenol (Fig. 3) increased. This trend suggests that an increase in adsorbent concentration yields an increase in the number of vacant sites on the titania particles available for attachment of phenol molecules. Adsorption of phenol almost leveled off upon further addition of titania beyond 10 mg/mL.

Pure titania was compared with the activated tar sands/titania mixtures. For an initial phenol solution of 100 ppm, equilibrium uptake of phenol using 5 mg/mL of tar sands with 2% TiO₂ is 4.16 mg/g while equilibrium uptake of phenol using 5 mg/mL of pure TiO₂ is 3.88 mg/g. This improvement is equivalent to an increase of 7.22% in uptake value for the titania/tar
sand mixture. By using the tar sands/titania mixture, the required cost of sorbent will substantially drop since tar sands are much cheaper than titania, being naturally available and surface-mined. Also, this minimizes the requirement for the regeneration step, since tar sands are so cheap. These data indicate that adding a very small amount of titania to tar sands yields a higher removal rate of phenol molecules than using pure titania. This advantage might be attributed to the fact that tar sands serve as a support for titania by permitting more exposure of surface area. This might be attributed to the fact that at pH 7, titania will have both neutral and negative surface charges (Weng et al. 1997), while tar sands will have negative surface charge (Riviello et al. 1988). Then, there will be a repulsive force between titania and tar sands with better suspension achieved.

Tar sands were thermally activated to determine if adsorption is enhanced upon activation. The amounts of phenol removed by both natural (i.e., non-activated) and activated tar sands were determined by varying the phenol initial concentration at constant sorbent concentration (5 mg/mL and 4% TiO₂) and sorption temperature, 25°C. The equilibrium data are presented in terms of Langmuir and Freundlich isotherms as shown in Fig. 4 and 5, respectively. It is obvious that the phenol uptake by activated tar sands is higher than that by non-activated tar sands. Also, Tables 1 and 2 show that the values of K_L and K_F for Langmuir and Freundlich models increase upon tar sands activation, indicating that the adsorbent capacity is positively influenced by thermal activation. When tar sands are activated, all volatile matter (bitumen) is removed from the particles of tar sands, increasing the number of available sites for adsorption. This leads to an increased amount of phenol removed. Similar results were previously reported for the removal of phenol by natural and activated oak shells (Al Asheh et al. 2003) and by raw and activated date pits prepared at 700°C (Banat et al. 2004). The combined effects of activation temperature and the amount of titania added have also been investigated. Figure 6 shows that increasing both the activation temperature and amount of titania increases the uptake of phenol. Increasing the activation temperature should expose more active sites and adding more titania will increase the surface area for adsorption, yielding an overall increase in the removal of phenol.

**Influence of Sorption Temperature**

To study the effect of sorption temperature on the removal of phenol by tar sands and titania, three experiments were conducted at 25, 35 and 45°C using different initial phenol concentrations between 10 and 100 ppm, using tar sands (pre-activated at 700°C, 4% titania added). As shown in Fig. 7, the uptake decreases as the
temperature increased, indicating that the adsorption process is exothermic. Similar findings were also obtained by other investigators (Zeatoun and Yousef 2004; Vinod and Anirudhan 2002).

Influence of Salt Addition

Phenol removal might be affected by the presence of dissolved salts in the aqueous solutions, so the effect of salinity on the adsorption of phenol was also studied. Solutions containing 100 ppm of phenol concentration were tested after addition of either sodium chloride (NaCl) or potassium chloride (KCl). Addition of either salt lowered the uptake rate appreciably for salt concentrations above 0.3 M, as shown in Fig. 8. This may be a result of competition between salt cations (Na+ or K+) and phenol for the available adsorption active sites. In addition, the presence of K+ ions hindered the phenol uptake more notably than the presence of Na+ ions (Fig. 8). This might be attributed to a higher rate of mass transfer of K+ ions than Na+ ions to the sorbent surface. The diffusion coefficient for K+ ions in water (1.957 × 10^{-5} \text{ cm}^2/\text{s}) is greater than for Na+ ions in water (1.334 × 10^{-5} \text{ cm}^2/\text{s}) at 25°C (Newman 1991). K+ ions will reach the sorbent surface faster than Na+ ions and consequently occupy more vacant sites. Similar results were reported by Banat et al. (2004), who studied the adsorption of Cd^{2+} ions by date pits.

Conclusions

These studies showed that tar sands mixed with small amounts of titania were capable of adsorbing appreciable amounts of phenols from wastewater over a range of concentration up to 100 ppm. The tar sands may be used as low-cost, naturally abundant sources for phenol removal and can remove 70% of the phenol from wastewater.

### Table 2. Freundlich model constants for phenol adsorption on activated and non-activated tar sands with 4% titania

<table>
<thead>
<tr>
<th>Type of tar sands</th>
<th>(K_F)</th>
<th>(1/n)</th>
<th>(R^2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Activated</td>
<td>0.21</td>
<td>0.72</td>
<td>0.96</td>
</tr>
<tr>
<td>Non-activated</td>
<td>0.17</td>
<td>0.67</td>
<td>0.93</td>
</tr>
</tbody>
</table>

![Fig. 6. Effect of activation temperature and TiO2 percentage on the adsorption of phenol uptake using initial phenol concentration of 100 ppm.](image)

![Fig. 7. Effect of solution temperature on the uptake of phenol. Sorbent concentration 5 mg/mL, 4% TiO2 added, activated tar sands at 700°C.](image)

![Fig. 8. Effect of the presence of salts on the uptake of phenol. Sorbent concentration 5 mg/mL, 4% TiO2 added, temperature 25°C, activated tar sands at 700°C.](image)
10-ppm phenol solutions. The adsorption process appears to be exothermic and fast since equilibrium was reached in a short period of time (within 15 min). The uptake of phenol was increased by increasing any of the following factors: percentage of titania, phenol concentration or activation temperature. In contrast, the presence of soft ions (Na+ or K+) or increase of solution (sorption) temperature lowered the uptake of phenol. Overall, these findings demonstrate tar sands/titania (sorption) temperature lowered the uptake of phenol.

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References


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