

Evaluation of Activated and Non-activated Tar Sands for the Removal of Phenol and Cadmium from Aqueous Solutions

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Locally available tar sands were used for the removal of phenol and cadmium ions from their aqueous solutions. Batch sorption experiments showed that tar sands did not remove phenol from aqueous solutions, but they were effective in cadmium adsorption. Cadmium uptake was found to increase with an increase in initial concentration of the metal ions, temperature, pH and sorbent amount. On the other hand, the presence of ions such as sodium, Na⁺, suppressed the uptake of cadmium ions. Physical activation of the tar sands influenced the adsorption process negatively. The sorption process was relatively fast and the equilibrium isotherm data were well represented by the Langmuir model.

Key words: tar sands, cadmium, adsorption, activation

Introduction

The presence of heavy metals, phenols and dyes has received great attention in the world due to their association with many human health problems and the aquatic environment. Adsorption is a process used widely to treat these contaminants, particularly at low concentrations. Since the adsorption process depends mainly on the availability and cost of the adsorbents, many researchers have utilized available natural and waste materials as adsorbents. Examples of these adsorbents include solid waste from the olive industry (Al Asheh and Banat 2001b), soils (Abu-Sharar 1997; Basta et al. 1993; Dar 1996; Halen and Vanbladel 1990), decaying leaves (Sayrafi et al. 1999), coconut shell granular activated carbon (Chang 1999), and low-grade bituminous coal (Chang 1999; Das and Sharma 1998). Other researchers have used inexpensive adsorbents such as fly ash (Finqueneisel et al. 1998), sugar beet pulp (Ozer et al. 1998), canola meal, pine bark and moss peat (Al Asheh and Duvnjak 1999).

Phenolic compounds are common contaminants generated by petroleum and petrochemical, coal conversion, and phenol-producing industries. Phenols are widely used for the commercial production of a vast variety of resins such as those used as construction materials for automobiles and appliances, epoxy resins, adhesives, and polyamide for various applications. Phenols are considered priority pollutants since they are harmful to organisms at low concentrations and many have been classified as hazardous pollutants because of their potential harm to human health. Thus, the United States Envi-

ronmental Protection Agency (U.S. EPA) limited the phenol content in water streams to less than 0.3 mg/L. Banat and Al Asheh (2001a,b) have used the low-cost adsorbents chicken feather and human hair for phenol removal from wastewater.

Cadmium is usually produced as a by-product of zinc extraction and is found in air, food, soil, plants and surface waters (World Health Organization 1984). Water is considered polluted when its cadmium content exceeds 1 µg/L (Friberg et al. 1974). Higher levels of cadmium in tap water are found with plated plumbing fittings, silver brass solders and galvanized iron piping materials (Browning 1969). Cadmium usually interferes with the ability of metallothionein to regulate zinc and copper concentrations in the body. Metallothionein is a protein that binds to excess essential metals to render them unavailable.

The objective of this study is to determine the possibility of using locally available tar sands for the removal of phenols and cadmium from aqueous solutions. The amount of solute uptake by tar sands will be investigated at different conditions, such as pH, temperature and initial solute and sorbent concentrations.

Material and Methods

Sorbent

Tar sands rocks were obtained from Wadi Isal in Jordan. The chemical analysis of tar sands is shown in Tables 1 and 2 (Harrison 1988). The analysis of trace elements showed neither phenol nor Cd content in the Jordanian tar sands as shown in Table 2. The average oil content in tar sands varies between 5.5 and 12.1% by weight and is

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TABLE 1. Chemical analysis of Jordanian tar sands

Components	Average wt. %
SiO ₂	74
CaO	0.07
MgO	0.03
Fe ₂ O ₃	0.77
Al ₂ O ₃	7
TiO ₂	0.44
Na ₂ O	0.04
K ₂ O	0.06

primarily composed of aliphatic and aromatic hydrocarbons (Harrison 1988). In order to use tar sands as sorbent, they were crushed and sieved to have a particle size in the range of 246 to 416 μm . This size was the most appropriate to provide high surface area for adsorption as well as to keep the particles suspended in the aqueous solution.

Physical activation of the tar sands was carried out in order to investigate the possibility of increasing active sites of adsorption by the removal of volatile materials. Thermal gas analysis on tar sands showed that the weight of the sample does not change after 500°C (indicating that all the volatile components were carbonized). Tar sands samples were activated using a fluidized bed reactor (Al Asheh et al. 2003) by passing N₂ gas at 520°C for 1.5 h, followed by flushing with CO₂ at the same temperature for 1.5 h.

Batch Sorption Tests

Batch adsorption was carried out to investigate the performance of non-activated and activated tar sands for phenol and cadmium removal. Phenol solution was prepared using deionized water to dilute phenol into six different initial concentrations in the range of 10 to 100 mg/L; initial pH of the solutions was in the range of 7 to 7.5 and was not adjusted during the course of the experiments. A solution of Cd²⁺ ions was prepared using 3CdSO₄·8H₂O salt and deionized water and then diluted to five desired concentrations in the range of 10 to 80 mg/L.

A known amount of tar sands was placed in vials containing 10 mL of different aqueous solutions of

either phenol or Cd²⁺ ions with predetermined concentration. The vials were placed in a temperature-controlled water bath shaker (Kottermann, Germany) to agitate the mixture at the desired temperature. Samples were withdrawn at different periods in order to study the kinetics of the adsorption process. The suspensions were then filtered to separate the tar sands from the solutions, and the filtrate was collected and analyzed.

The number of replicates required for this study was determined by running six experiments of identical conditions. It was noticed that the results of five experiments were within 7% and the sixth experiment was significantly out of this range. Therefore each test was carried out in duplicate, and the average results were presented in this study. The results of a duplicate test were discarded when they differed by more than 7%.

Phenol Analysis

Analysis of phenol was carried out spectrophotometrically using the produced colour from the reaction of phenol with 4-aminoantipyrine (Gales and Booth 1976). According to this method, buffer and potassium ferricyanide solution are added to the reaction mixture to adjust the pH and to give the desired colour, respectively. The final equilibrium concentrations were determined using a Spectronic 21 UVD spectrophotometer (Milton Roy Company) at a wavelength of 510 nm. Solutions of phenol, in which no tar sands were used, were analyzed to determine the calibration curve for phenol (Banat et al. 2000).

Cadmium Analysis

Cadmium ion concentration in the filtrate was measured using an atomic absorption spectrophotometer (Spectro AA10, Varian). Some of the runs were replicated to ensure reproducibility of the data.

The experimental conditions that were used throughout the study include the following parameters: temperature of 25°C, initial pH of 5.97 for Cd²⁺ ions, four hours of shaking, and 10 mg of tar sands per millilitre of solution. Each parameter was changed at a time, while fixing the others, to examine its influence on the sorption process. The adjustment of the pH was made by adding different amounts of 0.1 M HCl solution or 0.1 M NaOH. Sorption experiments were carried out at 18, 25 and 45°C to study the effect of temperature on the sorption process.

Adsorption Isotherm

Adsorption isotherm describes the relationship between the liquid phase concentration and surface concentration of adsorbate at equilibrium. The Langmuir and Freundlich isotherms are the most common models used to

TABLE 2. Average trace elemental analysis of Jordanian tar sands

Element	Content (ppm)
Cu	19
Cr	133
Mn	41
Ni	100
Pb	23
Zn	328
Ag	22

describe such a relation (Tien 1994). The Langmuir model is used in this study to examine the experimental data. It can be written in its linearized form as follows:

$$\frac{1}{q} = \frac{1}{K_L} + \frac{1}{K_L b} \frac{1}{C} \quad (1)$$

where q is the equilibrium solid-phase concentration (mg/g), C is the equilibrium liquid-phase concentration (mg/L), K_L is the Langmuir constant related to the adsorption capacity (mg/L), and b is the other Langmuir parameter related the energy of adsorption (L/mg). The parameter b is used to determine the following thermodynamic relations :

$$\ln(b) = \ln(b') - \frac{\Delta H}{RT} \quad (2)$$

$$\ln\left(\frac{1}{b}\right) = -\frac{\Delta G}{RT} \quad (3)$$

$$\Delta S = \frac{\Delta H - \Delta G}{T} \quad (4)$$

where b' is the adsorption energy constant, ΔH is the enthalpy of adsorption, R is the universal gas constant, T is the absolute temperature (K), ΔG is the Gibb's free energy, and ΔS is the entropy of adsorption. ΔG and ΔS are found from adsorption experiments at different temperatures.

Results and Discussion

Removal of Phenol

Three main experiments were conducted to study the adsorption of phenols onto tar sands. In one of the experiments, 5 mg/mL of non-activated tar sands was used with a different initial concentration of phenol in the range of 10 to 80 mg/L. No phenol uptake was detected onto this type of tar sands at all phenol concentrations used. In another set of experiments, 4-hour oven sintered (at 700°C) tar sands were used as an adsorbent. Adsorption tests with phenol using 10 to 80 mg/L initial phenol concentrations were conducted using the treated tar sands and again no adsorption was observed. In a third set of experiments, the concentration of tar sands was increased to 10 mg/mL, but still no phenol uptake was detected when using thermally treated tar sands. In all of these experiments, the temperature was kept at 25°C, no salt was added, and the vials were agitated for four hours.

The non-detectable adsorption in the above-mentioned tests could be attributed to the fact that tar sands are mostly silica and negatively charged in aqueous solutions (Riviello et al. 1988). Phenol particles act as weak acids releasing the H^+ ions into the solution, thus remaining with a negative charge as well. When silica

(tar sand) is in direct contact with a solution containing negatively charged molecules (phenols), repulsion forces are exerted between the two and thus no adsorption can take place (Banat et al. 2000; Riviello et al. 1988).

Removal of Cadmium Ions

Effect of contact time. The effect of contact time on Cd^{2+} ion adsorption using tar sands was investigated at an initial cadmium concentration of 60 ppm, 25°C and 10 mg/mL of non-activated tar sands. The results (Fig. 1) showed that the rate of cadmium uptake onto tar sands was relatively fast. Equilibrium was attained in almost 20 min. The high initial uptake was because of the likelihood that Cd^{2+} ions attachment occurred mainly at the surface of the sorbent (Al Asheh and Banat 2001b). This result was verified by plotting the square root of time versus the uptake. When the data was fitted to a straight line, the fitted line did not pass through the origin (the R^2 value of the straight line was 0.72). This showed that intraparticle diffusion was not the controlling step in the adsorption of Cd^{2+} ions by tar sands (Banat and Al Asheh 2001). This surface adsorption phenomenon could be due to the complex formation of Cd^{2+} ions with the functional groups available on the sand surface. Tar sands contain aromatics and aliphatic hydrocarbon; these contain carboxyl and hydroxyl groups which form the functional groups along with silica, titania and alumina compounds (Table 1) which might be responsible for the sorption process.

Effect of adsorbent. The effect of sorbent concentration on the removal of Cd^{2+} from aqueous solutions was considered. In this case, different amounts of tar sands were

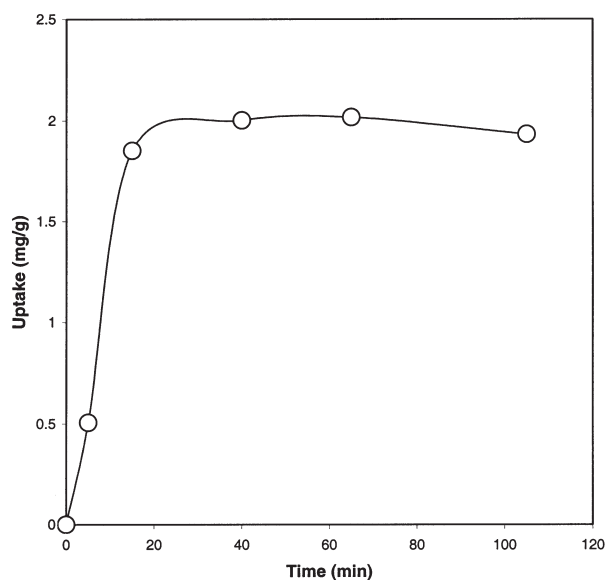


Fig. 1. Kinetics of Cd^{2+} ions uptake by non-activated tar sands.

used and adsorption was followed using different initial cadmium concentrations. Figure 2 shows that the residual concentration of Cd^{2+} ion was reduced upon increasing tar sand concentration from 1 to 10 mg/mL. This could be due to the increase of the number of active sites available for metal binding. Adsorption of cadmium did not improve upon further addition of tar sand beyond 10 mg/mL due to the saturation of the suspension.

Effect of temperature. Temperature has significant influence on adsorption processes. Adsorption might be exothermic or endothermic, thus it was decided to verify the nature of the adsorption system. For this purpose, three temperatures were used, namely 18, 25 and 45°C, to study the influence of temperature on Cd^{2+} ion uptake by tar sands. The equilibrium isotherms obtained at each of these temperatures were well represented by the linearized Langmuir model (equation 1) shown in Fig. 3. It was noticed that the uptake increased as the temperature increased. Table 3 shows high values of R^2 (a measure the goodness-of-fit), indicating that the Langmuir model was adequate to represent the experimental equilibrium data.

The enthalpy change of adsorption (ΔH) (equation 2) was obtained from the slope of $\ln(b)$ versus $1/T$ shown in Fig. 4; it was found to be -80.17 kJ/mol. The high value of ΔH (>62.7 kJ/mol) showed that the removal process was due to the chemisorption mechanism (Fogler 1999). The chemisorption mechanism could be due to the chemical reaction complexes formed between Cd^{2+} ions and the functional groups available on the surface of the tar sands. The negative sign of ΔH confirms the exothermic nature of the adsorption process. Accordingly, any increase in temperature will increase the available energy

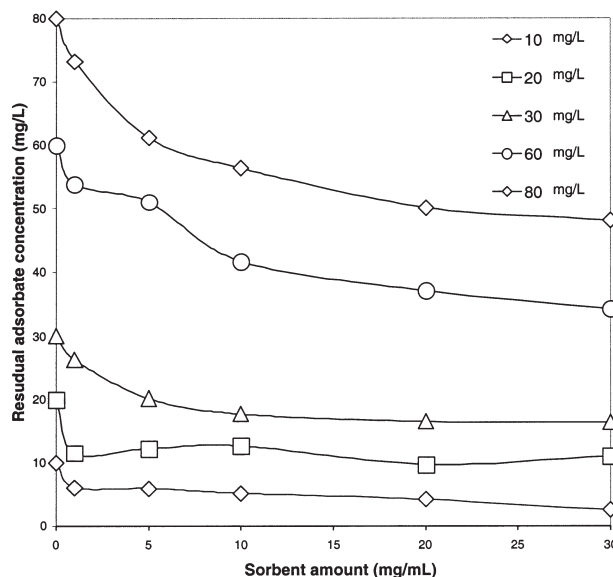


Fig. 2. Residual adsorbate concentration using different sorbent amounts.

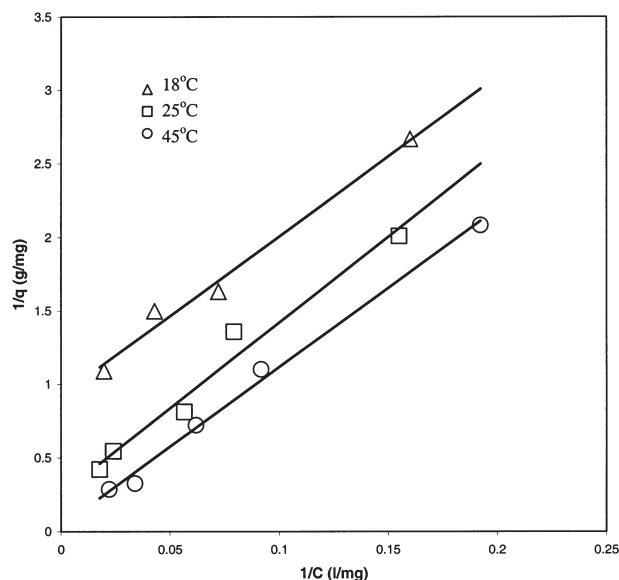


Fig. 3. Langmuir isotherms for different temperatures.

for complex formation, consequently increasing the uptake. Similar results were also obtained by other researchers (Al Asheh and Banat 2000).

Effect of pH. The nature of the adsorbent surface reflects different responses for the solution pH. Thus, it is necessary to investigate the interaction between solution pH and tar sands surface via this adsorption process. The initial pH of the metal solution was adjusted to give four values, namely 2.06, 2.77, 5.04 and 5.97. They did not exceed this range to avoid any possible precipitation of the Cd^{2+} ions. Solutions of 30 ppm Cd^{2+} ions were used, while the other conditions were fixed. Figure 5 shows that the increase in the initial pH of the solution resulted in an increase in the Cd^{2+} uptake by tar sands. This was expected because of the negative charges prevailing at the surface of the tar sands at high pH values. This increases the attraction forces between the tar sands and Cd^{2+} ions. At considerably low pH values the opposite occurs, where repulsive forces take place between Cd^{2+} ions and the positively charged surface of the sorbent, thus lowering the Cd^{2+} uptake (Al Asheh and Banat 2001a).

Effect of salt addition. The effect of salt addition on the adsorption of Cd^{2+} ions was also considered for solu-

TABLE 3. Langmuir isotherm constants at different temperature for Cd^{2+} adsorption

Temperature (°C)	Langmuir constants		
	K_L (mg/g)	b (L/mg)	R^2
18	1.45	0.050	0.95
25	2.80	0.038	0.95
45	27.1	0.003	0.99

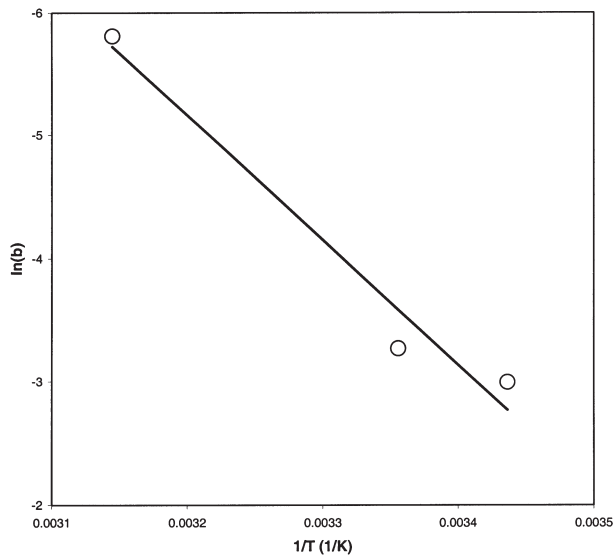


Fig. 4. Relationship between $\ln(b)$ and $1/T$ for the adsorption of Cd^{2+} ions adsorption on tar sands.

tions containing 60 mg/L metal concentrations and 0.0, 0.01 and 0.05 M Na^+ ions in the form of sodium chloride (NaCl). Other initial conditions were not adjusted. Addition of salt ions lowers the uptake (Fig. 6). This might be a result of the competition between Na^+ and Cd^{2+} ions to the active sites of adsorption available on the surface of the tar sand. In such a case, Na^+ ions hinder Cd^{2+} ions from reaching the sorbent-active sites due to the repulsive forces. The same results were obtained by Jha et al. (1988), when they studied the adsorption of Cd^{2+} ions by chitosan.

Effect of physical activation. Activated and non-activated tar sands were used in this part to examine the

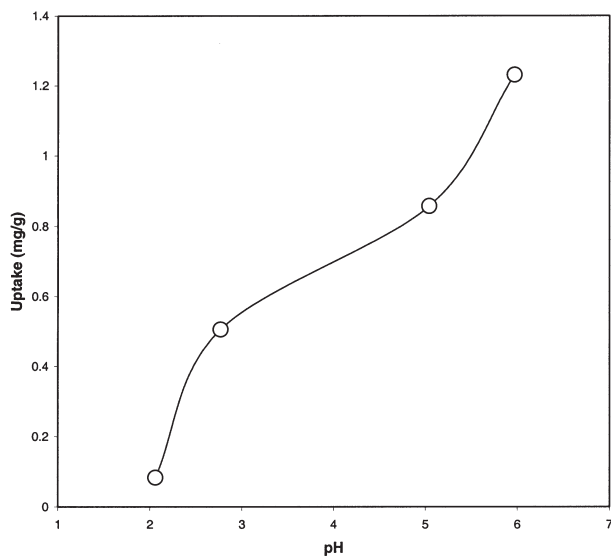


Fig. 5. Effect of pH on the adsorption of Cd^{2+} ions by tar sands.

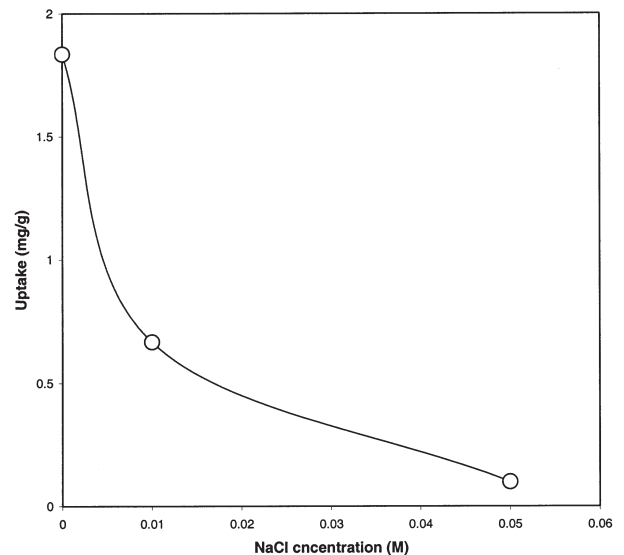


Fig. 6. Effect of salt addition on the adsorption of Cd^{2+} ions by tar sands.

potential of each for Cd^{2+} ion adsorption and to verify if any enhancement can be achieved upon activation. In this case, 10 mg/mL of tar sands was used, and none of the other conditions were altered. The adsorption data were well represented by the Langmuir isotherm shown in Fig. 7. It was clear that the Cd^{2+} uptake by activated tar sand was lower than that by non-activated sand. The values of K_L for the Langmuir model confirmed this conclusion (Table 4), which showed that the adsorbent capacity was negatively influenced upon activation. When tar sands were activated, all the volatile matter that contain the functional groups are removed; since adsorption could be due to chemical complexation this will render the sorbent to be less effective with fewer numbers of functional groups.

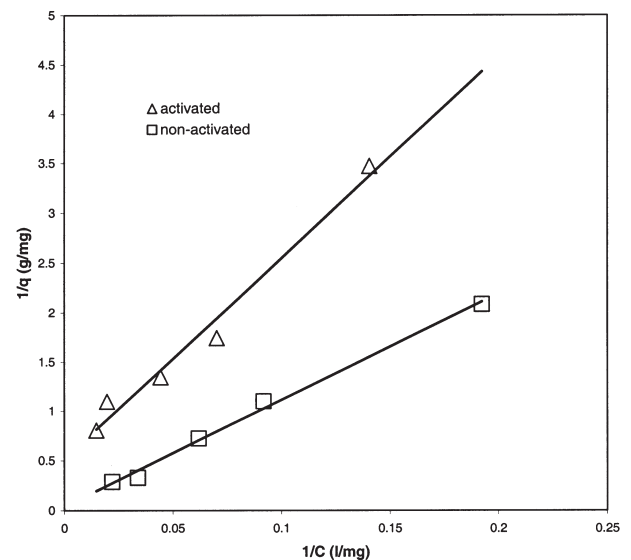


Fig. 7. Langmuir isotherms for Cd^{2+} ions adsorption on activated and non-activated tar sands.

TABLE 4. Langmuir isotherm constants for Cd²⁺ adsorption on activated and non-activated tar sands

Type of tar sands	Langmuir constants		
	K_L (mg/g)	b (L/mg)	R^2
Activated	1.95	0.025	0.98
Non-activated	2.80	0.038	0.95

Conclusions

Tar sands were found to be incapable of adsorbing phenols. In the case of cadmium ions, tar sands removed appreciable amounts of Cd²⁺ ions from the aqueous solutions. The cadmium ion adsorption process was affected by many factors. The increase in the metal ion concentration, tar sands amount, pH or temperature resulted in an increase in the uptake of cadmium ions by non-activated tar sands. On the other hand, the presence of ions such as Na⁺ lowered the adsorption of Cd²⁺ on the surface of the tar sands. A maximum amount of Cd²⁺ removal from the solution was achieved when using 10 mg/mL of tar sands. The sorption process was considered fast and equilibrium was attained in a short period of time. Activation was not economical since it resulted in a lower uptake of Cd²⁺ ions.

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