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ADSORPTION OF ORGANICS FROM TAR SAND WATER
BY ACTIVATED CARBON IN PACKED BEDS

Final Report

By
Anthony L. Hines
Enayat O. Pedram

Work Performed Under Contract No. AS20-81LC10686

University of Wyoming
Laramie, Wyoming

Technical Information Center
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FINAL REPORT
ADSORPTION OF ORGANICS FROM TAR SAND WATER
BY ACTIVATED CARBON IN PACKED BEDS

by

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Under Terms of Contract DE-AS20-81LC10686

SUMMARY

The adsorption of TS-1S and TS-2C tar sand waters were studied at 278 and 298 K on activated carbon in both batch and packed bed experiments. The isotherms were nonlinear over the entire liquid concentration ranges. Breakthrough curves were obtained in packed bed experiments as a function of bed lengths, particle size, and liquid velocity. A mechanistic approach was used to solve the mass transfer equations for the packed adsorber, the mass transfer coefficients and the rates of adsorption were calculated. Also the breakthrough curves were analyzed to establish the relative importance of the various individual mechanisms that contributed to the overall adsorption process.

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PART I

Adsorption of Organics from TS-1S Tar Sand Water on Activated Carbon in Packed Beds

INTRODUCTION

The adsorption characteristics of dissolved organic matter onto activated carbon from TS-1S tar sand product water was investigated in this part of the study. Equilibrium isotherms at 298 K were obtained and modeled. Breakthrough curves were obtained from column experiments as a function of bed length, carbon particle size, and liquid velocity.

Theoretical breakthrough curves were predicted by the Thomas approach using different rate controlling mechanisms. The second order surface kinetics model was found to predict the breakthrough over the entire concentration range. Mass transfer coefficients determined from the best fits to the experimental data are larger for smaller particle sizes and for the higher flow rates. The results are presented herein.

EXPERIMENTAL

Materials:

Granular DARCO activated carbon was selected as the adsorbent for this study. It had a total surface area of $667 \text{ m}^2/\text{g}$ (as found by a BET analysis), a bulk density of 0.357 g/ml , a total pore volume of 1.00 ml/g , and a mean pore radius of $29 \times 10^{-8} \text{ cm}$. Prior to use, the activated carbon was screened to 20 x 40 U.S. mesh, washed with distilled water, and dried in an oven at a temperature of 175°C for nine hours. It was then placed in a closed container until it was to be weighed for the adsorption study. The tar sand water used in this work was obtained from the Laramie Energy Technology Center steamflood experiment of a Utah Tar Sand. The test was conducted in the Northwest Asphalt Ridge deposit located near Vernal, Utah and the water is denoted as TS-1S. Total production during the test amounted to 1150 barrels of oil and 6250 barrels of water. Prior to the studies the water went through a

coagulation process with a FeCl_3 dosage of 250 mg/l. It was mixed in a rapid mixing unit at 100 rpm for 2 min, then in a slow mixing unit at 20 rpm for 30 min. This water was yellowish in color and had a pH value of about 4.0. The analyses of TS-1S tar sand water before and after coagulation are presented in Tables 1 and II.

Apparatus and Procedure:

The batch kinetic study was done to determine the time required for the organics and activated carbon to reach equilibrium. In the experiment, 0.5 g of 20 x 40 U.S. mesh activated carbon was added to a 250 milliliter Erlenmeyer flask with 100 ml tar sand water. The flask was sealed with a polyethylene cap and placed in a constant temperature gyratory shaker bath. Periodically, a 100 microliter tar sand water sample was withdrawn and analyzed with a total carbon analyzer to determine the total organic carbon (TOC) content. When there was no change in carbon content of the sample water, adsorption equilibrium was reached. Since the total amount of sample withdrawn was small enough to cause only slight volume changes, it had little effect on the study.

Batch adsorption isotherm data was based on the measurements of the total organic carbon content in the tar sand water before and after the solution was brought into contact with activated carbon. In this experiment, known amounts of activated carbon were accurately weighed (± 0.1 mg) and then placed in a 250 ml Erlenmeyer flask. The flask was then filled with 100 ml of TS-1S tar sand water. The Erlenmeyer flask was carefully sealed with teflon tape and polyethylene caps, and then was continuously shaken in a constant temperature shaker bath. After five days of shaking, each sample was allowed to settle for two hours before it was filtered to remove any carbon fines. The filtrate

Table I
Analysis of TS-1S Tar Sand Water Performed
by the Laramie Energy Technology Center

<u>Water Quality Parameters</u>	<u>Range (mg/l)</u>
Sodium	44
Potassium	22
Magnesium	11
Calcium	22 - 24
Chloride	17 - 20
Sulfate	116 - 133
Bicarbonate	87
Ammonia	2.3 - 2.6
Total Dissolved Solids	476 - 536
Total Alkalinity (CaCO_3)	71
pH	7.48 - 7.63
Silica	140 - 150
Conductivity (micromhos/cm)	440
Total Organic Carbon	3153 - 3236
Dissolved Organic Carbon	10
Total Inorganic Carbon	15 - 16

Table II
Analysis of TS-1S Tar Sand Water (after coagulation)
Performed by the Laramie Energy Technology Center

<u>Element</u>	<u>Concentration (ppm)</u>
Al	0.090
B	1.273
Ba	0.080
Ca	25.168
Fe	49.424
K	27.038
Li	0.228
Mg	13.993
Mn	1.096
Na	55.163
Ni	0.113
P	0.185
Pt	0.332
Sb	0.076
Se	0.333
Si	77.073
Sr	0.247

was then analyzed with a total carbon analyzer to determine its TOC content. In this study adsorption isotherms were determined at 298 K, using 20 x 40 U.S. mesh size activated carbon as the adsorbent. Because of the nonhomogeneous nature of the activated carbon, replicate runs were made to ensure the reproducibility of the data.

Adsorption breakthrough curve were found by determining the effluent TOC concentrations in the tar sand water at specified times. The parameters studied included adsorbent particle size, bed length, and aqueous flow rate. The experimental apparatus in this packed bed adsorption study consisted basically of pumps, stainless steel columns, and the carbon analyzer that was used to measure the effluent concentrations. The schematic diagram of the system is shown in Figure 1. A peristaltic pump was used to pump tar sand water through the columns at a specified flow rate. The rate was held constant throughout a runs. The fluid flowed upward through the columns, and the flow rates were controlled at either 151.6 or 400.9 ml/h-cm² by a calibrated rotameter. These flow rates gave contact times that ranged from 4 to 50 minutes. During the runs, the tar sand water in the storage tank was continuously mixed by a mixer and a circulation pump to ensure a uniform influent concentration at the inlet to the first column. Four half-inch O.D. stainless steel columns of various lengths were connected in series by short sections of quarter inch O.D. tubing and on-off needle valves. Each end of the column was packed with a half inch thick section of pyrex glass wool to prevent carbon fines from being carried away by the column effluent. The sizes of adsorbent particle used were 20 x 40 and 40 x 50 U.S. mesh. Special care was taken when packing the columns to ensure that the same amount of activated carbons was packed per unit length.

Figure 1. Adsorption Continuous Flow System

The columns were designed to run as four packed beds with lengths of 25.4, 50.8, 76.2, and 127.0 cm, respectively. When sampling, only one valve was open at any time, and the volume of the fluid sampled was very small compared to that leaving the top of the column. Therefore, the sampling had little effect on the continuous flow adsorption study. The samples were stored in vials and kept in a refrigerator at 277 K prior to the TOC analysis. The time interval between the sample collection and the analysis was as short as possible to minimize the change in the amount of TOC in the samples.

TOC Analysis

There are various organic materials present in tar sand waters, and it is difficult to identify each species. Therefore, the concentration is often expressed in terms of a nonspecific gross parameter such as total organic carbon content, which can be used as an indicator of the quantity of organics adsorbed by the adsorbent.

In this study an Oceanography International Total Carbon Analyzer was used to measure the TOC content in the tar sand water. A known amount of sample water was added to a glass ampule along with an oxidizing agent. The ampule was purged with oxygen to remove inorganic carbon components and then sealed with a microburner. After sealing, the ampules were stored in a pressure vessel and heated at an elevated temperature so that the organics in the water could be oxidized to carbon dioxide. The amount of carbon dioxide could then be measured with the TOC infrared analyzer. A standard curve was necessary to interpret the data obtained from the IR analyzer. The curve was prepared with sucrose used as the source of organic carbon. Various dilutions of standard sucrose solution were prepared in ampules and then

analyzed. The integrated peak areas from the analyzer were plotted versus TOC. A typical standard curve is presented in Figure 2. The curve is nearly linear, except in the low concentration range.

RESULTS

Equilibrium Studies:

The batch kinetic study was carried out at 298 K using the TS-1S tar sand water. The initial TOC concentration of this water was 36 mg TOC/l and the equilibrium time was found to be about 76 hours. The results of this study are presented graphically in Figure 3.

The equilibrium time was set at five days to ensure that the tar sand water and activated carbon reached equilibrium in each run. The adsorption isotherm was obtained at 298 K. Replicate runs were made for each measurement and the averaged values are tabulated in Table III.

The equilibrium data were compared with the Langmuir (1916, 1918) and Freundlich (1926) equations. A good fit of the data was obtained with the Langmuir isotherm over the complete concentration range. In the lower range of concentration, the data could also be fitted with the Freundlich isotherm. The data fit to the two models are presented in Figure 4 and the Langmuir and Freundlich constants are listed in Table III. The equilibrium data at the influent concentration was obtained by flowing tar water through a packed bed of activated carbon until effluent concentration reached that of influent. The uptake could thus be determined by evaluating the area above the breakthrough curve. This data point is represented by an asterisk in Figure 4.

Breakthrough Curves:

Experimental breakthrough curves for TS-1S tar sand water were

Table III
Equilibrium Isotherm Data, Langmuir and Freundlich
Constants for TS-1S Tar Sand Water

T = 298 K

C_A^* (mg/l)	q_a (mg/g)
1.2	2.9
1.45	3.45
1.7	4.28
1.9	5.68
2.1	8.48
3.3	16.35
7.4	28.6
8.7	34.1
13.4	45.0
21.5	72.5
36.0	92.1

Langmuir Constants:

$$K = 0.01497 \text{ l/mg}$$

$$KQ_m = 4.1705 \text{ l/g}$$

Freundlich Constants:

$$m = 3.01$$

$$1/n = 1.04$$

Figure 2. Typical Standard Curve for TOC Analyzer

Figure 3. Batch Kinetic Study of TS-1S Tar Sand Water Adsorption onto Activated Carbon at 298K.

Figure 4. Langmuir and Freundlich Isotherms for Adsorption of Organics from TS-1S Tar Sand Water' on Activated Carbon at 298K.

determined from adsorption experiments carried out in packed columns at 298 K. The column system was designed so that the data could be obtained at the bed lengths of 25.4, 50.8, 76.2, and 127.0 cm. The flow rate through the beds was set at either 151.6 ml/h-cm^2 or 400.9 ml/h-cm^2 . These flow rates gave contact times ranging from 4 to 50 minutes. These are consistent with the ASTM (D2910-75) suggestion that a minimum average contact time of two minutes be used for the removal of organics by activated carbon. Adsorbent particle sizes of 20 x 40 and 40 x 50 U.S. mesh were used.

Figures 5 through 7 show the breakthrough curves for TS-1S tar sand water. Effluent concentration profiles for various column heights with different flow rates and adsorbent particle sizes are shown in Figures 8 through 11. These experimental breakthrough curves show that the flow rate and particle size had definite effects on the slope of the breakthrough curves and hence the adsorption rate. The breakthrough time was longer for the smaller adsorbent particle size and the overall adsorption rate was higher for the higher flow rate. These curves were analyzed later to establish the relative importance of the various rate controlling mechanisms that influence the overall rate of adsorption. The mass transfer coefficients were found from the best fits of the theoretical breakthrough curves to the experimental data.

Analysis of the Breakthrough Curves:

There are essentially three consecutive steps in the adsorption of solutes by porous adsorbents and the rate of mass transfer is controlled by one or a combination of these steps. The first is the transport of the adsorbate from the bulk fluid phase to the external surface of the adsorbent granule. The second is the diffusion of adsorbate within the

Figure 5, Experimental Breakthrough Curves for 25.4, 50.8, 76.2, and 127.0 cm Column Heights Using TS-1S Tar Sand Water, with a Flow Rate of 400.9 ml/h-cm² and 40X50 Mesh Size Particles.

Figure 6. Experimental Breakthrough Curves for 25.4, 50.8, 76.2, and 127.0 cm Column Heights Using TS-1S Tar Sand Water, with a Flow Rate of 151.6 ml/h-cm² and 20X40 Mesh Size particles.

Figure 7. Experimental Breakthrough Curves for 25.4, 50.8, 76.2, and 127.0 cm Column Heights Using TS-1S Tar Sand Water, with a Flow Rate of $400.9 \text{ m}^3/\text{h-cm}^2$ and 20X40 Mesh Size Particles.

Figure 8. Effluent Concentration Profiles for a 25.4 cm Column Height Using TS-1S Tar Sand Water.

Figure 9. Effluent Concentration Profiles for a 50.8 cm Column Height Using TS-1S Tar Sand Water.

Figure 10. Effluent Concentration Profiles for a 76.2 cm Column Height Using TS-1S Tar Sand Water.

Figure 11. Effluent Concentration Profiles for a 127.0 cm Column Height Using TS-1S Tar Sand Water.

pores of the adsorbent, coupled with the surface diffusion. The third is the adsorption reaction that occurs on the surface of the adsorbent particle.

Effluent concentration-time profiles can be predicted by using the Thomas approach. This approach, proposed by Thomas in 1944 for ion exchange reactions, took into account the curved shape of the equilibrium relationship and assumed surface reaction to be rate controlling. This model has proven to be a very useful tool for adsorption design. It has been successfully extended by Hiester and Vermeulen (1956) to cases where other mechanisms are rate controlling, such as external film control and intraparticle diffusion control.

Starting with the general material balance, we obtain

$$\left(\frac{\partial q_A}{\partial t}\right)_Z + \frac{F}{S\rho_b} \left(\frac{\partial C_A}{\partial Z}\right)_t + \frac{\epsilon}{\rho_b} \left(\frac{\partial C_A}{\partial t}\right)_Z = 0 \quad (1)$$

For second order surface kinetics controlling, the rate of adsorption can be expressed by

$$\left(\frac{\partial q_A}{\partial t}\right)_Z = k_a [C_A (Q_m - q_A) - \frac{1}{K} q_A] \quad (2)$$

For intraparticle diffusion resistance controlling, the rate of adsorption can be expressed by

$$\left(\frac{\partial q_A}{\partial t}\right) = k_p a (q_A^* - q_A) \quad (3)$$

where q_A^* is the concentration of the adsorbate that would be in equilibrium with the instantaneous fluid-phase concentration outside the

particle, C_A , as related by the equilibrium isotherm. It is necessary that q_A^* be expressed in terms of C_A and q_A to get a solution.

For external film resistance controlling, the above approach can also be applied. The rate equation can be expressed by

$$\left(\frac{\partial q_A}{\partial t}\right) = \frac{k_F a}{\rho_b} (C_A - C_A^*) \quad (4)$$

where C_A^* is the adsorbate concentration at the liquid-solid interphase in equilibrium with the solid concentration q_A . Again, C_A^* should be expressed in terms of C_A and q_A to get a solution.

These rate controlling mechanisms were employed in the Thomas model to determine which one best described the rate of TOC uptake in this study. A good fit to the data was found for the case in which a second-order reversible surface reaction was assumed to be rate controlling. Comparisons of experimental data with theoretical curves obtained from the Thomas model are presented in Figures 12 through 14 for a column height of 50.8 cm. Comparable results were obtained for all column heights but are not presented. For each case, a family of theoretical breakthrough curves were generated for various values of the mass transfer coefficient. From matching the experimental breakthrough curve with the family of theoretical ones, a value for the mass transfer coefficient was determined. The mass transfer coefficients obtained from this curve fit are also given in Figures 12 through 14. mass transfer coefficients for different adsorption rate mechanisms are presented in Table IV. Mass transfer coefficient obtained for these models varied with flow rate, adsorbent particle size, and bed height. They varied directly with flow rate through the bed and inversely with

particle size raised to approximately the 0.5 power. The Thomas model would permit a designer to predict the rate of TOC uptake in a packed bed with reasonable accuracy. Since TOC represents several organic species, the rate of adsorption should not be attributed to any single mechanism. Furthermore, it is important to note that the presence of the wide variety of inorganics also influences the adsorption capacity. The presence of the inorganic species, however, cannot be dealt with conveniently.

The results obtained in this study indicate that the activated carbon is effective in adsorbing organic matter from tar sand water. The low cost of activated carbon as well as low capital investment requirements for an activated carbon treatment system offer an attractive method for removing dissolved organic contaminants from tar sand waters.

Table IV
Mass Transfer Coefficients for TS-1S Tar Sand Water in Packed Beds

T = 298 K

Bed Length (cm)	Surface Kinetics Model			Internal Model			External Model		
	$k_a \times 10^4$ (1/mg-h)			$k_p a \times 10^2$ (1/h)			$k_F a$ (1/h)		
	a	b	c	a	b	c	a	b	c
25.4	3.3	10.7	13.5	5.6	12.4	13.8	55	120	140
50.8	2.4	5.4	8.5	2.7	5.8	6.9	26	69	80
76.2	1.6	3.6	4.5	1.9	4.0	4.6	18	46	52.5
127.0	0.9	2.0	2.5	1.2	2.4	3.2	13	31	38

a - 20 x 40 mesh particle size; 151.6 ml/h-cm²

b - 20 x 40 mesh particle size; 400.9 ml/h-cm²

c - 40 x 50 mesh particle size; 400.9 ml/h-cm²

Figure 12. A Comparison of Experimental and Predicted Breakthrough Curves for a 50.8 cm Column Height Using TS-1S Tar Sand Water, with a Flow Rate of 400.9 ml/h-cm² and 40X50 Mesh Size Particles.

Figure 13. A Comparison of Experimental and Predicted Breakthrough Curves for a 50.8 cm Column Height Using TS-1S Tar Sand Water, with a Flow Rate of 151.6 mL/h-cm^2 and 20X40 Mesh Size Particles.

Figure 14. A Comparison of Experimental and Predicted Breakthrough Curves for a 50.8 cm Column Height Using TS-1S Tar Sand Water, with a Flow Rate of 400.9 $\text{m}^3/\text{h}\cdot\text{cm}^2$ and 20X40 Mesh Size Particles.

PART II

Adsorption of Organics from TS-2C Tar Sand Water on Activated Carbon in Packed Beds

INTRODUCTION

In the first part of this study the adsorption of organics from TS-1S tar sand water was investigated. The purpose of this work was to investigate the adsorption of dissolved organics onto activated carbon from a second tar sand water, TS-2C. This work in conjunction with the previous work on the TS-1S tar sand water provides a relatively comprehensive study of the application of activated carbon as a means for removing organics from tar sand waters produced by various processes.

EXPERIMENTAL

The process water used in this work was obtained from LETC's TS-2C field experiments. The analysis of the water is presented in Table I. As in the previous study, granular DARCO activated carbon was selected as the adsorbent. The experimental procedure used in this part of the study was the same as in Part I, except that equilibrium isotherms were obtained at 278 and 298 K.

RESULTS

The batch kinetic study was carried out at 298 K using TS-2C tar sand water. The initial TOC concentration in the TS-2C water was 760 mg/l. The time required to reach equilibrium was found to be about 80 hours. The results of this study is presented graphically in Figure 1. Isotherms were obtained at 278 and 298 K using an equilibrium time of five days. Replicate runs were made for each measurement and the average values are presented in Figures 2 and 3. Data at the highest concentrations were obtained by flowing the retort water through packed beds of activated carbon until the beds were exhausted; these data are represented by an asterisk. It is important to note that the equili-

Table I
Analysis of TS-2C Tar Sand Water Performed
by the Laramie Energy Technology Center

<u>Water Quality Parameters</u>	<u>Range (mg/l)</u>
Sodium	2.8 - 4500
Potassium	1.2 - 50
Magnesium	6.3 - 20
Calcium	11 - 18
Chloride	14 - 968
Fluoride	2.3 - 53
Sulfate	103 - 2430
Carbonate	0 - 1300
Bicarbonate	0 - 14000
Total Dissolved Solids	424 - 13800
Iron	1.4 - 52
pH	4.05 - 8.75
Chemical Oxygen Demand	2100 - 4600
Total Inorganic Carbon	10 - 3123
Total Organic Carbon	662 - 1126
Conductivity (micromhos/cm)	720 - 28000

Table II
Equilibrium Isotherm Data, Langmuir and Freundlich
Constants for TS-2C Tar Sand Water

T = 278 K

C_A^* (mg/l)	q_A (mg/g)
35	10.2
68	20.4
98	28.8
142	34.8
172	43.6
200	52.8
295	63.4
385	75.0

T = 298 K

C_A^* (mg/l)	q_A (mg/g)
32	8.8
65	17.4
100	25.6
142	34.8
172	43.6
205	51.8
300	62.4
380	76.0
760	130.0

Langmuir Constants

	K (l/mg)	KQ_m (l/g)
T = 278 K	0.0012	0.310
T = 298 K	0.00119	0.322

Freundlich Constants

m	1/n
0.6598	0.8052
0.5076	0.8483

Figure 1. Batch Kinetic Study of TS-2C Tar Sand Water Adsorption onto Activated Carbon at 298K

Figure 2. Langmuir and Freundlich Isotherms for Adsorption of Organics from TS-2C Tar Sand Water on Activated Carbon at 298K.

Figure 3. Langmuir and Freundlich Isotherms for Adsorption of Organics from TS-2C Tar Sand Water on Activated Carbon at 278K.

brium uptake of total organic carbon from the tar sand water by the activated carbon does not decrease with increasing temperature as expected theoretically. Dissolved oxygen, biodegradable TOC, and bacteria react with the tar sand water to produce oxidation products and additional bacteria. Since the oxidation products usually include carbon dioxide and inorganics, the overall effect is to decrease the TOC level in the equilibrium solution at the higher temperature. This effect was observed by Maqsood and Benedek (1977), by Young and Clark (1965), and by Pedram et al. (1982).

The equilibrium data are compared with the Langmuir (1916, 1918) and Freundlich (1926) equations in Figures 2 and 3 and the Langmuir and Freundlich constants are listed in Table II. The equilibrium adsorption study shows that the removal of organics from the TS-2C tar sand water by activated carbon is less than for the TS-1S tar sand water studied in Part I. This is due to the different types and amounts of organic and inorganic species that are present in the two waters. The mass of adsorbate for TS-2C tar sand water at a concentration of 35 mg/l is equal to 10.2 mg TOC per gram of adsorbent, but for TS-1S the uptake is 95.0 mg TOC per gram of adsorbent; this is an 89% difference in the amount adsorbed.

Experimental breakthrough curves for TS-2C tar sand water were determined from adsorption experiments carried out in packed columns at 298 K. These are shown in Figures 4 through 6. Effluent concentration profiles for various column heights with different flow rates and adsorbent particle sizes are shown in Figures 7 through 10. As in Part I the breakthrough curves show that the flow rate and particle size had

definite effects on the slope of the breakthrough curves and hence the adsorption rate.

Several rate controlling mechanisms were employed in the Thomas model to determine which one best described the rate of TOC uptake in this study. A good fit to the data was found for the case in which a second-order reversible surface reaction was assumed to be controlling. Comparisons of experimental data with theoretical curves obtained from the Thomas model are presented in Figures 11 through 13 for a column height of 76.2 cm along with the mass transfer coefficients obtained from this curve fit. A summary of the mass transfer coefficients for different adsorption rate mechanisms are presented in Table III.

Table III
Mass Transfer Coefficients for TS-2C Tar Sand Water in Packed Beds

T = 298 K

Bed Length (cm)	Surface Kinetics Model			Internal Model			External Model		
	$k_a \times 10^5$ (1/mg-h)			$k_p a \times 10^2$ (1/h)			$k_F a$ (1/h)		
	a	b	c	a	b	c	a	b	c
25.4	4.0	8.5	11.0	8.5	18.0	21.5	6.0	13.0	15.0
50.8	2.0	4.8	6.0	3.5	10.0	11.4	2.6	7.0	7.9
76.2	1.5	3.4	4.3	2.4	6.5	7.5	1.8	4.5	5.0
127.0	1.0	2.2	2.7	1.5	4.0	4.6	1.2	2.8	3.1

a - 20 x 40 mesh particle size; 151.6 ml/h-cm²

b - 20 x 40 mesh particle size; 400.9 ml/h-cm²

c - 40 x 50 mesh particle size; 400.9 ml/h-cm²

Figure 4. Experimental Breakthrough Curves for 25.4, 50.8, 76.2, and 127.0 cm Column Heights Using TS-2C Tar Sand Water, with a Flow Rate of 400.9 ml/h-cm^2 and 40X50 Mesh Size Particles.

Figure 5. Experimental Breakthrough Curves for 25.4, 50.8, 76.2, and 127.0 cm Column Heights Using TS-2C Tar Sand Water, with a Flow Rate of $151.6 \text{ m}^3/\text{h-cm}^2$ and 20X40 Mesh Size Particles.

Figure 6. Experimental Breakthrough Curves for 25.4, 50.8, 76.2, and 127.0 cm Column Heights Using TS-2C Tar Sand Water, with a Flow Rate of 400.9 mL/h-cm^2 and 20X40 Mesh Size Particles.

Figure 7. Effluent Concentration Profiles for a 25.4 cm Column Height Using TS-2C Tar Sand Water.

Figure 8. Effluent Concentration Profiles for a 50.8 cm Column Height Using TS-2C Tar Sand Water.

Figure 9. Effluent Concentration Profiles for a 76.2 cm Column Height Using TS-2C Tar Sand Water.

Figure 10. Effluent Concentration Profiles for a 127.0 cm Column Height Using TS-2C Tar Sand Water.

Figure 11. A Comparison of Experimental and Predicted Breakthrough Curves for a 76.2 cm Column Height Using TS-2C Tar Sand Water, with a Flow Rate of 400.9 ml/h-cm² and 40X50 Mesh Size Particles.

Figure 12. A Comparison of Experimental and Predicted Breakthrough Curves for a 76.2 cm Column Height Using TS-2C Tar Sand Water, with a Flow Rate of 151.6 ml/h-cm² and 20X 40 Mesh Size Particles.

Figure 13. A Comparison of Experimental and Predicted Breakthrough Curves for a 76.2 cm Column Height Using TS-2C Tar Sand Water, with a Flow Rate of 400.9 ml/h-cm² and 20X40 Mesh Size Particles.

NOMENCLATURE

- A - Subscript for component of TOC
- a - Interfacial area of solid phase per volume of bed, cm^2/cm^3
- C - Effluent concentration of TOC, mg/l
- C_0 - Inlet concentration of TOC, mg/l
- C^* - Equilibrium fluid phase concentration of TOC, mg/l
- F - Volumetric flow rate of fluid, ml/hr
- K - Adsorption equilibrium constant, l/mg
- k_a - Rate constant for adsorption, l/mg-hr
- k_F - Mass transfer coefficient for fluid phase, cm/hr
- k_p - Mass transfer coefficient for solid phase, cm/hr
- q - Average concentration of adsorbed TOC, mg/g
- q^* - Equilibrium concentration of adsorbed TOC, mg/g
- Q_m - Mass of one monomolecular layer of adsorbate, mg/g
- S - Cross sectional area of packed bed, cm^2
- t - Time, hr
- Z - Bed length, cm
- ϵ - Void fraction of packed bed
- ρ_b - Bulk density of packed bed, g/cm^3

REFERENCES

- Freundlich, H., "Colloid and Capillary Chemistry," Dutton: New York, (1926).
- Hiester, N.K., and Vermuelen, T., Chem. Eng. Prog., 48, No. 10, 505 (1952).
- Langmuir, I., J. Am. Chem. Soc., 28, 2221 (1916).
- Langmuir, I., J. Am. Chem. Soc., 40, 1368 (1918).
- Maqsood, A., and Benedek, A., J. Water Pollut. Control Fed., 49, No. 10, 2107 (1977).
- Pedram, E., Hines, A.L., Poulson, R.E., and Cooney, D.O., Chem. Eng. Commun., 15, 291 (1982).
- Thomas, H.C., J. Amer. Chem. Soc., 66, 1664 (1944).
- Young, J.C., and Clark, J.W., J. San. Eng. Div., Proc., ASCE, 91, No. SA1, 43 (1965).