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Application of organophilic clay

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ABSTRACT

Application of Organophilic Clay

by
Koshy Koshy

The overall goal of this project is to asses the feasibility of using clay to filter water contaminated with organic contaminants. The clays that were used were provided by the Union Carbide Corporation and the Industrial Mineral Ventures (IMV), a division of Floridin company. The organic contaminants that this project concentrated on were, naphthalene, 1,4-dioxane, and phenol. The feasibility studies were done by batch isotherm studies. The protocol for the batch studies were the same as the ones used previously for granular activated carbon. This project looked at a total of six Union Carbide clays and five IMV Floridin clays. The batch studies reduced the number of clays that could be used for the removal of organics by eliminating the clays that adsorbed the least amount of contaminants. This showed which of the clays were best for removing the contaminants. The batch studies showed that the IMV Floridin clays were the best for adsorbing the contaminants.

APPLICATION OF ORGANOPHILIC CLAY

by
Koshy Koshy

A Thesis
Submitted to the Faculty of
New Jersey Institute of Technology
in Partial Fulfillment of the Requirements for the Degree of
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To Mom, Dad, Shuba, Jesse, Monica, Kevin, Zack, Larry, Mike, Ara and Pam thanks for everything.

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CHAPTER 1

INTRODUCTION

1.1 Purpose of This Study

The integrity of our drinking water is one of the primary environmental concerns of our time. Many federal and state regulations have been passed with regard to water supply. Through industrial, agricultural, and urban use, water quality has seriously deteriorated. Regulations such as RCRA (Resource Conservation and Recovery Act) attempt to get waste generators to minimize and better treat their wastes [1]. Some of the technologies presently available to dispose of hazardous waste include treatment (biological, neutralization), incineration, landfilling, well injection, and surface impoundment. The predominant method for disposal of hazardous waste in the United States has been placement of these wastes in injection wells or landfills [13]. As the amount of land available for these facilities decreases, alternatives are being sought for better treatment systems.

The proposed method of waste removal in this study, adsorption of contaminants on organoclays, is a nondestructive method for removing organic contaminants from water. Unlike biological treatment and incineration, the contaminants are adsorbed onto the organoclay from the water and not destroyed. This can be beneficial because the compounds can be desorbed and recycled.

1.2 Focus of This Study

The feasibility of removing three organics from water was tested in this study. The three compounds are naphthalene, phenol, and 1,4-dioxane. These three organic compounds have a variety of domestic and industrial applications. They also have a variety of epidemiological effects reported in the next sections.

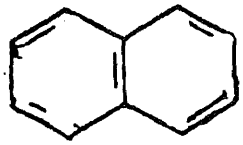

Figure 1
Naphthalene

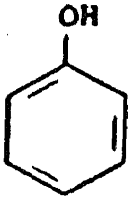

Figure 2
Phenol

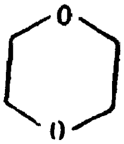

Figure 3
1,4-Dioxane

1.3 Epidemiological Effects of Naphthalene

Naphthalene (see Figure 1) is used extensively in industrial processes. It is used in manufacturing phthalic and anthranilic acids used in making indigo, indanthrene and triphenyl methane dyes. Another use of naphthalene is in synthetic resins, cellulose, lamp black and smokeless powder. In the past it was used extensively in the production of moth repellents and insecticides, although for this particular use it has recently been replaced by p-dichlorobenzene [8]. Naphthalene can cause nausea, vomiting, headaches, hematuria, hemolytic anemia, fever, hepatic necrosis, convulsion, and coma. The maximum daily allowance of Naphthalene is set at 47 ppb [10].

1.4 Epidemiological Effects of Phenol

Ingestion of small quantities of phenol (see Figure 2) can cause nausea, vomiting, circulatory collapse, tachypnea, paralysis, convulsions, coma, narcosis of mouth and GI tract, icterus, and death from respiratory failure. Chronic exposure can cause renal and hepatic damage [3]. The maximum chronic exposure allowed 47 ppb [8]. Phenol has traditionally been used in disinfectant solutions for toilets, stables, cesspools, floors, drains and other places. It has also been used to manufacture colorless and light colored artificial resins.

1.5 Epidemiological Effects of 1,4-Dioxane

1,4-Dioxane, also known as diethyl dioxide (see Figure 3), is used as a solvent for cellulose acetate, ethyl cellulose, benzyl cellulose, resins, oil, waxes, and spirit soluble dye synthesis as well as in the manufacture of inorganic compounds. 1,4-Dioxane can cause central nervous system depression, necrosis of the liver, kidney damage, skin irritation and mucous membrane irritation. 1,4-Dioxane is also suspected of being a carcinogen. Because of this, the maximum allowed exposure level for humans is zero in the United States [8].

CHAPTER 2

LITERATURE REVIEW

2.1 Introduction

The majority of the work done on adsorption of organic contaminants from waste water is done with granular activated carbon. The experimental protocol for testing the organoclays in this experiment will be the same as the one used for granular activated carbon.

The activated carbon process has been used extensively in the past for removal of color from dye mill waste water, removal of taste and/or odor from potable water, removal of surface activated agents, removal of TOC and BOD_5 from industrial and sanitary waste water, and for the purposes of this project, removing organic contaminants from waste water streams [12].

This project will use two methods to evaluate the potential of the clay to remove organic contaminants from water. First, a batch isotherm technique will be used. The batch test is a quick method to find the general adsorption capability of the organoclay. This will give a quick comparison for the general ability of organoclays to adsorb the organic contaminants. The column study is a more involved technique. Here, a small scale model (section 2.3) of the actual process is reproduced.

2.2 Batch Study

As stated earlier, the technique for determining the adsorption potential of the clay was similar to work done with granular activated carbon [11]. For the batch isotherm study, an aqueous solution of organic contaminants was kept in contact with the adsorptive material (organoclay) for a fixed period of time (the time should be sufficient to ensure attainment of equilibrium) at a set ratio of liquid/organoclay. Then, the amount of organic contaminants left in the supernatant was determined to see how much of the organic contaminant is adsorbed on the organoclay. This procedure is known as an equilibrium batch study. A graphical presentation of the data follows in the results section of this thesis. The adsorption equilibrium can be represented using the Freundlick Equation [2]

$$S=K_f\,C^b$$

S = Mass of Contaminant adsorbed on the soil

C = Concentration of Contaminant in solution.

b = Exponent

K_f= Freudlick Constant

2.3 Clay

The use of clays in various environmental applications has become standard practice. One very important area in particular is landfill protection. The 1984 amendment to the Hazardous and Solid waste amendments mandated that all landfills have to have a double liner of clay [3]. The most important reason that these double liners came into law is that they greatly decrease the chance of leaching of hazardous waste into local water supplies.

Clay is also used in the disposal of hazardous material. One of the most important properties of clay is that it is not biodegradable which is essential for the disposal of hazardous waste. Clay is used as packing material for hazardous waste drum disposal. If other biodegradable materials like wood chips or cardboard were used, void space would develop and drum collapse could result, increasing probability of widespread contamination. Another important reason for the use of clay is that it is relatively inexpensive. All these reasons together make the use of clay quite practical.

CHAPTER 3

BACKGROUND

3.1 Organoclay

The clays used in the adsorption batch studies will be elaborated upon in this chapter. The objective of this study is to develop a method to filter out organic contaminants from waste water stream, using treated clay (organoclay). Fundamentally, two processes are used to determine the best clay, the batch adsorption study, and column filtration study.

The organoclays used for determining the adsorption potential were supplied by Industrial Mineral Venture and the Union Carbide Corporation of South Charleston, West Virginia. Four organoclays from Union Carbide and five organoclays from IMV Floridin were used. In addition to these organoclays, granular activated carbon was also used. The granular activated carbon (GAC) was used as a standard because most of the previous work on adsorption/removal of organic contaminants has involved GAC as the adsorbing material.

An organoclay is a clay that has been treated with organic compounds to change its characteristics. In this study, the adsorption potential of the clay was changed. The starting materials for the organoclays in this study are bentonite, smectite, and sepiolite. Each of these clays has been changed in industrial processes into organoclay by the addition of quaternary ammonium compounds with different functional groups and chlorides in different patented treatment processes.

3.2 Chemical Properties and Commercial Uses of Industrial Mineral Venture Clays Used in This Work

1 IMVISPERSE 50:

This is a smectite clay modified by a quaternary ammonium compound, bis (hydrogenated tallow alkyl) dimethyl chloride compound. This organoclay is used as an additive to finish coatings, traffic paint, asphalt coating, stains, sealants, and drilling fluids.

2 IMVISPERSE 200:

This is a bentonite clay modified by a quaternary ammonium compound, dicoco alkyldimethyl chloride compound. Imvisperse 200 is used to disperse aromatic and oxygenated solvent systems.

3 IMVISPERSE 100:

This is a smectite clay modified by a quaternary ammonium compound, bis(hydrogenated tallow alkyl) dimethyl chloride compound. It is added in the paint making process in the grind phase, in the letdown, and post-addition to correct the viscosity.

4 SEPIOTONE:

This is a sepiolite clay modified by a quaternary ammonium compound bis (hydrogenated tallow alkyl) dimethyl chloride compound. Sepiotone is used to thicken and suspend filters in systems such as asphalt roofs coating, automotive under body, mastics, and sealants.

5 IMVISPERSE 90B:

This is a smectite clay modified by a quaternary ammonium compound, bis (hydrogenated tallow alkyl) dimethyl chloride compound. Imvisperse 90B is used to make pigments.

6 IMVISPERSE 95B:

Imvisperse 95B has the same chemical identity as Imvisperse 90 B but it higher gelling efficiency. The main difference is its production process.

3.3 Union Carbide Clays

Six clays from the Union Carbide company were used in the experiment. Four of them were treated organoclays. The other two were untreated clays.

7 BASCM A & B:

This is a bentonite clay modified by the addition of benzyldimethylstearylammonium chloride monohydrate. Unlike the other clays discussed earlier from the Floridin company, these clays are made for the adsorption studies with the hope that they can be used to filter out organic contaminants from the waste water.

8 CPC. A & B:

This is a bentonite clay modified by the addition of cetylpyridinium chloride Monohydrate. Like the BASCM A & B the CPC's were also made for the adsorption studies.

9 Untreated Clay:

Enviroplug bentonite and Natural gel bentonite were also analyzed. These two clays are the starting materials for the treated organoclays BASCM A&B and CPC A&B. They were used to compare how good the treated organoclays were compared to the untreated clay.

CHAPTER 4

EXPERIMENTAL APPARATUS AND PROCEDURES

4.1 Experimental Equipment

The apparatus used in this study is described in the following subsections:

4.1.1 Preparation of Samples

(1) Rotating Mixer

Manufacturer: Dayton Electronics
Model: 3M137B
Speed: 34 rpm
Description: The mixer holds a total of 16 reaction vessels at a time. It spins the vessels in a circular direction 34 times a minute.

(2) Reaction Vessel

Manufacturer: Alltech
Size: 125 ml
Description: The vessels are made of glass with a teflon coated stoppers and the vessels are 110 mm in height and 45 mm in diameter.

(3) Sampling Bottles

Manufacturer: Alltech
Size: 2 ml
Purpose: Specially made for use with the HPLC autosampler

(4) Filters

Manufacturer: Gelman Sciences
Size: 0.45 micrometer pore size
3 mm diameter

(5) Syringe

Manufacturer: Popper & Sons, Inc.
Description: Interchangeable hypodermic syringe/capacity 5 cc.

(6) Pipettes

Manufacturer: VWR
Model : 2 ml capacity/disposable 9 inch length

4.1.2 Chromatographic Equipment

A HPLC (High Pressure Liquid Chromatography)

A1 Column

Manufacturer: Waters, Inc.
Model: Nova Pak C18 -3.9*150mm col part no. 86344

A2 UV-VIS Detector

Manufacturer: Waters
Model: Millipore 994, Photodiode Programmable detector

A3 Pump

Manufacturer: Waters, Inc.
Model: Millipore 600E

A4 Autosampler

Manufacturer: Hewlett Packard
Model: Series 1050

A5 HPLC Solvent filter for mobile phase

Manufacturer: Waters

Model:	0.45 micrometer pore size
	HV- Volatile solvents
	HA- Aqueous solvents

B GC (Gas Chromatography)

B1 Gas Chromatography

Manufacturer:	Varian
Model	3700

B2 GC Column- Packed

Model:	1.5% OV-1, 100/120
	Chromasorb WHP, 6' 1/4" mo 9179

B3 Integrator

Manufacturer:	Hewlett Packard
Model:	3390 A

B4 Recorder:

Manufacturer:	Kipp & Zonen
Model:	BD 41

B5 Detector

Manufacturer	Varian
Type	FID

4.1.3 pH Meter

Manufacturer:	Corning
Model:	Meter 200

4.1.4 Electrical Precision Balance

Manufacturer:	Soiltest Company
Model:	E 4000
Capacity:	4000 g
Readability:	0.1 g
Stabilizing time:	2.5 seconds

4.1.5 Electronic Precision Balance

Manufacturer:	Sartorius Company
Model:	H-110
Capacity:	120 g
Readability:	0.0001 g
Stabilization Time:	3.5 seconds

4.2 Reagents

The solvents, methanol and acetonitrile used in this experiment were HPLC grade or better. Only deionized water was used for the dilution of Naphthalene, 1,4-Dioxane, and Phenol. Also each of the solvents used in the mobile phase was filtered with the filters described in A5.

4.3 Experimental Procedure

4.3.1 General Batch Study Procedure

A 125 ml vial was used as the reaction vessel for the batch isotherm studies. Ten milliliters of contaminated liquid were used with 5 grams of organoclay [6]. This ratio of solution:clay (2:1) was determined based on the fact that certain clays, will not leave supernatant liquid after equilibrium if less liquid is used.

The bottles (after clay and contaminant solutions are added) were put into the rotating mixer. This is done to allow the clay and contaminants to come to equilibrium. This equilibrium process is allowed to proceed for 72 hours [12]. The vials are rotated at 34 RPM for this 72 hour period. All the batch isotherm studies were done at room temperatuie.

After the equilibration process, the bottles are removed from the rotator and the supernatant is removed. This is done as follows; the supernatant is pipetted out of the 125 ml vial and filtered with a syringe filter tip (the filtering is done to keep stray clay particles from going into the HPLC Column). The filtered supernatant is placed into a 2 ml vial. These vials are used to analyze for the contaminant (phenol or naphthalene) with the HPLC.

4.3.2 Exception to Batch Protocol

During the evaluation of the untreated clays, (Natural Gel Bentonite & Enviroplug) there was insufficient supernatant after the equilibrium process for analysis. Therefore, the ratio of clay to solution had to be changed. The new ratio was 10:1 (10 ml of water to 1 gram of clay).

4.3.3 Phenol Analysis

A 1% (wt/vol.) solution of phenol was used as the starting contaminant for this analysis in the batch studies. This phenol was diluted to different concentrations for the batch studies. The batch studies were conducted at room temperature. The concentration of the supernatant for the isothermal batch studies range from 100-10,000 ppm (mg/liter).

4.3.4 HPLC Analysis of Phenol

The mobile phase for the phenol analysis was acetonitrile and water. For this analysis, the concentration of the mobile phase was as follows: 80% water with 1% acetonitrile, and 20% acetonitrile. The acetonitrile and the water was filtered through a 0.45 micrometer filter and degassed with ultrasound for 15 minutes. This was done to ensure that the HPLC pump was not damaged. The flow rate was adjusted to 0.80 ml/min, and the sample size was 10 microliters. The pressure for the pump was approximately 1600 psi for the whole analysis.

For the analysis, seven concentrations of standards were run. These concentrations were 25, 50, 125, 250, 500, 750, and 1,000 ppm. Then, the samples were run followed by the 125 ppm standard to make sure that the concentrations were properly identified. If the concentration of a sample was above 1000 ppm then the sample was diluted by half to bring it into the working linear range of the detector. The retention time for the phenol ranged from 3.5-3.9 minutes.

4.3.5 Naphthalene Analysis

A 500 ppm solution of naphthalene was made by diluting naphthalene crystals with methanol. This sample was diluted with distilled water to different concentrations for isothermal batch studies. The initial concentration of naphthalene for the tests ranged from 100-500 ppm. The high initial concentrations of supernatants were used because all concentrations at and below 30 ppm (solubility limit in water) were below the detection limit. The naphthalene was analyzed by HPLC using acetonitrile and water as the mobile phase with a concentration of 65% acetonitrile and 35% water at a flow rate of 1 ml/min. The same mobile phase concentration could not be used for the phenol and naphthalene analysis because a higher percent of organic solvent had to be used with the naphthalene to get a sufficient retention time. The retention time for the naphthalene was 5.8-6.1 minutes. The pressure at which the solvent was pumped was roughly 1200 psi for each analysis. As with the phenol, 10 microliters of sample were injected into the HPLC to be analyzed. The standards used for the HPLC for the generation of standard curves were of concentrations, 5, 25, 100, 125, 250, and 500 ppm.

4.3.6 1,4-Dioxane Analysis

Unlike the other two contaminants, 1,4-Dioxane does not absorb UV- radiation. Therefore, another analytical technique must be used to analyze concentrations of 1,4-Dioxane. GC/FID was chosen because the sample was in an aqueous media, and a capillary column could not be used. A packed column must be used for this analysis. The carrier gas for this analysis was nitrogen, and the flame was fueled by hydrogen and air.

4.3.7 The Operating Conditions for the GC were:

(1) Injector temperature:	160^{0}C
(2) FID temperature:	180^{0}C
(3) Column temperature:	Init. 88^{0}C, final 110^{0}C at 2^{0}C per minute, initial hold time 2 min.

For the analysis, a 1000 (wt/vol.) ppm initial concentration of 1,4-Dioxane was diluted to make the initial concentrations for the analysis. The isothermal batch study uses the same procedure as the phenol and naphthalene studies. In this 1,4-Dioxane analysis, extra care was taken to make sure that it did not come into contact with air because of its potential carcinogenic nature. For standards, concentrations of 10-1000 ppm were used depending on the initial concentration of the 1,4-Dioxane used for the batch isothermal studies. The retention for the 1,4-Dioxane was between 2.4-2.6 minutes

4.4 Water Content

An additional set of experiments were conducted to determine the water content of the clay. For this analysis, the clay was oven dried at 120^{O}C. Then, the weight was recorded after letting the samples cool in a dessicator until stabilization. The wet weight of the clay was taken before it was placed in the oven [13].

$$\text{\% of water in the clay} = \frac{\text{Wet Weight - Dry Weight of Sample}}{\text{Wet Weight of Sample}} * 100$$

4.5 Final Volume of Supernatant

Also another additional set of experiments were done to determine what volume of the supernatant had adsorbed onto the clay at equilibrium. In this analysis, the same initial ratio of clay to the solution for the contaminant analysis were used. The final volume of each of the supernatant at the point of equilibrium is given in table 5-24.

Chapter 5

RESULTS AND DISCUSSION

5.1 Calculation of the Batch Studies

The Freundlick equation is used to evaluate the adsorption capacity of the clays.

$$S = K_f C^b$$

$$\log S = \log K_f + b \log C_f$$

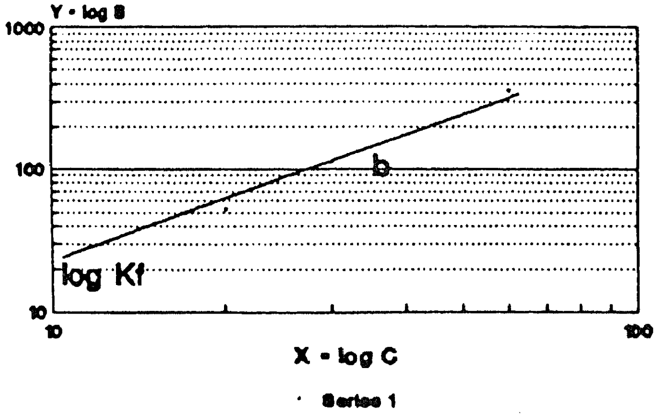

Figure 4 Plot of the Freundlick isotherm

K_f=Partition Coefficient

$S = V_iC_i - V_fV_f$/grams of wet clay

V_i=initial volume of the supernatant

V_f= final volume of the supernatant

C_i=initial concentration of the supernatant

C_f=final concentration of the supernatant

5.2 Results of the Batch Studies of Phenol

Phenol was the first chemical studied with the batch system. All of the clays except for the untreated clays were analyzed in the same manner. Ten ml of liquid was used with 5 grams of organoclay. For the untreated clay, 10 ml of liquid was used with 1 gram of clay.

The data are presented as follows:

The results from the six Union Carbide organoclays are presented in Tables 5-1 to 5-6. The tables contain the following information: the initial concentration of the solution, the final concentration of the supernatant after the equilibrium, the amount of contaminant adsorbed on the clay, and the partition coefficient. A graphical presentation of this data is given in Figure 5. Tables 5-7 to 5-11 contain the analagous information from the batch studies of the Floridin clays.

TABLE 5-1 Batch Isotherm for the Adsorption of Phenol by CPC A

Init. conc. (mg/L)	Final conc. Supernatant (mg/L)	Amount Adsorbed (mg/kg)	partition coefficient K_f [(L/mg)b-1- L/kg]
100	16.7	175.6	10.6
500	84.3	876.9	10.5
900	156.8	1571.1	10.1
1000	172.3	1748.4	10.2
2500	422.0	4383.9	10.5
3000	534.5	5219.6	9.8
5000	1000.0	8540.0	9.0
7500	1400.0	12956.0	9.3
10000	1640.0	17605.6	10.8

Statistical Information from the plot of Cetylpridinium Chloride Natural Gel Bentonite: (CPC A):

Correlation : 0.9988
Intercept : 0.9984 +/- 0.03181
Slope : 0.9440

Table 5-2 Batch Isotherm for Adsorption of Phenol by BASCM A

Init. conc. (mg/L)	Final conc. of supernatant (mg/L)	Amount adsorbed on clay (mg/kg)	partition coefficient K_f [(L/mg)b-1- L/kg]
80	7.9	151.2	31.2
100	10.5	188.2	31.3
200	24.6	372.4	32.4
250	27.5	469.2	39.4
300	32.7	563.4	39.4
900	105.2	1682.2	46.7
3000	380.3	5574.1	60.0
9000	585.3	11444.6	88.6
7500	798.1	14106.1	86.2
10000	1200.0	18656.0	86.6

Statistical information from the plot of Benzyldimethyl Stearyl ammonium chloride Monohydrate Natural Gel Bentonite (BASCM A):

Slope	: 0.7628
Intercept	: 1.5744 +/- 0.2906
Correlation	: 0.9395

Table 5-3 Batch Isotherm for Adsorption of Phenol by BASCM B

Init. conc. (mg/L)	Final Conc. of supernatant (mg/L)	Amount adsorbed on clay (mg/kg)	partition coefficient K_f [(L/mg)b-1- L/kg]
100	8.1	190.6	21.4
500	25.6	970.3	32.8
1000	65.7	1926.4	24.3
5000	279.9	9686.5	26.9
10000	632.0	19292.2	22.9

Statistical information from the plot of Benzyldimethyl Stearyl ammonium chloride Monohydrate Natural Gel Bentonite (BASCM B):

Slope	:1.0447
Intercept	:1.4041+/- 0.08411
Correlation	:0.9959

TABLE 5-4 Batch Isotherm for Adsorption of Phenol by CPC B

Init. conc.of solution (mg/L)	Final conc. Supernatant (ml/L)	Amount Adsorbed (mg/kg)	partition coefficient K_f [(L/mg)b-1- L/kg]
100	10.2	184.7	18.3
500	42.2	936.7	22.5
1000	84.4	1873.4	22.6
5000	432.0	9352.0	22.2
10000	1029.7	18455.5	18.4

Statistical information from the plot of Cetylpyridinium Chloride Monohydrate (CPC B):

Slope : 0.9959

Intercept : 1.3164 +/- 0.04559

Correlation : 0.9988

Table 5-5 Batch Isotherm for Adsorption of Phenol by Enviroplug

Init. conc. (mg/L)	Final conc. of Supernatant (mg/L)	Amount adsorbed on clay (mg/kg)	partition coefficient K_f [(L/mg)b-1- L/kg]
50	11.5	85.5	22.9
100	21.9	172.4	32.9
500	98.5	875.9	82.7
1000	177.9	1775.8	108.4
5000	3689.3	5351.5	62.6
10000	8789.3	8925.5	19.0

Statistical information from the plot of Enviroplug

Slope :0.5397

Corr. :0.9021

Int. :1.6440 +/- 0.3376

Table 5-6 Batch Isotherm for Adsorption of Phenol by Natural Gel Bentonite

Init. conc. (mg/L)	Final conc. of Supernatant (mg/L)	Amount adsorbed on clay (mg/.kg)	partition coefficient K_f [(L/mg)b-1- L/kg]
50	16.7	77.3	11.8
100	29.1	160.4	17.0
500	121.7	834.5	34.0
1000	317.9	1567.7	33.7
5000	4359.1	4071.6	15.3
10000	9385.5	7235.7	16.3

Statistical information from the plot of Natural Gel Bentonite:

Slope :0.6663

Int. :1.2959 +/- 0.2125

Corr. :0.9694

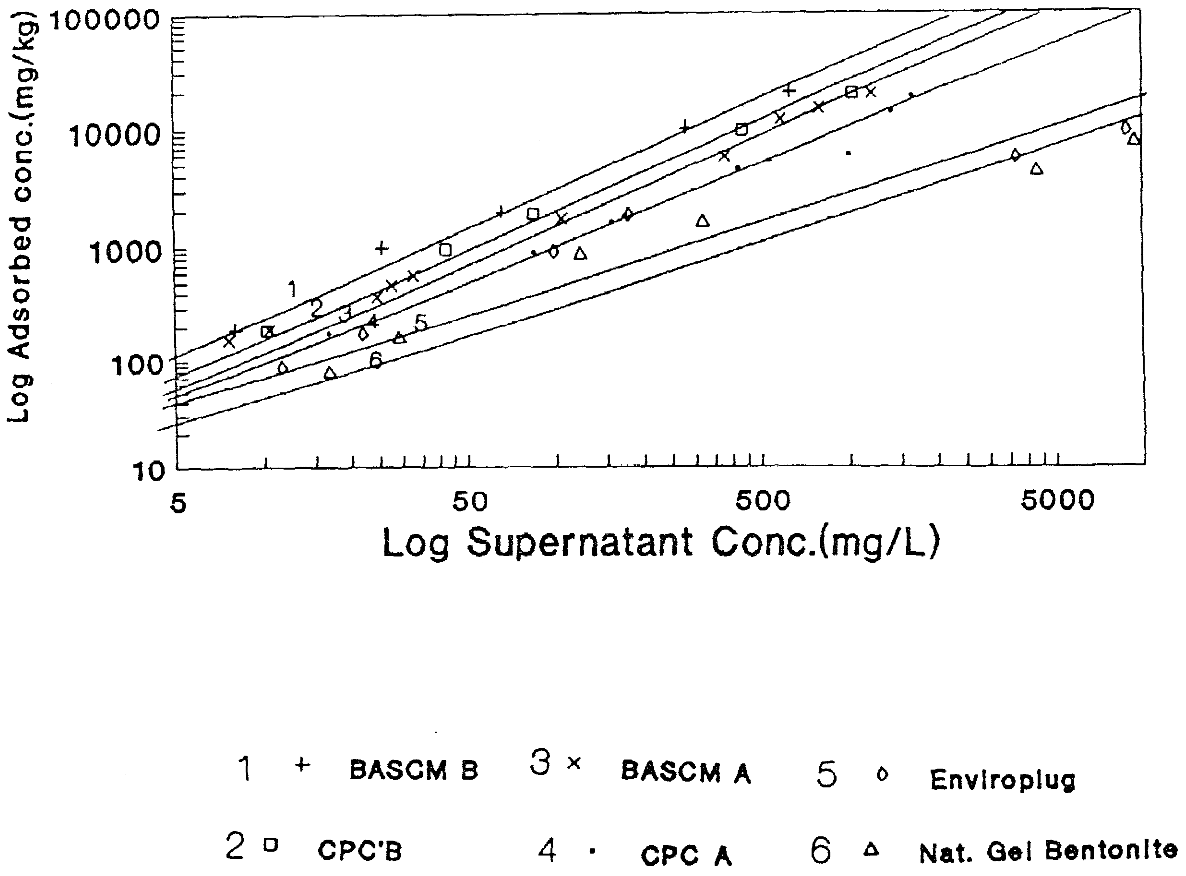

Figure 5. The contaminant in this analysis is phenol. Union Carbide Corporation clays BASCM A & B and CPC A & B as well as Natural Gel Bentonite and Enviroplug are analyzed with this contaminant for adsorption potential.

Table 5-7 Batch Isotherm for Adsorption of Phenol by IMV 50

Init. Conc. (ml/L)	Final conc. Supernatanat (ml/L)	Amount Adsorbed (mg/kg)	partition coefficient K_f [(L/mg)h-1- L/kg]
100	3.0	197.5	72.0
250	8.8	492.8	66.8
500	19.2	984.3	62.8
750	32.2	1473.3	61.1
900	35.9	1770.6	66.0
1000	40.4	1966.9	65.8
2500	104.9	4914.0	68.4
3000	120.1	5901.5	72.6
6000	288.3	11763.6	64.7
7500	365.1	14700.6	65.1
10000	451.7	19629.6	71.5

Statistical information from the plot of IMVISPERSE 50 (IMV 50):

Slope	: 0.9186
Intercept	: 1.8263 +/- 0.02599
Correlation	: 0.9993

Table 5-8 Batch Isotherm for Adsorption of Phenol by IMV 200

Init. conc. (ml/L)	Final conc. Supernatant (ml/L)	Amount Adsorbed (mg/kg)	partition coefficient K_f [(L/mg)b-1- L/kg]
500	BDL	UNKNOWN	UNKNOWN
1000	0.5	1999.7	2703.4
5000	23.0	9983.9	2646.1
6000	35.8	11947.9	2631.5
7500	69.8	14951.1	2476.3
10000	96.3	19932.6	2880.7

Statistical information from the plot of IMVISPERSE 200 (IMV 200):

Slope	:0.4235
Intercept	:3.4234+/- 0.02957
Correlation	:0.9978

Table 5-9 Batch Isotherm for Adsorption of Phenol by IMV 95 B

Init. conc. (ml/L)	Final conc. Supernatant (ml/L)	Amount Adsorbed (mg/kg)	partition coefficient K_f [(L/mg)b-1- L/kg]
600	1.9	1198.8	812.0
750	2.0	1498.7	984.0
1000	5.4	1996.5	717.3
2500	25.5	4983.7	697.9
3000	30.0	5980.8	758.8
6000	74.5	11952.3	873.5
7500	101.5	14935.0	904.2
10000	182.1	19883.5	844.3

Note: All concentrations below 600 mg/L were below detection limit.

Statistical information from the plot of Imvisperse 95 B (IMV 95 B):

Slope :0.6070

Intercept :2.9150 +/- 0.05651

Correlation :0.9938

Table 5-10 Batch Isotherm for Adsorption of Phenol by IMV 90 B

Init. Conc. (ml/L)	Final conc. Supernatant (ml/L)	Amount Adsorbed (mg/kg)	partition coefficient K_f [(L/mg)b-1- L/kg]
750	1.7	1498.9	1098.4
1000	4.5	1997.0	827.4
2500	25.5	4983.2	747.4
5000	61.4	9959.5	892.7
7500	99.9	14934.1	1006.5
10000	150.1	19900.9	1056.7

Statistical information from the plot of Imvisperse 90B (IMV 90B)

Slope :0.5858

Intercept :2.9686 +/- 0.07314

Correlation :0.9899

Table 5-11 Batch Isotherm for Adsorption of Phenol by Sepiotone

Init. conc. (ml/L)	Final conc. Supernatanat (ml/L)	Amount Adsorbed (mg/kg)	partition coefficient K_f [(L/mg)b-1- L/kg]
500	0.5	999.7	1470.8
5000	28.4	9981.3	1547.7
10000	112.1	19926.0	1436.1

Note: All concentrations below 500 mg/L were below detection limit.

Statistical information from the plot of Sepiotone:

Slope :0.5573

Intercept :3.1722+/- 0.02507

Correlation :0.9997

Figure 6 represents a graphical presentation for the five IMV Floridin clays, from the figure it is obvious that the IMV 200 showed the best adsorption potential followed by the Sepiotone.

Figure 7 represents the graphical presentation of all the organoclays together with phenol. From this, it is apparent that IMV organoclays outperform the Union Carbide organoclays. The IMV 90 B and IMV 95 B adsorbed similar amounts of phenol and they have similar chemical makeup, so it was decided that only one would be studied further. Since IMV 90 B showed the better performance of the two, it was the one used.

GAC of 100-400 mesh was also analyzed. The protocol for this analysis was the same as the Enviroplug and Natural Gel Bentonite. All the initial concentrations other than 10,000 mg/l showed supernatant concentrations below the detection limit. The initial supernatant concentration of 10,000 mg/l shows a final concentration of 10.4 mg/l after equilibrium.

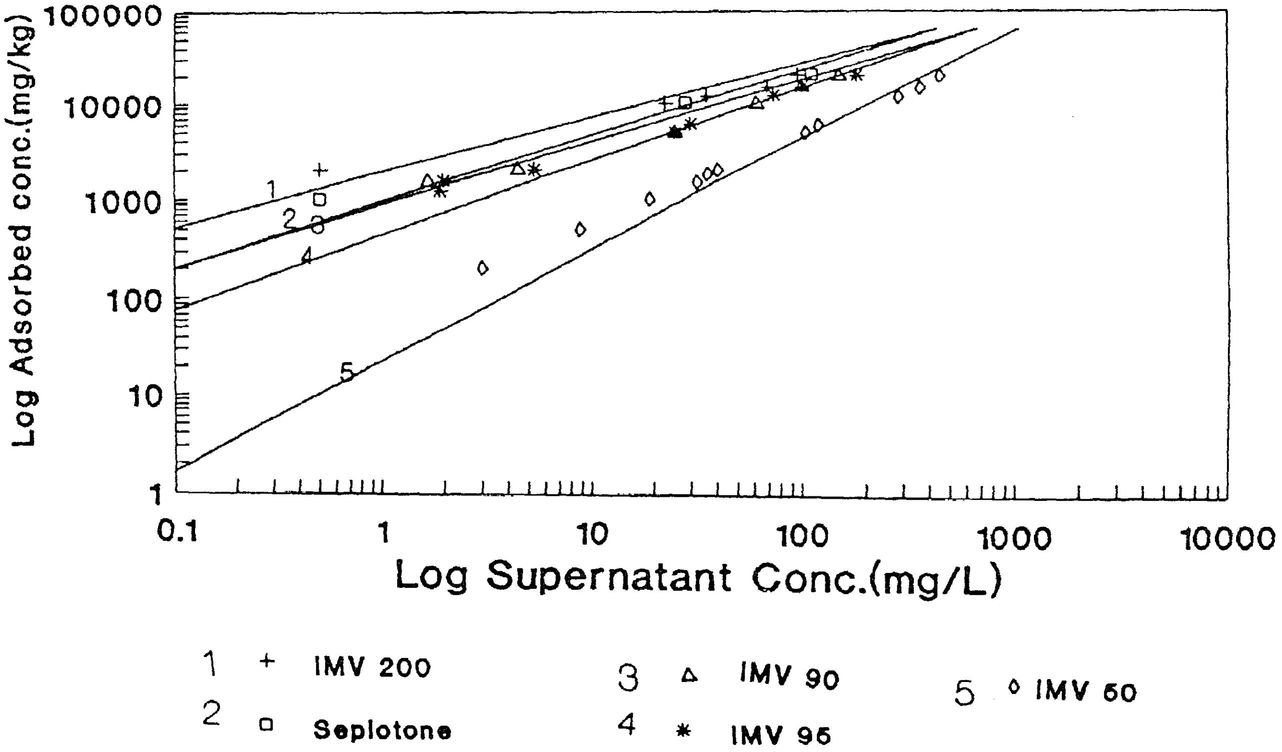

Figure 6. The contaminant in this analysis is phenol. IMV Floridin clays IMV 200, 95, 50, and 90 as well as Sepiotone are analyzed with this contaminant.

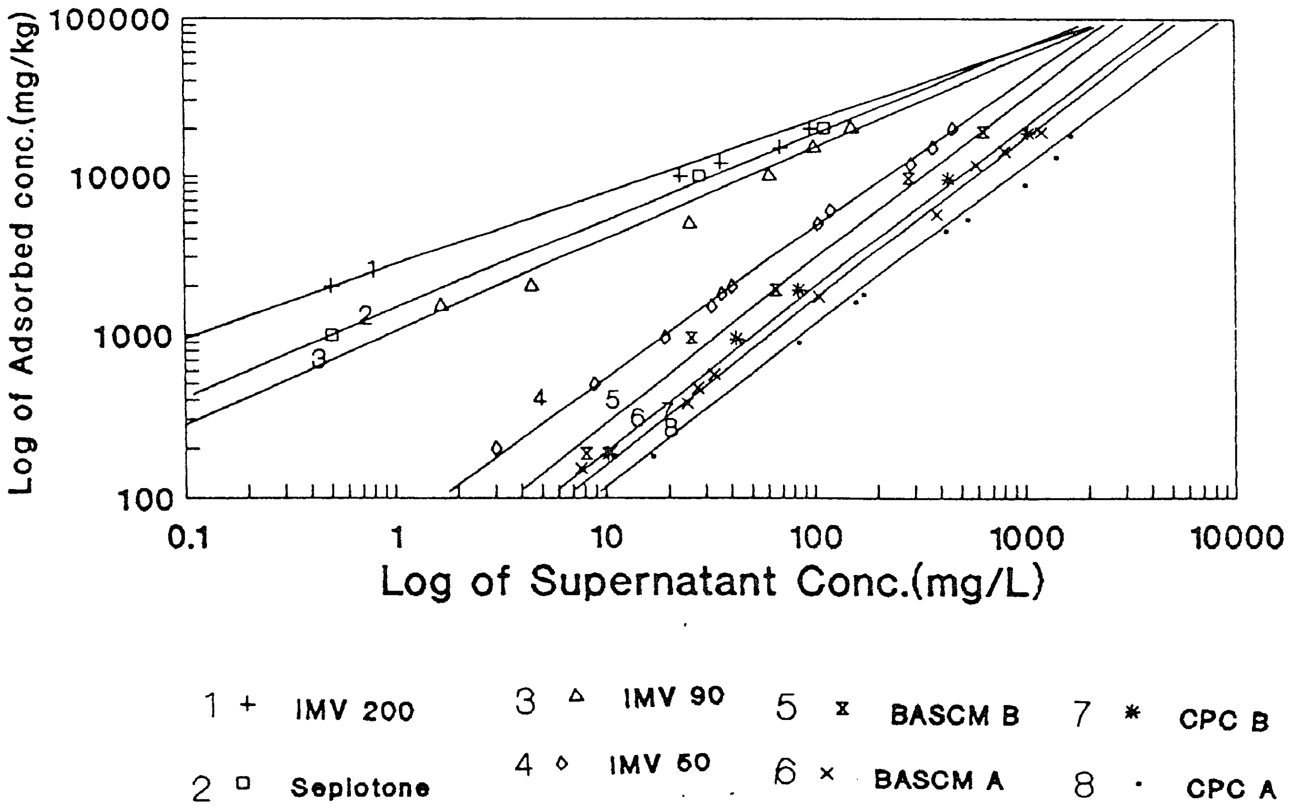

Figure 7. The contaminant in this analysis is phenol. The IMV Floridin clays Sepiotone, IMV 200, 50, 90, and 95 are analyzed for adsorption potential along with the Union Carbide Corporation clays CPC A & B and BASCM A& B.

5.3 Results of the Batch Studies of Naphthalene

Naphthalene was the second contaminant considered in the adsorption studies. One important difference between naphthalene and the other contaminants is that it has a very low solubility in water. Therefore, the naphthalene had to be dissolved in methanol first before it could be used. For this purpose, 1000 mg/l (wt./vol.) solution was first prepared. From this solution, the other concentrations were made by dilution.

First, a method blank was run for each of the concentrations that were going to be used for the adsorption studies. Here, the objective was to see how much of the contaminant would be adsorbed on the reaction vessel. For this purpose, different concentrations of naphthalene from 100-1000 mg/l were used.(A method blank was also run for phenol but there was not any significant amount of phenol adsorbed on the vessel.)

Table 5-12 Blank Naphthalene Analysis.

Initial concentration (mg/L)	Final concentration
100	96.0
150	145.0
250	228.5
300	281.3
500	475.0
750	608.5
1000	690.1

From this blank analysis, it was apparent that initial concentrations of naphthalene over 500 mg/L would show inaccurate concentrations because a lot of the naphthalene would be adsorbed onto the wall of the vessel. Therefore, for all samples only initial concentrations of less than or equal to 500 mg/L were used.

The same method of presenting the data as the phenol analysis will be used here also. First the results from the six Union Carbide clays will be presented in Tables 5-13 to 5-18. Then a plot of their performance, Figure 8 will be presented. The data from the Floridin clay analysis is presented in Tables 5-19 through 5-20. After this, a graphical presentation of the IMV Floradin organoclay will be presented in Figure 9. Finally, a comparison of all the organoclays will be done for naphthalene, Figure 10.

5.3.1 Discrepancies with the Naphthalene Analysis

In order to determine the Freundlick isotherm a linear first order regression was done with the naphthalene as well as the phenol data. The phenol regression showed good correlations. The correlations were between 0.9186-0.9997. The naphthalene regression however showed many variations. The correlations were between 0.4858-0.9738. This discrepancy in correlation indicates that the use of the Freundlick isotherm could be incorrect in determining partition coefficients for the naphthalene.

5.3.2 Discrepancy with the Batch Study

If there was water trapped in the pores of the clay, there could be less contaminants adsorbed than indicated in these tables. This could also be another source of error in the batch studies. One way this problem could be alleviated is to saturate the clays with deionized water before the batch studies are done.

Table 5-13 Batch Isotherm for Adsorption of Naphthalene by CPC A

Initial conc. (mg/L)	Final conc. of Supernatant (mg/L)	Amount adsorbed on clay (mg/kg)	partition coefficient K_f [(L/mg)b-1- L/kg]
100	5.3	184.3	6.6
150	12.5	271.8	25.8
250	14.0	436.6	21.9
500	14.8	928.4	43.8

Statistical information from the plot of Cetylpyridinium Chloride Monohydrate (CPC B):

slope :1.1335

intercept :1.1335 +/- 0.7002

correlation :0.7531

Table 5-14 Batch Isotherm for Adsorption of Naphthalene by BASCM A

Initial conc. (mg/L)	Final conc. of supernatant (mg/L)	Amount adsorbed on clay (mg/kg)	partition coefficient K_f [(L/mg)b-1- L/kg]
100	4.8	186.6	13.7
150	7.8	281.3	9.2
250	9.5	446.4	10.5
500	12.1	936.4	14.7

Statistical information from the plot of BenzyldimethylStearylammonium Chloride A (BASCM A):

slope :1.6670

intercept :1.07222 +/- 0.1182

correlation :0.9468

Table 5-15 Batch Isotherm for adsorption of Naphthalene by BASCM B

Init. conc. (mg/L)	Final conc. of Supernatant (mg/L)	Amount adsorbed on clay (mg/kg)	partition coefficient K_f [(L/mg)b-1- L/kg]
100	BDL	UNKNOWN	UNKNOWN
250	BDL	UNKNOWN	UNKNOWN
300	3.8	555.1	
500	11.5	927.0	

Table 5-16 Batch Isotherm for Adsorption of Naphthalene by CPC B

Init. conc. (mg/L)	Final conc. of Supernatant (mg/L)	Amount adsorbed on clay (mg/kg)	partition coefficient K_f [(L/mg)b-1- L/kg]
100	BDL	UNKNOWN	UNKNOWN
250	14.1	435.9	119.3
300	18.9	534.3	121.8
500	56.6	865.1	121.8

Statistical information from the plot of Cetylpyridinium Chloride Monohydrate B (CPC B):

slope :0.4858

intercept :2.09300 +/- 0.01950

correlation :0.9960

Table 5-17 Batch Isotherm for Adsorption of Naphthalene by Enviroplug

Init. conc. (mg/L)	Final conc. of Supernatant (mg/L)	Amount adsorbed on clay (mg/kg)	partition coefficient K_f [(L/mg)h-1- L/kg]
100	45.1	676.9	17.0
250	115.7	1555.7	15.8
500	203.0	3471.1	20.4
750	309.7	4133.9	16.2
1000	348.2	4707.3	16.4

Statistical information from the plot of Enviroplug:

Slope :0.9666

Correlation :0.9912

Intercept :1.2359 +/- 0.05445

Table 5-18 Batch Isotherm for Adsorption of Naphthalene by Natural Gel Bentonite

Init. conc. (mg/L)	Final conc. of Supernatant (mg/l)	Amount adsorbed on clay (mg/Kg)	partition coefficient K_f [(L/mg)h-1- L/kg]
100	50.2	658.6	16.9
250	123.8	1658.2	18.3
500	225.8	3464.6	21.9
750	325.8	3869.6	17.3
1000	395.2	4213.6	15.8

Statistical information from the plot of Natural Gel Bentonite:

Slope :0.9347

Intercept :1.2530 +/- 0.06702

Correlation : 0.9857

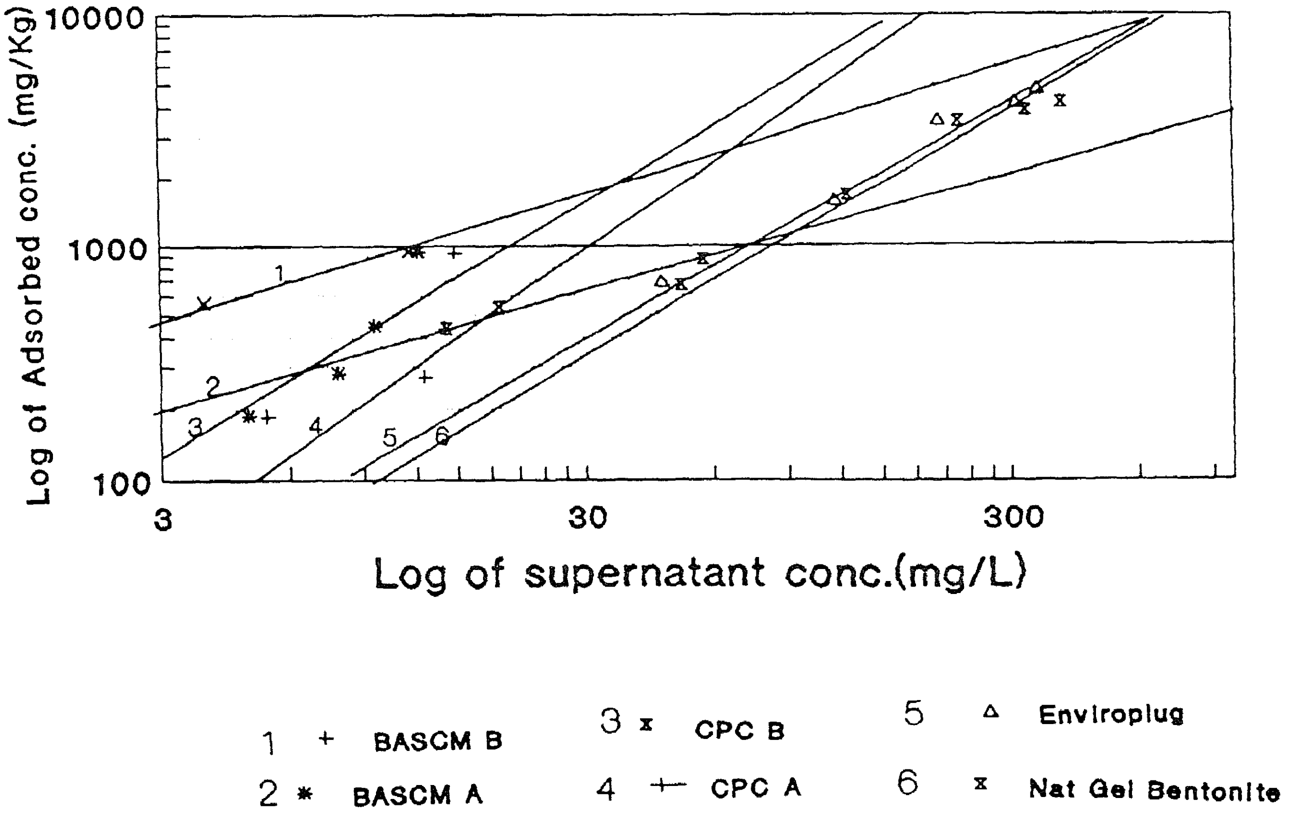

Figure 8. The contaminant in this analysis is naphthalene. Union Carbide Corporation clays BASCM A & B and CPC A & B as well as Natural Gel Bentonite and Enviroplug are analyzed with this contaminant for adsorption potential.

Table 5-19 Batch Isotherm for Adsorption of Naphthalene by Sepiotone

Init conc. (mg/L)	Final conc. of Supernatant (mg/L)	Amount adsorbed on clay (mg/kg)	partition coefficient K_f [(L/mg)b-1- L/kg]
100	3.8	188.7	32.7
150	6.6	284.2	23.8
250	8.2	449.4	28.3
500	12.8	938.7	33.0

Statistical information from the plot of Sepiotone

slope :1.3137

intercept :1.4643 +/- 0.08252

correlation :0.9738

Table 5-20 Batch Isotherm for Adsorption of Naphthalene by IMV 90B

Init. conc. (mg/L)	Final conc. of Supernatant (mg/L)	Amount adsorbed on clay (mg/kg)	partition coefficient K_f [(L/mg)b-1- L/kg]
100	4.9	188.3	22.2
150	10.0	283.3	12.8
250	11.5	449.4	16.8
500	13.2	941.3	28.8

Statistical information from the plot of Imvisperse 90B (IMV 90B):

slope :1.3447

intercept :1.2840 +/- 0.1887

correlation :0.8580

The IMV 200 and 50 showed concentrations below the detection limits at equilibrium for all initial concentrations. From this analysis, it was apparent that the Union Carbide clay BASCM B showed the best adsorption capacity of all the Union Carbide clays. For the overall performance IMV Floridin clays, the IMV 200 and 50 showed the best performance.

Granular activated carbon was also analyzed with the naphthalene. As in the case of the phenol, the protocol for analyzing the GAC is the same as the untreated clays. All the final concentrations of naphthalene tested were below the detection limit.

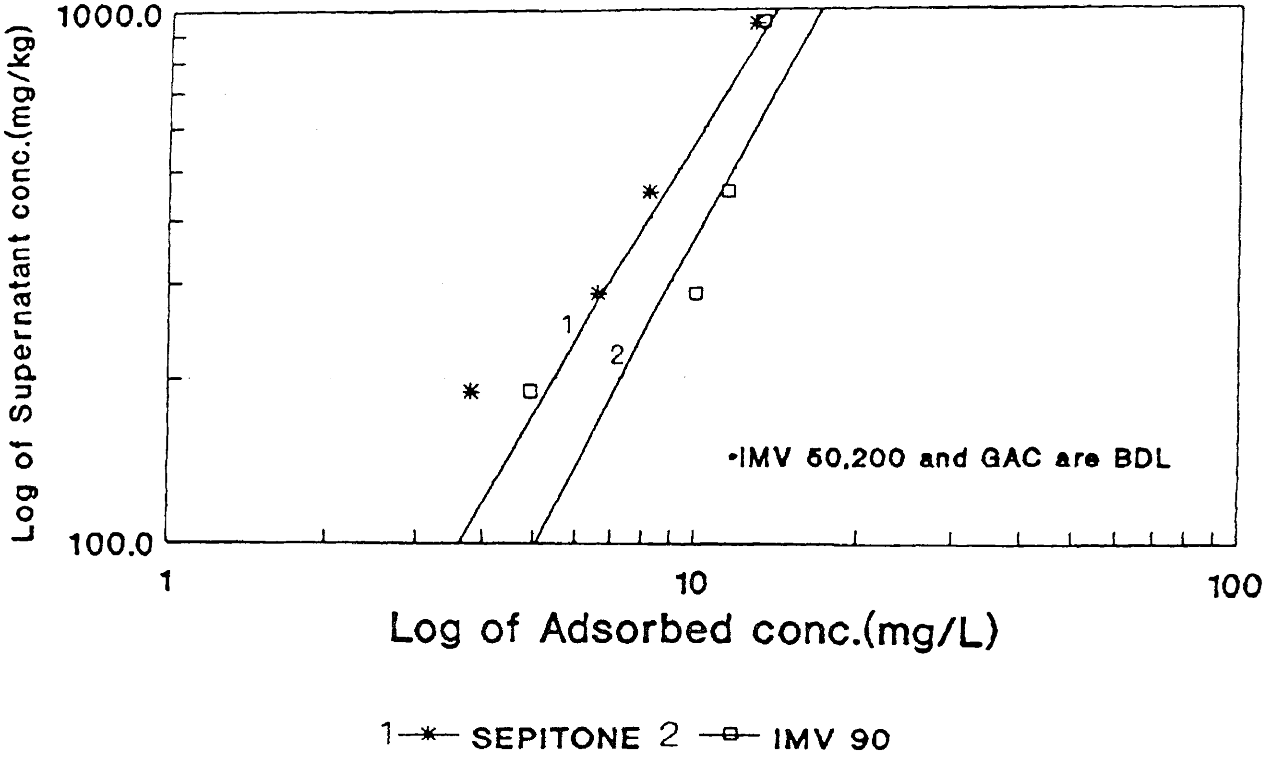

Figure 9. The contaminant in this analysis is naphthalene. The IMV Floridin clays Sepiotone, IMV 90, 50, and 200 are analyzed with this contaminant for adsorption potential

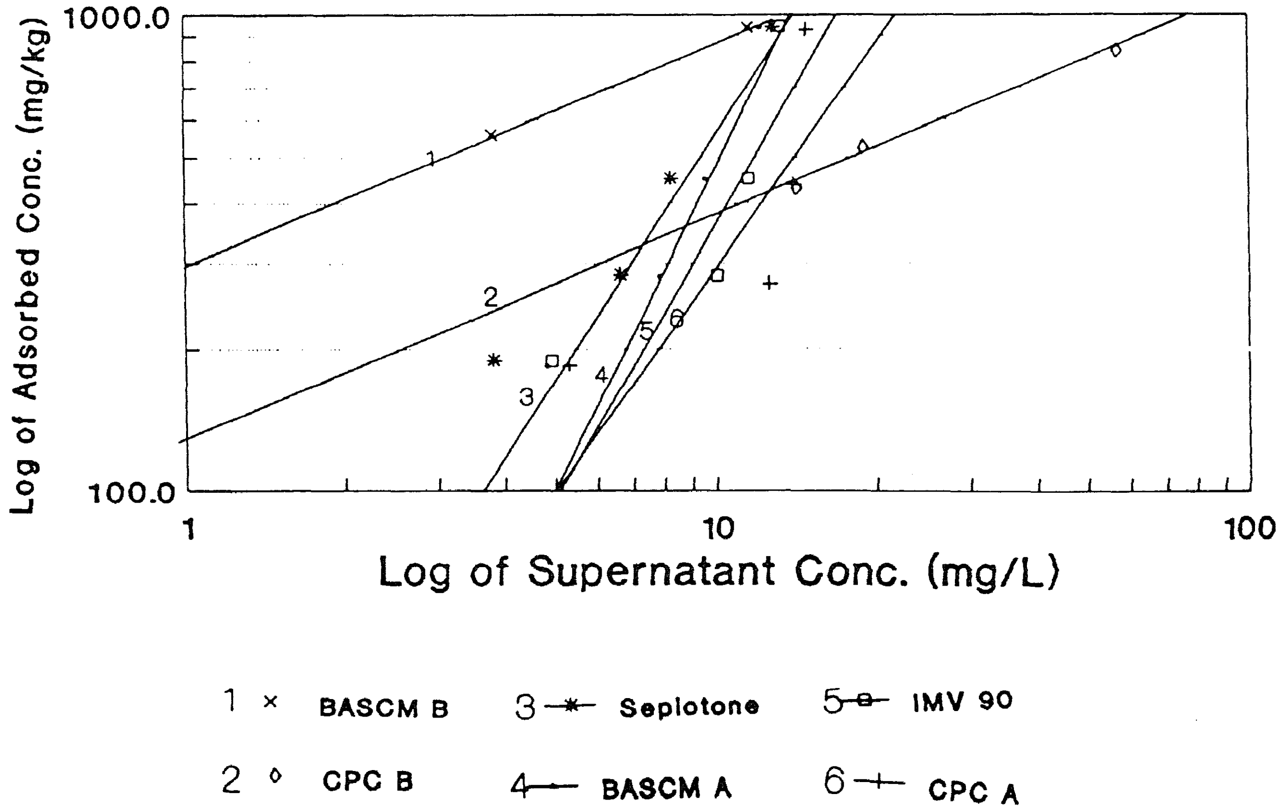

Figure 10. The contaminant in this analysis is naphthalene. Union Carbide Corporation clays BASCM A & B and CPC A & B are represented here as well as the IMV Floridin clays IMV 90, 200, 50 and Sepiotone.

5.4 Results of the 1,4-Dioxane Batch Studies

1,4- Dioxane was the final organic compound considered for analysis. Like phenol, it is miscible with water. A 1000 mg/L (wt./vol.) was used for this analysis. This solution was diluted to various initial concentrations for use in the adsorption study.

The detection limit of the gas chromatograph for 1,4-Dioxane is 5 mg/l. All the clays except for IMV 50 could not be analyzed with less than 50 mg/l initial concentration. The graph for the adsorption potential of 1,4-Dioxane can found in Figure 11.

The adsorption studies of 1,4- Dioxane with these organoclays showed a very poor adsorption potential. One possible reason could have been that the pH for the initial solution of 1,4- Dioxane was too high or low. The initial pH was 8.4. This pH was adjusted to 10.4 with NaOH (aq) and 6.4 with HCl (aq) to see if this would affect the adsorption capacity. The initial concentration of 50 mg/l was tested at these two pH.

Table 5-21 Batch Isotherm for Adsorption of 1,4-Dioxane

Clay	Init. conc. (mg/L)	Final conc. of Supernatant (mg/L)	Amount adsorbed on clay (mg/kg)
IMV 90B	50	24.8	83.6
	200	151.6	100.0
	1000	915.7	1395.6
IMV 200	50	28.8	79.8
	200	169.5	281.4
	1000	899.7	1370.2
SEPIOTONE	50	19.5	82.8
	200	141.0	275.9
	1000	898.6	1209.2
CPC B	50	35.5	46.8
	200	185.4	121.9
	1000	955.8	566.3
BASCM B	50	31.8	75.8
	200	190.9	254.9
	1000	913.2	1306.0
BASCM	50	29.7	66.7
	200	195.1	181.4
	1000	958.8	926.1
IMV 50	10	6.5	14.7
	50	40.4	66.9
	200	189.3	244.8
	1000	955.3	1216.7

Table 5-22 Analysis of 1,4-Dioxane at 50 mg/l conc. in acidic and basic pHs

Clay	Final conc. supernatant at pH 6.4(mg/L)/ Amount adsorbed on clay (mg/kg)	Final conc. of Supernatant at pH 8.4(mg/L)/ Amount adsorbed on clay (mg/kg)	Final conc. of Supernatant at pH 10.4 (mg/L)/ Amount adsorbed on clay (mg/kg)
SEPIOTONE	17.1/65.8	19.5/61.0	25.7/48.6
CPC B	32.7/34.6	35.5/29.0	40.2/19.6
IMV 50	36.4/27.2	40.4/19.2	43.7/12.6
IMV 200	20.4/59.2	28.8/42.4	32.7/34.6
BASCM B	29.7/40.6	31.8/36.4	38.9/22.2
BASCM	28.3/43.4	29.7/40.0	33.0/34.0
IMV 90	17.5/65.0	24.8/50.4	32.2/35.6

Note: The changing of the pH did not significantly improve the adsorption capacity of the organoclays.

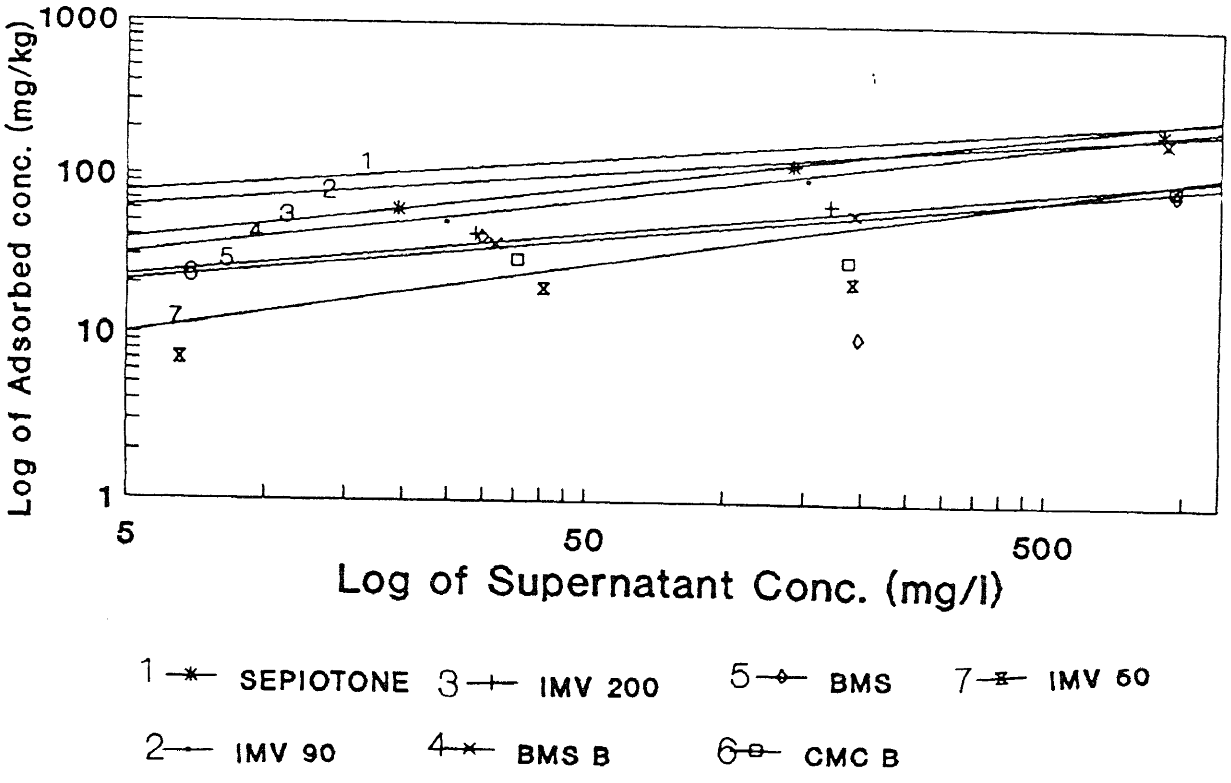

Figure 11. The contaminant in this analysis is 1,4-Dioxane. All of the clays from the Union Carbide Corporation and IMV Floridin are analyzed with this contaminant.

5.5 Water Content

The water content measurements of the clays are given in table 5-23. The water content analysis shows that the Natural gel bentonite and the Enviroplug are the most hydrophilic. This could explain why the batch analysis protocol had to be changed to evaluate these two compounds. After equilibrium, these two clays left no supernatant for the original clay/solution ratio of 5 grams of clay to 10 milliliters of solution.

Table 5-23 Water Content of the Clays

Name of the clay	% of water
BASCM A	2.1
BASCM B	3.8
CPC A	2.4
CPC B	2.8
SEPIOTONE	1.9
IMV 50	2.1
IMV 200	1.5
IMV 90B	1.9
IMV 95B	2.0
NAT. GEL. BENTONITE	5.9
ENVIROPLUG	6.1

Table 5-24 Final volume of supernatant

Name of the clay	Final volume(ml)
BASCM A	5.6
BASCM B	5.8
CPC	7.3
CPC B	7.5
SEPIOTONE	4.4
IMV 50	4.1
IMV 200	3.5
IMV 90B	3.3
IMV 95B	3.2
NAT. GEL. BENTONITE	6.8
ENVIROPLUG	6.3

CHAPTER 6

CONCLUSION AND FURTHER WORK

6.1 Conclusion

From the batch isotherm studies of 1,4-Dioxane, it is apparent that it cannot be removed to any safe concentration with any of the organoclays analyzed in these studies. So, no further studies will be done with the 1,4-Dioxane.

Naphthalene is soluble at less than 30 mg/L in water. The concentrations of naphthalene used for the isotherm batch studies ranged up to 500 mg/L (initial stock naphthalene solution was diluted in methanol). At these concentrations, all the organoclays removed the naphthalene to safe levels. The organoclays IMV 200 and 50 removed all the naphthalene with initial concentrations up to 500 mg/L. The best organoclay from the Union Carbide Corporation was the BASCM B. Still, it was not as good as the IMV 200 and 50 but it was better than the IMV 90 B (see Figure 10).

The phenol is very soluble in water. For this reason, a high initial concentration of phenol was used in the batch studies. The initial concentration ranged up to 1% (wt/vol.). The IMV 200 had the best performance in the isotherm studies followed by the Sepiotone. The Floridin clays performed much better than any of the Union Carbide Clays. The best Union Carbide Clay was the BASCM B.

This study also considered GAC as a potential adsorber for the removal of phenol and naphthalene. It was determined that GAC was as good as IMV 50 and 200 for the removal of naphthalene. It was also determined that GAC was better than all the organoclays for the removal of phenol. At the same time GAC is much more expensive than the organoclays so it has the advantage of cost efficiency over the GAC for its use.

6.2 Further Work

Section 5.3.2 described a discrepancy in the batch study. Water could have been adsorbed onto the pores of the clay. This could have affected the clays adsorptivity. One way to prove or repudiate this hypothesis is to saturate the clay with water and then do the batch isotherm studies again.

The batch isotherm studies were done over a 72 hour period of time. It could be beneficial to see how the concentrations of contaminants changed over the 72 hours. This can be done by checking the supernatant concentration during the 72 hour equilibrating period.

The next step of this project is to conduct the column studies. The RSSCT (Rapid small scale column test) is a laboratory version of a full-scale adsorber. The use of RSSCTs in industry have gained wide range of popularity because they are cost effective, they use very small volumes of water and they are time saving [4]. The RSSCT will determine how the organoclays can remove the contaminants in a continues flow system.

The IMV 200 and the Sepiotone had the best batch isotherm potential for the phenol. The IMV 200 and the IMV 50 had the best isotherm adsorption potential for the naphthalene but the IMV 50 had a very low adsorption potential with the phenol.

Since the IMV 200 had the best batch isotherm potential, it will be used for the column study. The second clay that will be used for the column study will be Sepiotone. It had the second best batch isotherm with phenol and it had a reasonable performance with the naphthalene. The IMV 50 cannot be used since it had such a poor performance with the phenol.

This project only looked at the effect of a single contaminant on the clays. Another possible study would be to investigate the affect of multiple contaminants simultaneously to see if there is a competition for adsorption potential between the different contaminants.

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