To the Graduate Council:

I am submitting herewith a thesis written by James K. Cable entitled "An Evaluation of the Adsorption and Flotation of Nonpolar Organic Compounds in Clay Colloid Suspensions." I recommend that it be accepted in partial fulfillment of the requirements for the degree of Master of Engineering, with a major in Civil Engineering.

Dennis W. Weeter, Major Professor

We have read this thesis and
recommend its acceptance:

Wayne T Davis

Accepted for the Council:

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Vice Chancellor
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AN EVALUATION OF THE ADSORPTION AND FLOTATION OF NONPOLAR ORGANIC COMPOUNDS IN CLAY COLLOID SUSPENSIONS

A Thesis
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Master of Engineering
Degree
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ABSTRACT

The objective of this study was to evaluate the adsorption and volatilization of organic compounds onto clay coagulated using cationic surfactants. Dissolved air flotation (DAF) was used to remove the clay from the water. Three clays were used in the study which were: bentonite, kaolinite, and illite. Benzene, toluene, and chlorobenzene were the organic compounds used. Hexadecyltrimethylammonium bromide and dodecyltrimethylammonium bromide were the cationic surfactants used as coagulating aides.

Jar test were run to determine the amount of adsorption that occurred. A bench scale DAF unit was used for the flotation process. The samples were analyzed using an ultra-violet spectrophotometer.

The following results were determined from the research. As the surface area (SA) and cation exchange capacity (CEC) increased with each clay, the amount of adsorption that occurred increased. Adsorption was found to be essentially complete after 30 minutes. It was found that the amount of adsorption occurring did not increase proportionally as the amount of clay increased. This indicates that there was a limiting factor in the process. The attraction for adsorption by hydrophobic bonding was not significantly greater than the attractive forces between the water and the organic compounds which results from dipole-dipole interaction and hydrogen bonding. The DAF process was effective in removing the clay and a certain amount of volatilization of the compounds occurred.

The overall process does not remove the compounds to trace levels. Because of this the usefulness of the process is limited in its application. Continued research on selected industrial wastestreams should be done to determine the effectiveness of the overall process.

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CHAPTER I

INTRODUCTION

Background

Organic compounds have become a major concern in the aquatic environment because of their adverse risk to health and the difficulty in their removal. Industrialization has increased the number and concentration of organic compounds found in river water, primary and secondary effluents of waste treatment plants, ground water, rainwater, and water purification plants (Keith, L. H.; 1976). The Federal Water Pollution Control Act of 1972 required that effluent limitations be set for industries discharging into waterways based on "Best Practical Technology" (BPT) and "Best Available Technology" (BAT). In 1977, partially as a result of a suit filed against the EPA by several environmental organizations, Congress passed the Clean Water Act. Toxic pollutants became the major focus, overriding the initial concern over the conventional pollutants such as BOD, COD, TSS and pH. A list of 129 toxic pollutants developed from 65 classes of toxic pollutants. Effluent limitation guidelines were also to be set for 36 industries which would require BAT, BPT, and Best Conventional Technology (BCT). The difficulties that the EPA faced in developing effluent limitations using BAT involved categorizing the industries according to the processes used and the facilities' age, and by taking into account the possible differences in applicability and the cost of the control technology. The EPA was given the discretion by Congress to choose alternative control technologies based on the age of the equipment and the facility, the processes used, and the cost of the technology. After sampling the industrial discharges to determine the toxic pollutants present, the EPA identified possible control technologies and the effectiveness of the chosen technology. Final effluent standards do not require installation of a particular type of control technology. Instead, the achievement of effluent standards equivalent to proper operation of the "model" control technologies is required (CEQ Draft Report, 1980).

The Clean Water Act of 1977 requires that the 36 industrial categories meet the effluent discharge limitations placed upon them by July 1, 1984. With the opportunity to choose a treatment process that will reach the required effluent standards, there is an increased interest in research in the area of water treatment for trace organic compounds which is both effective and economical.

Objective

Naturally occurring clay colloid suspensions are found in water courses. Cationic surfactants are long chain hydrocarbons with ionic characteristics which make them useful as coagulating aides. As cationic surfactants adsorb to the surface of the clay particles, coagulation occurs which results in the formation of a hydrophobic surface. The hydrophobic surface in this process may be useful as an adsorbent for trace nonpolar organic compounds in water.

The adsorption process is dependent upon many factors (Weber, 1972). They are:

1. Nature of the adsorbent;
2. Nature of the adsorbate;
3. pH;
4. Temperature.

This study will investigate the effectiveness of three types of clays in adsorbing different organic compounds after being flocculated by quaternary ammonium compounds.

The following variables will be considered:

1. What effect does the type and concentration of clay have on the adsorption process?
2. What effect does the type of surfactant have on the ability of the clay to adsorb the organic compounds?
3. Are certain compounds removed to a greater extent than other compounds?
4. Is the time of interaction between the clay floc and the organic compounds a significant factor in the adsorption process?
5. Will Dissolved Air Flotation (DAF) adequately remove the clay floc?
6. Does DAF play any role in the removal process?

The results from this study will have practical application to water purification processes. It will be determined whether removal of organic compounds occurs with the addition of cationic surfactants to clay colloid solutions. If it proves to be effective, variables which are important in a design analysis would be determined.

CHAPTER II

LITERATURE REVIEW

Clay Chemistry

Clay minerals belong to the phyllosilicates. These minerals are composed of two-dimensional arrays of silicon-oxygen tetrahedra and aluminum or magnesium-oxygen hydroxy octahedra. These sheets are superimposed in different fashions to form the different types of clays. The three layer clays are termed montmorillonites and illites. A two layer clay is kaolinite (van Olphen, 1977).

These are three principle groups of phyllosilicates which are: montmorillonites, kaolinites, and illites. Two other groups of clay minerals are chlorites and attapulgite clays. The different groups vary in clay structure, chemical composition, surface area, and cation exchange capacity (van Olphen, 1977).

Clays, by their chemical nature, carry a net negative charge. This net negative charge is neutralized by positive counterions present at the surface of the clay. The net negative charge is believed to be caused by isomorphic substitution, broken edges of the edge of the clay layers, and exposed structural hydroxyl groups (Swartzen-Allen and Matijevic, 1974).

Montmorillonite clays are expanding 2:1 layer clays. Trivalent aluminum sometimes replaces silica in the tetrahedral sheet. In the octahedral sheet, magnesium sometimes replaces aluminum while leaving a vacant octahedral position, thus a net negative charge on the particle results (van Olphen, 1977). An example of a montmorillonite clay is bentonite.

In the presence of water, interlayer swelling occurs which results in the increase of basal spacing by approximately 12.5-20 Å (van Olphen, 1977). This interlayer swelling causes the volume of clay to double. Several hypotheses have been proposed to explain the swelling behavior of montmorillonites. The most widely accepted reason for the interlayer swelling is that interlayer cations become hydrated and the large hydration energy involved is greater than the attractive forces between the layers. In other nonexpanding clays, these interlayer cations are not present for hydration and no energy is generated to overcome the attractive forces (McAttee, Jr., 1958). The cation exchange capacity of montmorillonites was found to range from 85-160 meq./100 grams (Am. Petroleum Inst., 1951).

Illites are nonexpanding 2:1 layer clays. In the presence of water there is no interlayer swelling. Substitution occurs only in the tetrahedral sheet. The total net negative charge of illite clays is generally one and a half times larger than the net negative charge of montmorillonites. Illites have nonswelling characteristics because of the specific electrostatic linking effect between layers by the potassium ions. The potassium ions are present to compensate for the absence of one positive charge in the tetrahedral sheet after the substituion of one aluminum atom (Grim et al.; 1934). The literature cites values of the cation exchange capacity ranging from 20-40 meq./100 grams (van Olphen, 1977).

Kaolinites are 1:1 layer clays with nonexpanding characteristics. The absence of interlayer swelling is primarily caused by electrostatic forces, Vander Waals forces of attraction, and hydrogen bonding (Giese, R. F., Jr., 1972; Wolf, R. W. and Giese, R. F., Jr., 1974). Kaolinites have only a small amount of isomorphic substitution which results in a small net negative charge. The cation exchange capacity values found in the literature for kaolinites range from 1.5 to 20.2 meq./100 grams (Am. Petroleum Research Inst., 1951).

Cationic Surfactants

Surfactants are defined as surface active agents that adsorb to surfaces and interfaces when present in solutions at low concentrations. The adsorption process results in a decrease of the surface free energies at the interfaces. Surfactants have two structural groups composing the molecule. One structural group has little attraction to the solvent and is termed lyophobic. When water is the solvent, the structural group is said to be hydrophobic. The remaining structural group has a strong attraction for the solvent and is described as lyophilic. In water this structural group would be termed hydrophilic. The presence of the lyophobic group causes a distortion in the free energy of the system and the surfactant tends to concentrate at the surface of the solvent. The lyophillic group prevents the complete separation of the two phases (Rosen, 1978).

Flocculation—The Interaction of Clay Colloid Suspensions and Cationic Surfactants

Clay minerals in solution form colloidal suspensions. The net negative charge of the clay minerals is compensated by positive counterions at the surface of the particle. The positive ions are electrostatically attracted to the negatively charged surface. The positive ions are diffused away from the surface. At the surface the concentration of counterions is high. As it diffuses outward the concentration of counterions decreases. In 1910 Goy and in 1913 Chapman recognized this counterion diffusion from the surface and they gave a theoretical interpretation of the counterion distribution (Chapman, 1913). This theory was developed with some unrealistic elements. The ions are not considered in terms of ion size and they are treated as point charges. The surface, the counterions and the medium have certain interactions which are neglected. The theory developed by Stern in 1924 took into account the distance between the counterions and the surface. This effect of counterion size is accounted for in the theoretical development of a fixed Stern layer at the surface of the particle (Stern, 1924; Adamson, 1967). The presence of the positive counterions at the surface of the clay produces a stable colloidal suspension in which the electrostatic repulsive forces are greater than the Vander Waal forces of attraction. Figure 1 illustrates the effects of the attractive potential energies and repulsive potential energies. Cationic surfactants adsorb to surfaces in an oriented fashion. This adsorption of surfactants at the surface is influenced by the following factors (Rosen, 1978):

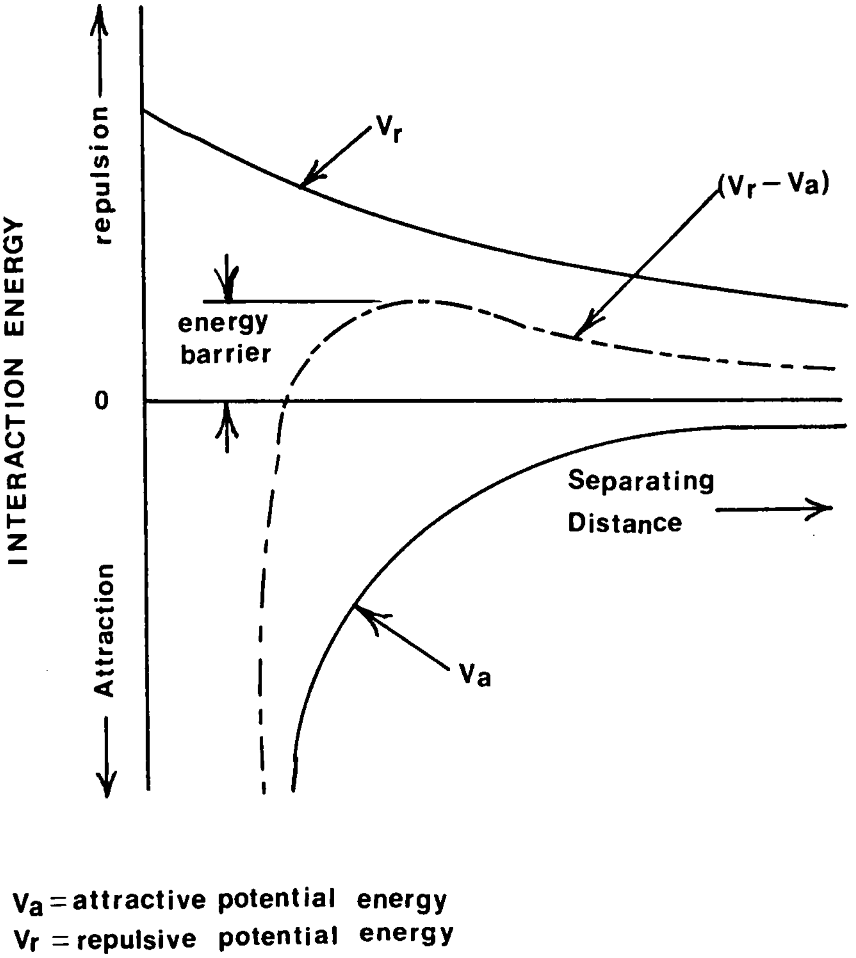


Figure 1. Interaction energy diagram of a colloidal system.

1. The nature of the structural group;
2. The type of surfactant used;
3. The condition of the aqueous phase.

The surfactants adsorb to the surface by four mechanisms. In ion exchange similarly charged surfactant molecules replace counterions (Law, 1966). Ion pairing involves adsorption of surfactants onto unoccupied sites. Hydrogen bonding occurs between the surfactant and the adsorbate (Snyder, 1968). Adsorption also occurs when dispersion forces are overcome between adsorbent and adsorbate (Law, 1966). Hydrophobic bonding occurs from the mutual attraction of hydrophobic groups of the surfactant and other hydrophobic molecules in the aqueous phase (Dick, 1971; Giles, 1974).

Previous research has been done to determine the actual effects of the addition of cationic surfactants to clay colloidal suspensions. The stability of the hydrophobic sol was found to be a minimum at certain concentrations of cationic surfactant, but the sol became destabilized as the amount of surfactant increased (Ottewille et al., 1960; Ottewille and Rastogi, 1960). Amine salts were added to kaolinite and bentonite suspensions to produce hydrophobic surfaces and it was found that the amount of amine salt needed decreased as the molecular weight of the salt increased (Kobalchidze and Shishniashvili, 1964).

In addition to the amount needed decreasing as the molecular weight increased, it was also found that, regardless of the surfactant used, the flocculation concentration of each surfactant added produced a floc having nearly an identical surface area (Kay, 1971). Amine salts were also used to look at their arrangement and orientation on the solid interfaces of clay (Lagaly et al., 1970).

Adsorption of Organic Molecules Onto Clays

Research in the area of adsorption indicates that the process takes place by adsorption onto the crystal lattice by ion-dipole interaction, Vander Waals forces, and hydrogen bonding. Complexation with the clay may also occur or the molecules may undergo anion or cation exchange with the original ions (Swartzen-Allen and Matijevic, 1974).

Many studies have been made on the adsorption of organic molecules on clay without the addition of surfactants. Low molecular weight alcohols were adsorbed to clays saturated with inorganic ions (Swartzen-Allen and Matijevic, 1974). Ethylene glycol and ethanol were adsorbed to montmorillonite (Dowdy and Mortland, 1967). Montmorillonite was also used as an adsorbent for ketones (Parfitt and Mortland, 1968). Kaolinite and bentonite were used as adsorbents for aromatic hydrocarbons. Contact time was 2 days. Considerable amounts of clay were required to remove appreciable amounts of the compounds (El-Dib et al., 1978).

The literature indicates that while a significant amount of work has been done with the adsorption of compounds onto clays and surfactants onto clays, there has been very little research on the adsorption of organic molecules onto clay floc made hydrophobic by the addition of cationic surfactants. The interaction of benzene, phenol, and chlorobenzene with hydrophobic floc was investigated. Short chain quaternary ammonium compounds were used to produce a hydrophobic surface on the clay. The adsorption of benzene was attributed to the interaction of the π-electrons with the clay. Phenolic adsorption was felt to occur primarily through ion dipole interaction. Chlorobenzene adsorption was not significant and it was felt that the molecule was too large for significant adsorption (Mortland and Pinnavaids, 1971). An additional study showed that chlorobenzene was not appreciably adsorbed (Gast and Mortland, 1971).

Studies have shown that the addition of quaternary ammonium compounds open up the lamellae and increase the adsorptive capacity of montmorillonites. Benzene was found to adsorb to a greater extent than aliphatic hydrocarbons. It was suggested that the planar benzene molecule was packed in a manner which was more suitable to the shape of the interlamellar cavity. The aliphatic hydrocarbons have less regular configurations and, therefore, will not allow easy packing (Barrer and MacClead, 1955).

Another study was done using phenol, chlorobenzene and benzene as molecules to be adsorbed to montmorillonites saturated with short chained quaternary ammonium compounds. It was found that the replacement of the inorganic ions by surfactant ions on the clay surface greatly increased the adsorptive capacity of the clay. The primary adsorption mechanism was Π-election interaction with the oxygen atoms of the silicate tetrahedral. Chlorobenzene was found not to adsorb readily McBride et al., 1977).

Dissolved Air Flotation

Dissolved air flotation has been applied to many processes in the past, both on municipal and industrial waste. A review done by K. L. Roberts in his dissertation for his doctorate degree illustrates these widespread applications (Roberts, 1980). Municipal applications of the DAF process involve treatment of raw and settled sewage and sludge thickening. Industrial waste applications involve processing oil refinery waste, cold reduction steel mill wastes, slaughterhouse waste, pulp and paper mill waste, and paint-containing waste (Nemerow, 1971). The DAF process was also found applicable to the cannery industry, coal industry, chemical industry, meat products industry, mining industry, metal finishing industry, soap manufacturing, sugar refineries, and on laundry waste (Vrablik, 1951). Other industrial processes are using DAF treatment for paper board mill white water, toilet tissue wastes, and glue wastes (Barry, 1951).

CHAPTER III

MATERIALS AND METHODS

Materials

Clays. Three types of clays were used in this study. They were: bentonite, kaolinite, and illite. The bentonite and kaolinite were laboratory grade samples obtained from Fisher Scientific Company. The illite was obtained from a sample of shale found in Fithian, Illinois. It was received from Ward's Natural Science Establishment, Inc., Rochester, N.Y. The sample of illite was prepared by crushing the shale and collecting the portion passing the number 200 sieve (74μm). No separation by differences in specific gravity was done so the sample of illite actually contained siltaceous material.

Organic compounds. Benzene, chlorobenzene, and toluene were the organic compounds used for this study. All three chemical reagents were laboratory grade purity obtained from Fisher Scientific Company. Table 1 shows the molecular weights and the solubilities of each compound that was needed for the study.

Cationic surfactants. The surfactants used in this study were all quaternary ammonium compounds. Two types were used that varied only in the difference in their chain length. Dodecyltrimethylammonium chloride and hexadecyltrimethylammonium chloride were chosen for

TABLE 1

PHYSICAL PROPERTIES OF ORGANIC COMPOUNDS USED

	MW	Solubility in HOH (ppm)
Benzene	78.11	1780
Chlorobenzene	112.56	490
Toluene	97.14	54

the study. Both compounds were obtained from Eastman Kodak Company in Rochester, N.Y.

Instruments. A Perkin-Elmer Hitachi 200 ultraviolet-visible spectrophotometer was used to determine the concentrations of the chemical compounds in the aqueous solution. The ultraviolet light was used with a slit width of 2 nm and a spectrum ranging from 200 to 300 nm.

Corning stir plates and teflon magnets were used to enhance the flocculation process. One thousand milliliter volumetric flasks were placed on the stir plates for reactor vessels.

Samples were prepared by placing them in an IEC-International centrifuge and running them at 600 rpm for 30 minutes.

A bench scale DAF unit was used in the study. The unit would withstand pressures up to 100psi. Compressed air was used with the system.

Colloidal suspensions were prepared by mixing at a medium speed in a mixer for one minute.

Cation exchange capacities were also determined. An Orion Research Microprocessor Ion Analyzer 901 with a model 95-01 Orion ammonia electrode was used in the analysis.

Surface areas of the clays were also measured in the study. The instrument used was a Micromeritics Surface Area Analyzer.

Methods

Cation exchange capacity measurements. The cation exchange capacity was one parameter used to characterize the clays. The method followed was the ammonia electrode method. The procedure followed was the same as that outlined in the literature (Busenberg, E., and Clemancy, C. V., 1973; Chapman, H. D., 1965).

Surface area measurements. The surface area was the second parameter used to characterize the three types of clays. The method used was the same as is outlined in an instruction manual supplied with the Micromeritics Surface Area Analyzer.

The adsorption process. Colloidal suspensions were put into 1000 ml. volumetric flasks containing teflon stir bars and then placed on Corning stir plates. Stoichiometric amounts of surfactant were added up to one CEC of each clay. Samples were taken every 5, 10, 15, 30, and 60 minutes. These samples were then placed in IEC centrifuges at 6000 rpm for 30 minutes in preparation for the UV spectrophotometer. The samples were then run on the instrument according to the procedures outlined in the Perkins-Elmer Manual.

The concentration of clay in suspension was varied to determine if the adsorption increased as the amount of clay increased. The time of interaction between the clay floc and the organic compounds was varied to determine if there was an optimum time for adsorption to occur. The various types of clay used in the study offered a means of determining the effects of a change in physical properties on the adsorption process. To a small extent, the chain length of the surfactant was varied to determine if the type of surfactant affected the adsorption process.

The Volatilization process. Colloidal suspensions containing low concentrations of an organic compound were flocculated using hexadecyltrimethylammonium bromide. The clay floc was allowed to interact with the solution for 10 minutes and a sample was drawn. Water supersaturated with air from the DAF unit was added to the solution. After a bubble-clay interaction time of 5 minutes, another sample was drawn. These two samples plus the sample taken to determine the initial concentration were centrifuged for 15 minutes in the IEC centrifuge at 6000 rpm. The UV-spectrophotometer was then used to determine the residual concentration of the organic compounds.

Benzene and toluene were used in this study. The clays used were bentonite, kaolinite, and illite.

CHAPTER IV

RESULTS

CEC and SA of the Clays

Table 2 summarizes the results obtained in the cation exchange capacity and the surface area analysis. The values obtained in the study were comparable to those found in the literature (Swartzen-Allen and Matijevic, 1973). The surface area and cation exchange capacity of the illite sample appear to be low which probably results from the presence of silty material which was not removed during the sample preparation. The surface area of bentonite in Table 2 represents the surface area in a dry state. Because of the expansive properties of bentonite in water, the actual surface area in the solution would be approximately ten times greater than the value given.

TABLE 2

CEC AND SA VALUES FOR THE VARIOUS CLAYS

	CEC (meq/100 g.)	SA (m^2/g)
Bentonite	97	34.8
Kaolinite	12	18.8
Illite	24	42.7

Effects of the Type of C.S

Two types of quaternary ammonium compounds were used in this study. Dodecyltrimethylammonium chloride contains a 12 carbon chain connected to the ammonium group. Hexadecyltrimethylammonium chloride contains a 16 carbon chain. These two compounds were used to flocculate a bentonite suspension containing benzene. As can be seen from Figure 2, the residual concentration of the benzene in solution was not effected by the chain length. The increase in chain length from 12 to 16 carbons is not significant when compared to the size of the clay floc. The length of a carbon-carbon single bond is approximately 1.54 Å (Solomons, 1978). The surface area of bentonite is much larger than this. In comparison of size, the difference between the two is significant and, therefore, does not enhance the adsorption process.

Effects of the Type of Clay on Adsorption

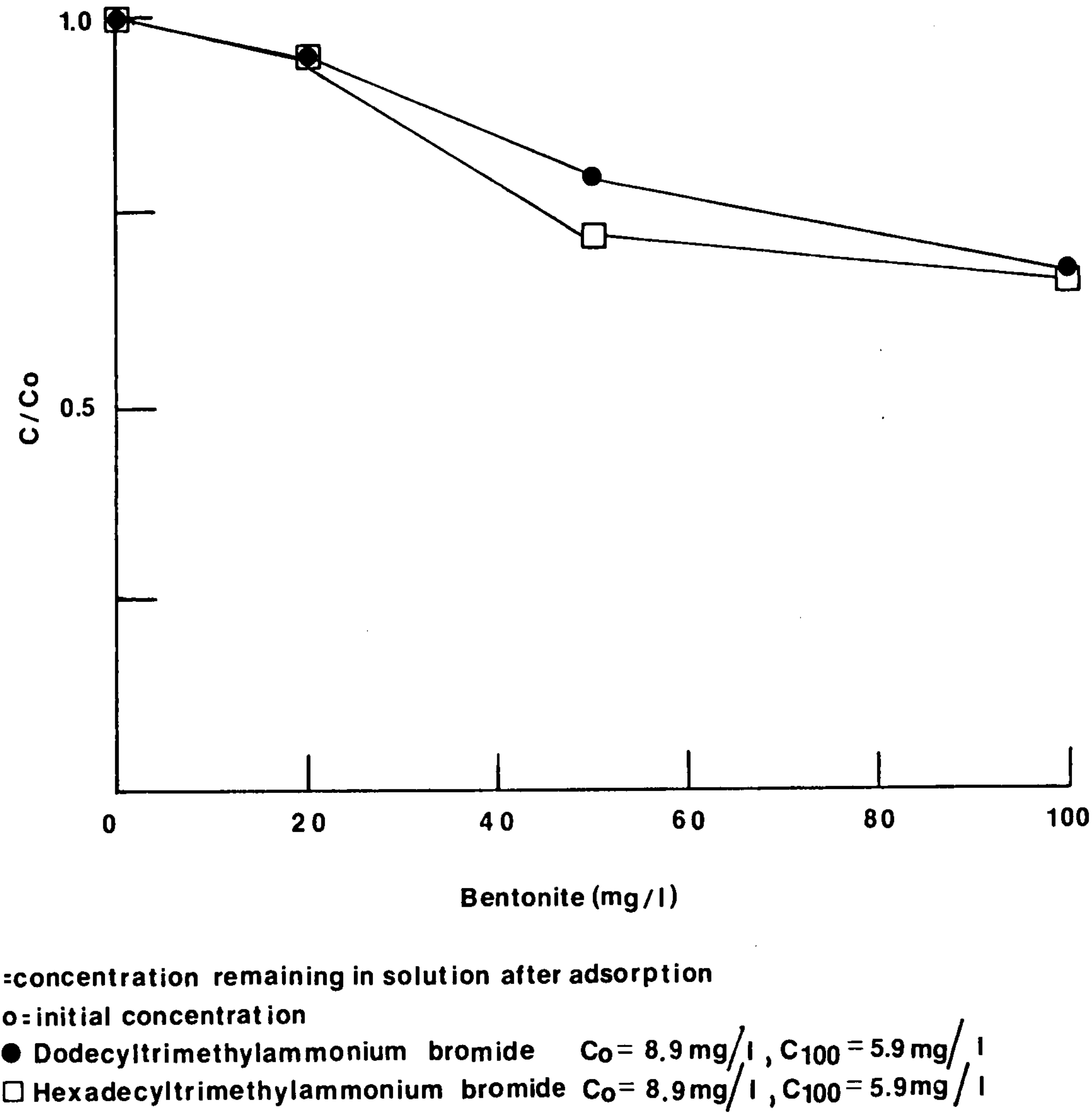
The three types of clay were put into suspensions containing three different types of organic compounds. In the solutions containing benzene and toluene, the order of adsorption was (see Figures 3 and 4):

Bentonite > Illite > Kaolinite

As was noted earlier, the order of increasing CEC and SA area is:

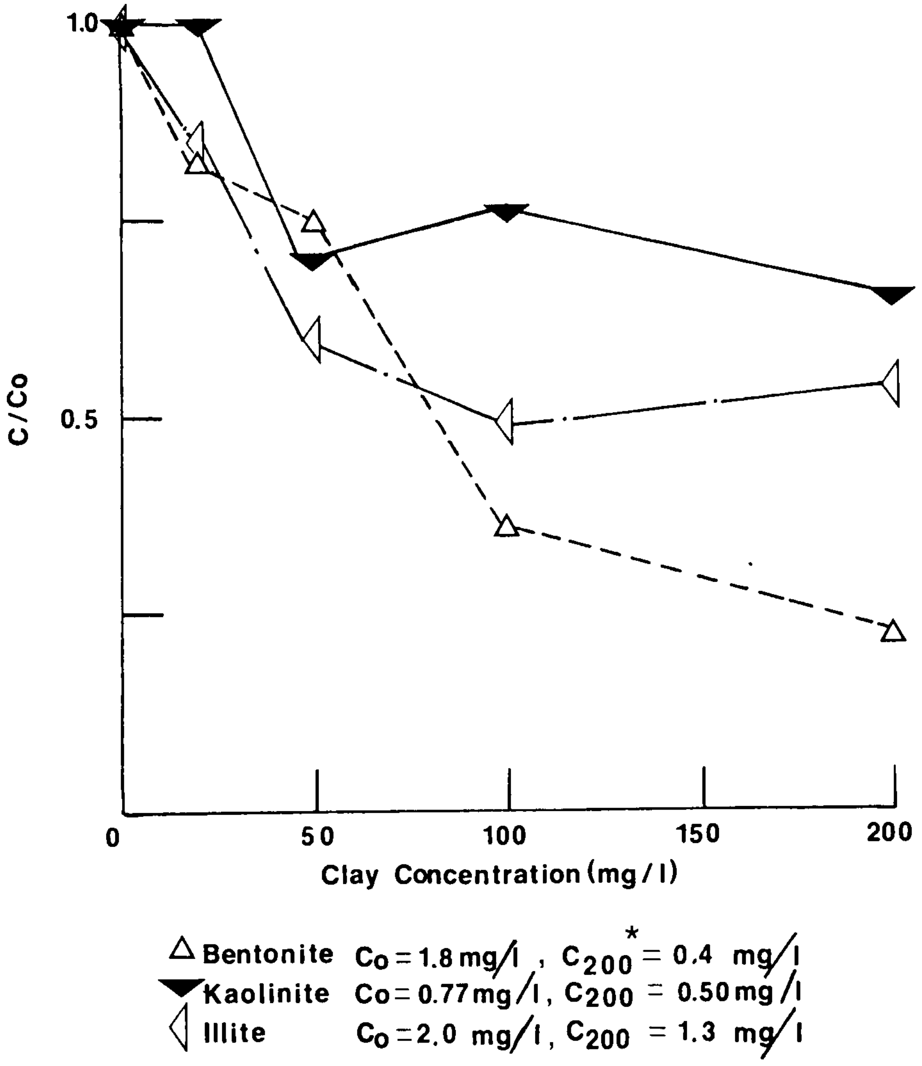
Bentonite > Illite > Kaolinite

The increase in both CEC and SA would produce a more hydrophobic surface which would result in greater adsorption capacity. This is illustrated in Figures 3 and 4.



*Subscript 100 indicates values for suspensions with clay concentrations at 100mg/l.

Figure 2. Adsorption of benzene onto bentonite using hexadecyltrimethylammonium bromide and dodecyltrimethylammonium bromide.



*Subscript 200 indicates clay concentrations of $200^{mg}/l$.

Figure 3. Adsorption of benzene onto kaolinite, illite, and bentonite.

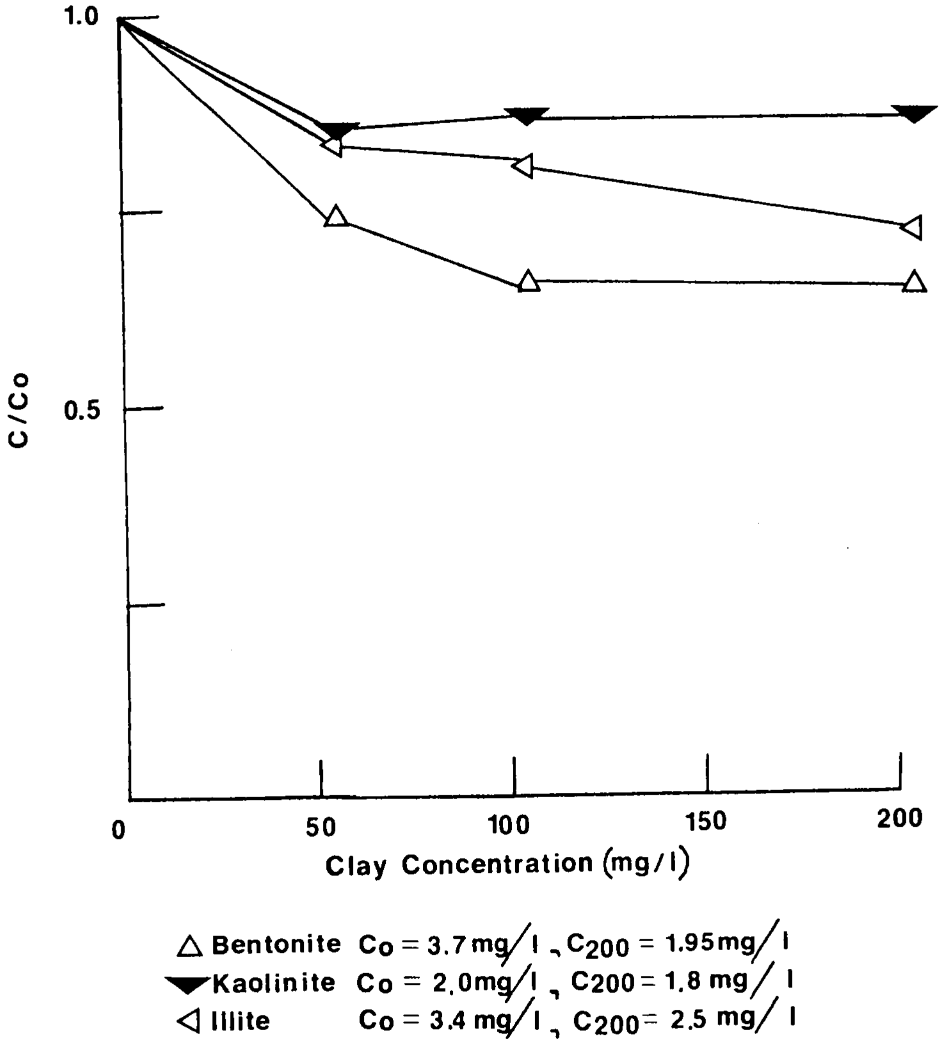


Figure 4. Adsorption of toluene onto kaolinite, illite, and bentonite.

The solution containing chlorobenzene produces different results from those obtained from the solutions of benzene and toluene. As can be seen from Figure 5, the order of increased adsorption is:

Kaolinite > Bentonite > Illite

Very little adsorption is seen to occur for any of the clays. It is felt that the type of organic compound and its polarity inhibits the adsorption process.

Effects of the Time of Interaction on Adsorption

Figures 6 and 7 illustrate the adsorption of benzene and toluene as a function of time. In these solutions it was found that the adsorption leveled off after approximately 30 minutes. As can be seen in Figure 6 with the illite as an adsorbent, the adsorption process seems to reverse after 30 minutes. This apparent desorption is most likely an effect of experimental error. It seems that the adsorptive capacity of the clays is reached in a short period of time, after which very little adsorption occurs.

The sample containing chlorobenzene could not be investigated for the effects of time of interaction because of the small degree of adsorption that occurred. Figure 8 illustrates the problem.

Effects of the Type of Organic Compound on Adsorption

It was found that the type of organic compound present in solution had an important effect on the amount of adsorption that took place. The order of increased adsorption was found to be:

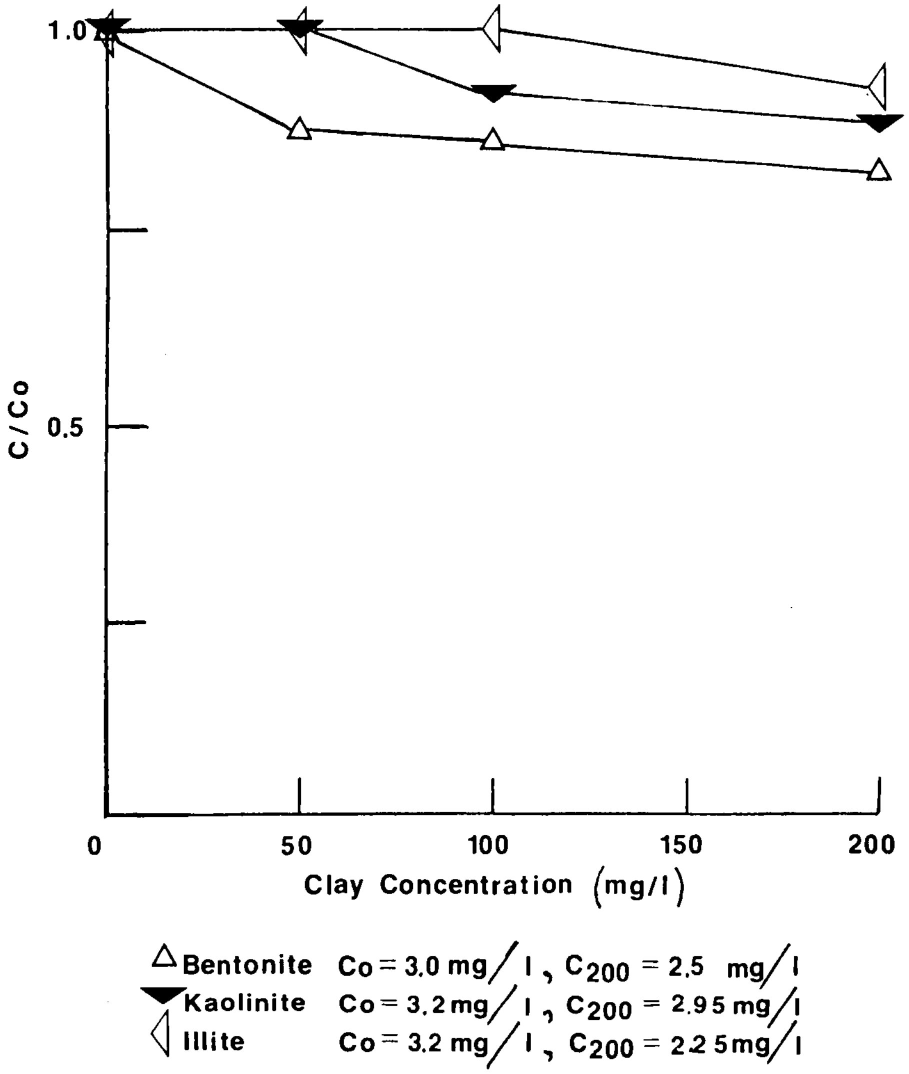
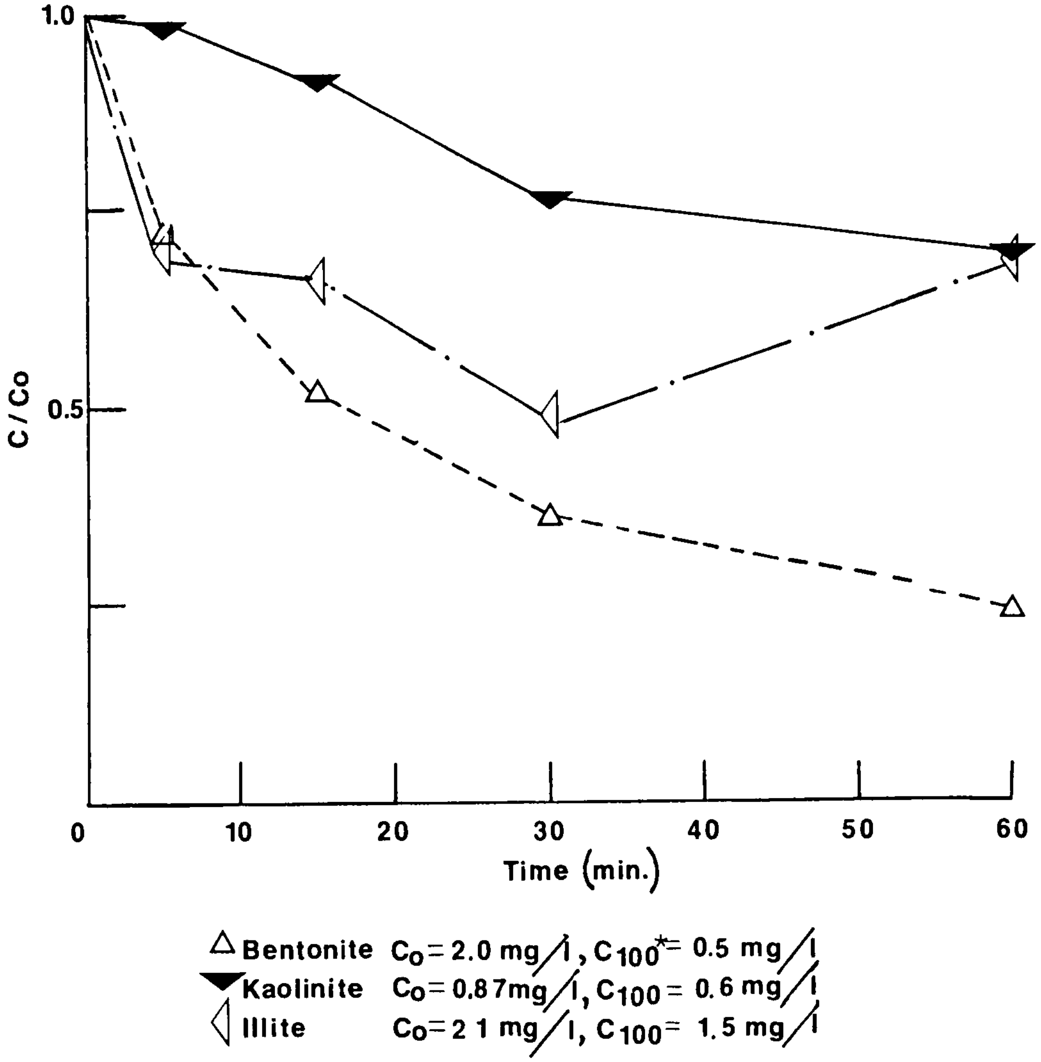
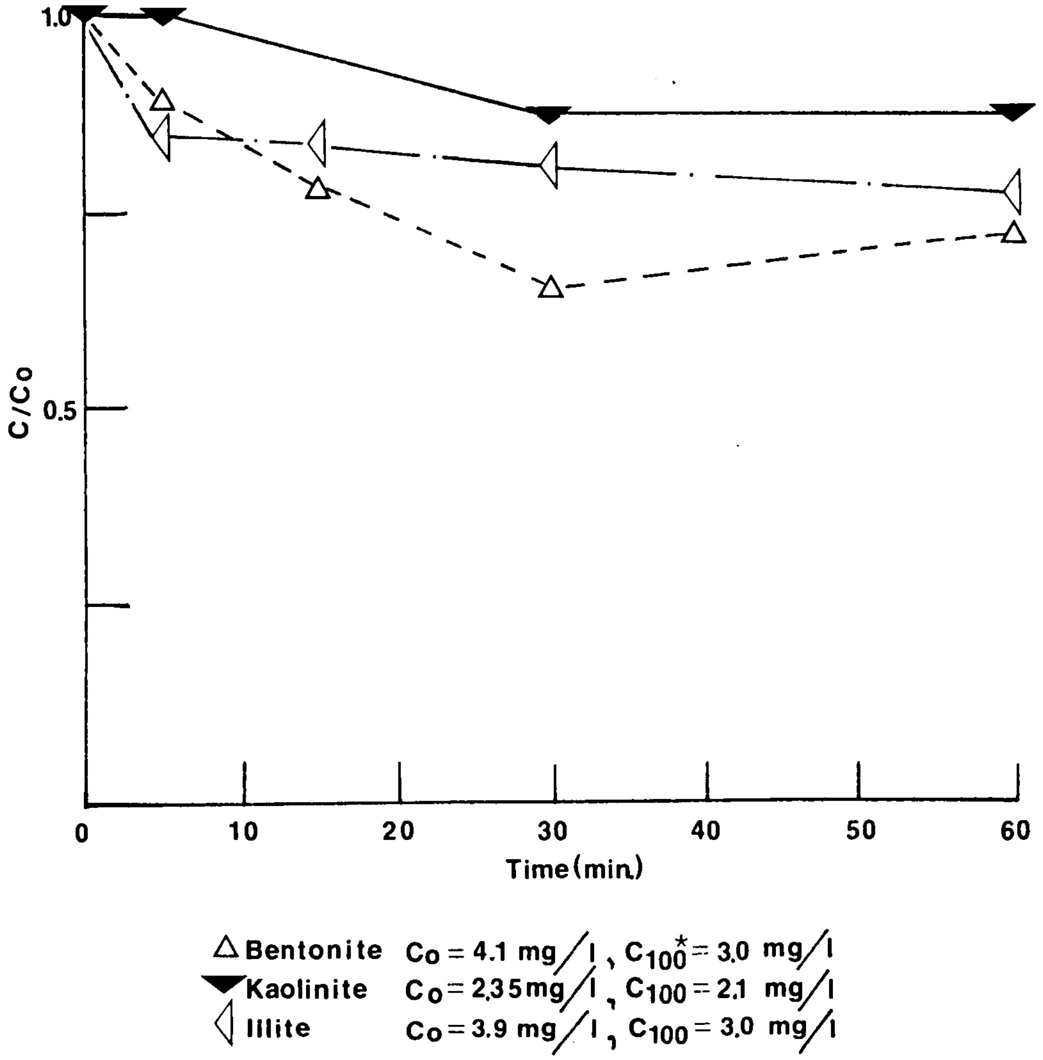


Figure 5. Adsorption of chlorobenzene onto kaolinite, illite, and bentonite.



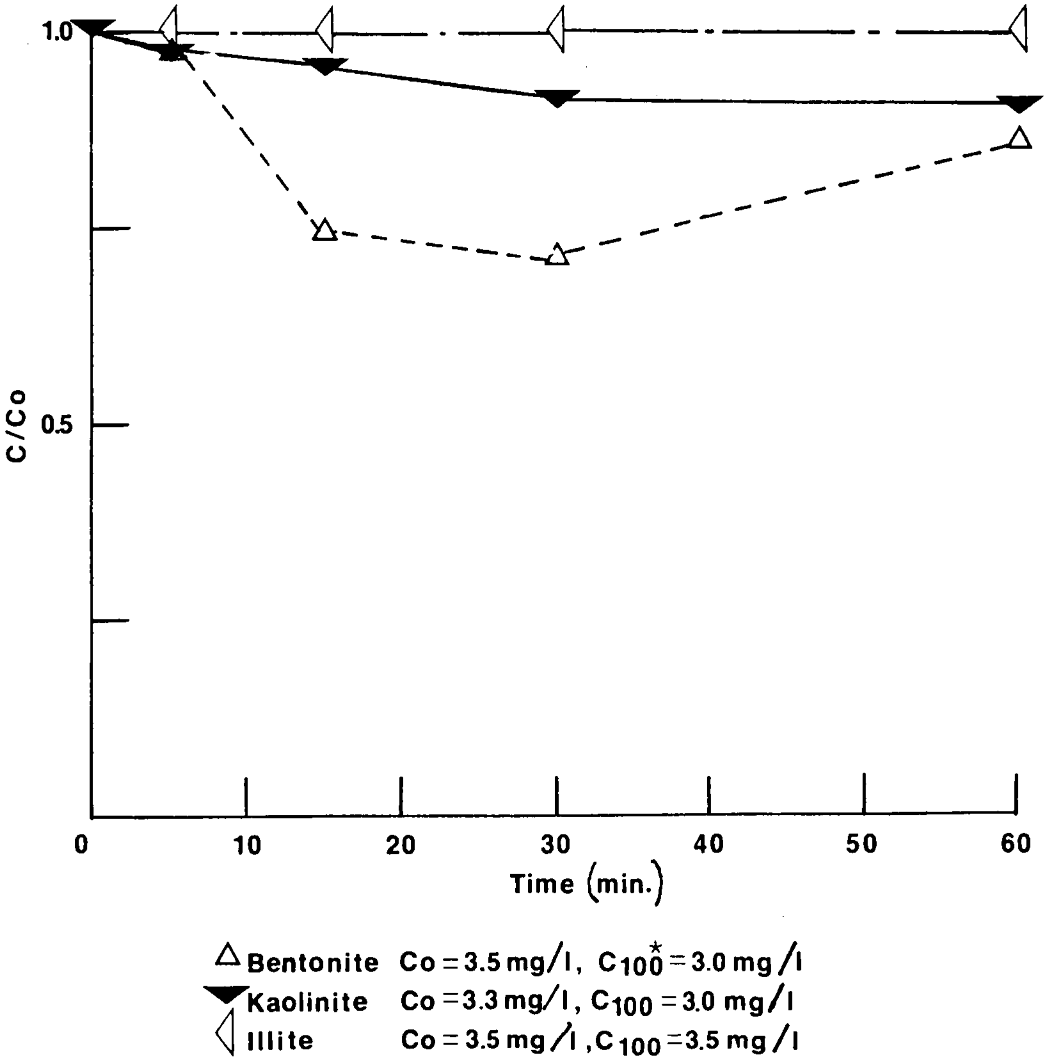
*Subscript 100 indicates values for suspensions with clay concentrations of 100mg/l.

Figure 6. Adsorption of benzene as a function of time.



*Subscript 100 indicates values for suspensions with clay concentrations of 100mg/l.

Figure 7. Adsorption of toluene as a function of time.



*Subscript 100 indicates values for suspensions with clay concentrations of 100mg/l.

Figure 8. Adsorption of chlorobenzene as a function of time.

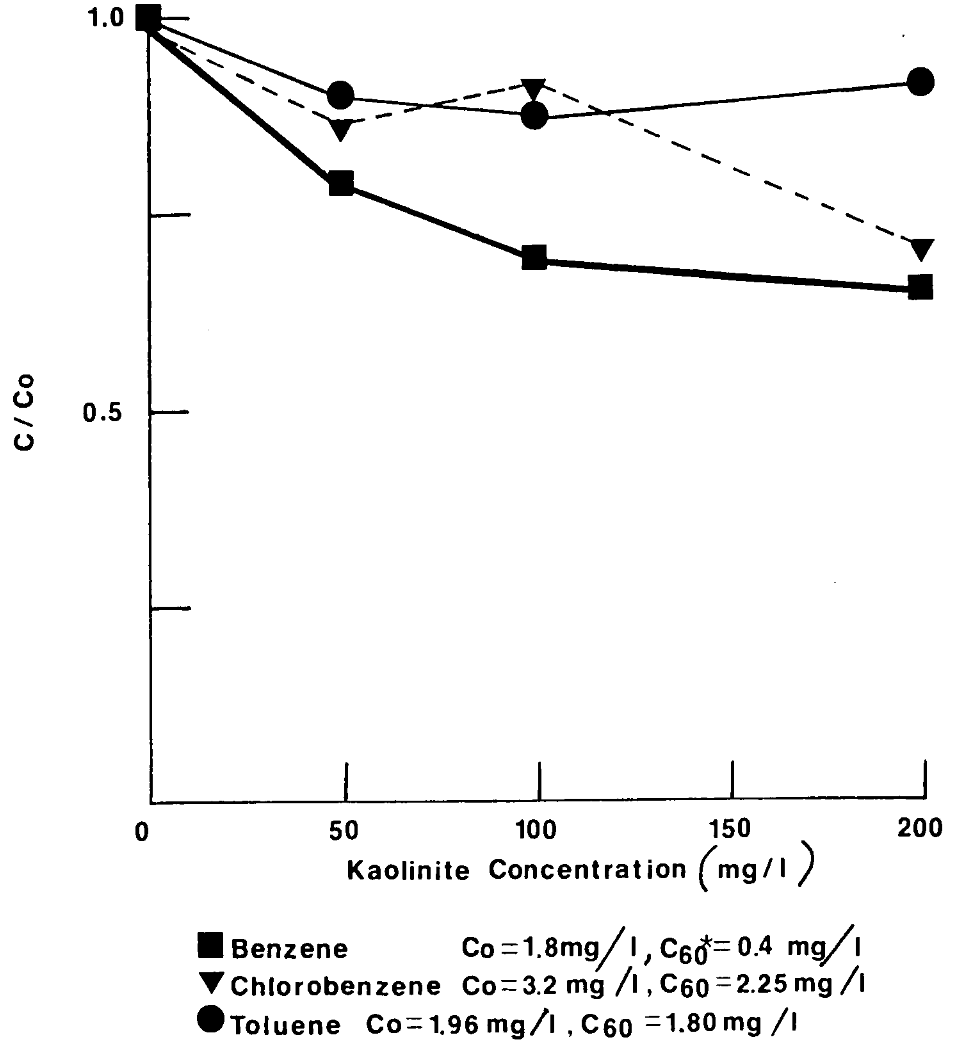
Benzene > Toluene > Chlorobenzene

See Figures 9, 10, and 11.

An explanation of these results can be found in the interaction of a hydrophobic surface with compounds of different degrees of polarity. Most organic compounds are neither ionic nor nonpolar. Instead they have permanent dipoles resulting from the nonuniform distribution of the bonding electrons. As a result of this nonuniformity, the organic compounds orient themselves in solution such that the negative end of the molecule will be directed toward the positive end of another molecule. These interactions or intermolecular forces are important in explaining the solubility of various compounds. As the nonuniform distribution of bonding electrons increases, the permanent dipole increases in polarity. The increased polarity of the permanent dipole of a compound increases the interaction between other dipole molecules, such as water, and their solubility increases. The compounds become more hydrophillic as their solubility increases.

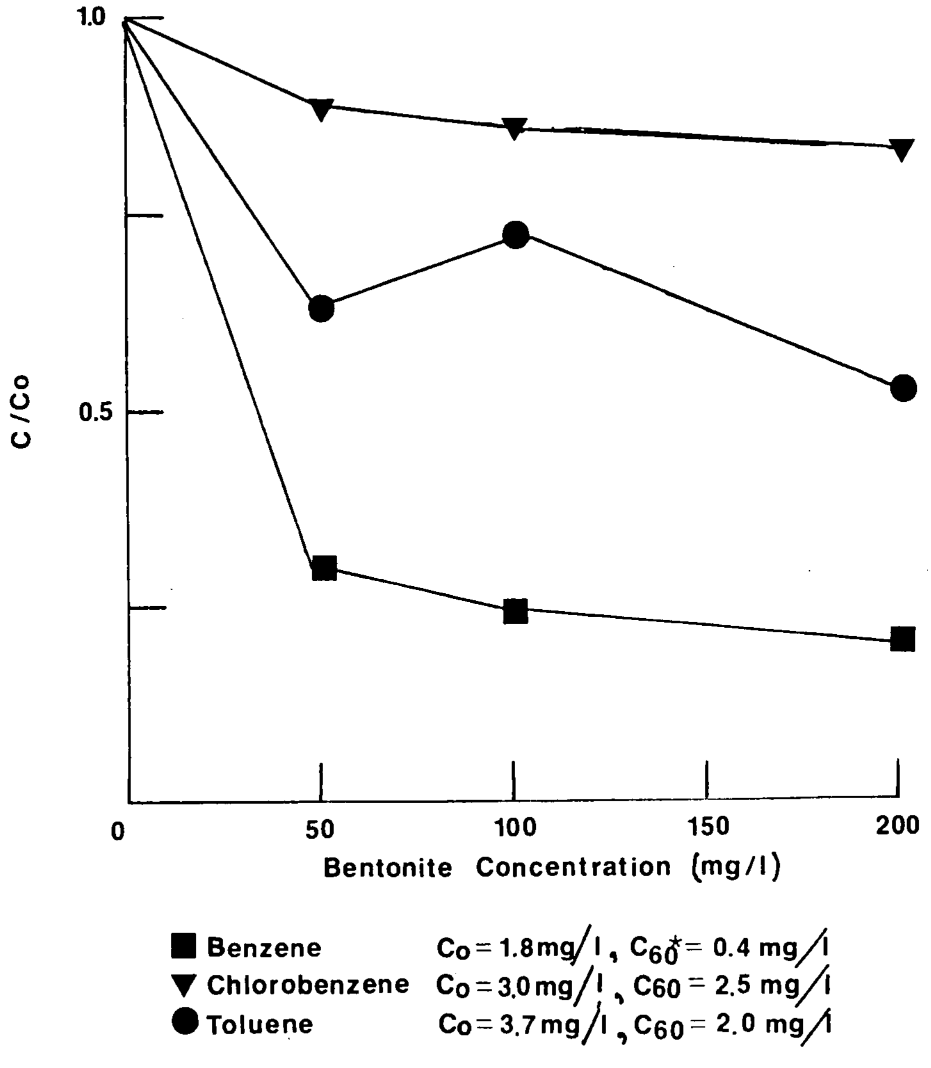
The surfactants were added to the clay solution to form a hydrophobic surface. There is a repulsion between hydrophobic and hydrophillic surfaces. As a result, compounds which are more soluble in aqueous solution (or more hydrophillic) have little attraction to hydrophobic surfaces and, therefore, the adsorption process is inhibited.

In this study, chlorobenzene was the compound with the strongest permanent dipole because of the presence of the chlorine atom on the aromatic ring. The interaction of the unpaired electrons in the chlorine atom with those electrons in the aromatic ring produces a



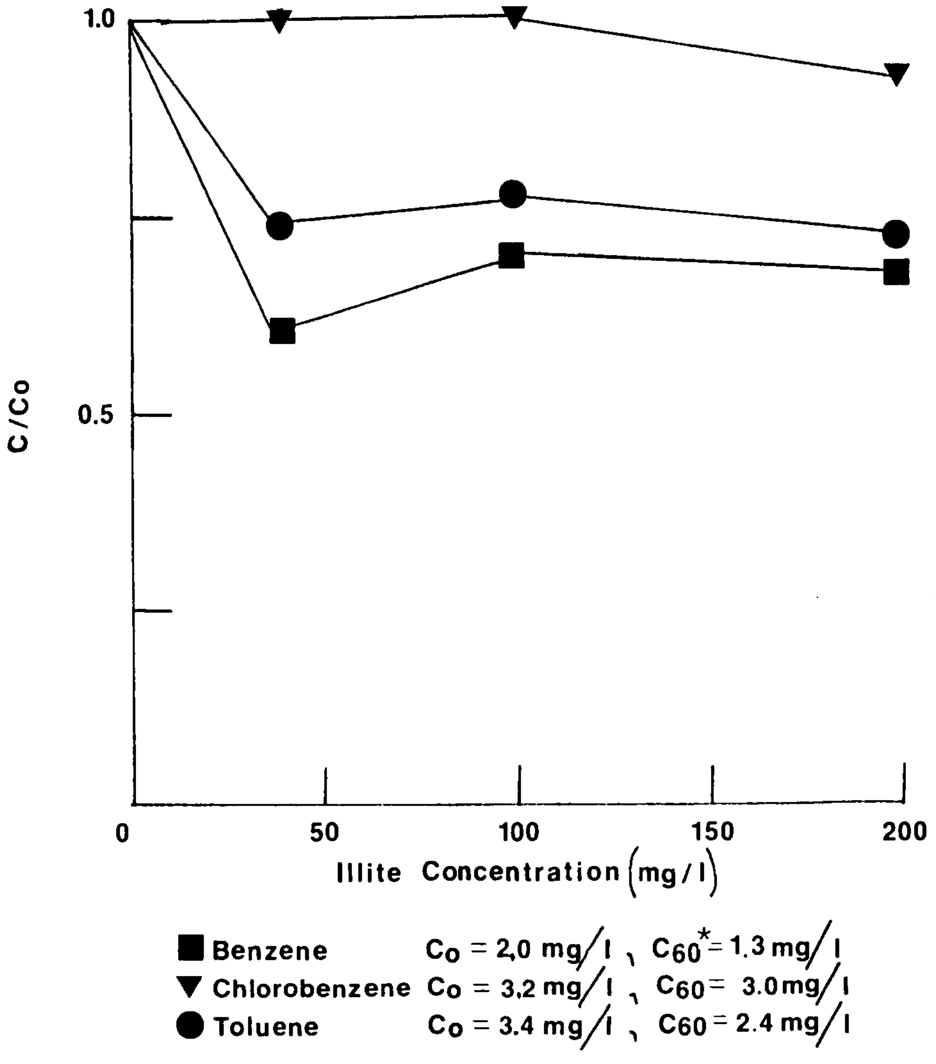
*Subscript 60 indicates concentration after 60 minute contact time.

Figure 9. Residual concentration of the organic compounds as a function of the amount of kaolinite present.



*Subscript 60 indicates concentration after 60 minute contact time.

Figure 10. Residual concentration of the organic compounds as a function of the amount of bentonite present.



*Subscript 60 indicates concentration after 60 minute contact time.

Figure 11. Residual concentration of the organic compounds as a function of the amount of illite present.

partially negative charge on the chlorine atom and partially positive charge on the aromatic ring. In chemistry, resonance structures can be used to illustrate the interaction of all the electrons in the molecule. Figure 12 illustrates this interaction and the partial dipole which results.

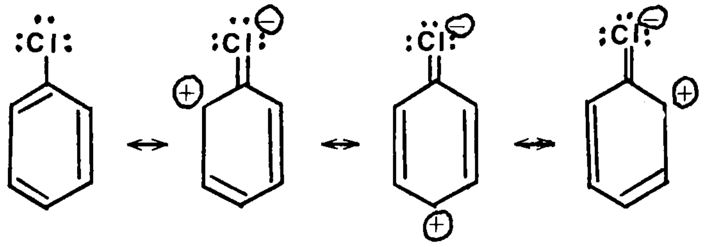


Figure 12. Resonance structures of chlorobenzene.

Toluene was adsorbed less than benzene but more than chlorobenzene. The presence of the methyl group on the aromatic ring produces a permanent dipole which is not as strong as the permanent dipole produced from the presence of the chlorine atom on the aromatic ring. The methyl group becomes partially positive and the aromatic ring becomes partially negative.

Benzene is an aromatic compound in which all the constituents on the aromatic ring are the same. This results in no permanent dipole produced from a nonuniform distribution of the bonding electrons. The lack of a permanent dipole would cause a greater attraction to a hydrophobic surface because of lower solubility of water. Greater adsorption would result.

The order of increasing permanent dipole was:

Chlorobenzene > Toluene > Benzene

The results obtained in this study match the results that should theoretically be found.

Effects of Clay Dosage on Adsorption

There were some discrepancies in the amount of adsorption occurring between different amounts of clay present. In most cases, as the amount of clay increased, the amount of adsorption also increased, but not in a linear or logarithmic manner. (See Figures 9, 10, 11.) It would be theoretically expected that as the amount of clay increased, the amount of adsorption occurring would increase in some mathematically measurable amount. As the amount of clay increases, the surface area of the clay floc would increase. An increase in the surface area of floc would result in a larger hydrophobic surface for adsorption to occur. The increase in adsorption was not found to be proportional to the increase in clay concentration. Figures 9, 10, and 11 illustrate this. Samples containing 200 mg/l clay do not adsorb four times as much as samples containing 50 mg/l clay. There are several possible explanations for this. Three explanations are in reference to the experimental error in the tests run. These are:

1. Varying clay concentrations;
2. Varying CEC between clay samples;
3. Varying amounts of cationic surfactant.

The fourth reason is the most likely reason for the effects mentioned. In the adsorption process, the attraction or driving force for adsorption to the clay surface is not sufficiently greater than the attraction between the water molecules and organic molecules in solution. This inadequate driving force limits the effectiveness of the process.

The experimental errors previously mentioned all effect the resultant hydrophobicity of the clay floc. As the clay concentrations in solution and the CEC of the clays vary, the addition of the surfactant fails to reach the same point of floc stability in a repeatable manner. The stability of the floc determines the hydrophobicity of the surface and the amount of adsorption that will occur. These changes in the floc stability would result in variations in the amount of measurable adsorption that can be seen.

The limiting mechanism in the overall process seems to be the inadequate driving force behind the adsorption process. Hydrophobic bonding is a vague term defined only as the mutual attraction between hydrophobic groups of the adsorbate and the adsorbent (Rosen, 1978). This attraction is partially caused by van der Waals forces, but other interactions occur which are less well defined (Ben-Naim, 1980). The adsorption of the cationic surfactants onto the clay produces a hydrophobic surface. This resultant hydrophobicity acts as an adsorbent for the organic molecules in the aqueous phase.

The organic molecules also interact with the aqueous phase. This interaction involves hydrogen bonding and dipole-dipole interaction.

The driving force for adsorption, which is the hydrophobic interaction between the clay floc and the organic molecules, is not significantly greater than the attraction of the organic molecules to remain in the aqueous phase. As a result, the adsorption process is limited in its effectiveness.

Removal Effects of DAF Process

In the flotation study, adsorption of the compounds onto the clay floc lasted for 10 minutes. After this period, the water saturated with air in the DAF unit was added to the sample. After 5 minutes, sufficient bubble-particle interaction had occurred to float the clay. In the total treatment process, 3 samples were taken for each run. The first sample indicated the initial concentration C_o. The sample taken after the 10 minute adsorption period was felt to indicate adsorption only and was given the nomenclature C_{ads}. The sample taken after the 5 minute interaction between the clay and the water from the DAF unit indicated the concentration remaining after both adsorption and volatilization had occurred and was given the nomenclature C_{daf}. A mass balance relationship illustrates the removal efficiency for adsorption and volatilization. This can be seen in the following equation.

$$(1)\ \Delta C = C_o - C_{daf}$$

where ΔC = total change in concentration.

(2) $\Delta C_{vol} = C_{ads} - C_{daf}$

where ΔC_{vol} = Concentration lost through volatilization.

(3) $\Delta C_{ads} = C_o - C_{ads}$

where ΔC_{ads} = amount removed by adsorption.

In Figures 13, 14, 15, the effectiveness of each individual clay on removing the organic compounds by both adsorption and volatilization can be seen. Comparisons can be seen in each graph of the two compounds for each clay. Figures 16 and 17 compare the effectiveness of removal by both volatilization and adsorption of all three clays on each compound.

For all the sample wastes, it was found that the residual organic concentration level was the same for each clay regardless of the initial clay concentration. While the residual concentration was not the same between different clays and the different compounds, each individual clay-organic waste reached the same concentration after flotation. This indicates that the concentration of clay has little effect on the volatilization process. More specifically, the bubble-particle interaction is not a reducing factor for volatilization. Figures 13, 14, and 15, illustrate the residual concentration effect.

The two compounds used in the study, toluene and benzene, were compared in the amount volatilized by the DAF process. Analysis of the Figures 13, 14, and 15 indicates that benzene was volatilized to

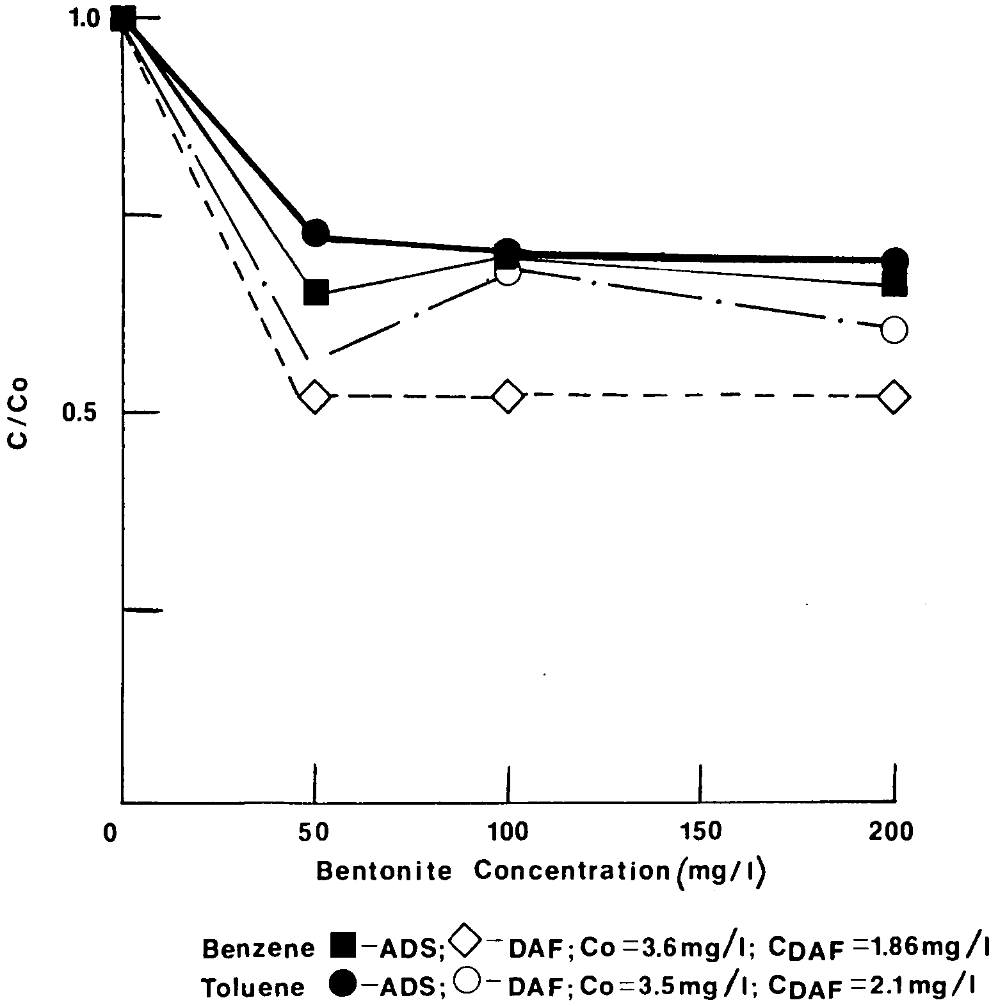


Figure 13. Comparison of the amount of adsorption and volatilization of benzene and toluene occurring in solutions containing bentonite.

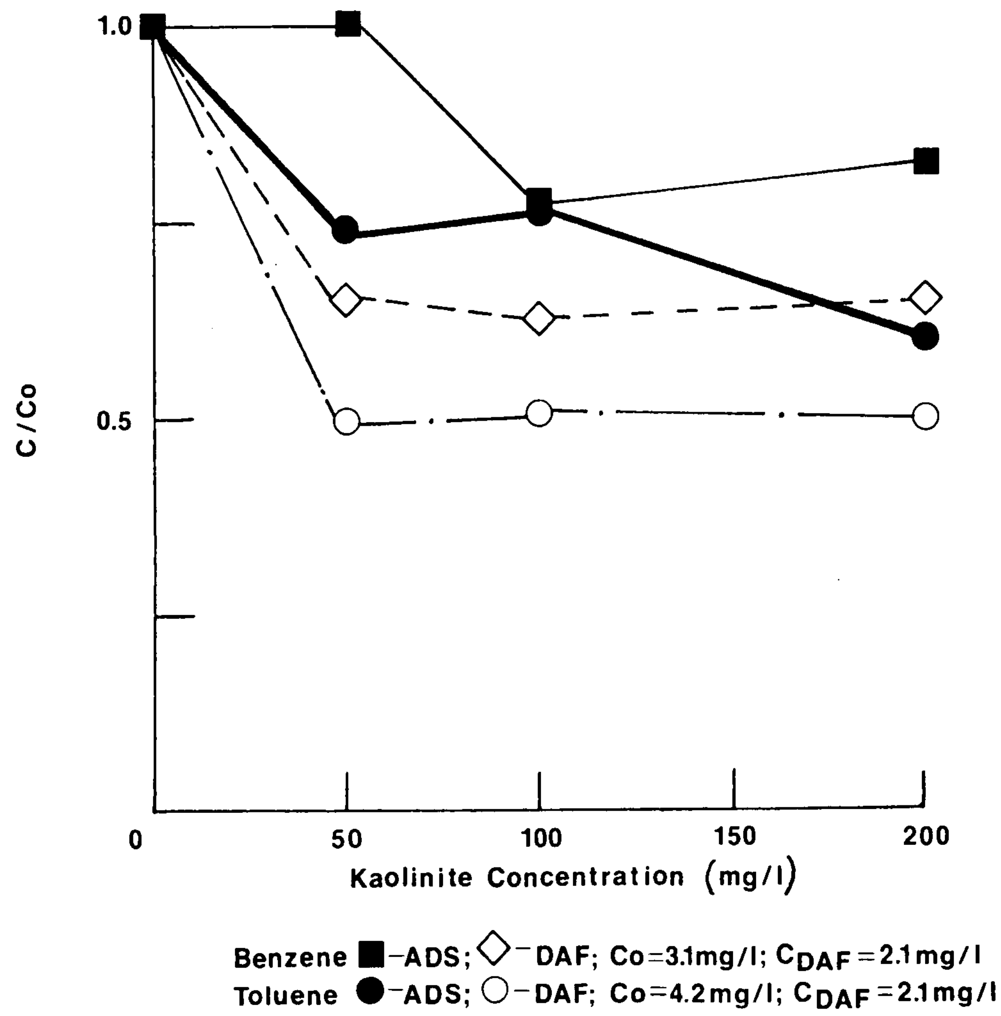


Figure 14. Comparison of the amount of adsorption and volatilization of benzene and toluene occurring in solutions containing kaolinite.

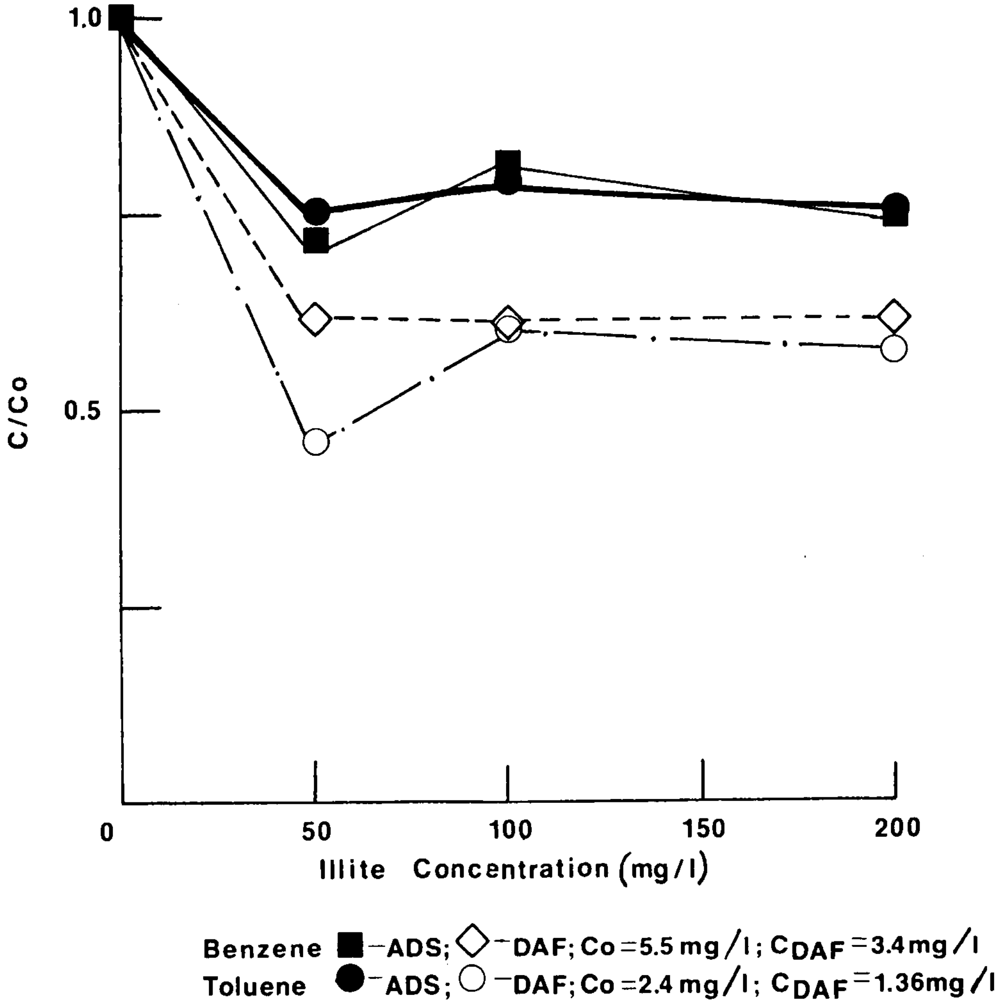


Figure 15. Comparison of the amount of adsorption and volatilization of benzene and toluene occurring in solutions containing illite.

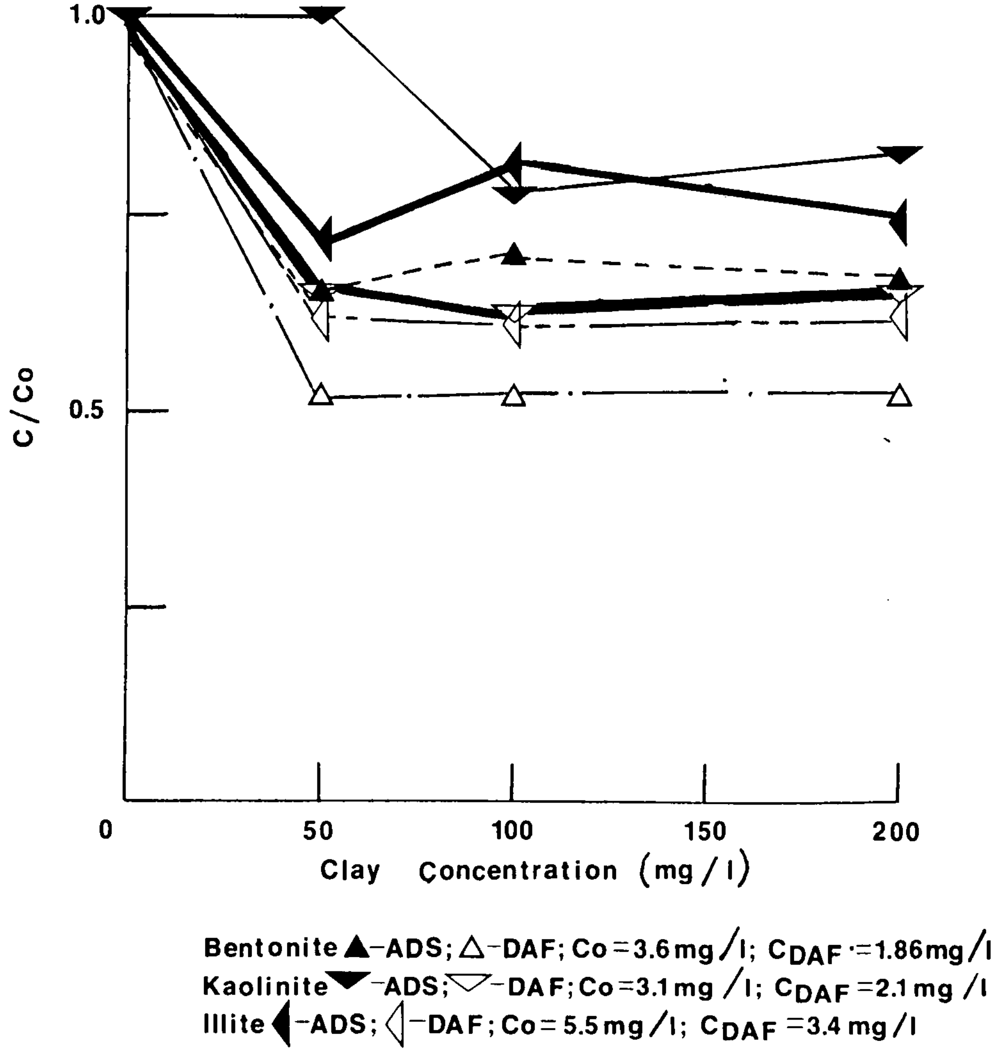


Figure 16. Comparison of the amount of adsorption and volatilization occurring between the three clays in solution containing benzene.

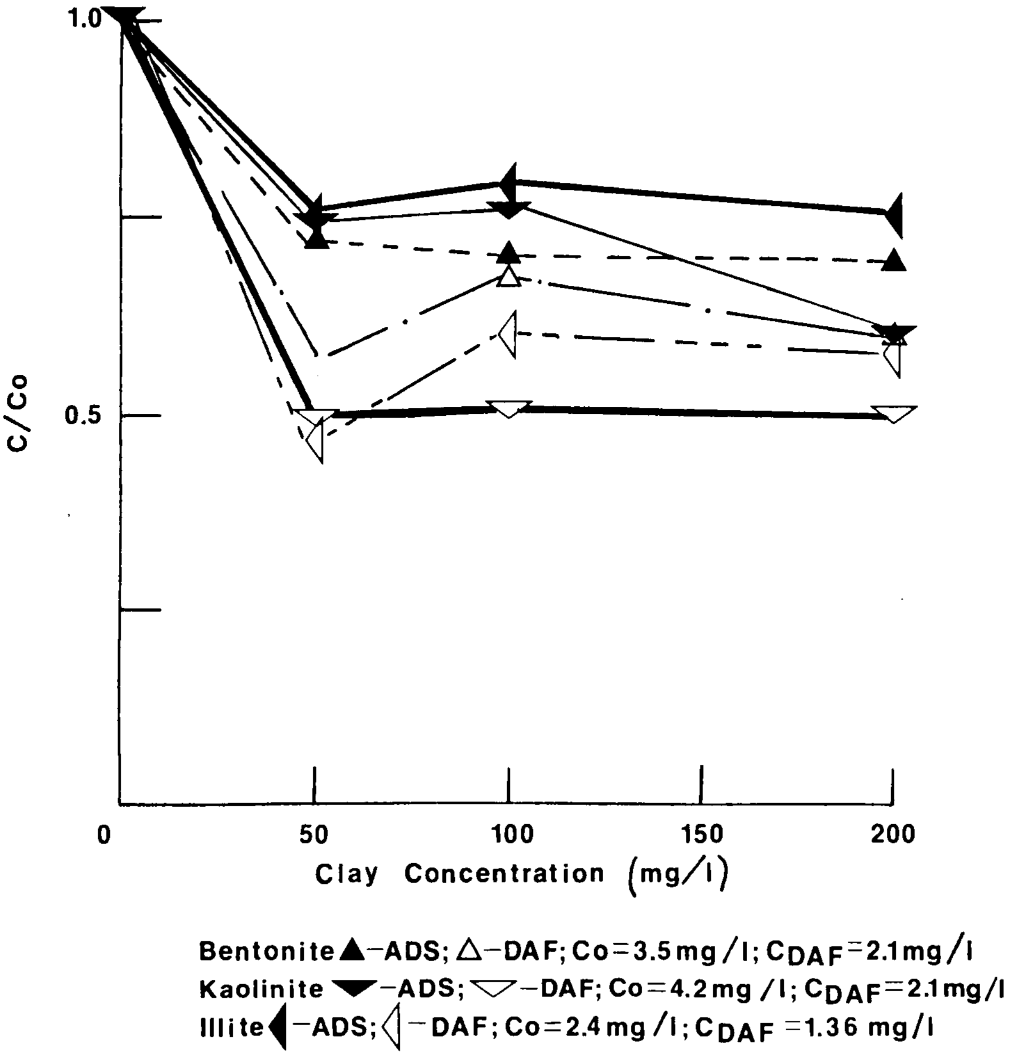


Figure 17. Comparison of the amount of adsorption and volatilization occurring between the three clays in solutions containing toluene.

a greater extent than toluene in the bentonite solution, but in the kaolinite and illite solutions, the volatilization of both compounds was approximately the same.

Figures 16 and 17 illustrate the comparative removal efficiencies of the three clays. In Figure 16 for the benzene solutions, the following overall removal efficiency was found:

Bentonite > Illite > Kaolinite.

In Figure 17 for the solution containing toluene, the overall removal efficiency followed this pattern:

Kaolinite > Illite > Bentonite.

The effect of the adsorption process resulted in what was expected to the benzene solution:

Bentonite > Illite > Kaolinite.

Figure 17 shows the effect of adsorption in the following sequence:

Bentonite > Kaolinite > Illite

These results tend to follow those found in the adsorption study described earlier if it is remembered that adsorption took place for only 10 minutes.

In a comparison of the two mechanisms of removal, volatilization and adsorption, it can be seen in Figures 13, 14, and 15 that adsorption is the major removal mechanism. In all cases for both change in clay type or change in organic compound, adsorption occurred to a greater extent than volatilization. This indicates that desorption does not occur from the DAF process. In other words, the bubble-particle interaction is not destructive to the interaction between the hydrophobic surface of the clay and the organic compound.

Summary

The results of the study indicate that the following parameters are important for adsorption:

1. Type and amount of clay;
2. Time of interaction between clay floc and compounds;
3. Type of compounds present.

It was found that bentonite adsorbed the best for all the compounds. Maximum adsorption seemed to take place in the first 30 minutes. After that adsorption leveled off or desorption occurred. The degree of adsorption was greatly influenced by the type of organic compound present.

In the flotation study, the following parameters were found or considered to be important:

1. Effective flotation of the flocculated clay;
2. Volatilization of the compound in solution;
3. DAF recycle capabilities.

The bentonite floc was best removed by flotation. Although no turbidity data was taken, visual observation indicated this to be true. Volatilization did produce identical residual levels regardless of the clay concentration, but it was felt that volatilization of potentially harmful compounds is not an adequate treatment method.

The design of a system which could utilize this process would include a chemical mixing tank with a rapid mix unit, a DAF unit with recycle capacity, and a reaction tank with a skimmer. Treatment of the incoming waste would include chemical addition and mixing, addition of air and subsequent pressurization, release of the pressure, flotation, skimming for float removal, and recycling of effluent. Parameters important for operation would include amount of clay necessary for sufficient surface area, concentration of surfactant necessary for flocculation, air injection and pressure requirements, and recycle rate. The organic compounds would be removed through both adsorption and volatilization mechanisms. In the case of application of this process to an industrial waste containing high concentrations of potentially toxic and/or carcinogenic compounds, adequate care would be required to minimize ambient air concentrations resulting from volatilization.

From the study it is indicated that the type and concentration of clay used as an adsorptive media affects the removal of compounds from the waste stream. The flotation process gave best removal of the floc when bentonite was the clay used. Bentonite also adsorbed the compounds to the greatest extent. The type of organic compounds present in solution and their time of interaction with the clay floc affects the amount of adsorption that occurs.

Operation of the system would require a characterization of the waste if an industrial process was being treated. This characterization of the waste would include the type of organic compounds present and their respective concentrations, if possible. From this information, an idea of whether adsorption would readily occur and what ranges of clay concentrations would be required for adsorption to occur could be estimated. Adjustment of the recycle rate would offer control over the final effluent quality.

This process could be applied to industrial waste streams as well as water treatment plant influents. Water treatment plant influents have been found to contain a high number of organic compounds, some at levels of 1 $^{mg}/l$ (Keith, 1976). Conventional treatment has little effect on the removal of these compounds and they remain in the finished water. In regions of the country where clay is a major constituent of the soil, these influent waters would also contain relatively high concentrations of naturally occurring clays in suspension. Depending on the type and concentration of clay in the water as well as the concentration of the compounds in solution, removal of the natural turbidity resulting from the clay by addition and flocculation of the surfactants might also offer enough adsorptive capacity to effectively remove many of the compounds present. In regions where clayey soils do not prevail, clay suspensions could be added to the influent stream and subsequently removed by the flocculation and flotation process.

Industrial wastestreams containing low concentrations of organic compounds could be treated by this method. Many industrial processes utilize organic compounds in the production of their products. These wastestreams may contain levels of organic compounds too high to allow discharge into municipal treatment plants or surface waters. This process with its adsorption capacity might adequately remove the compounds present to within acceptable discharge limits. However, this process would be waste specific and each industry would require treatability studies.

CHAPTER V

CONCLUSIONS AND RECOMMENDATIONS

Conclusions

1. The SA and the CEC of clays have an effect on the amount of adsorption that occurs when a surfactant is added to the clay suspension. As the SA and CEC increase, the amount of adsorption increases. In this study this could be seen in comparing the three clays. The order of decreasing adsorption, SA, and CEC was:

Bentonite > Illite > Kaolinite

2. The chain length of the cationic surfactant has little effect on the amount of adsorption that occurs between the clay surface and the organic molecule.

3. Time plays an important part in the adsorption process. It was found that maximum adsorption occurred after 30 minutes. After that time adsorption leveled off.

4. The strength of the permanent dipole moment in the molecule affected the adsorption process. As the permanent dipole moment increased, the amount of adsorption decreased. The order of decreasing adsorption was:

Benzene > Toluene > Chlorobenzene

5. While adsorption did occur, an increase in amount of clay added did not increase the adsorption in a linear or logarithmic manner.

The attraction between the organic compounds and the clay from hydrogen bonding and dipole-dipole interaction is not sufficiently greater than the attraction between the organic compound and the water molecules. Adsorption to low concentration would not result from this process.

7. In the volatilization process, a constant residual organic concentration was reached for all clay concentrations. There was a minimum level that the volatilization would reach.

8. Adsorption was a greater removal mechanism than the volatilization process.

Recommendations

The study indicates that adsorption does occur to an appreciable extent for certain compounds. Because of the concern in the environmental engineering field over the effective removal of nonpolar organic compounds, the following recommendations can be made:

1. Surface waters containing natural clay concentrations should be used to determine the amount of adsorption occurring when in the presence of humic acids and other substances in water.

2. Additional compounds should be studied which are found in natural waters after being discharged from industrial sources. These compounds should be considered alone and in competition with one another.

3. Selected industrial wastestreams should be treated by this process to determine its effectiveness.

4. A more indepth study should be done in comparing the energies of the hydrophobic interactions between the clay and the organic

molecules and the attraction for the organic molecules to remain in the aqueous phase.

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APPENDIX

TABLE 3

ADSORPTION DATA FOR BENZENE ONTO BENTONITE, KAOLINITE, AND ILLITE

Clay type and Concentration (mg/l)	Residual Concentration ($^{mg}/l$) at Time t (min.)				
	0	5	15	30	60
Bentonite					
50	2.1	1.6	1.6	1.74	0.63
100	2.0	1.44	1.04	0.72	0.5
200	1.8	0.8	0.65	0.4	0.4
Kaolinite					
50	0.94	0.8	0.8	0.66	0.74
100	0.87	0.85	0.8	0.66	0.6
200	0.77	0.74	0.74	0.4	0.5
Illite					
50	2.2	1.9	1.6	1.32	1.32
100	2.1	1.6	1.6	1.1	1.5
200	2.0	1.4	1.3	1.0	1.3

TABLE 4

ADSORPTION DATA FOR TOLUENE ONTO BENTONITE, KAOLINITE, AND ILLITE

Clay type and Concentration (mg/l)	Residual Concentration ($^{mg}/l$) at Time t (min.)				
	0	5	15	30	60
Bentonite	4.2	3.6	3.4	3.1	2.7
50	4.1	3.6	3.2	2.7	3.0
100	3.7	2.9	2.6	2.4	2.0
200					
Kaolinite	3.2	3.2	--	2.7	2.9
50	2.4	2.4	--	2.0	2.0
100	2.0	2,0	--	1.7	1.8
200					
Illite	4.1	3.8	3.6	3.4	3.0
50	3.9	3.3	3.3	3.2	3.0
100	3.4	2.7	2.7	2.45	2.4
200					

TABLE 5

ADSORPTION DATA FOR CHLOROBENZENE ONTO BENTONITE, KAOLINITE, AND ILLITE

Clay type and Concentration (mg/l)	Residual Concentration ($^{mg}/l$) at Time t (min.)				
	0	5	15	30	60
Bentonite					
50	3.7	3.5	3.2	3.1	3.2
100	3.5	3.4	2.6	2.5	3.0
200	3.0	--	2.7	2.6	2.5
Kaolinite					
50	3.5	3.2	3.5	3.5	3.0
100	3.3	3.2	3.2	3.0	3.0
200	3.2	3.1	2.5	2.8	2.2
Illite					
50	3.5	3.5	3.5	3.5	3.5
100	3.5	3.5	3.5	3.5	3.5
200	3.2	3.1	2.9	3.0	2.9

TABLE 6

ADSORPTION AND VOLATILIZATION DATA FOR BENZENE USING KAOLINITE, ILLITE, AND BENTONITE

Clay type and Concentration (mg/l)	Initial Concentration (mg/l)	Concentration After Adsorption (mg/l)	Concentration After Volatilization (mg/l)
Bentonite			
50	4.3	2.8	2.2
100	4.1	2.8	2.1
200	3.6	2.4	1.9
Kaolinite			
50	3.7	3.7	2.4
100	3.5	2.7	2.24
200	3.1	2.6	2.1
Illite			
50	6.3	4.5	3.9
100	6.2	5.0	3.8
200	5.5	4.1	3.4

TABLE 7

ADSORPTION AND VOLATILIZATION DATA FOR TOLUENE USING KAOLINITE, ILLITE, AND BENTONITE

Clay type and Concentration (mg/l)	Initial Concentration (mg/l)	Concentration After Adsorption (mg/l)	Concentration After Volatilization (mg/l)
Bentonite			
50	4.1	3.0	--*
100	3.9	2.7	2.6
200	3.5	2.4	2.1
Kaolinite			
50	4.9	3.6	2.4
100	4.7	3.6	2.4
200	4.2	2.4	2.1
Illite			
50	2.35	2.2	1.3
100	2.7	2.1	1.6
200	2.4	1.8	1.4

*Experimental error.

VITA

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