TREATMENT OF WATER SUPPLIES CONTAMINATED WITH TOXIC POLLUTANTS

USING TAILORED SOILS

by

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ABSTRACT

Natural clays have a large internal surface area that is potentially available for adsorption of hazardous organic compounds. The exchangeable cations in clays occupy the interlamellar spaces that separate the clay platelets. Water molecules form a hydrated shell around the exchangeable cations due to the hydrophilic nature of these ions. The presence of such water molecules hinders adsorption of hydrophobic organic pollutants. Therefore, the interlamellar area in clays is normally inaccessible to organic pollutants.

The natural cation in the clay may be exchanged with tetraalkylammonium (TAA^+) ions. These quaternary amines are rigid tetrahedrons capable of displacing the natural exchangeable cations and associated interlamellar water. Clays tailored by this process have a predictable basal spacing, which is a function of the TAA^+ molecule size. According to Theng et al. (1967), basal spacing in moist conditions vary from 13.8 A for tertamethylammonium (TMA^+) to 16.5 A for tetra-n-butyl ammonium). The interlamellar space created by TAA^+ treated clays favors the selective removal of low molecular weight organic pollutants, which due to their steric properties can conform to the interlamellar space of the tailored clay. Other larger organic pollutants are prevented access into the clay by this selective straining mechanism.

Restoration of aquifers affected by petrochemicals may be accomplished by flushing the aquifer through natural soils that have been previously tailored with TAA^+ molecules. The modified soils can be selectively tailored to preferentially adsorb targeted hazardous substances, while allowing innocuous materials to pass unaltered through the treated layers of soil (or be retained in underlying soil strata). This innovative process for the removal of BTX (benzene, toluene and xylenes) from ground waters contaminated by gasoline and other petrochemical spills is expected to be both economically and technically feasible.

The adsorptive properties of TAA^+ tailored soils for the selective removal of hazardous organic pollutants found in waters contaminated by petrochemical spills was investigated. Effectiveness of the tailoring agents was evaluated by comparing adsorption isotherms of BTX on treated and untreated soils. Column studies were performed to estimate kinetic properties of the tailored and untailored natural soils. Modelling of pollutant transport in the column studies was used to obtain engineering design parameters.

KEYWORDS: Adsorption, Hazardous Materials, Organic Compounds, Clays, Pollutants, Ground Water Pollution.

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JUSTIFICATION OF WORK PERFORMED

Reported pollution cases involving hazardous waste spills have become quite numerous in recent years. The tally of communities and private water users affected by this problem is increasing at an accelerating rate. This rapid growth in‑reported pollution cases is attributed to mismanagement of a large number of chemicals generated by the chemical industry, that have been improperly released into the environment. Also, more environmental awareness and improved chemical detection techniques have brought to light cases that would otherwise have gone unreported.

Ground water contamination by private and governmental facilities is common throughout the United States. The problem of ground water pollution by leaking underground storage tanks became evident in the 1970's (Mates 1971; Williams and Wilder 1971; McKee, Laverty, and Hertel 1972). Thus, the solubilization of benzene from petrochemical products is of particular concern due to its carcinogenic, teratogenic, and leukemogenic properties (Laskin and Goldstein 1977). Consequently, the drinking wate𝗂 standard for this particular chemical is much lower than for other organics (1 ug/l). Gasoline contains approximately 3% benzene and 9 - 11 % toluene. Xylenes in gasoline may add up to 10 to 12% (Jercinovic 1984). Benzene has been selected by the New Mexico Health and Environment Department as an indicator for petroleum-byproduct contamination of water supplies due to its

high toxicity, high solubility (1,780 mg/l at 25°C) and its ubiquitousness in gasoline and other petrochemicals.

The State of New Mexico alone reported 261 cases of refined petroleum-product contamination between 1972 and 1984. Since the majority of pollution cases by petroleum derivatives remains unreported, this figure represents a small fraction of actual pollution incidents (Jercinovic 1984). Twenty-six of these cases occurred in Bernalillo County alone (Jercinovic 1982).

The New Mexico Environmental Improvement Division (NMEID) estimates that the total volumes of gasoline and diesel fuel involved in 148 out of the 261 reported cases were 750,000 and 800,000 gallons respectively (Jercinovic 1984). Recently discovered cases include pollution of ground water supplies by petroleum derivatives at Ballard Wells (near Carlsbad), Carlsbad Caverns Visitor Center, Flora Vista, Monument, and Ruidoso, New Mexico[*]. Ground water contamination by the energy industries is not limited to the State of New Mexico (Jercinovic 1984). For instance, extensive contamination of the Ogallala and Vamoosa-Ada aquifers has been attributed to the oil and gas industry (Bingham 1986; US Water News 1984).

Underground storage tank spills represent a serious threat to ground waters. Compounds such as benzene, toluene and xylenes (the BTX group) are contaminants of particular interest due to their relatively high solubility and carcinogenicity.

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[*] Simpson O., Telephone conversation, New Mexico Environmental Improvement Division, Santa Fe, New Mexico, December 27, 1984.

The State of New Mexico is particularly vulnerable to contamination by leaky underground storage tanks because over 95% of the population depends on ground water supplies (McQuillan 1984). The problem is compounded in urban areas where fuel storage tanks are in close proximity to underground drinking water supplies.

The U.S. House of Representatives Proposal on Groundwater Protection emphasizes that "groundwater destruction will be one of the most serious environmental problems of the 1980's" and recommends swift control of contamination sources (House Report 98-1136 1984)). The Ground-Water Protection Strategy identifies leaky underground storage tanks and chemical oil and brine spills among the major ground water problems in the United States, and points out that among the main contaminants of concern in this category are benzene and toluene (Ground-Water Protection Strategy 1984). A reasonable perspective of the problem is quoted from a recent scientific publication: "EPA estimates that 3 to 5 million underground tanks in the U. S. contain petroleum or hazardous substances and that thousands of them may be leaking, with more expected to leak within the next five years" (Environmental Engineering News 1986).

A recent U.S. Environmental Protection Agency (EPA) survey showed that 35% of the existing underground storage tanks in the U.S. leak or are not liquid tight (Underground Storage Tanks Receiving Closer Scrutiny 1987). Present estimates of leaky gasoline storage tanks vary between 75,000 and 100,000. This number is expected to increase by 350,000 over the next decade

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(Manko 1985). The environmental impact of these leaky
petrochemical products on ground water is also expected to
increase in the same proportion.

The latest EPA Status Report on the Ground-Water Protection
Strategy continues to accentuate the need to solve the problem of
ground water contamination by leaky underground storage tanks
(Status Report on the Implementation of EPA's Ground-Water
Protection Strategy 1987).

The treatment technique proposed herein represents a new
approach to mitigate the complex, and widely distributed problem
of ground water contamination by petrochemical spills. The scope
of this project concentrates on the removal of toxic compounds
typically found in gasoline and other petrochemical spills, even
though the methodology selected has potential application for the
removal of a wide variety of wastes. Thus, practically every
site plagued by contamination with hazardous organic compounds
may benefit from the results obtained in this investigation. In
the following sections of this report, conventional treatment
techniques are compared with selective adsorption processes to
place in perspective the usefulness of this innovative process.

BACKGROUND

Commonly, hazardous wastes travel vertically through the unsaturated (i.e. vadose) zone until they are deflected by impermeable strata or by an aquifer. Several mechanisms retard and/or remove hazardous compounds in the vadose zone. Biodegradation, adsorption, and volatilization are three main mechanisms that mitigate the impact of hazardous wastes on the quality of ground water supplies (Jury, Spencer, and Farmer 1983). Insoluble and other large molecular weight organics are more readily adsorbed onto the soil particles in the vadose zone, where biodegradation and volatilization may reduce their impact upon underlying ground waters.

Low molecular weight compounds, on the other hand, tend to be relatively more soluble and move more freely through the vadose zone. Compounds such as single ring aromatics are of particular interest due to their high water miscibility, and their relative abundance in gasoline and petroleum derivatives. The BTX group (benzene, toluene, xylene) is detected in most instances where ground water contamination by petroleum by-products has occurred. This aromatic family has been linked with cancer and other adverse effects, and represents a major concern to environmental agencies (Jercinovic 1984).

Conventional treatment techniques are often technically inadequate (or economically unfeasible) to eliminate hazardous wastes present in ground water supplies. Contamination of ground water supplies by gasoline spills and other petroleum derivatives

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has reached alarming proportions. The problem is compounded due to the large number of small gasoline storage tanks. Even in cases when pollution liability is established, the probability of executing remedial action is remote, as the financial burden on the gas station owner is overwhelming. Frequently, communities affected by such problems are forced to request federal cleanup funds (Superfund), or more likely to abandon the water source.

The solution to contamination of ground water supplies by petroleum derivatives is not simple. The most common techniques used to remove hazardous petroleum derivatives from ground water supplies are based on three basic processes: adsorption onto a solid phase, chemical oxidation, and volatilization by air stripping (Symons 1981). These techniques to remove toxic organic compounds have both advantages and disadvantages.

Air stripping, although simple, has limited applicability for removal through volatilization since large volumes of air are required (Symons 1981) and only highly volatile solutes may be removed by this technique (Kavanaugh and Trusell 1980). Air stripping is an energy intensive process limited to the removal of volatile organic compounds (VOC) from a liquid phase. Thus, non-volatile compounds and most heavy metals are not significantly affected by this technique. Pollutants removed by this process are released into the atmosphere, unless VOC adsorbers are installed.

Chemical oxidation of trace concentrations of toxic compounds is typically difficult due to the refractory nature of large numbers of contaminants. For example, removal of trihalomethanes

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(THM) is not feasible, since oxidation reactions with THM occur only when ultraviolet light is used in combination with strong oxidizing agents such as ozone (Symons 1981).

Various types of adsorbents have been experimentally tested for removal of organic compounds at trace concentrations from water. These adsorbents typically include granular and powdered activated carbon (Proceedings of the Specialized Conference on the use of Activated Carbon 1979; Proceedings EPA/NATO/CCMS Conf. on Adsorption Techniques 1979; Activated Carbon Adsorption of Organics From the Aqueous Phase 1980), synthetic carbonaceous adsorbents (Neely 1980) and ion exchange resins (Oehme and Martinola 1973; Gauntlett 1975; Evans and Mallman 1979). Due to current economic and efficiency factors, activated carbon has been the most commonly used adsorbent for the treatment of contaminated water supplies. Moreover, use of activated carbon can be expensive, but it is generally more economical than synthetic resins.

A crucial need exists to develop alternative treatment procedures for the removal of dissolved organics that are both efficient and economical. This study addresses such need by applying novel experimental technologies developed and tested at New Mexico State University (NMSU) through an ongoing National Science Foundation (NSF) grant. Such technologies have demonstrated the technical feasibility to remove selectively hazardous wastes at the laboratory level using tailored clays. The goal of this project is to apply these novel technologies to the removal of the BTX group, which is commonly found in ground

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waters contaminated by fuel hydrocarbons and other petroleum derivatives. This project is particularly relevant to facilities that experience ground water contamination by organic compounds. However, potentially any site affected by hazardous waste contamination could benefit from the results of this study.

An application of tailored clays for the removal of ground water contaminants would consist of applying the water source over a field of tailored soil. Water treated by this adsorption process infiltrates back into the original unconfined aquifer. Thus, treatment of the contaminated water, in combination with aquifer recharge from process effluent, may be used to restore the aquifer back to acceptable environmental conditions. Exposure of the spent tailored soil to the atmosphere, aided by natural solar radiation and biodegradation, may be used to regenerate the spent material in the field (by volatilization of adsorbed VOC). The goal of the present study was to investigate the technical feasibility of using typical tailored soils for the removal of BTX found in ground waters contaminated by petrochemical wastes. Regeneration by this process may result in some air pollution problem. However, such problem would be mitigated by biodegradation in the soil and by dispersion of the source over a large application area.

ADSORPTIVE NATURE OF NATURAL AND TAILORED CLAYS

The large surfaces found in most natural clays account for
the excellent capacity of these minerals to adsorb certain types
of pollutants. For example, the smectite group, which includes
montmorillonite and bentonite clays, has a good potential to
adsorb certain hazardous organic compounds. However, neutral or
uncharged compounds with molecular weights near or below 150
g/mole are poorly retained through liquid-solid adsorption on
clays.

Smectites are naturally occurring clays with effective sizes
below 2 um. A simplified representation of a common smectite
mineral is shown in figure 1. The large surface area of up to
800 m^2/g in smectites accounts for their excellent adsorptive
capacity. Molecular adsorption on smectites may involve chemical
as well as physical effects. Even neutral molecules, such as
hydrocarbons, have been reported to exhibit weak interactions
with the net negative charge of smectites and the positive charge
of associated cations. However, these interactions are much
weaker than ion-ion or ion-dipole interactions found in certain
priority pollutants such as phenols and aromatic amines. The
total external surface area of smectites is generally larger than
that of other soil minerals due to their small particle size
(Minerals in Soil Environments 1977). The rate of adsorption in
porous materials is usually limited by diffusion through pores
(Weber 1972).

CLAY PLATELET
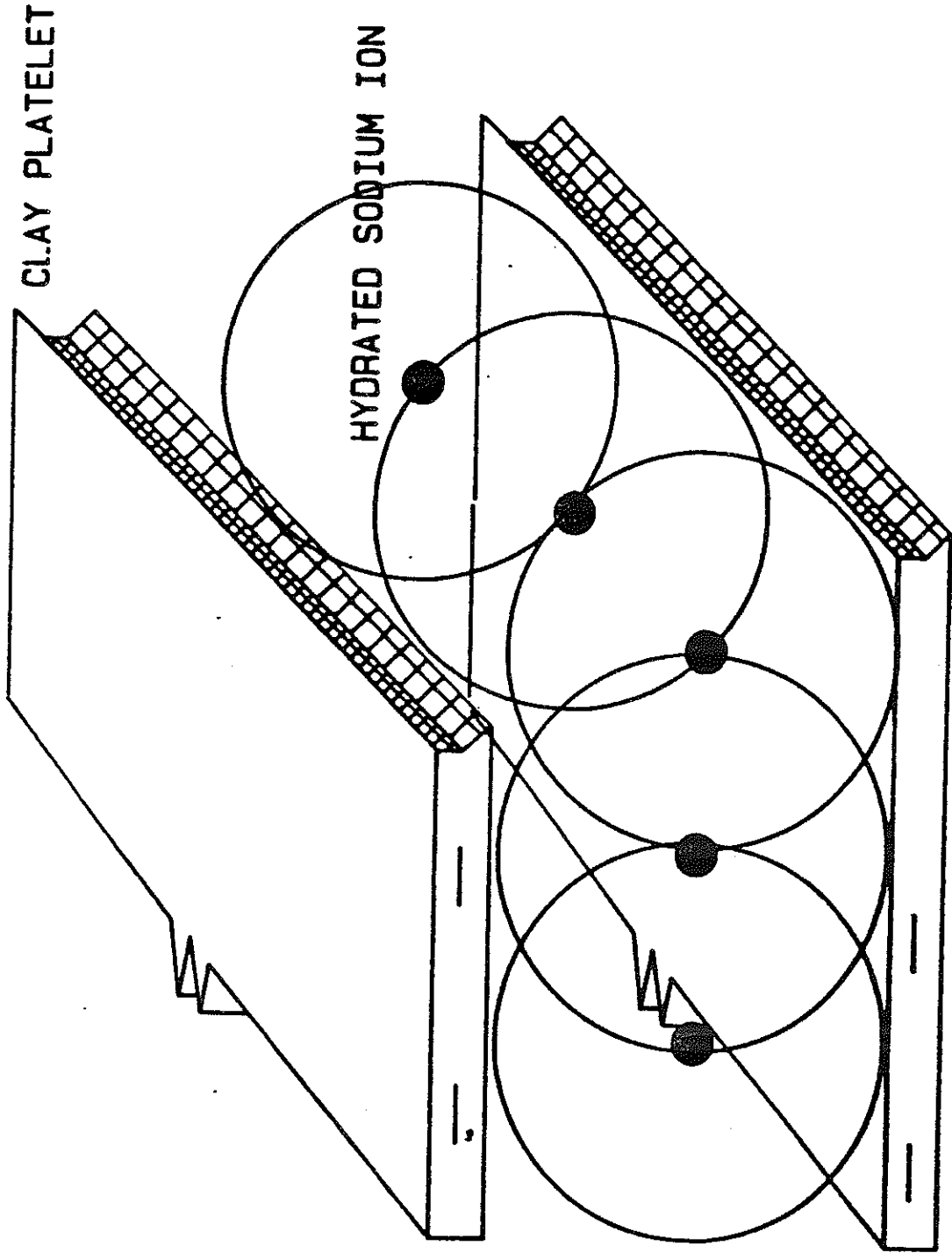
HYDRATED SODIUM ION

Figure 1. Natural Clay in Sodium Form.

Thus, the small size and large surface available on smectites should be associated with a fast and efficient adsorption process.

Organic compounds with molecular weights below 150 g/mole are weakly adsorbed or not adsorbed by pure smectites, unless they carry a charge and can enter into ion-exchange reactions. The interaction forces under these conditions are the same in magnitude as hydration forces, so that competition reactions with water molecules for the surface dominate (De Boer 1953). Although a certain amount of anion exchange may occur on the edges of smectite, most exchange adsorption will be cationic, with positively charged organic molecules displacing inorganic cations (Minerals in Soil Environments 1977). Thus, negatively charged compounds are not readily adsorbed on the negative charges of smectite (De Boer 1953). However, soluble compounds with molecular weights above 150 g/mole, whether or not charged, are strongly adsorbed by smectites (Greenland 1965).

The ability of clays to adsorb small organic compounds (molecular weight below 150 g/mole) is dependent upon the electrostatic interaction between the negative charge of the clays and the valence and polarity of the organic molecule. Thus, adsorption of organic molecules is less significant for neutral molecules and non-existent for negative compounds. However, significant adsorption of negatively charged organic compounds can occur through a polyvalent exchangeable cation (Greenland 1965) such as Cu^{++}, Ca^{++} or Mg^{++}. The exchange of Na^+ for a multivalent cation in the interlamellar spaces of smectites

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improves considerably the adsorptive capacity of smectites for organic anions. It is likely that the multivalent cation acts as a bridge between the negatively charged molecule and clay (Weiss 1959). Therefore, adsorption by pure smectites is feasible for large molecules (which include a substantial number of key related pollutants such as polycylic aromatic hydrocarbons), but unworkable for smaller molecules (such as BTX) except those with a polar or charge moiety (e.g., phenol, aniline).

Thus, clays may be modified using an adsorbed or charge-exchanged organophilic (i.e., organic-liking) coating to yield materials that strongly adsorb molecules such as benzene and chlorinated hydrocarbons. Different coatings generate significantly varied adsorption characteristics, such that a family of adsorbent clays might be tailored to fit the steric properties of a particular pollutant. Recent studies also show that smectites may be modified using organophilic cations in order to yield materials that strongly adsorb low molecular weight molecules (Cadena and Jeffers 1987, Cadena [in press]).

The work by McBride et al. (1977), and Wolfe, Demirel T. and Baumann (1985,1986), shed light on the nature of smectites tailored with organic cations. These researchers agree that preparation of effective clay adsorbents requires careful selection of the cationic tailoring agent. Optimum dose of coating material, and selectivity of tailored clay and kinetic rates have been experimentally determined in our laboratories for bentonitic clays (Cadena [in press]; Cadena and Jeffers 1987; Jeffers 1985). Different coatings generate significantly varied

adsorption constants, such that a family of adsorbent materials might be tailored to fit the steric properties of a particular pollutant. Technologically, this process is particularly attractive since clays are inexpensive, ubiquitous, and an entire family of adsorbents might be prepared from a single substrate.

Quaternary ammonium cations have been successfully used to improve the adsorptive capacity of clays. For instance, tetramethylammonium cations (TMA$^+$), which are small rigid tetrahedrons, occupy minimal interlamellar space in the clay. McBride et al. (1977), demonstrated that adsorption of single-ring aromatic hydrocarbons onto TMA$^+$ exchanged smectites greatly favored adsorption of small planar molecules (such as phenol and benzene) but not by larger chlorinated benzenes. However, the use of an organic coating of the larger hexadecyltrimethyl-ammonium cations (HDTMA$^+$) on the same smectite reduced considerably the solution concentrations of o-dichlorobenzene and 1,2,4-trichlorobenzene. Their results suggest that the chlorinated benzene molecules are too large to enter into the interlamellar regions of the TMA$^+$ smectite, and that adsorption may only occur because of the additional swelling of the clay provided by the HDTMA$^+$. Therefore, tailoring may be designed to accommodate the steric nature of a given pollutant, while eliminating the adsorption of larger, non-targeted compounds.

On the other hand, high molecular weight quaternary amines, which contained straight-chain hydrocarbons, only marginally improved the adsorptive nature of natural montmorillonite. The relative poor performance of these tailoring agents may be

explained by the tendency of the flexible hydrocarbon end of the ammonium salts to lie flat along the interlamellar plane. The adsorptive capacity of these tailored clays was thus reduced by the obstructions created by the hydrocarbons chains (Wolfe, Demirel, and Baumann, 1986, Cadena [in press]).

Adsorption of small neutral molecules from aqueous solutions has been demonstrated by the investigators using specially tailored smectites. By exchanging organophilic cations onto smectites, the adsorption of all sizes of organic (neutral) molecules can be enhanced.

The organophilic substance utilized as tailoring agent plays a crucial role on the adsorptive properties of smectites as discussed before. This agent must be water miscible, but readily adsorbed by smectites. Additionally, the compound selected must be non-toxic, and relatively inexpensive. The compounds selected in our studies, TMA salts, readily dissolve in water according to the following reaction:

$$TMA\ Cl \longrightarrow TMA^+ + Cl^- \text{ (For a chloride form)} \qquad (1)$$
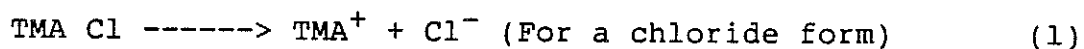
Commercial salt anions include chloride, iodide, and perchlorate. TMA presents the following advantages over other organophilic compounds:

a) The TMA^+ radical undergoes a strong (and apparently irreversible) ion exchange reaction with the natural cation in the clay.

b) The cation exchange process is favored by those ions that are in close contact with the clay surface since the contribution

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of Van der Waals forces decrease rapidly with distance. The small and spherically shaped TMA ions fulfill this requirement, as illustrated in figure 2.

c) TMA-exchanged smectites are sodium free, and due to the strong electrostatic interaction between clay and TMA molecule, the resulting tailored smectite is highly coagulating, and non-expansive. Thus, separation of the spent adsorbent from the treated product, when needed, does not cause any technical difficulties.

d) The large surface area in the interlamellar spaces, crucial for effective adsorption, becomes available to adsorbates, once the naturally occurring cations are exchanged with quaternary amines. This phenomenon is illustrated in figure 3, where benzene (the adsorbate), occupies the basal space between the TMA molecules.

Benzene, C_6H_6, is a low molecular hydrocarbon with moderate polarity and high solubility in water. Due to these properties, benzene is normally difficult to remove from aqueous wastes by adsorptive processes. For example, the adsorption of benzene on pure smectites has been reported to be below limits of detection (McBride et al. 1977). However, once they are tailored with TMA, their adsorptive capacity for benzene increases dramatically. Further, these soils are highly selective for benzene, while closely related aromatic compounds are removed to a lower extent (Cadena and Jeffers 1987).
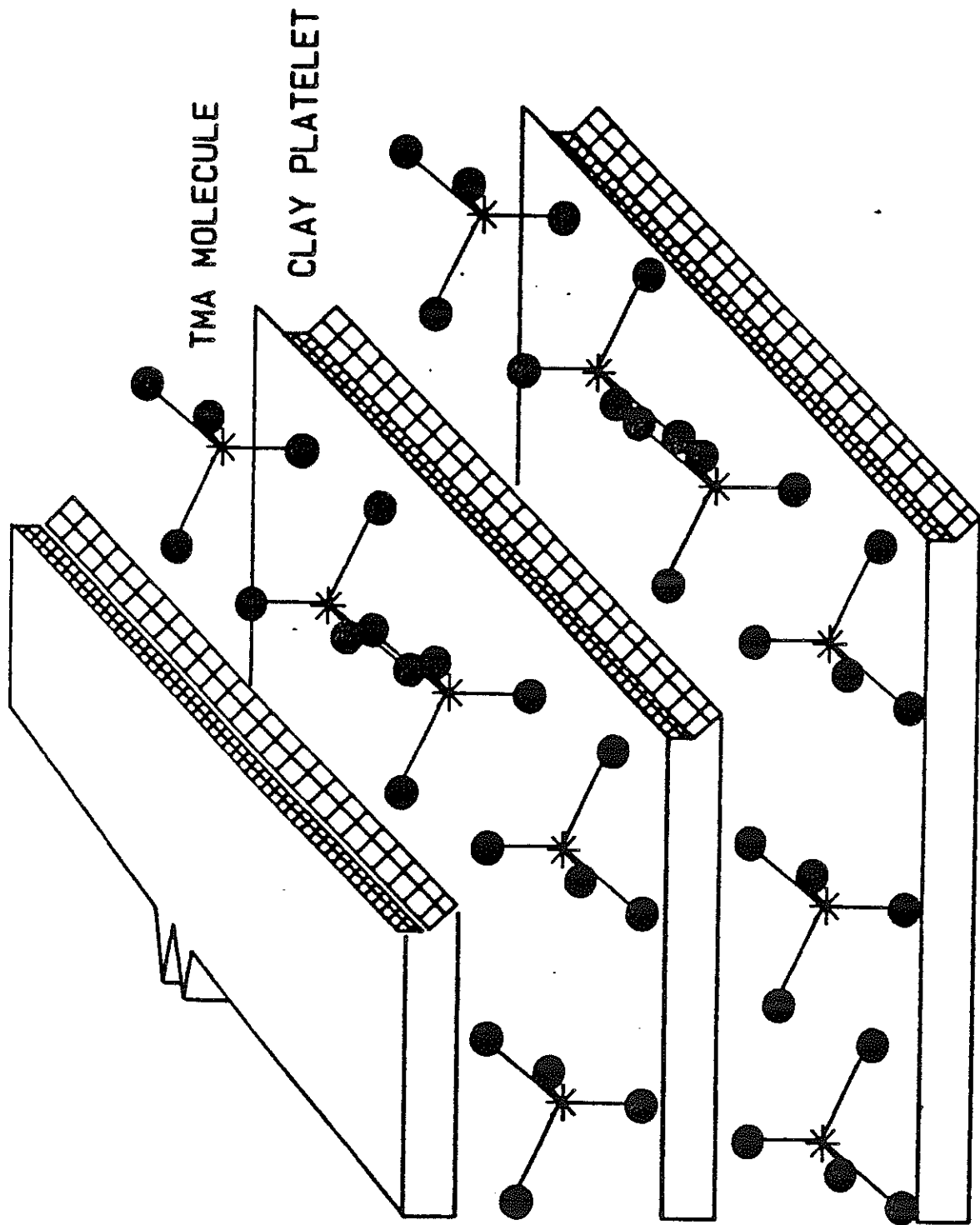
TMA MOLECULE

CLAY PLATELET

Figure 2. Clay Tailored with TMA$^+$.

CLAY PLATELET
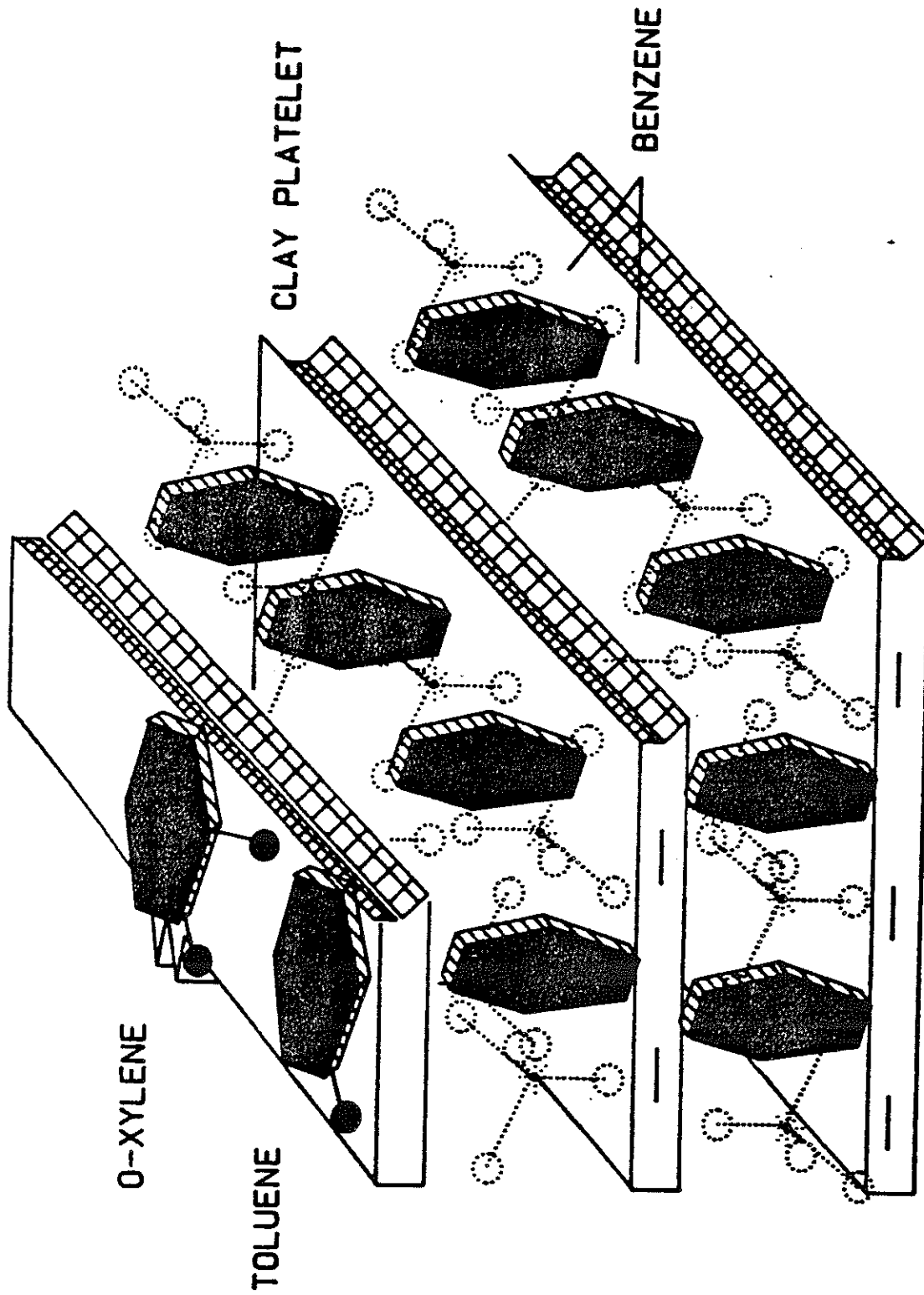
BENZENE

O-XYLENE

TOLUENE

Figure 3. Removal of Aromatic Compounds by Tailored Clay.

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EXPERIMENTAL PROCEDURES

Batch Studies

Stock suspensions of TMA^+ tailored soils were prepared by adding 0.5 l of tap water to 10 g of natural soils. The volume of the suspension was then adjusted to 1.0 l. Soils used·in equilibrium studies were: Aladdin, Glendale, and Dalby soils and Wyoming bentonite. The first three adsorbents are typical New Mexico soils with significantly different clay content (clay is the main component in Wyoming bentonite). Cation exchange capacity (CEC) of the soils was determined by the New Mexico State University Soils and Water Testing Laboratory, a commercial soil chemistry laboratory.

The soil stock suspensions were mixed with a magnetic stirrer for at least 24 hours prior to adsorption tests in order to insure that the suspensions are homogeneous. Aliquots were transferred from the stock suspension into 14 ml centrifuge tubes (the tubes were filled to capacity). Dilute solutions of TMA-Cl were added during the tailoring process using a microsyringe. The TMA-treated soils were then mixed in a revolving apparatus at 20 rpm for 24 hours prior to adsorption tests. Two glass beads were added at this time to each tube to eliminate the headspace, and to help in the mixing process described later.

A thin plastic layer was placed as a septum over the tubes, taking care to displace completely any trapped air. Dilute solutions of the pollutants to be tested were injected through the septum (chromatographic grade benzene, toluene, and o-xylene

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were used for these tests). The tubes were then sealed with teflon caps to minimize volatilization losses (losses by this procedure were reduced to below 5% of the original concentration). The tubes were then turned at 20 rpm in the revolving apparatus. The falling effect of the glass beads insured that adequate mixing was effected.

Time required from initial mixing to the end of centrifugation was used as the contact time in the adsorption studies. Reactor temperature in the tests was approximately 25 ($^+_-$ 2^{O}C). The solid phase (adsorbent) was separated from the liquid phase by centrifugation of the tubes at 3,500 rpm for 3 minutes (prior investigation shows that such contact time is sufficient to obtain adequate solids separation). Liquid supernatant samples were withdrawn with a microsyringe through the septum. These samples were immediately analyzed in a gas chromatograph by direct aqueous injection (DAI). The gas chromatograph was calibrated prior to each experimental run by injecting samples of known pollutant concentration from tubes that contained no soil suspension.

The gas chromatograph used to detect remaining solution concentrations was equipped with an OV-101 column and a flame ionization detector. Chromatographic data were obtained through a computerized chromatographic station as illustrated in figure 4. Data from the chromatograph was transmitted to an IBM-PC compatible computer via an analog to digital interface. This computer was used to collect and interpret the experimental information.

GAS CHROMATOGRAPH

A/D
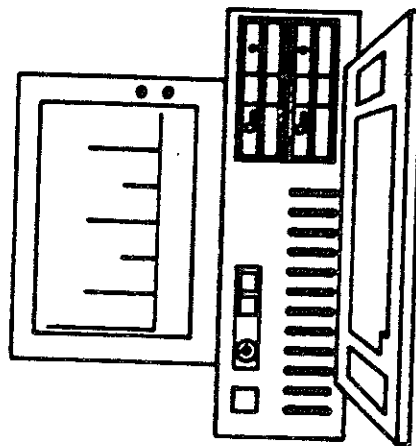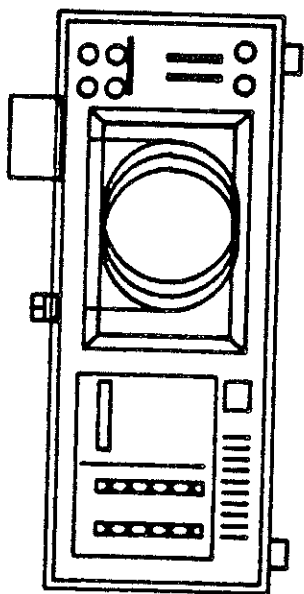
PC COMPUTER

TEFLON CAP

D.A.I.
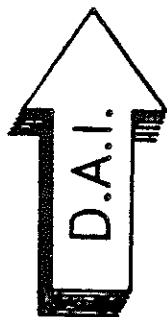
ROTATING
GLASS TUBE
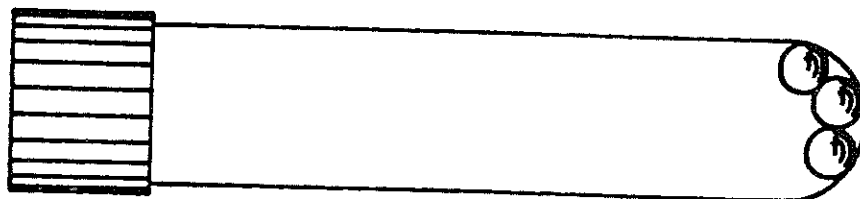
GLASS BEADS

REACTOR

Figure 4.   Experimental Setup for Batch Studies.

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Column Studies

Shallow-column studies were conducted using Aladdin, Glendale and Dalby soils. Reagent grade TMA-Cl, the exchangeable organophilic cation, was used to replace the natural exchangeable cations in the soil. The soils were treated in dry conditions by mixing as a crystal the tailoring agent into the soils. This procedure simulates the simplest approach to implementation of this treatment to field conditions. However, irregular distribution of this tailoring process should yield a heterogeneous adsorbent, with adsorptive capacities lower than those obtained by a homogeneous application of the tailoring agent.

Several short column configurations were tried for the breakthrough studies. Dye was injected at the inlet of each column arrangement to evaluate possible short-circuiting. Short-circuiting was reduced by installing a baffle ring at the inlet side, a layer of sand approximately 3.0 cm thick, and a porous stone at the outlet of the column. Figure 5 depicts the plexiglass column that provided the minimum short-circuiting. This experimental configuration which minimized short-circuiting was used in all the breakthrough studies.

The internal diameter of the column was 6.4 cm, while the soil depths between 5.1 to 12.0 cm could be studied by varying the length of the plexiglass tube. These depths were selected to simulate potential treatment in field conditions, where the tailoring agent would be applied by tilling it into a thin soil layer which could be regenerated by solar radiation.

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EFFLUENT PORT

POROUS STONE

SAND

COLUMN
(6.4 cm ID)

SOIL

BAFFLE RING

INFLUENT PORT

SOIL DEPTH = 5.1 cm
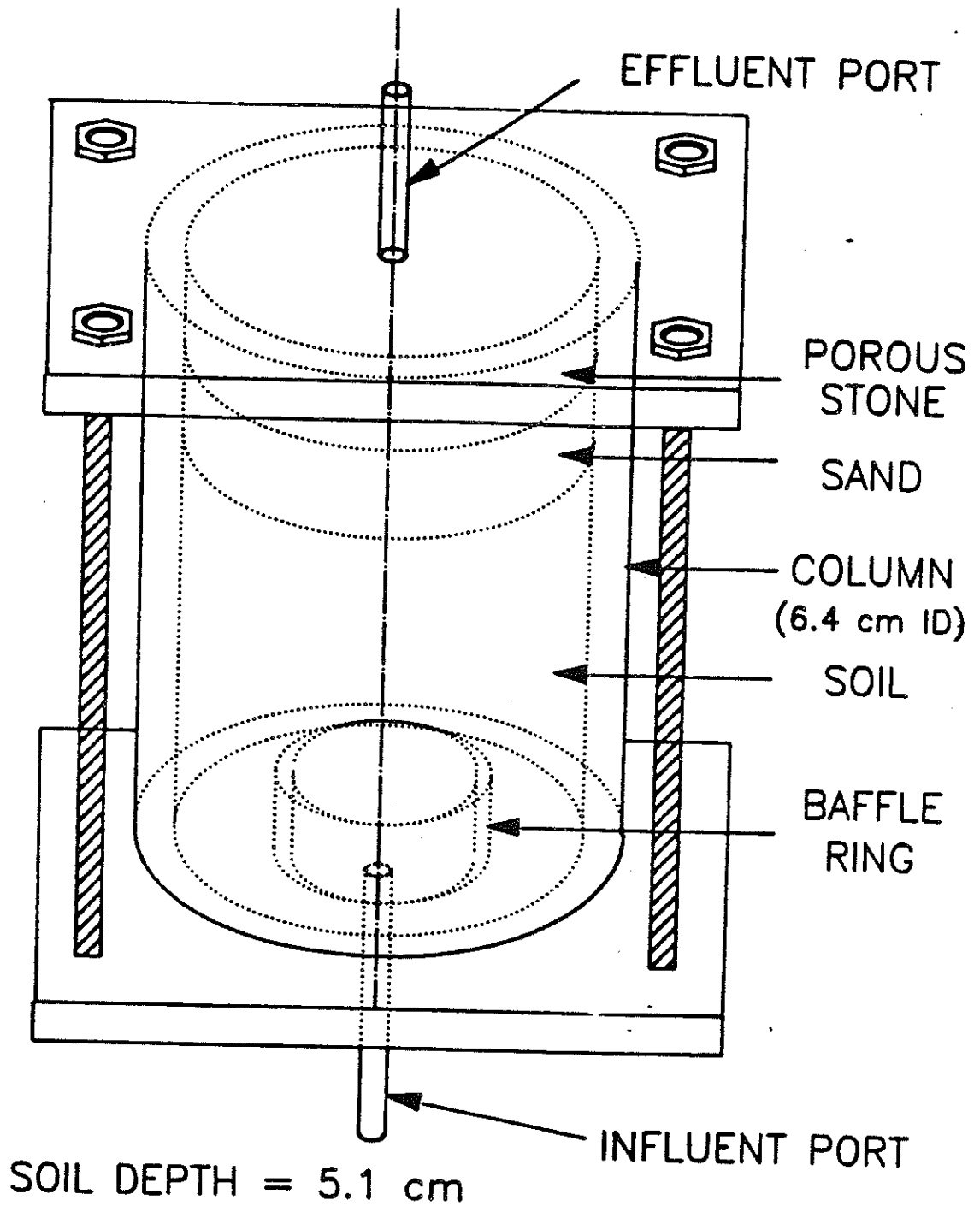
Figure 5. Column for Continuous Flow Studies.

Air was evacuated from the soil-filled columns by flushing the soil (amended with TMA^+) with tap water for 24 hours prior to breakthrough studies. The column was operated during flushing and breakthrough tests as an upflow adsorption system to eliminate any entrained air (and thus reduce interferences created by volatilization losses). Tap water contaminated with a known initial concentration of benzene (C_O) was introduced through the column inlet during breakthrough tests. Effluent concentrations were measured by extracting with a microsyringe a portion of the effluent. Analyses were conducted using the gas chromatograph and chromatographic station described previously.

The possibility of using solar radiation for regeneration of spent tailored soils was also investigated. A sample of spent Glendale soil from a prior column study was placed in a glass terrarium. This terrarium was partially covered to prevent atmospheric precipitation. The terrarium was then exposed to the elements for a period of one month to simulate the effects of typical field regeneration conditions. A column study was then conducted with the regenerated soil.

RESULTS

Nature of Adsorbents

Table 1 summarizes the main physical characteristics of the four soils investigated. Results from both batch (i.e., equilibrium) and continuous flow (i.e., breakthrough column studies) are presented in this section of the report. The Aladdin, Glendale and Dalby soils, commonly found in the southwestern part of the United States, present low organic content. Wyoming bentonite has significant advantages over the other soils due to its high clay content as shown in Table 1.

TABLE 1.

Physical Characteristics of Soils Studied

===

Soil Name	CEC (meq/100g)	Soil Fraction (%)			Organic Content (g/Kg)
		Sand	Silt	Clay	
Aladdin	7.0	67	23	10	0.84
Glendale	21.8	40	26	34	0.65
Dalby	29.2	6	30	64	0.58
Bentonite	72.9	0	0	100	< 0.10

===

Adsorption Isotherms

The adsorptive capacity of a tailored soil depends upon the amount of tailoring agent used and on the nature of the adsorbate. The effect of TMA^+ (the tailoring agent used in these studies) dose on the adsorptive properties of the tailored soils was evaluated by determining the equilibrium concentration, C_e, of benzene solutions exposed to the tailored adsorbent. Table 2 summarizes the experimental results of this experimental phase.

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Table 2 shows that the amount of benzene adsorbed (x) per unit weight of soil (m) increases for TMA^+ concentrations below the CEC of the soil. For instance, the capacity of the tailored soils to remove benzene is greatly improved by as little as 0.25 meq of TMA^+ per meq of CEC. Smaller incremental improvements occur at TMA^+:CEC ratios greater than 0.5 for most soils.

TABLE 2.

Effect of TMA^+ on the Adsorption Properties of Benzene by Tailored Soils.

TMA+:CEC meq/meq	x/m (mg/g)			
	ALADDIN[a]	GLENDALE[a]	DALBY[a]	BENT.[b]
0.00	0.00	0.00	0.00	0.00
0.25	0.39	0.39	0.37	--
0.50	0.99	0.12	0.23	3.09
0.75	--	--	--	3.84
1.00	1.15	0.46	--	4.50
1.50	0.00	0.86	0.20	4.59
2.00	0.00	0.21	0.55	4.55

a. C_o = 60.2 mg/l, m = 10,000 mg/l
b. C_o = 100.0 mg/l, m = 20,000 mg/l

Maximum benzene adsorptive capacity occurs at TMA^+ doses close to the CEC of the soil. Further experimental results (Cadena [in press]) show that addition of TMA^+ at doses greater than 2.0 times the CEC of the clay is not effective. This phenomenon is due to the limited capacity of the clay to retain TMA^+ cations. Excessive concentrations of TMA^+ result in increasing concentration of TMA^+ in solution (rather than in the interlamellar spaces of the clay). Therefore, the partitioning

effect between the TMA-tailored soil and the pollutant is reduced by the competing effect of TMA^+ in solution.

Measurements of solution concentration of benzene were conducted at varying contact times (i.e., kinetic tests). Measured solution concentrations reached equilibrium conditions within 5 minutes contact time. The adsorptive capacity and selective nature of the TMA-treated soils were experimentally evaluated in several adsorption studies at times greater than 5 minutes in order to insure equilibrium conditions. These studies were conducted using fixed initial concentrations of benzene, toluene, o-xylene and chloroform and variable concentrations of tailored and pure soil at contact times greater than 5.0 minutes.

Results from benzene adsorption tests on TMA-tailored soils are presented in linear fashion in figures 6 and 7 (adsorption of this pollutant on the natural soils was below detection levels).

Several adsorption isotherm models (BET, Freundlich, Langmuir and Linear) were used to describe the data presented in figures 6 and 7. The Linear and Freundlich isotherm models described the experimental data equally well. These two isotherm models are used throughout this report to represent mathematically adsorption data since these models are common in design of adsorption process and in solute transport modeling, respectively.

The linear isotherm model assumes that the pollutant removed per unit mass of adsorbent (x/m) is a linear function of the equilibrium concentration (i.e., the 1/n exponent in the Freundlich isotherm equals 1.0):
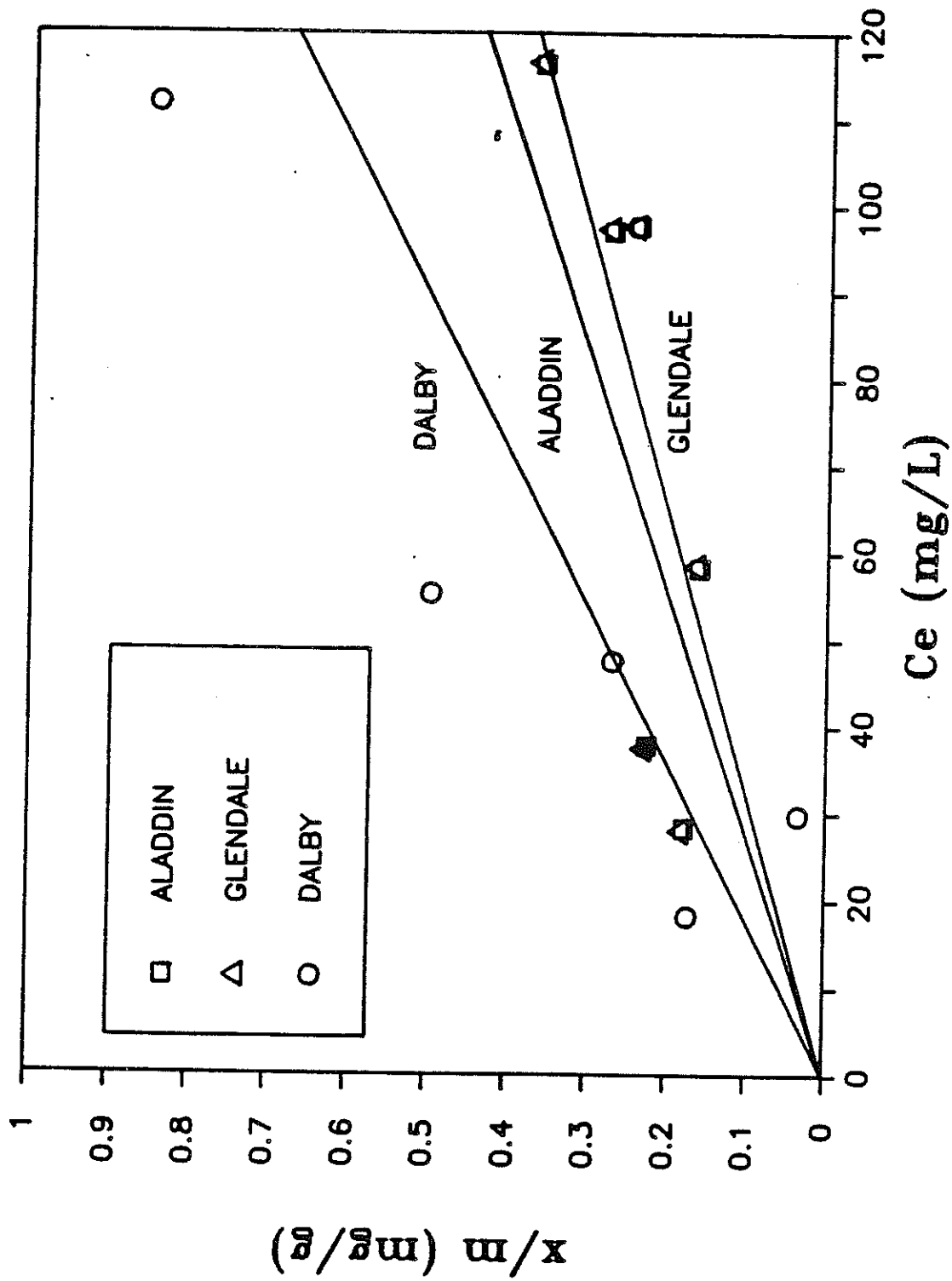
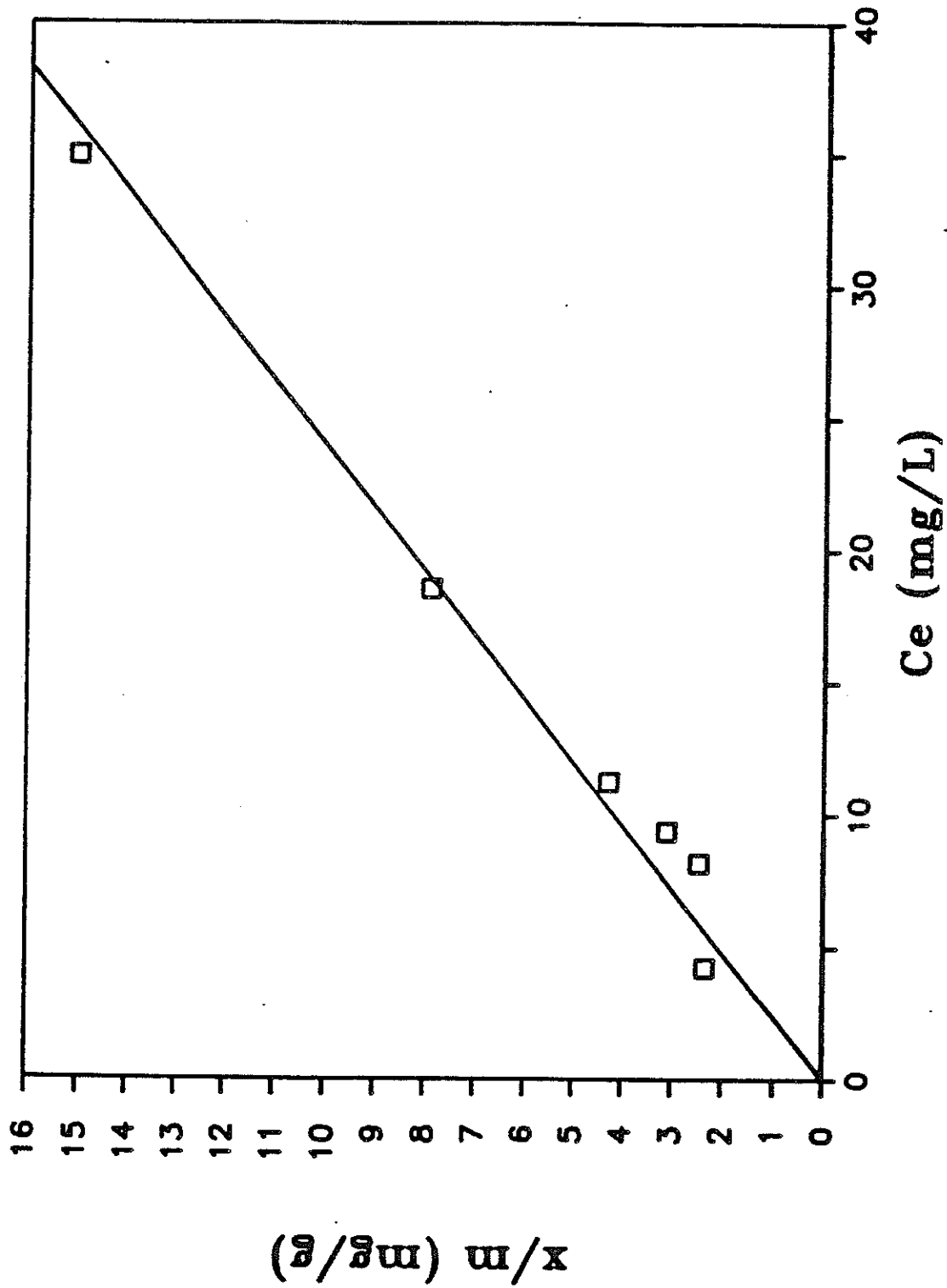Figure 6. Linear Adsorption Isotherms for Dalby, Glendale and Aladdin Soils Tailored with TMA$^+$.

Figure 7. Linear Adsorption Isotherm for TMA-Bentonite.

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$$x/m = K_d \, Ce \qquad\qquad (2)$$

Figure 6 shows that the tailored southwestern soils have a significant adsorptive capacity, which is represented by the slope of the corresponding best-fit lines. Interestingly, the adsorptive capacity of TMA-bentonite is much greater than the capacities for the other three soils, as shown in figure 7. This difference is probably due to the large clay content of the bentonitic soil. Table 3 summarizes the adsorptive capacities, K_d, for the four soils studied.

TABLE 3.

Benzene Adsorption Isotherm Constants

	Isotherm		
Soil	Linear	Freundlich	
Name	$K_d \times 10^3$	$K \times 10^2$	$1/n$
	(1/g)		
Aladdin	3.66	2.72	0.52
Glendale	3.15	6.21	0.32
Dalby	5.68	0.42	1.03
Bentonite	420	40.6	0.99

Freundlich isotherms are represented by power equations that depend on the adsorptive capacity coefficient, K, and the exponent $1/n$. Equation (3) represents the Freundlich model:

$$x/m = K \, (Ce)^{1/n} \qquad\qquad (3)$$

where x is the mass of pollutant adsorbed, in mg by m grams of adsorbent, and Ce is the solution equilibrium concentration in mg/l.

Equation (3) may be linearized by plotting the logarithm of the independent variable (C_e) against the logarithm of the dependent variable (x/m) as shown in figures 8 and 9. Best-fit values corresponding to the Freundlich isotherms of the four tailored soils are also presented in table 3. It is evident from this table that the adsorptive capacity of TMA-bentonite is much greater than for the other soils.

Selective Nature of TMA-Tailored Soils

The selective nature of TMA-treated soils was investigated in a series of batch studies exposing tailored soils to benzene, toluene, o-xylene and chloroform. Benzene adsorption on TMA-tailored soils was significant in all soils investigated as described before. However, adsorption of toluene, o-xylene and chloroform was only detected when using TMA-bentonite as adsorbent. This finding is important considering that non-selective adsorbents, such as granular activated acrbon (GAC), show greater affinity for these three compounds than for benzene (i.e., the TMA-tailored soils are highly selective).

Adsorption isotherm constants for the four compounds tested on TMA-bentonite are shown in table 4. Figure 10 compares these isotherms with granular activated carbon (GAC) isotherms for the four pollutants tested. The TMA-bentonite lines in this figure correspond to the experimentally determined isotherms while the

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Ce (mg/L)

x/m (mg/g)

1.00

0.10

0.01

10

·100
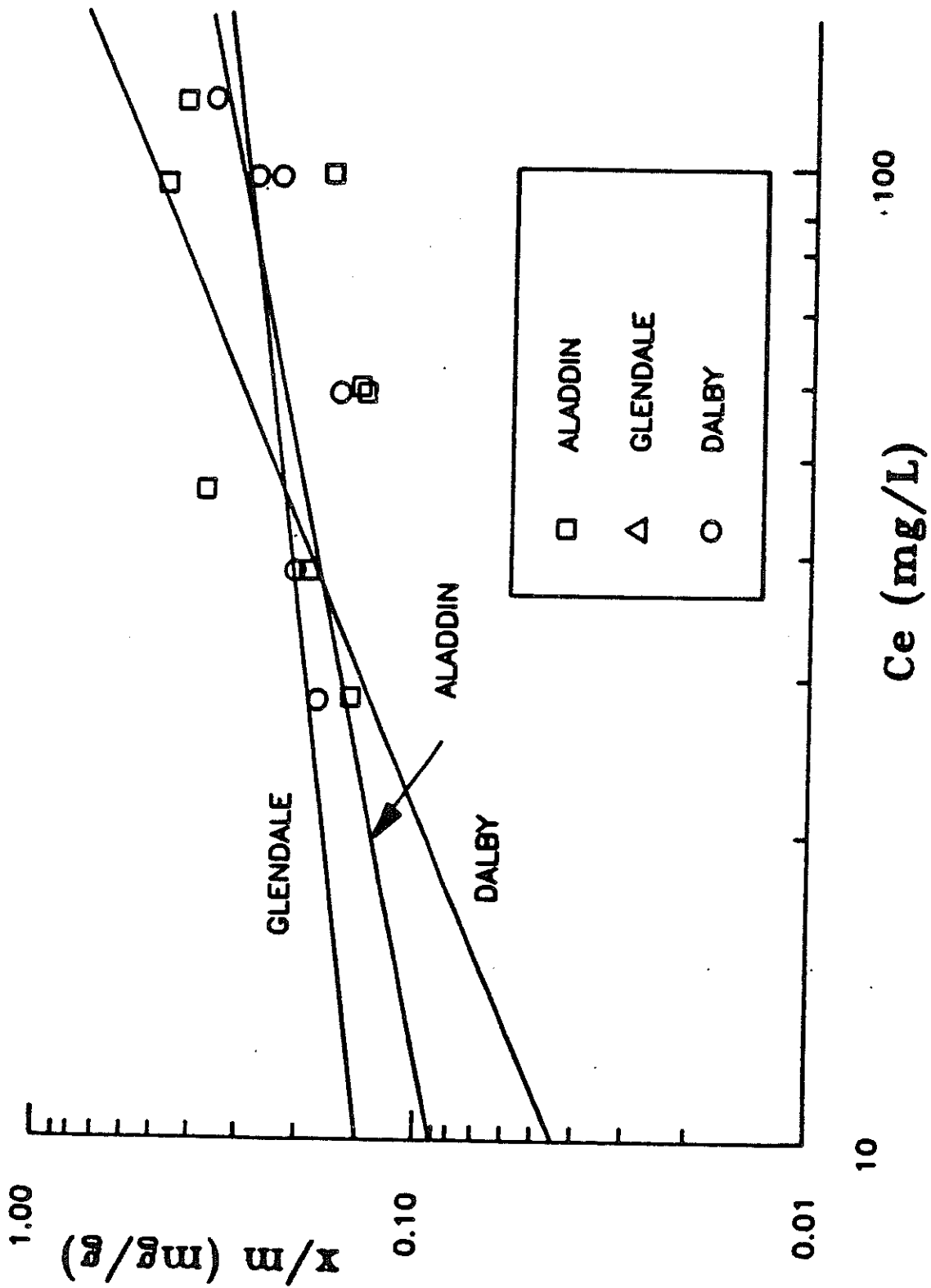
GLENDALE

ALADDIN

DALBY

ALADDIN

GLENDALE

DALBY

Figure 8. Freundlich Adsorption Isotherms for Dalby, Glendale and Aladdin Soils Tailored with TMA$^+$.
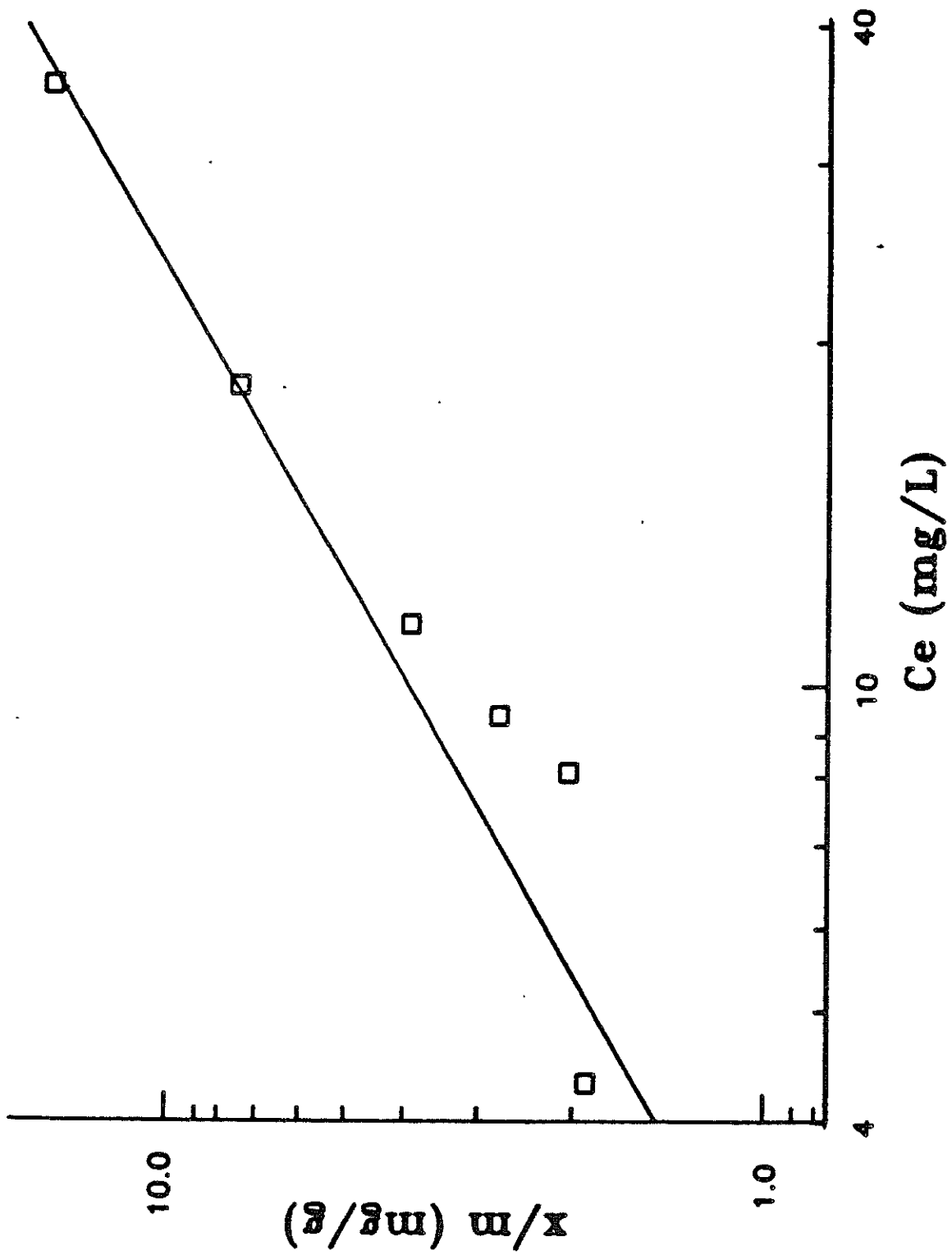
Figure 9. Freundlich Adsorption Isotherm for TMA-Bentonite.

GAC lines are calculated from the coefficients determined by Dobbs and Cohen (1980). Solid lines in figure 10 represent the experimental range, and dashed lines are extrapolations from this range.

TABLE 4.

TMA-Bentonite and GAC Freundlich Adsorption Isotherms

		TMA-Bentonite		GAC[a]	
Compound	M.W. in g/M	K mg/l	1/n	K mg/l	1/n
Benzene	78.1	0.41	1.00	1.0	1.60
Toluene	92.1	8.4×10^{-4}	2.52	26.1	0.44
Xylene	106.2	1.5×10^{-3}	1.71	85.0	0.19
Chloroform	119.4	3.5×10^{-5}	3.40	2.6	0.73

[a]Filtrasorb 300

Figure 10 shows that the amount of benzene adsorbed per gram of GAC is approximately two to five times greater than for TMA-bentonite in the range of equilibrium concentrations tested. On the other hand, the non-selective adsorptive capacity of GAC increases, as predicted by Traube's Rule (Weber 1972), with the molecular weight of the aromatic compounds, since the solubility in a homologous series decreases.

The adsorptive capacity of TMA-bentonite and GAC was divided by the benzene adsorptive capacity Ce = 1.0 mg/l in order to compare the selective nature of the adsorbents. These computed ratios are presented in table 5. Results from this table show that benzene adsorption on TMA-bentonite is greatly favored over the other compounds tested (benzene >> o-xylene > toluene).
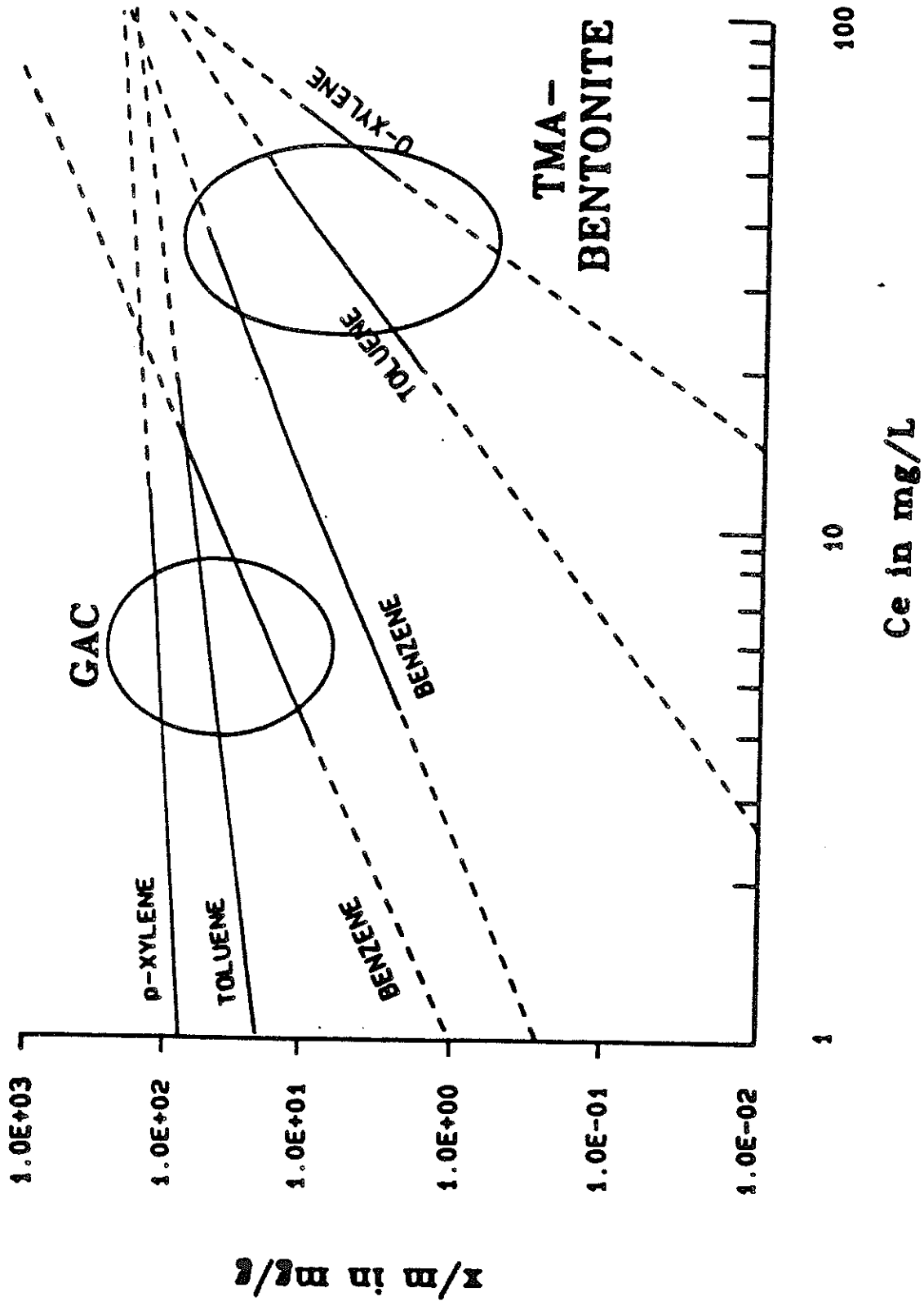
Figure 10. Freundlich Isotherms for Various Organics Adsorbed by Granular Activated Carbon and TMA-Bentonite.

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On the other hand, the trend for GAC is benzene < toluene < xylene; a logical result for this non-selective adsorbent.

TABLE 5

Calculated Selectivity with Respect to Benzene for
TMA-Bentonite and GAC

Compound	Molecular Weight, in g/M	TMA-Bentonite	GAC
Benzene	78.1	1.0	1.0
Toluene	92.1	2.1×10^{-3}	26.1
Xylene	106.2	3.7×10^{-3}	85.0
Chloroform	119.4	8.5×10^{-5}	2.6

Effect of Tailoring Agent Type on Adsorptive Capacity

The work by Boyd, Mortland, and Chiou (1988), shows that the adsorptive capacity of natural bentonite is also enhanced by tailoring with hexadecyltrimethylammonium ($HDTMA^+$). Similar experimental results by Wolfe, Demirel, and Baumann (1986), reveal that adsorption of benzene by other quaternary amines decreases as the molecular weight of the alkyl chains increases.

Table 6 compares the results obtained in various investigations with the results from this study. Linear partition coefficients, K_d, are used in this table to compare the results of disparate research work in order to maintain a consistent frame of reference. The length of the alkyl chain (as carbon atoms), n, is also presented for each tailoring agent in table 6.

TABLE 6

Effect of Alkyl Chain Size on the Partition Coefficient of
Benzene onto Tailored Montmorillonite.

===

Tailoring Agent[a]	Formula	C_n	K_d, L/g	Reference
TMA^+	$C_4H_{12}N$	1	0.421	This work[b]
PAM^+	$C_3H_{10}N$	3	0.356	Wolfe et al. 1986
DAM^+	$C_{12}H_{28}N$	12	0.124	Wolfe et al. 1986
$HDTMA^+$	$C_{19}H_{42}N$	16	0.062	Boyd et al. 1988

===

[a]TMA^+ = Tetramethylammonium, PAM^+= Propylammonium,
DAM^+ = Dodecylammonium, $HDTMA^+$ = Hexadecyltrimethylammonium
[b]Bentonite containing approximately 80 percent montmorillonite

The partition coefficient (i.e., K_d) of benzene decreases
with the length of the alkyl chain (presented in table 6 as the
number of carbon atoms in the chain, C_n). The effect of
tailoring agent size on benzene adsorption is illustrated in
figure 11. The excellent correlation coefficient (0.991)
obtained by a best-fit line through the points in figure 11 is a
clear indication that the type of molecule used to tailor the
soil plays a crucial role on the adsorption of the pollutant.

The decreasing trend in figure 11 is due to molecule crowding
by the longer chains in the interlamellar spaces. Such crowding
phenomenon was observed by Wolfe, Demirel, and Baumann (1986),
who reported that alkyl chains in molecules greater than PAM^+ are
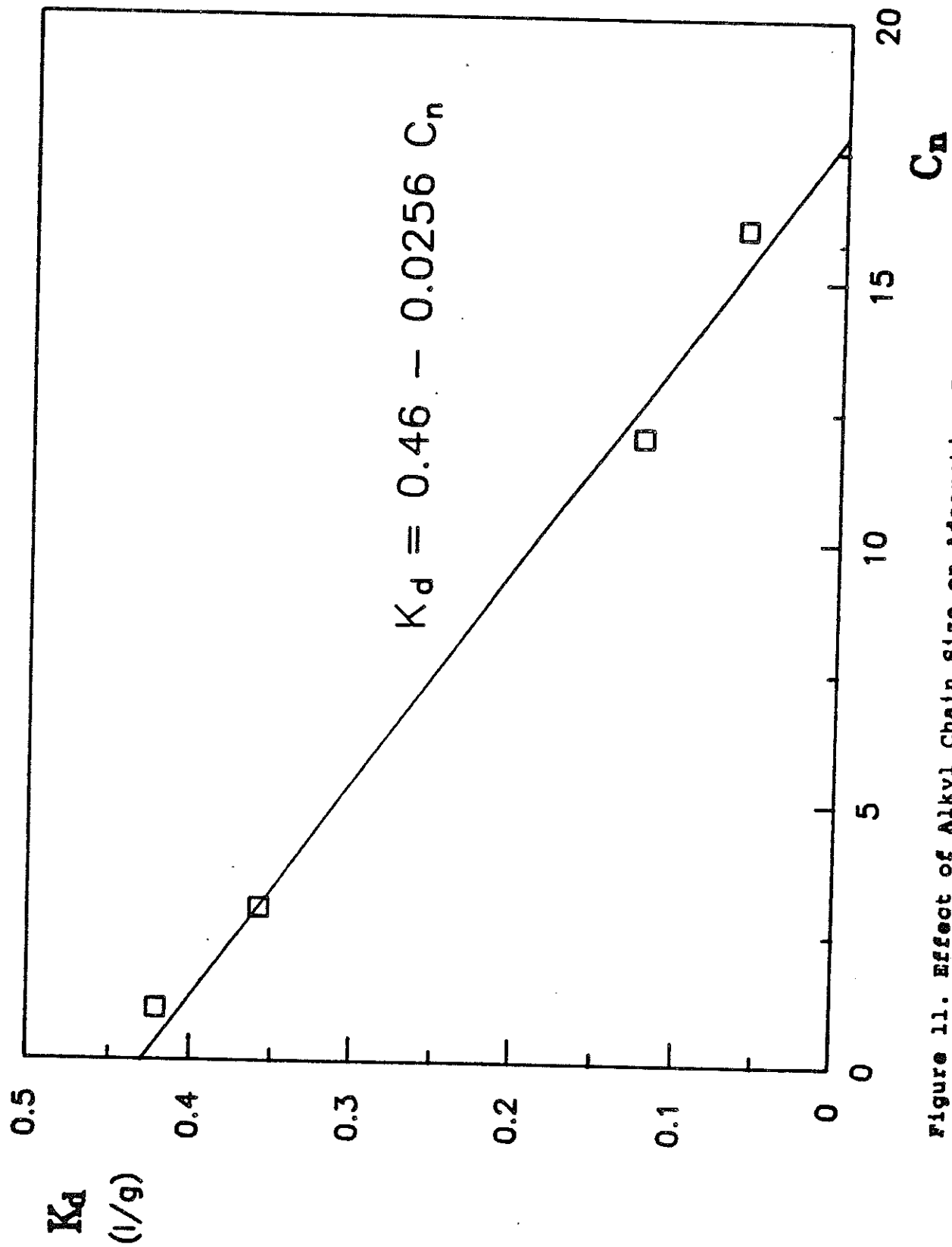oriented flat, along the ineterlamellar space, while the propyl

$$K_d = 0.46 - 0.0256 \ C_n$$

Figure 11. Effect of Alkyl Chain Size on Adsorptive Properties of Tailored Montmorillonite.

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chain in PAM^+ (a smaller and more rigid molecule) is not bent and remains perpendicular to the silicate layer.

Consequently, the crowding effect associated with long alkyl chains tends to reduce the interlamellar space available for adsorption of benzene molecules. Therefore, smaller molecules, such as TMA^+, are preferred tailoring agents for the removal of benzene from aqueous solutions over larger compounds such as DAM^+ and $HDAM^+$. Such results confirm the superiority of the TMA^+ cation as a tailoring agent for the removal of benzene.

This conclusion is not valid for the removal of alkylated aromatic compounds, whose adsorption is limited by the narrow space created by molecules such as TMA^+ and PAM^+. This conjecture is validated by experimental results presented by Wolfe, Demirel, and Baumann (1986), who detected greater toluene uptake by DAM^+ than by PAM^+ tailored montmorillonite.

Column Studies

Several breakthrough curves were obtained using natural and TMA-tailored soils. Soils used for these dynamic tests included Aladdin, Glendale and Dalby soils. Column studies with bentonite were impossible in the time domain of this study because of the low hydraulic conductivity of this soil. Other soils enriched with bentonite at concentrations as low as 5% by weight experienced the same low permeability and were not studied either.

Benzene, the most toxic and mobile of the three pollutants tested, was selected as the adsorbate for all column studies.

Experimental results obtained from column studies with the natural and tailored soils are shown in figures 12 through 14.

One-dimensional solute transport through saturated porous media has been studied by Lindstrom et al. (1967). These authors introduced a solute transport model that assumes steady state influx conditions (of both flow and adsorbate concentration), linear adsorption, absence of pollutant degradation and volatilization and a homogeneous adsorbent. The validity of this model for short laboratory columns has been tested by van Genuchten and Parker (1984). This model, with modifications to include the combined effects of molecular and mechanical diffusion effects, is described below.

The average pore velocity (v) may be calculated by dividing the approach velocity, v_o, by the porosity, p, of the solid medium:

$$v = v_o/p \tag{4}$$

The approach velocity (i.e., application rate) is a function of the applied flowrate, Q, and the application area, A:

$$v_o = Q/A \tag{5}$$

The pollutant front does not necessarily match the water front. Molecular diffusion of the solute, which occurs inside the porous medium, promotes migration of the solute in the direction of the concentration gradient. Mechanical dispersion, which is induced by mixing in the pores, is of high importance in
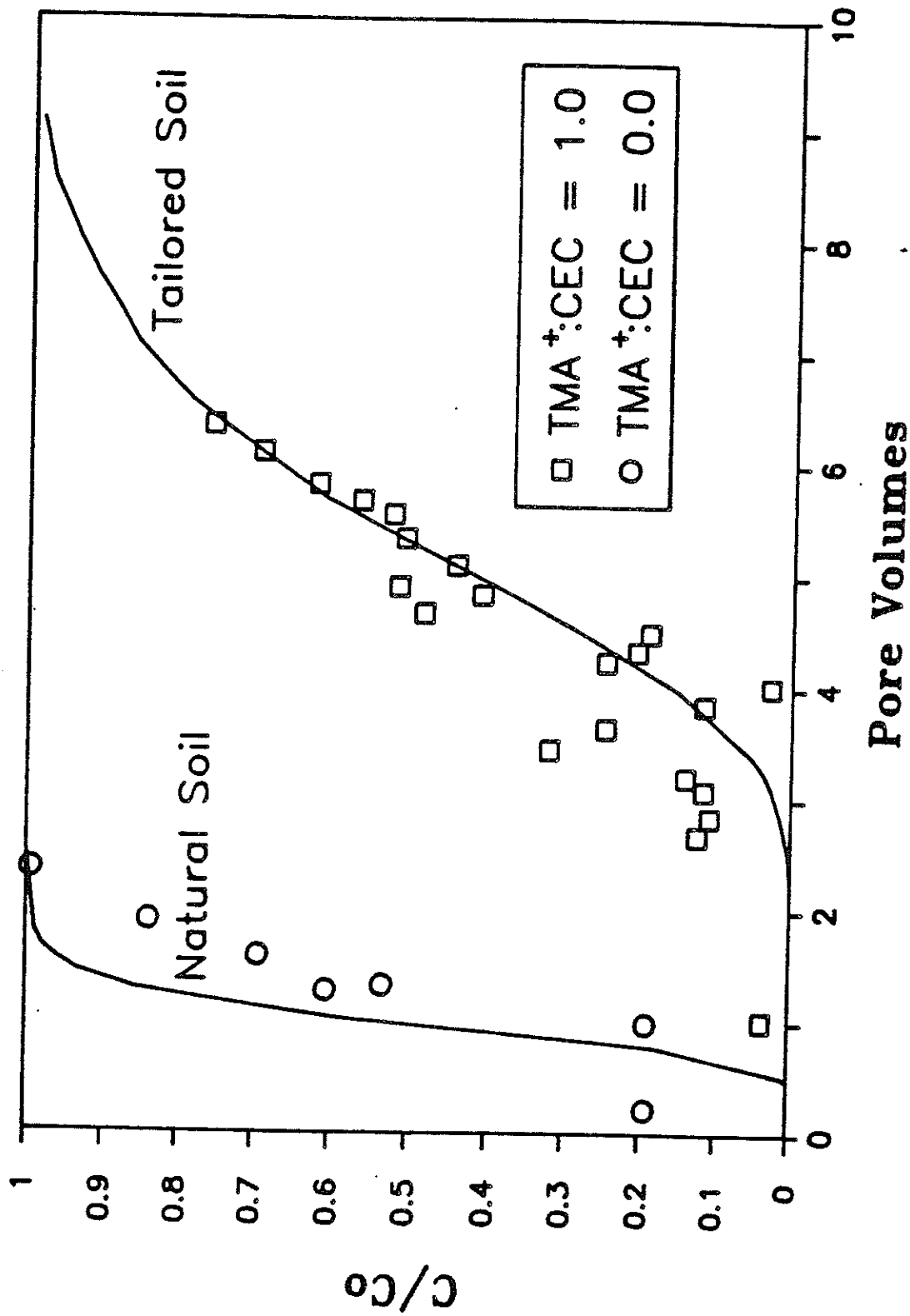
39

Figure 12. Experimental and Predicted Breakthrough Curves for Column Studies with Natural and Tailored Dalby Soil.
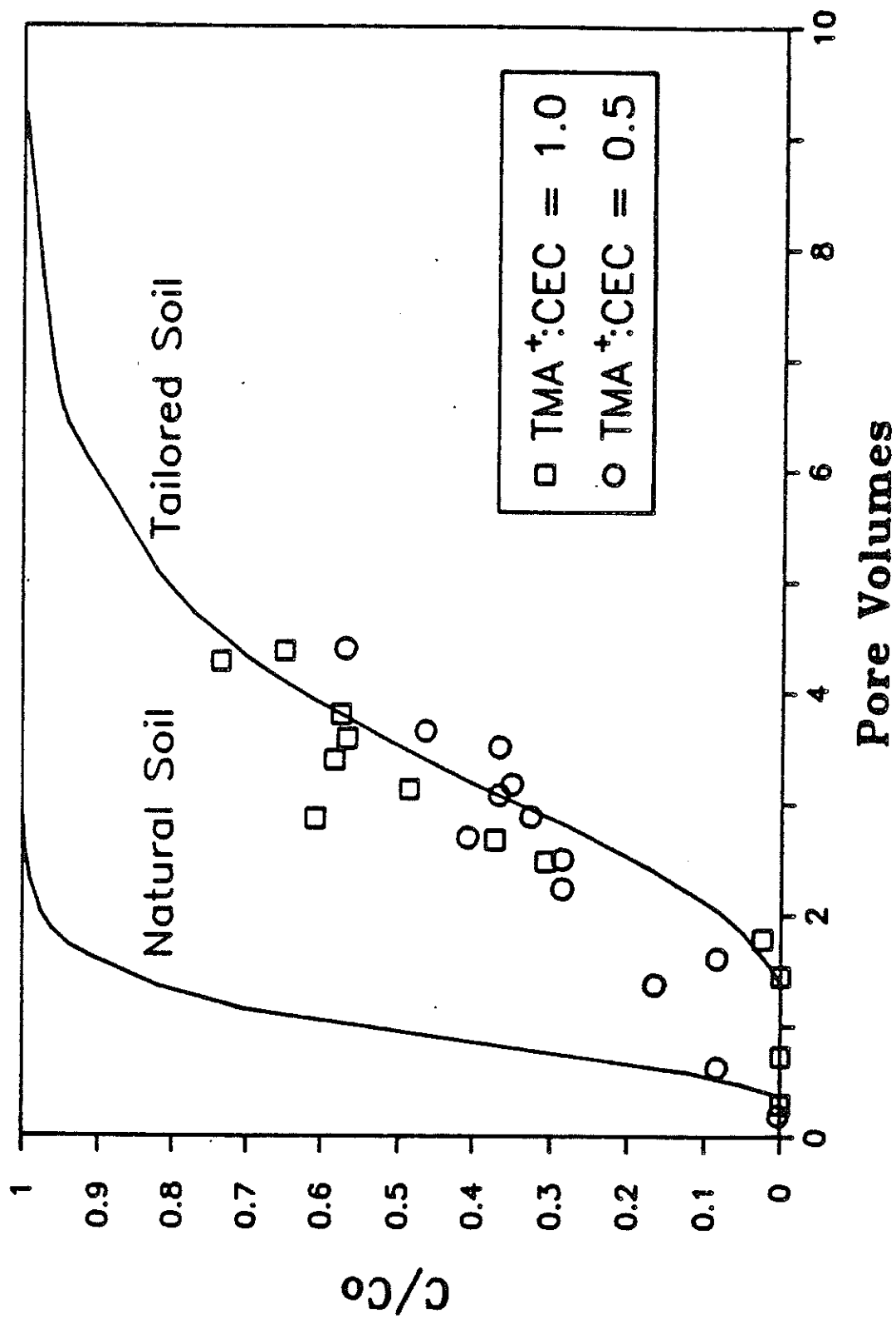
Figure 13. Effect of TMA$^+$ Dose on Column Breakthrough Curves for Column Studies with Natural and Tailored Aladdin Soil.
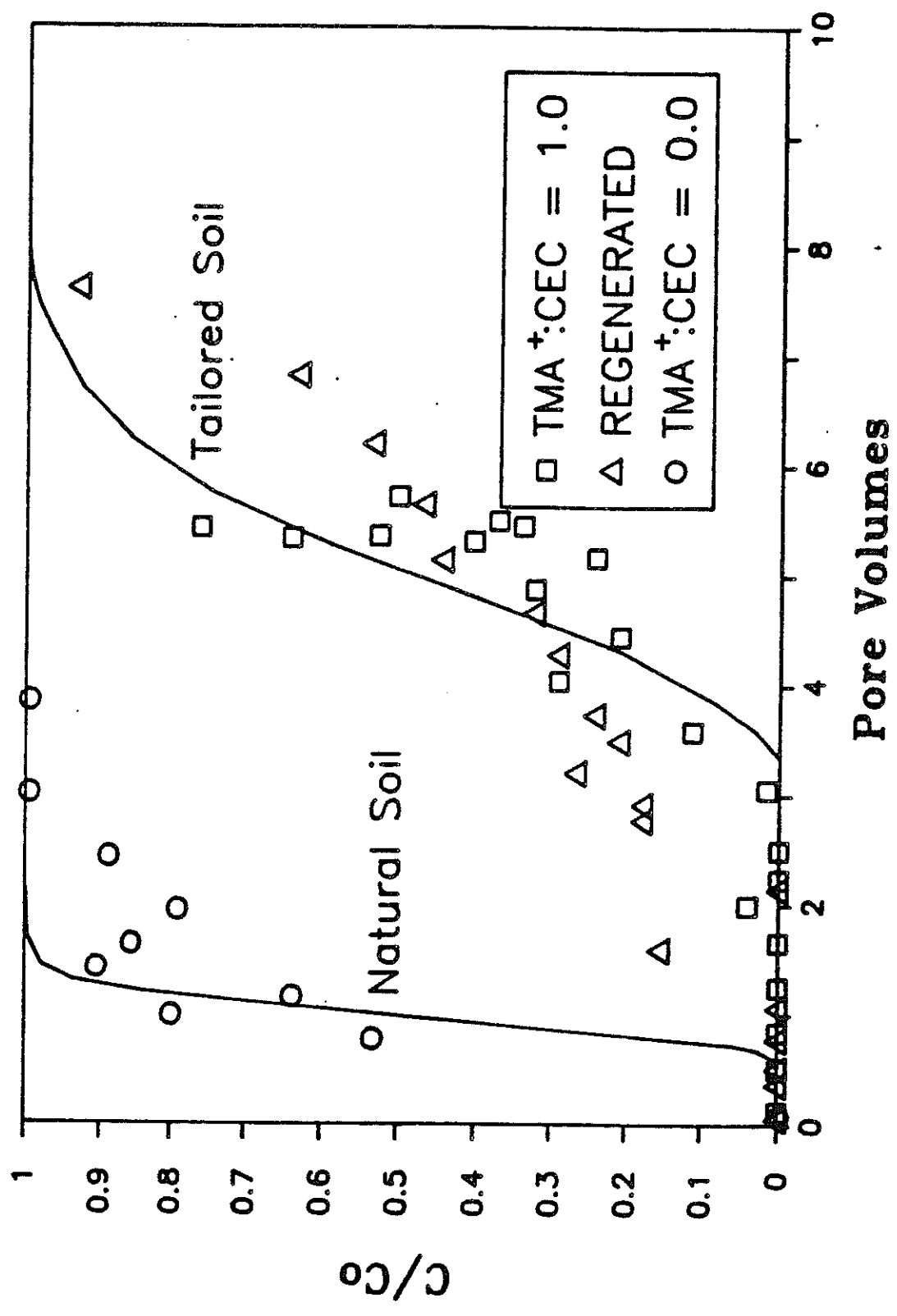
Figure 14. Effect of Solar Regeneration on Column Breakthrough Studies Using Natural and Tailored Glendale Soil.

more turbulent conditions created by rapidly moving fluids (Jury, Spencer, and Farmer 1983).

Molecular diffusion may be estimated by using the Wilke-Chang relationship, as proposed by Reid, Prausnitz, and Sherwood (1977). The molecular diffusion coefficient for benzene at 25°C obtained with this relationship is 3.61×10^{-4} cm^2/min. Mechanical diffusion effects are more difficult to evaluate. These effects depend on the pore velocity, v, and on the dispersivities of the porous medium, a. According to Wilson and Miller (1978), this parameter varies greatly depending on scale and nature of soil. For instance, the dispersivity in field conditions may be very large (several meters) due to aquifer stratification, nonuniformity and fractures. In laboratory conditions this parameter is small, of the order of the grain size of the medium (a few millimeters).

The total dispersion coefficient, D_T, is a summation of the combined effects of molecular diffusion and mechanical dispersion:

$$D_T = 3.61 \times 10^{-4} + va \qquad (6)$$

The first term in equation (6) represents the molecular diffusion coefficient, and the second one corresponds to the effects of mechanical dispersion. It may be noticed from this equation that the magnitude of mechanical diffusion effects increases linearly with the pore velocity. At high application rates desirable in treatment processes, the second term dominates.

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Two main mechanisms affect solute transport: the advection transport due to the hydraulic front, and dispersion. Equation (7) defines the Peclet number, P_e, of the flow in porous media, which is used to describe the relative effects of hydraulic to dispersion phenomena.

$$P_e = vL/D_T \qquad (7)$$

Where L is the depth of soil (i.e., the column length in laboratory experimentation).

The pollutant may be delayed from the hydraulic front due to adsorption onto the solid phase. The retardation coefficient, R, is used in solute transport modeling to describe this phenomenon:

$$R = 1 + (d\ K_d)/p \qquad (8)$$

Where K_d is the slope determined by the Linear Adsorption Model, d is the bulk density of the adsorbent, and p is the porosity of the adsorbent.

Equation (9) summarizes the model for short laboratory columns presented by van Genuchten and Parker (1984). This equation is a normalized time function of the concentration at the outflow of the column:

$$C/Co = 0.5\ erfc[(P_e/4RT)^{1/2}(R-T)]$$
$$+ 0.5\ exp(P_e)\ erfc[(P_e/4RT)^{1/2}(R+T)] \qquad (9)$$

Where C is the effluent pollutant concentration, C_o is the constant influent pollutant concentration, P_e is the Peclet Number, R is the retardation coefficient, and T is the pore

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volume (i.e., bed volume). The pore volume, T, is the normalized time function:

$$T = vt/L \qquad\qquad\qquad (10)$$

Where t is the time elapsed since the breakthrough study started.

Equations (4) through (10) were programmed in MATHCAD, an advanced MS-DOS computer software. The results of the model output are compared against experimental data in figures 12 through 14. Experimental T values in these figures were corrected for the lag-time produced by dead volumes at the inlet and outlet of the column.

Parameters used in the model are summarized in table 7. Influent benzene concentrations (i.e., C_O) used in these studies were in the range of 22.4 to 36.4 mg/l. Adsorption coefficients used in the model are lower than the ones found in the batch studies. This is due to the decreased adsorptive properties of the soil tailored by crystalline TMA^+ (rather than a homogeneous coating obtained in the thermodynamic studies). Adsorptive capacities obtained by this simpler application method are reduced by 40 to 75% from the ideal isotherm values.

The dispersivity coefficients, a, used to model the three types of soils investigated were 0.06 cm in the Glendale and Dalby soils, and 1.0 cm in the Aladdin soil. The change from the lower to the higher value is consistent with the grain size, which is much greater in the sandy Aladdin soil.

TABLE 7

Breakthrough Curve Parameters

Soil Name	d (g/l)	p	v_o (cm/min)	Co mg/l	a (cm)	$Kx10^3$ (1/g)	R
Aladdin	1,410	0.46	0.070	36.4	1.00	0.92	3.82
Glendale	1,160	0.54	0.022	33.2	0.06	1.89	5.06
Dalby	1,090	0.58	0.002	22.4	0.06	2.27	5.27

The pollutant holdup, H, in a soil column is computed using equation (11):

$$H = R [1 + (1/P_e)] \tag{11}$$

At the high Peclet numbers obtained in this experimental work ($P_e > 20$), the value of H approximately equals the retardation coefficient, R (the retardation coefficient equals 1.0 for non-adsorbent soils and increases with the value of K according to equation (8)).

Table 7 shows that the TMA-Aladdin soil (which has a low clay content) improves the characteristics of the bed by a factor of 3.8 over the untreated soil (the untreated soil contains the pollutant not by adsorption but as a solution inside the pores). A more dramatic effect is observed in the TMA-treated Dalby and Glendale soils which have retardation coefficients of approximately 5.0. Thus, the latter soils are capable of holding up to more than five times the amount of pollutant retained in the corresponding natural soils.

The effect of tailoring on benzene removal is clearly visible in figure 12, where the breakthrough pore volume of the Dalby soil is increased from 0.5 to 2.5 pore volumes by tailoring with TMA^+. A more marked difference occurs between the exhaustion times for the natural and tailored soils.

It was shown in the batch studies that the effect of the tailoring agent is more pronounced at doses below 50% of the CEC. Therefore, little difference in adsorptive properties should be noticed between soils treated at 50 and 100% of the CEC. The validity of such assumption was tested in a parallel test using two Aladdin soil columns. The columns were tailored by addition of TMA salt (as a crystal) at 50 and 100% of the CEC. Breakthrough results for these two tests are presented in figure 13.

The relatively small difference in results between two TMA-dose tests confirms the assumption that TMA application may be reduced to 50% of the CEC of the soil without loosing significant adsorptive capacity. From an economic viewpoint this finding is highly relevant since the cost of tailoring natural soils could be reduced by at least 50%.

The economics of using tailored natural soils for the removal of targeted pollutants becomes more attractive if the adsorbent is regenerable. Exposure of the soil (in outdoor conditions) may regenerate an adsorption field. Volatilization and biodegradation in the soil may be used to reduce the adsorbate concentration to acceptable levels in the adsorption field.

Biodegradation of the tailoring agent may, on the other hand, reduce the adsorptive capacity of the regenerated product.

It is currently unknown at what rate the tailoring agent biodegrades, and what is the potential life-time of these adsorption fields. Most favorable conditions for regeneration are currently unexplored. It is also unknown how weather-related factors could affect such process. These issues are of importance and merit further investigation.

The possibility of regenerating spent tailored soils was tested by drying the contents of a spent TMA-treated Glendale soil in a glass terrarium. Breakthrough results for both, freshly-tailored and regenerated soil, are presented in figure 14. Even though breakthrough in the regenerated soil appears before the one for the fresh soil, exhaustion of the regenerated soil occurs at a greater normalized time than that of the fresh soil. In other words, the net removal is approximately the same in both cases. These preliminary results represent a favorable indication of the regeneration potential of tailored soils.

CONCLUSIONS

1. The adsorptive properties of soils for benzene are dramatically improved by using organophilic coatings. The nature of the organic coating greatly influences the adsorption process. The high efficiencies obtained when organic coatings are used show that hydrocarbons occupy interlamellar positions in the clay structure. This phenomenon is due to ion exchange of the natural cation in the clay fraction of soils with TMA^+.

2. Results with adsorption isotherms showed that tailored bentonites have lower adsorptive capacities than those of activated carbon. However, the tailoring process results in a highly selective adsorbent; a property that is absent in activated carbon.

3. Tailored bentonitic clays have a greater capacity to remove BTX due to their large clay fraction. However, all four soils tailored showed a significant adsorptive capacity improvement after tailoring with TMA^+.

4. Maximum removal of benzene occurs at doses of TMA^+ that are approximately equal to the cation exchange capacity, CEC, of the soil. Doses much greater than the CEC of the soil result in impaired adsorption efficiency, as a result of excess TMA^+ molecules occupying the interlamellar space in the clay fraction of the soils. The largest adsorption improvement occurs at TMA^+:CEC doses below 0.5, while little improvement occurs at doses between 0.5 and 1.0.

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5. The TMA-bentonite shows high selectivity for benzene adsorption, and limited adsorption for toluene and xylene.

6. Column studies demonstrate that the capacities of three local soils to remove benzene (at concentrations ranging between 22.4 and 36.4 mg/l) are greatly improved by tailoring with crystalline TMA^+. These capacities are 40 to 75% lower than predicted from batch studies possibly due to heterogenicity during tailoring process.

7. Breakthrough of TMA-tailored soils is predicted by conventional one-dimensional solute transport models. Both, molecular and mechanical diffusion must be considered to predict effectively effluent concentrations.

8. Soils tailored at TMA^+ doses as low as 50% of the CEC of the soil (in both column and batch applications) removed significant amounts of benzene from solution. Marginal improvement in adsorptive capacity occurs at doses greater than this value. Therefore 50% TMA:CEC ratios are recommended in treatment applications.

9. Preliminary results show that exhausted TMA-soils may be regenerated using solar radiation. No detectable loss in adsorptive capacity was observed in a soil that was regenerated using solar radiation for a period of one month.

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