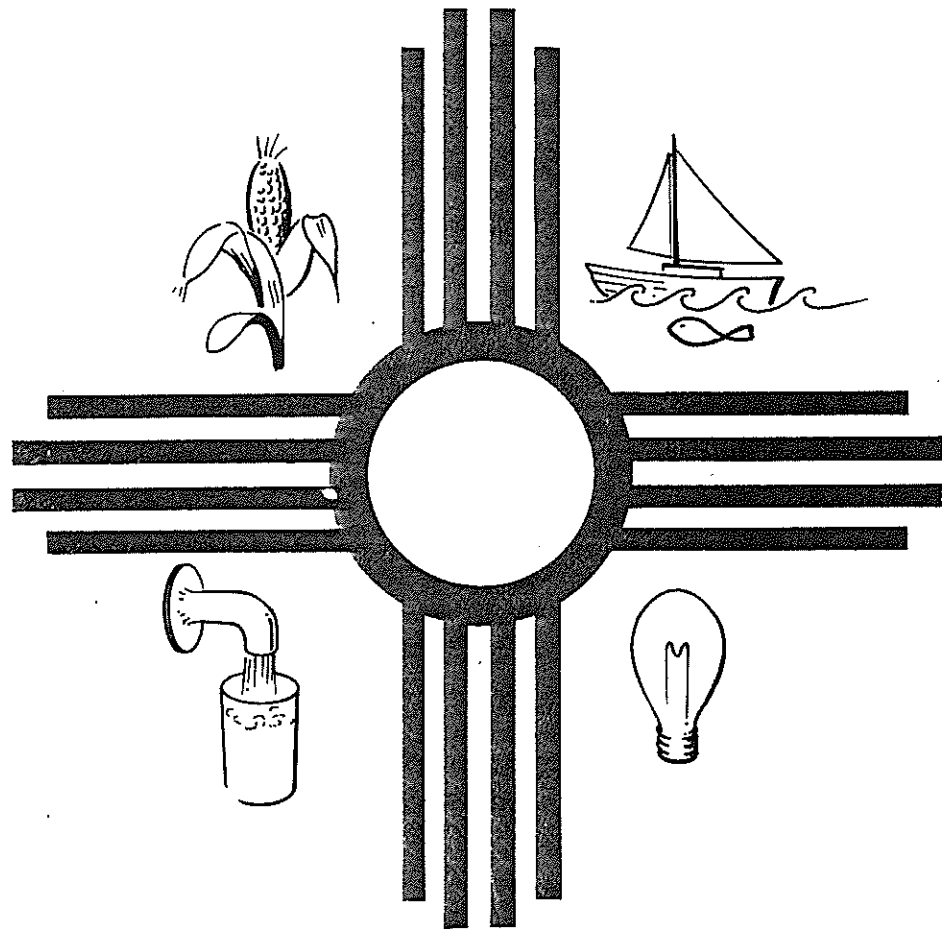


REGENERATIVE PROPERTIES OF SPENT TAILORED SOILS

Technical Completion Report

Project No. 1345690



New Mexico Water Resources Research Institute

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ABSTRACT

Natural clays have a large internal surface area potentially available for adsorption of hazardous organic compounds. The exchangeable cations in clay 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 pollutants. Therefore, the interlamellar area in clays is normally inaccessible to organic pollutants.

Adsorption of organic pollutants with low molecular weight onto natural soils may be greatly enhanced by chemical modification, that is, tailoring, of the clay fraction of the soil. Tailoring agents include tetraalkylamine compounds which can effectively replace the natural exchangeable cation in the clays. Prior studies show that the adsorption capacity of soils for benzene and toluene are greatly increased by tailoring with tetramethylammonium (TMA^+) cations.

Economic feasibility of using this process hinges on the potential to regenerate the spent soils. Regeneration by volatilization of the adsorbate was investigated for three different tailored soils: Wyoming bentonite, Glendale clay-loam, and a clay-loam soil collected in the Los Angeles area.

A 48 percent decrease from the original value of K (the linear adsorption constant) was observed for bentonite after six regeneration cycles. The Los Angeles soil showed no significant degradation in its adsorption capacity for benzene after six regeneration cycles. The Glendale soil decreased its K values 62 percent from the original value after the same number of regeneration cycles.

The adsorption capacity of tailored bentonite for toluene was reduced by 97 percent after six regeneration cycles. This decaying effect does not necessarily represent a decrease in equilibrium adsorption capacity. Rather, the kinetics of adsorption may play a significant role as the adsorbent becomes more granular after repeated regenerations. Adsorption studies with o-xylene showed minimal adsorption for both virgin and regenerated tailored bentonite. For this reason, no regeneration studies were performed with o-xylene.

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

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JUSTIFICATION OF WORK PERFORMED

Ground-water contamination by private and governmental facilities is common throughout the United States. Reported pollution cases involving hazardous waste spills have become quite numerous in recent years. The problem of ground-water pollution by leaking underground storage tanks became evident in the 1970s (Mates 1971, Williams and Wilder 1971, McKee, Laverty, and Hertel 1972).

It had been estimated that between 10 and 30% of the total number of underground gasoline storage tanks in the U.S. have leaked gasoline. These represents between 140,000 and 420,000 underground storage tanks (Connor 1988). This number is expected to increase by 350,000 over the next decade (Manko 1985). The environmental impact of these petrochemical products leaking into ground water is likely to increase in the same proportion.

The American Petroleum Institute reports that the nationwide average concentrations of benzene in regular and premium gasoline are 1.6 and 1.7%, respectively. However, concentrations as high as 5% have been reported in Atlanta, Georgia (Las Cruces Sun News 1990). In the state of New Mexico, gasoline contains approximately 3% benzene and 9-11% toluene. Xylenes in gasoline may be up to 10 to 12% by volume (Jercinovic 1984). Benzene has been selected by the New Mexico Health and Environment Department as an indicator for petroleum by-product 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. Benzene's solubilization from petrochemical products is of particular concern due to its carcinogenic, teratogenic, and leukemogenic properties (Laskin and Goldstein 1977). Consequently, the drinking water standard for this particular chemical is much lower than for other organics (1 $\mu\text{g}/\text{l}$).

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

The solution to contamination of ground-water supplies by petroleum derivatives is not simple. The most common techniques used to remove hazardous hydrocarbon derivatives from ground-water supplies are based on three principles: adsorption onto a solid phase, chemical oxidation, and volatilization by air stripping (Symons et al. 1981).

Air stripping, although simple, has limited applicability for removal of petroleum derivatives through volatilization since large volumes of air are required (Symons et al. 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 (VOCs) from a liquid phase. Thus, non-volatile compounds and heavy metals are not removable by this technique.

Chemical oxidation of trace toxic compounds represents a difficult alternative due to the refractory nature of a large number of key contaminants even with suitable compounds. For example, removal of trihalomethanes (THM) is not feasible, since oxidation reactions with THM occur only when ultraviolet light is used with strong oxidizing agents such as ozone and chlorine dioxide (Symons et al. 1981).

Various types of adsorbents have been tested experimentally for removal of organic compounds at trace concentrations from water. These adsorbents include granular and powdered activated carbon (DiGiano 1983), 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 treatment of contaminated water supplies. Using activated carbon can be expensive, though commonly it is less expensive than using synthetic resins.

Unfortunately, the three methodologies mentioned are non-selective for hazardous wastes removal. Common innocuous organics, which are typically present at much higher concentrations than hazardous pollutants, interfere with the treatment process. Consequently, significant capacity to remove hazardous wastes by adsorption and chemical oxidation is frequently reduced by competing non-hazardous substances.

Economic factors also impose important constraints on the nature of treatment selected and the degree of removal obtained.

Due to economic and other technological limitations, the three technologies discussed are not easily embraced in many cases. Thus, communities and other affected parties are often forced to abandon permanently their water supplies and to search for alternative water resources outside the contaminated area.

A crucial need exists to develop alternative treatment procedures for hazardous wastes removal that are efficient and economical. This research project addresses such needs by using technically and economically feasible technologies to remove selective hazardous wastes at the laboratory level. This technology involves the use of tailored soils as adsorbents that may reduce benzene removal costs in comparison with adsorption by granular activated carbon (GAC). Regeneration of tailored soils should reduce these costs even more making them more attractive than other conventional processes.

CHEMISTRY OF TAILORED CLAYS

The adsorption capacity of certain types of pollutants by most natural clays has been extensively studied (McBride, Pinnavaia, and Mortland 1977, Wolfe, Demirel, and Baumann 1985 and 1986). This capacity is directly related to the molecular arrangement of clays. Clays are a group of phyllosilicates with definite macroscopic and molecular properties that make them different from other types of silicates. They are composed of intercalated layers of silicon-oxygen (tetrahedral layer) and aluminum-oxygen (octahedral layer). In some clays, aluminum is replaced by magnesium, iron, or other metal ions. The relative number of each layer in the clay's structure defines a specific type of clay. In particular, montmorillonites consist of 1 aluminum-oxygen layer between 2 silicon-oxygen layers (2:1 relation).

In this kind of clay, some aluminum ions (Al^{+3}) are replaced by magnesium (Mg^{+2}). This kind of replacement is called isomorphic substitution that creates a negative charge in the clay that is balanced with additional ions, referred to as counterions, external to the silicon-oxygen layers. In the case of montmorillonite, these counterions are sodium.

The counterions, along with their hydrating water molecules, create a definite distance between adjacent silicon-oxygen layers, also referred to as interlamellar distance. In montmorillonites, the intensity of the charge in the intermediate layers, created by isomorphic substitution, and the resulting

interlamellar distance permits the penetration of polar molecules like water. Water molecules, penetrating the interlamellar region, surround the sodium counterions and enlarge the interlamellar distance to produce a swelling of the clay (see Figure 1A). This swelling also increases the internal surface area of the clay to values as large as 800 m²/g (Greenland 1965). The large surface area accounts for the excellent capacity of these materials to adsorb certain types of hazardous organic compounds.

If clays are used for adsorption of hydrophobic pollutants like BTX's (benzene, toluene, and xylenes), the water of hydration in the interlamellar space presents an adverse environment for this process. Small organic compounds with molecular weights below 150 amu are weakly adsorbed or not adsorbed by pure montmorillonites due to their relatively large solubility in water (unless they carry a charge and can enter into ion exchange reactions with the counterions).

Recent studies show that montmorillonite may be tailored using an organophilic cation in order to yield materials that strongly adsorb low molecular weight organic molecules. These organophilic cations are exchanged with natural counterions of the clay.

Recent works (Boyd, Mortland, and Chiou 1988, Jeffers 1985, McBride, Pinnavaia, and Mortland 1977, Cadena and Jeffers 1987, Cadena 1989, Wolfe, Demirel, and Baumann 1985, Lara 1990, and Cadena, Garcia, and Peters 1990) have shed light on the nature of clays tailored with organophilic cations. Preparation of tailored

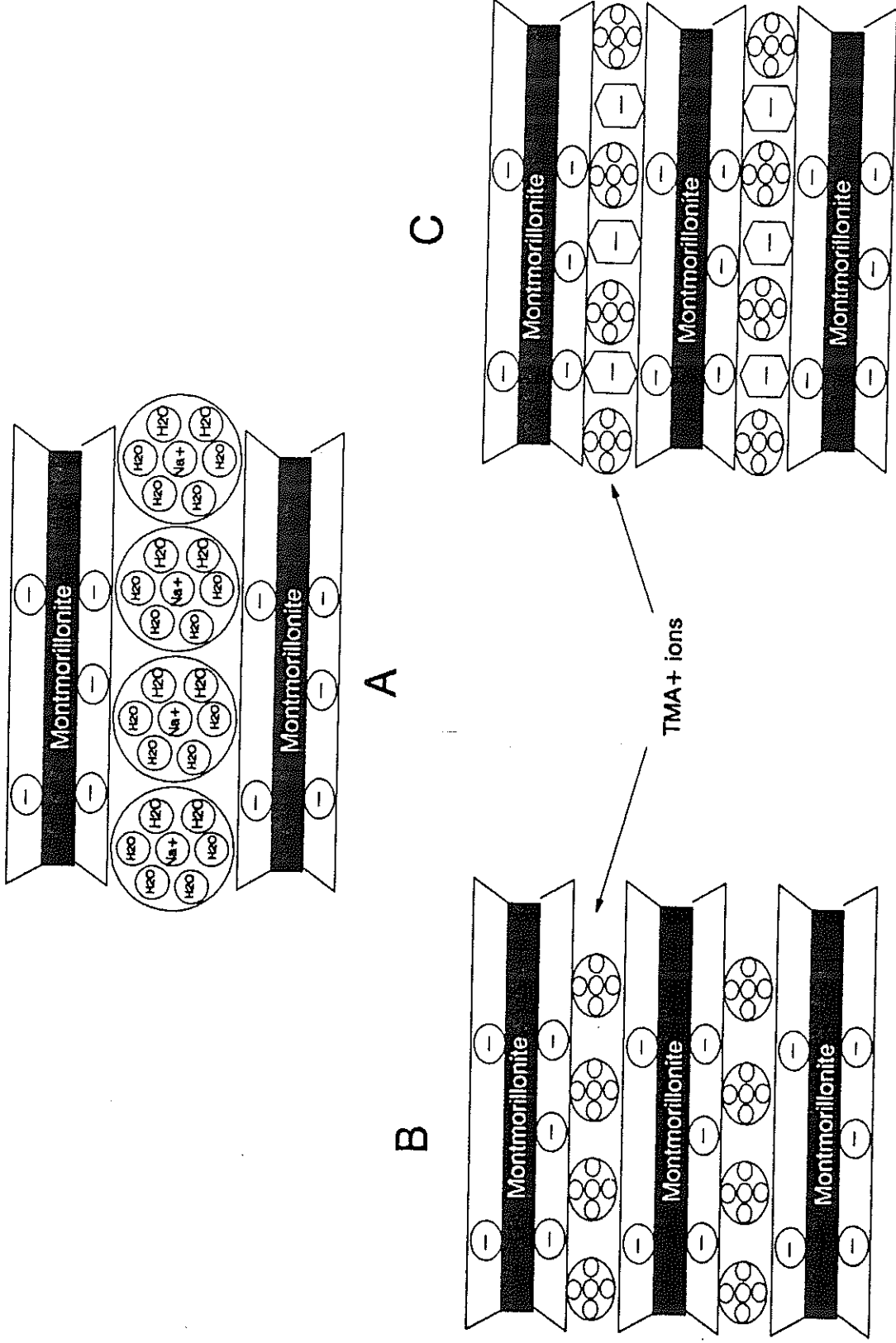


Fig. 1 A. Hydrated Sodium Montmorillonite. B. TMA Tailored Montmorillonite
 C. TMA Saturated Montmorillonite with Benzene

clay adsorbents requires carefully selecting the cationic tailoring agent. Different coatings generate significantly varied adsorption constants. In principle, a family of adsorbent materials might be tailored to fit the steric properties of a particular pollutant.

Using pure montmorillonite as an adsorbent is unlikely in practical applications due to difficulties associated with separation and purification of montmorillonite from the clay mineral source. On the other hand, the availability, high montmorillonite content (up to 80% by weight), and the low cost of Wyoming bentonite favored its selection in this investigation. Two soils, one from Los Angeles, California and the local soil Glendale clay, were also studied to determine if regional soils have also effective adsorptive properties.

The tailoring agent selected in the experimental studies was TMA⁺ (Tetramethylammonium ion), which is highly compatible with benzene (McBride, Pinnavaia, and Mortland 1977). Commercial TMA salt anions include chloride, iodide, and perchlorate. Chloride TMA salt was selected. TMA presents the following advantages over other organophilic compounds:

- a) The TMA⁺ radical undergoes a strong ion exchange reaction with the natural cation in the clay.
- b) Since the contribution of Van der Waals forces decrease rapidly with distance, their effect would be greatest for those ions in close contact with the clay surface. The small

and spherically shaped TMA^+ ions fulfill this requirement, as illustrated in Figure 1B.

- c) TMA exchanged montmorillonites are sodium free. Also, due to the strong electrostatic interaction between the clay and the TMA^+ ion, the resulting tailored montmorillonite is highly coagulating, and non-expansive. Thus, separation of the spent adsorbent from the treated product does not cause technical difficulties.
- d) The large surface area in the basal spaces, which are crucial for effective adsorption, becomes readily available to adsorbates once the naturally occurring cations are exchanged by TMA cations. This phenomenon is illustrated in Figure 1C, where benzene (the adsorbate), occupies the basal space between the TMA molecules.

The feasibility of adsorption of low molecular weight contaminants using tailored clays has been demonstrated in recent studies (Jeffers 1985, Cadena and Jeffers 1987, Wolfe, Demirel, and Boumann 1985, Lara 1990, and Cadena, Garcia, and Peters 1990). However, the economical aspects of the process have not been analyzed. The possibility of using the same tailored soil for adsorption of pollutants from water several times may be an attractive alternative over other common adsorption processes. This investigation aims to determine the feasibility and the optimal conditions of time and temperature needed to accomplish the regeneration of tailored soils for its repetitive use as adsorbents of organic pollutants.

EXPERIMENTAL PROCEDURES

Stock soil suspensions were prepared by adding 10 g of Wyoming bentonite or 100 g of the soils (Los Angeles or Glendale) to 1 liter of tap water. Wyoming bentonite was obtained through a commercial distributor of drilling well supplies. The suspensions were stirred over a 24-hour period using a magnetic stirrer and a magnetic stirring bar. Varying amounts of the tailoring agent, TMA-Cl, were then added to the suspensions. The soil suspensions tailored with the TMA-Cl were stirred for an additional 24-hour period. Thirteen-milliliter volume test tubes containing two glass beads were filled with the tailored soil suspension. The pollutant to be tested was added to the test tubes using a Jet Pipet to yield the desired initial concentration. A layer of Saran Wrap was placed over the tubes to act as a septum. At this time, trapped air was completely displaced. Then, the tubes were sealed with Teflon caps to minimize volatilization losses.

The tubes were placed in a revolving apparatus and turned at 20 rpm for 5 min. Solids were separated from the liquid phase by centrifugation at 2000 rpm for 10 min. A 5 ul sample was taken from the supernatant of each tube with a microsyringe. The sample was then injected into a gas chromatograph apparatus using direct aqueous injection to measure the supernatant concentration of the pollutant.

The gas chromatograph was equipped with an OV-101 column and a flame ionization detector. The operation parameters of the gas

chromatograph are shown in Table 1. The chromatograph was calibrated prior to each test run by injecting samples of known pollutant concentration from test tubes containing no soil suspension. Data generated by the gas chromatograph were transmitted to a microcomputer which compiled and interpreted the experimental information.

TABLE 1
Gas Chromatograph Operation Parameters

<u>Parameter</u>	
Oven temperature	70 ^o C
Detector temperature	200 ^o C
Injector temperature	200 ^o C
Nitrogen flow (ml/min)	8.5
Hydrogen flow (ml/min)	65
Air flow (ml/min)	220

Physical and Chemical Properties of the Soils

The physical and chemical properties of the different soils were determined by the Soil, Water, and Plant Testing Laboratory at New Mexico State University. Some of these properties are shown in Table 2.

Isotherm Tests

Varying amounts of TMA-Cl were added to the soil suspensions. The amounts of TMA-Cl used were 0%, 10%, 20%, 40%, 60%, 80%, and 100% of the cation exchange capacity (CEC) of the soil. To each tailored soil suspension, varying amounts of

TABLE 2
Properties of the Soils

Soil	CEC* (meg/100g)	Soil fraction (%)			Organic matter (g/kg)
		Sand	Silt	Clay	
Bentonite	72.9	0	0	100	< 0.10
Glendale	21.8	40	26	34	0.65
Los Angeles	13.27	29	35	36	0.02

* cation exchange capacity

pollutant were added. The range of pollutant concentrations varied from 0 to 130 mg/l for benzene and from 0 to 50 mg/l for toluene. These tests were performed to find the optimal amount of the tailoring agent, TMA-Cl, that should be added to the soil suspensions to provide the maximum adsorption capacity in the soil.

Preliminary Tests

In these tests, bentonite was the adsorbent soil and benzene was the targeted contaminant. The TMA-Cl added to the soil suspension was 100% of the bentonite's CEC, as was determined from the isotherm tests, and the benzene's concentration was 55 mg/l. After injecting the contaminated supernatant into the gas chromatograph, the rest of the supernatant was removed from the tubes and the compacted soil was spread throughout the tubes by manual agitation. The soil in the tubes was then dried at different temperatures, to allow the pollutant volatilization. These tests were carried out with different drying times.

After drying, the tubes were refilled with tap water. The soil was resuspended by hand shaking until no granules were observed. The tubes were sealed, mixed, and centrifuged according to the procedure described previously. Once again the supernatant concentration of the pollutant was measured using the gas chromatograph.

The amount of pollutant remaining in the soil was calculated according to the procedure indicated in the results section using the measured equilibrium concentration of the pollutant in the liquid phase. These tests were run to find the optimal combination of regeneration temperature and drying time to maximize the pollutant volatilization from the soil so that the soil may be reused.

Regeneration Tests

In these tests, the amount of TMA-Cl added to the soil suspensions was 100% of the bentonite's CEC and 40% of the CEC for the soils (Los Angeles and Glendale). The concentration of the contaminant used was 55 mg/l for benzene and 20 mg/l for toluene. The sealing, mixing, and centrifugation of the tubes was accomplished following the procedure described previously. The concentration of the pollutant in the supernatant was then measured. The supernatant was removed from the tubes and the compacted soil was spread throughout the tubes by manual agitation. The tubes were placed in an oven at 35°C for two days to allow pollutant volatilization. The tubes containing the dried soil were refilled with tap water, and the original concentration

of the pollutant was also added. The soil was resuspended by hand shaking until no granules were visible. The tubes were sealed, mixed, and centrifuged. The concentration of the pollutant in the supernatant was measured. This regeneration process was repeated up to six cycles for the same soil sample.

A set of control tubes was run at the same time. After each regeneration cycle, some of these control tubes were not re-injected with the contaminant. Instead, they were refilled with tap water only, to verify if all the pollutant that could be desorbed from the soil had been evaporated. (Some contaminant could still remain in the soil and not be detected in solution if its concentration was below the detection limit of the gas chromatograph. However, the main concern of this project is the reuse of the soil in aqueous suspensions. Therefore, the objective is the detection of the pollutant in water).

RESULTS

Isotherm Tests

Isotherm tests were conducted to find the optimal amount of the tailoring agent, TMA-Cl, to be added to the soil suspensions to produce the soil's maximum adsorption capacity. In these tests, soil suspensions were tailored with different amounts of TMA-Cl, and the test tubes were injected with different amounts of contaminant for each tailored soil suspension. The linear isotherm model was used as the adsorption simulation. For this model:

$$x/m = K C_e \quad (1)$$

where x = amount of pollutant adsorbed in the soil (mg)

m = amount of soil (g)

K = linear adsorption constant, or partition coefficient
(l/g)

C_e = equilibrium concentration of the pollutant in the liquid phase (mg/l)

The values of the linear adsorption constant were used as a measure of the soil's adsorption capacity. Figure 2 shows the values of K vs TMA^+ for the adsorption of benzene using bentonite. This figure shows that little improvement in the adsorption capacity of the bentonite, that is, K , is observed after 60% of the CEC of TMA^+ . The same effect was observed in previous work (Cadena 1989, and Cadena, Garcia, and Peters 1990).

When the amount of TMA-Cl added to the soil suspension is increased within the range of values below the soil's CEC, an

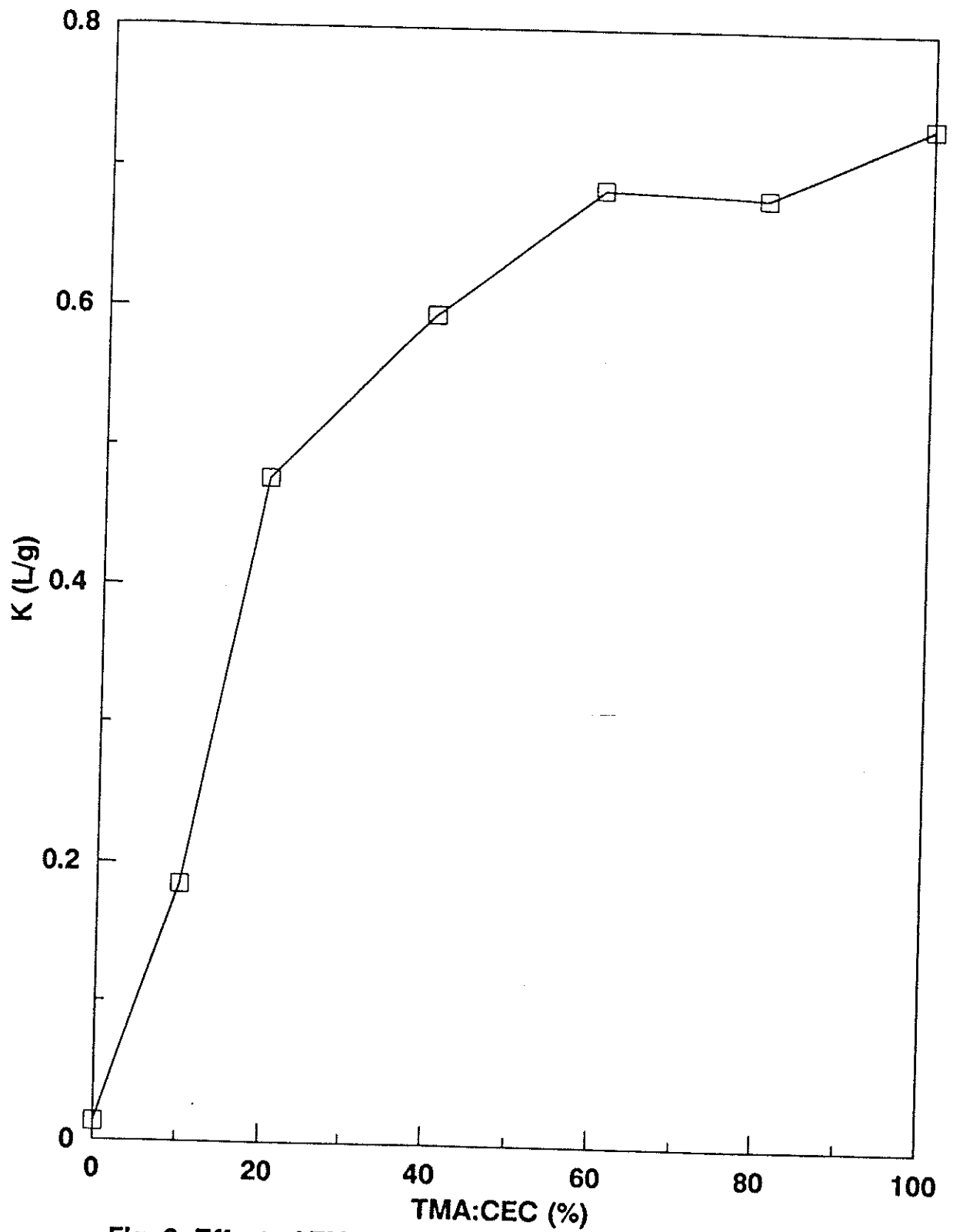


Fig. 2 Effect of TMA Dose on Benzene Adsorption Using Bentonite as Adsorbent

increasing number of TMA^+ ions are exchanged with the natural sodium ions between the clay's silicate plates. The affinity of these TMA^+ ions with the benzene molecules, and the limited space that they create between the silicate plates may explain the bentonite's increasing adsorption capacity of benzene.

An increasing number of TMA^+ ions remain in solution when the amount of TMA-Cl added to the soil suspension approaches the soil's CEC. The dissolved TMA^+ ions compete for benzene molecules with the TMA^+ ions exchanged in the clay. Also the TMA^+ ions exchanged are not distributed in optimal arrangement in the clay. Consequently, some of these ions could hinder adsorption of benzene between clay plates. These two phenomena along with the increasing number of benzene molecules adsorbed in the soil may explain the marginal improvement in the adsorption capacity for benzene as the amount of TMA^+ added approaches the soil's CEC.

The values of K vs TMA^+ for the adsorption of toluene using bentonite are shown in Figure 3. The pattern of this adsorption process is very similar to the adsorption of benzene. The same explanations given above could also explain this process. Comparing the K values on Figures 2 and 3, the values for benzene adsorption are about 10 times greater than the values for the adsorption of toluene.

This significant difference supports the model of adsorption on tailored clays proposed in previous works (Cadena 1989, and Lara 1990). The tailoring agent, TMA^+ in this case, creates a fixed interlamellar distance in the clay. This distance between

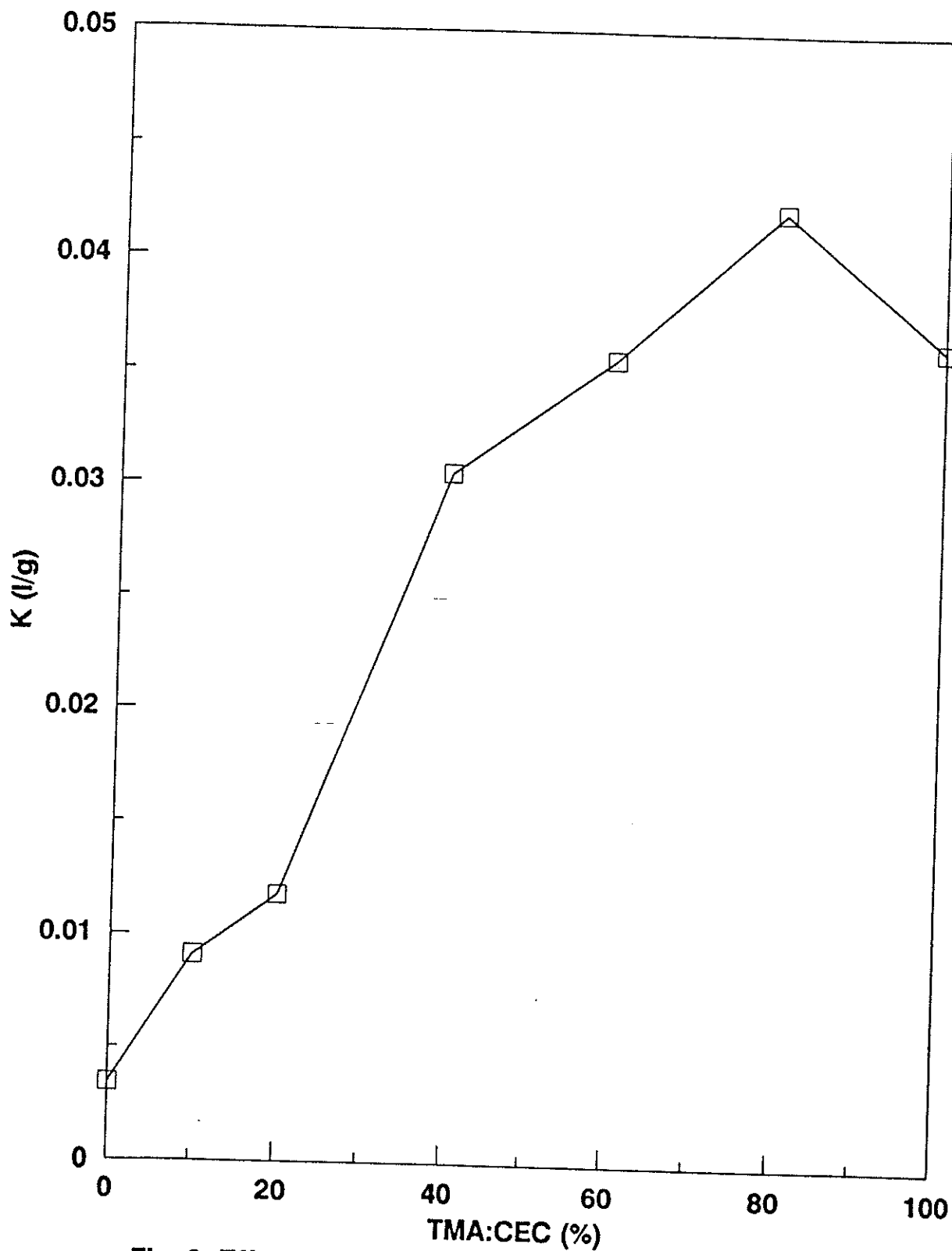
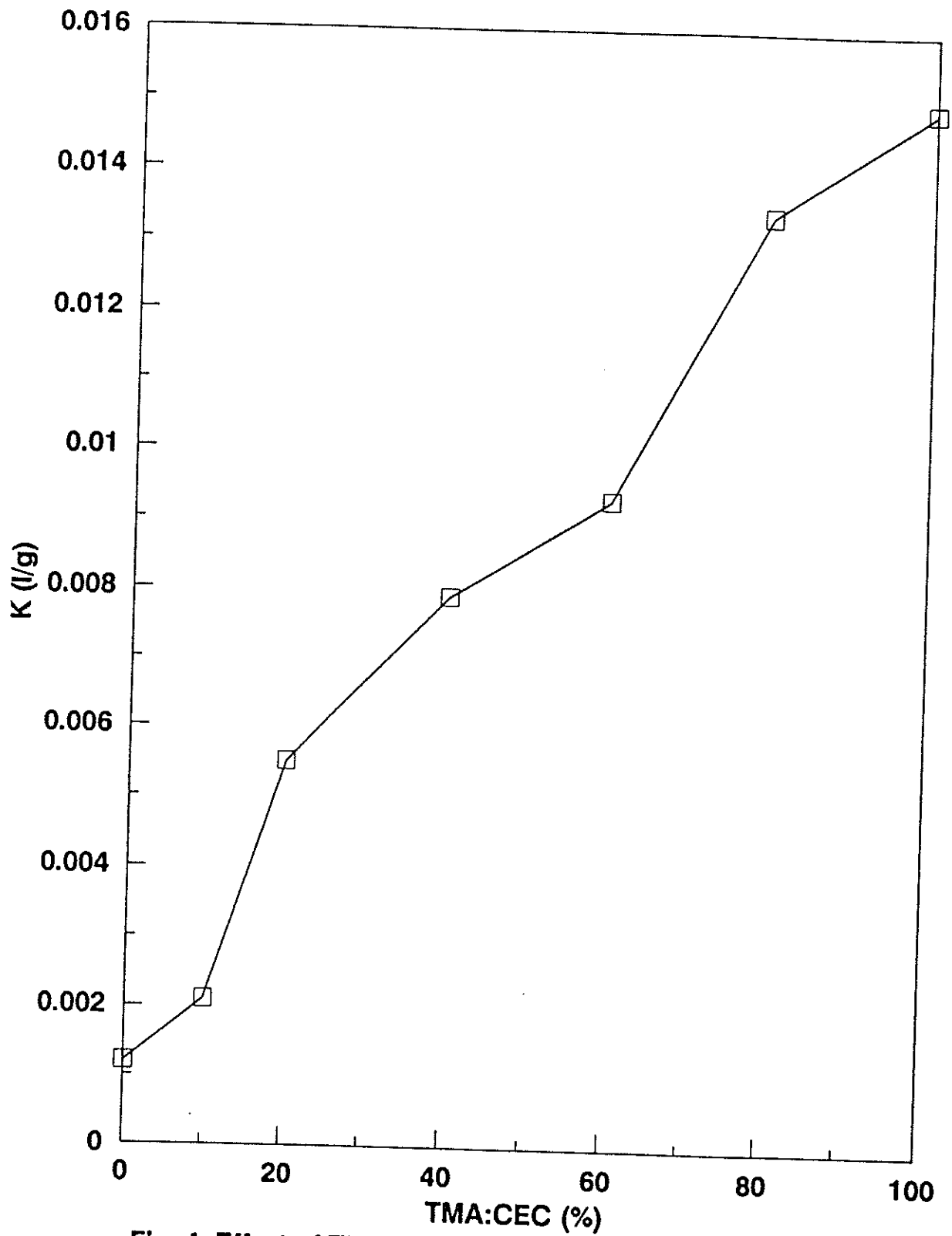


Fig. 3 Effect of TMA Dose on Toluene Adsorption Using Bentonite as Adsorbent

clay plates permits the selective adsorption of contaminants. Molecules equal or smaller in size than the interlamellar distance will be more readily adsorbed than molecules larger than the interlamellar distance. In other common adsorption processes, like adsorption using GAC, these adsorption trends are reversed. Larger molecules are adsorbed more easily than smaller ones of the same family. This difference makes the adsorption of contaminants using tailored soils a selective process.

Based on these results, the amount of TMA^+ selected for further use in the regeneration tests was 100% of the bentonite's CEC. This amount provides the maximum adsorption capacity in the bentonite for both benzene and toluene. Also, at this concentration of TMA^+ , 100% of the bentonite's CEC, the values of K show little variation from its maximum (see Figures 2 and 3). The isotherms for bentonite suspensions using o-xylene as the contaminant (at initial concentrations of 12 mg/l) were below the detection limit of the gas chromatograph. For this reason o-xylene was not further used in the regeneration tests.

Isotherms for the adsorption of benzene and toluene using the Los Angeles soil as adsorbent were also performed. The values of K against the amount of TMA^+ added are shown for benzene and toluene in Figures 4 and 5. The general pattern of the curve in Figure 5 is similar to that of bentonite. Little improvement is achieved in the adsorption capacity of the soil for toluene at doses higher than 40% of the soils' CEC. For this reason, this



**Fig. 4 Effect of TMA Dose on Benzene Adsorption
Using Los Angeles Soil as Adsorbent**

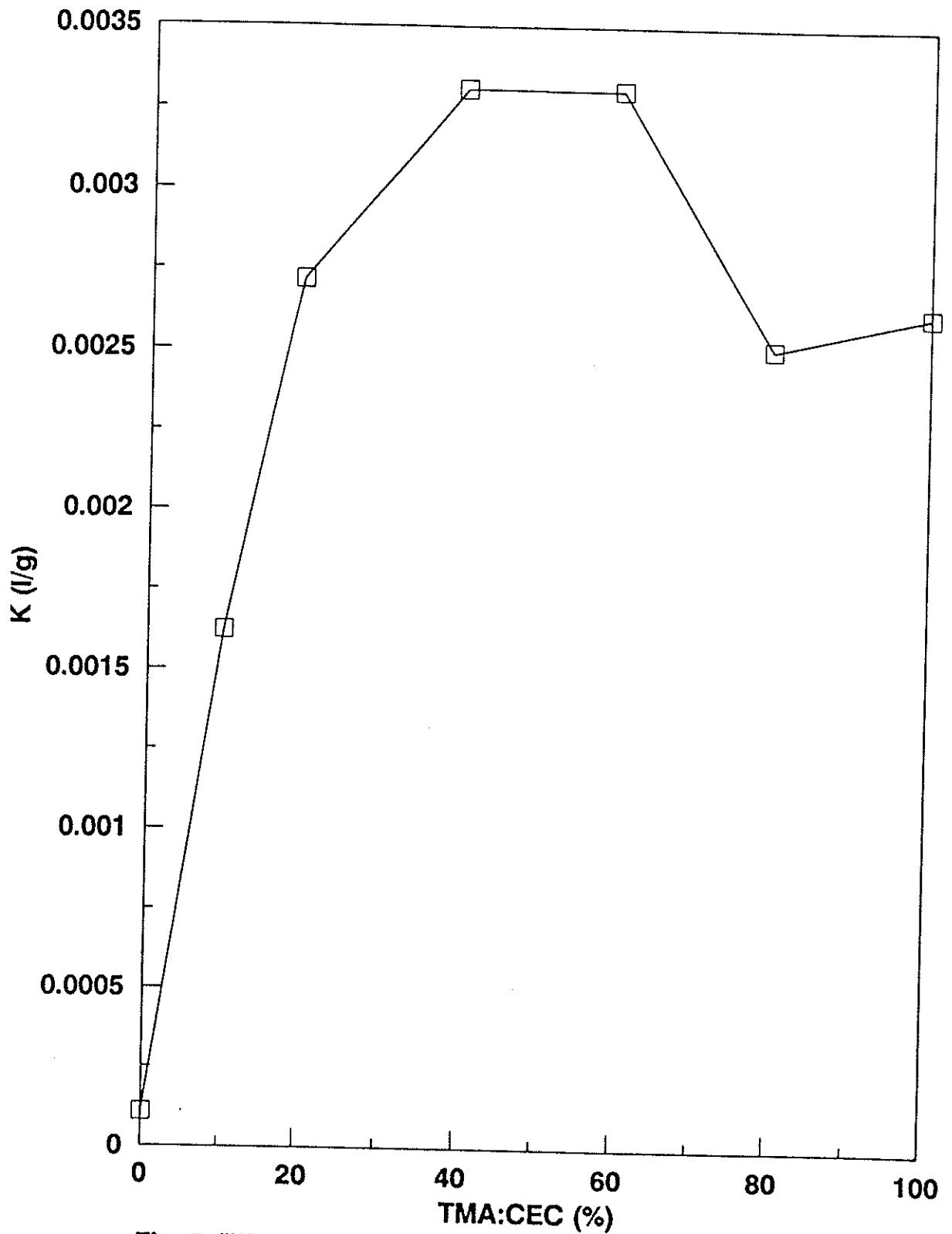


Fig. 5 Effect of TMA Dose on Toluene Adsorption Using Los Angeles Soil as Adsorbent

concentration was used for the Los Angeles soil in all regeneration tests.

The amount of TMA+ used for the regeneration of the Glendale soil was based on previous research results (Cadena 1989). This amount was 40% of the soil's CEC.

Preliminary Tests

The objective of these tests was to determine the temperature and drying time required for complete pollutant volatilization from the soil between regeneration cycles. These conditions were then used in further regeneration tests. Bentonite was used as the adsorbent soil and benzene as the contaminant in all tests. The concentration of benzene used in the test tubes was 55 mg/l and the amount of TMA-Cl added to the soil suspension was 100% of the bentonite's CEC.

Assuming a complete liquid-solid separation, the mass of benzene adsorbed by the bentonite in each test tube was calculated using the following equation:

$$x_{b1} = x_T - x_{s1} \quad (2)$$

where: x_{b1} = mass of benzene adsorbed in bentonite before the drying process (mg)

x_T = total mass of benzene added to each tube (mg)

x_{s1} = mass of benzene in the supernatant before the drying process (mg)

The values of x_{s1} were evaluated according to the following expression:

$$x_{s1} = V_t C_e \quad (3)$$

where: V_t = volume of the liquid phase in the test tube(l).

C_e = equilibrium concentration of the pollutant in the liquid phase (mg/l).

The value of x_{b1} is the mass of benzene that remains in the soil after the supernatant is removed and before the drying process is started. The linear adsorption constant is calculated using the following expression:

$$K = \frac{x_{b1}/m}{C_e} \quad (4)$$

After the drying time, the tubes were refilled with tap water and the soil was resuspended by hand shaking. The benzene concentration in the supernatant of each tube was then measured using gas chromatography. This concentration was used to calculate the amount of benzene that remained in the soil after the drying time and before the tube was refilled with water using the following expression:

$$x_{b2} = K C_{ei} m + x_{s2} \quad (5)$$

where: x_{b2} = mass of benzene in the bentonite after the drying process and before the tube was refilled with water (mg)

C_{ei} = equilibrium concentration of the pollutant in the liquid phase after the i th cycle of use (mg/l)

x_{s2} = mass of benzene in the supernatant after the drying process and after the tube was refilled with tap water (mg)

Finally, the percentage of benzene that remained in the soil after the drying time was evaluated according to:

$$\% \text{ of benzene remaining in the soil} = (x_{b2}/x_{b1}) 100 \quad (6)$$

Table 3 shows the percentage of benzene remaining in the contaminated and dried bentonite at different temperatures and drying times.

The general trend observed in Table 3 is that the benzene remaining in the soil diminished, as expected, when the drying time was increased. Also, as expected, the benzene remaining in the soil at 35°C after drying for 24 hours was greater than at 45°C for the same drying time.

TABLE 3
Percent Benzene Remaining in Bentonite after Different
Temperatures and Drying Times

Temperature	Drying Time (hr)	Benzene remaining in soil (%)
80°C*	1	69
	2	56
	3	40
	4	45
45°C**	24	0
	46	0
	70	0
35°C**	23	15
	47	0
	71	0

* Soil Conc.= 3 g/l

** Soil Conc.= 10 g/l

Table 3 also shows that no detectable benzene remains in the soil after two-days drying time at any temperature above 35°C. Thus, 35°C and two-days drying time were the selected conditions for further regeneration tests. Table 3 shows that no benzene remained in the soil after 47 and 71 hour drying time at 35°C. Because no benzene was detected in solution, the mass of benzene

in the soil calculated with equation (5) was zero. However, benzene traces are theoretically expected to remain in the soil.

Regeneration Tests

The goal of these tests was to evaluate the adsorption capacity of benzene and toluene by the different tailored soils after the contaminants had been adsorbed and volatilized several times. In these tests, the test tubes containing the dried soil were refilled with the contaminant after the drying time. The concentrations used are shown in Table 4. The regeneration studies were carried out at 35° C for two-days drying time. Two drying times of two and three days were used only in the case of bentonite and benzene.

TABLE 4
Pollutant Concentrations Used in Regeneration Tests

Soil	Soil conc. (g/l)	Amount of TMA+ as % of the CEC	Contaminant	Conc. of the contaminant (mg/l)
Bentonite	10	100	Benzene	55
	10	100	Toluene	20
Glendale	100	40	Benzene	55
Los Angeles	100	40	Benzene	55

The linear adsorption constant, K , was evaluated after each regeneration cycle using the following equation:

$$K_i = \frac{x_i/m}{C_{oi}} \quad (7)$$

where x_i = mass of contaminant adsorbed in soil after the i^{th} cycle of use (mg)

C_{oi} = equilibrium concentration of the pollutant in the supernatant after the i^{th} cycle of use (mg/l)

K_i = linear adsorption constant of the soil after the i^{th} cycle of use (l/g).

After six regeneration cycles (with two-days drying time) the values of K for bentonite and benzene decreased about 40% from their initial value as shown in Figure 6. The regeneration of bentonite for the adsorption of benzene was also tested using three-days drying time between regeneration cycles. The K values for this case were similar to those using two-days between regeneration cycles as shown in Figure 7.

The removal efficiency of the contaminant from the liquid phase is another parameter that could be used for the evaluation of the soil's adsorption capacity. This efficiency can be calculated as a function of the total mass of pollutant added to each tube, x_T , according to:

$$R.E._i(\%) = x_i/x_T (100) \quad (8)$$

where $R.E._i$ is the removal efficiency of the contaminant as a percentage after the i^{th} cycle of use.

The values of the bentonite's removal efficiency for the adsorption of benzene using two and three days between regeneration cycles are shown in Figures 8 and 9, respectively. In these cases, the removal efficiency decreased only about 13% of its initial value after six and four regeneration cycles, respectively.

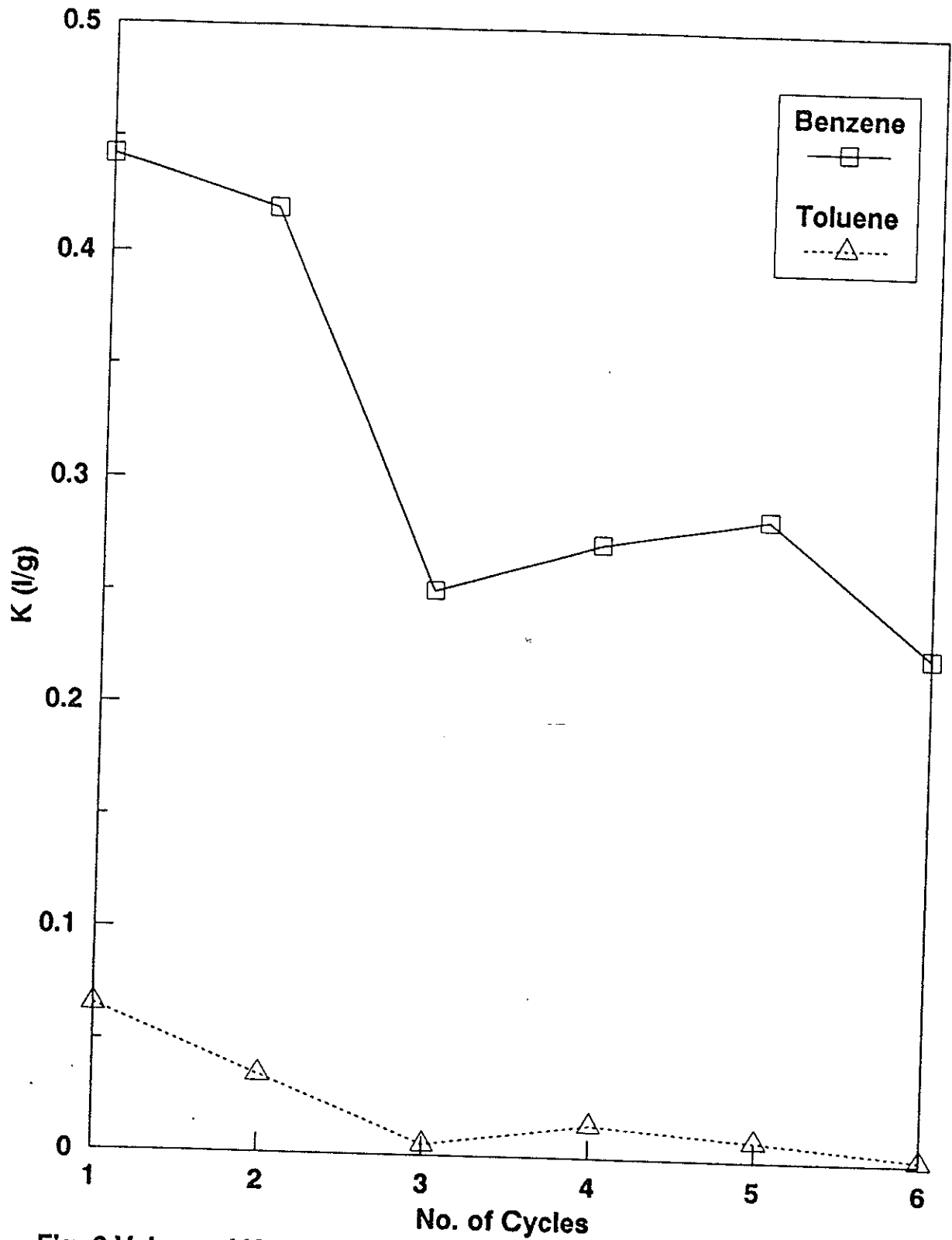


Fig. 6 Values of K vs No. of Cycles for Benzene and Toluene with Two Days Drying Time at 35°C Using Bentonite as Adsorbent

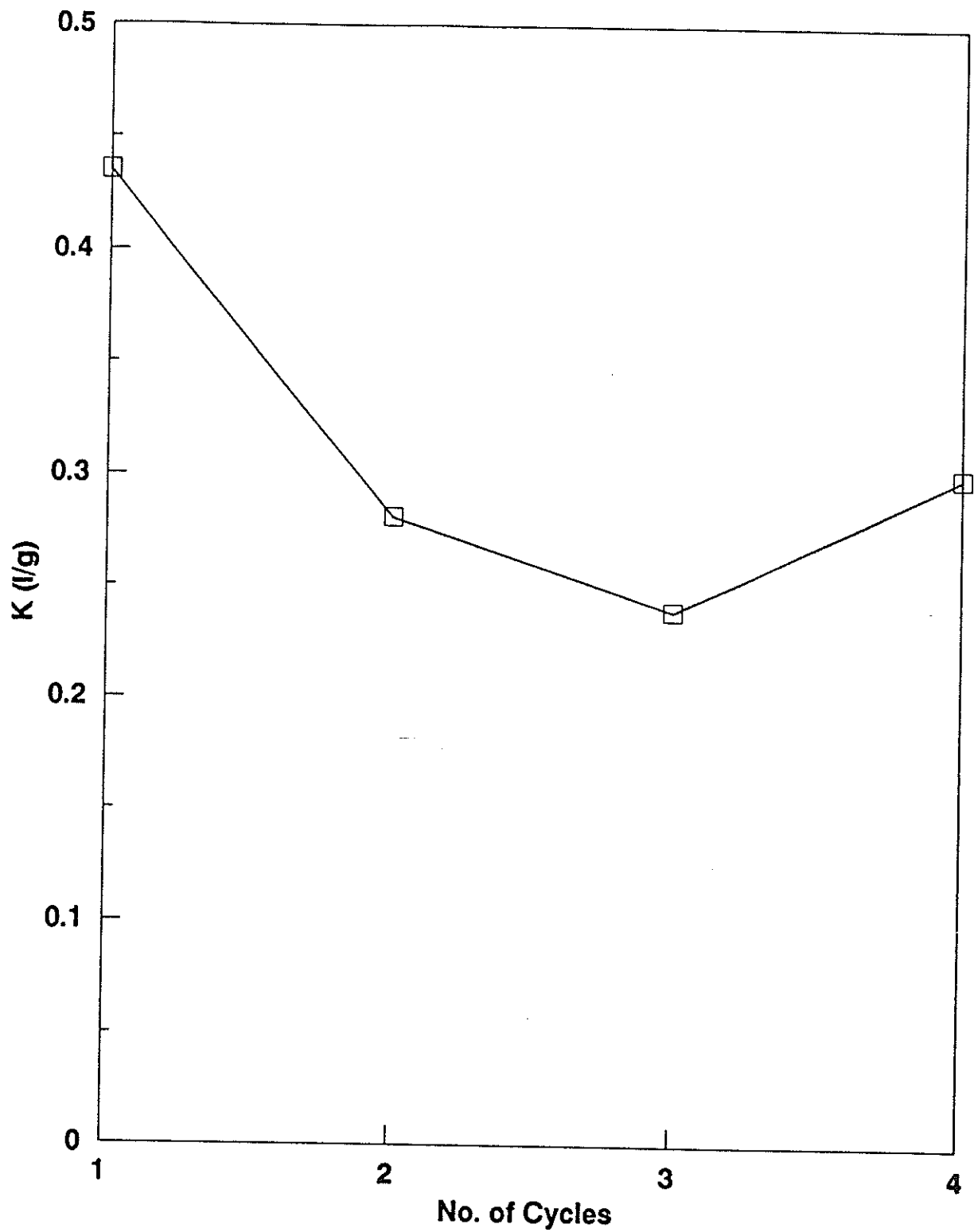


Fig. 7 Values of K vs No. of Cycles for Benzene with Three Days Drying Time at 35oC and Bentonite as Adsorbent

However, the bentonite's adsorption of toluene showed different behavior. Its adsorption capacity dramatically decreased after each cycle of use in this case. The K values and the removal efficiency for each regeneration cycle are plotted in Figures 6 and 8.

The K values for the bentonite's adsorption of benzene are greater than the K values for its adsorption of toluene. As stated earlier, this finding supports the model of adsorption of tailored clays based on the interlamellar distance created by the tailoring agent.

The significant decrease in the bentonite's adsorption capacity of toluene is not well understood, and merits further research. A possible explanation of this decrease could be related to the kinetics of the adsorption process. As the number of regeneration cycles increases, the bentonite becomes more difficult to resuspend.

After six cycles of use it became impossible to resuspend all the clots completely, and some soil remained attached to the walls of the tubes. As the soil particles became greater, the contaminant molecules took more time to be adsorbed into the soil flocs. If the time between the addition of the contaminant and measurement by the gas chromatograph is not sufficient for the completion of the process, some toluene will remain in solution. This could explain the low toluene adsorption after two cycles of use, when the soil particles tend to aggregate after the drying process.

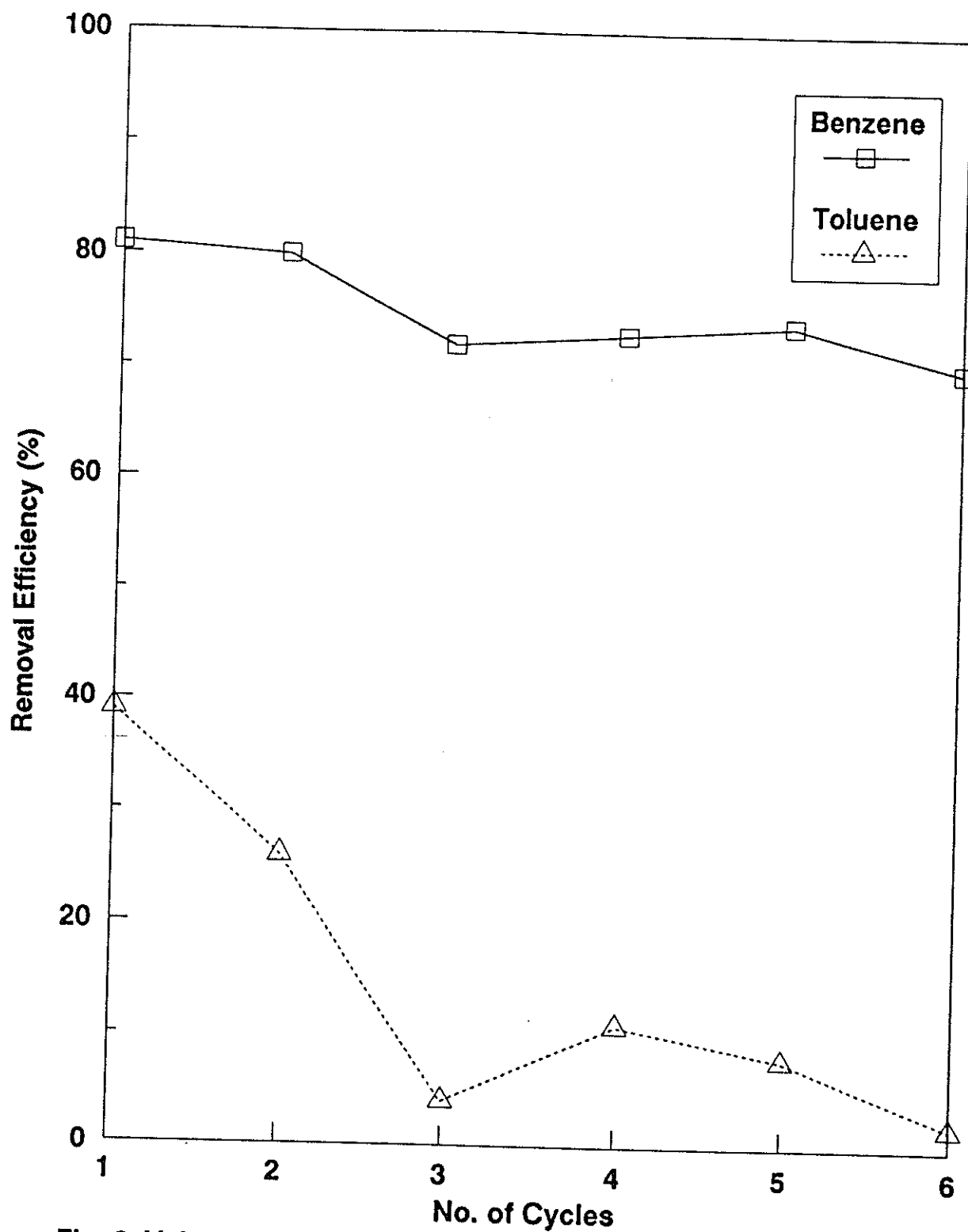


Fig. 8 Values of Removal Efficiency vs No. of Cycles for Benzene and Toluene with Two Days Drying Time at 35oC Using Bentonite as Adsorbent

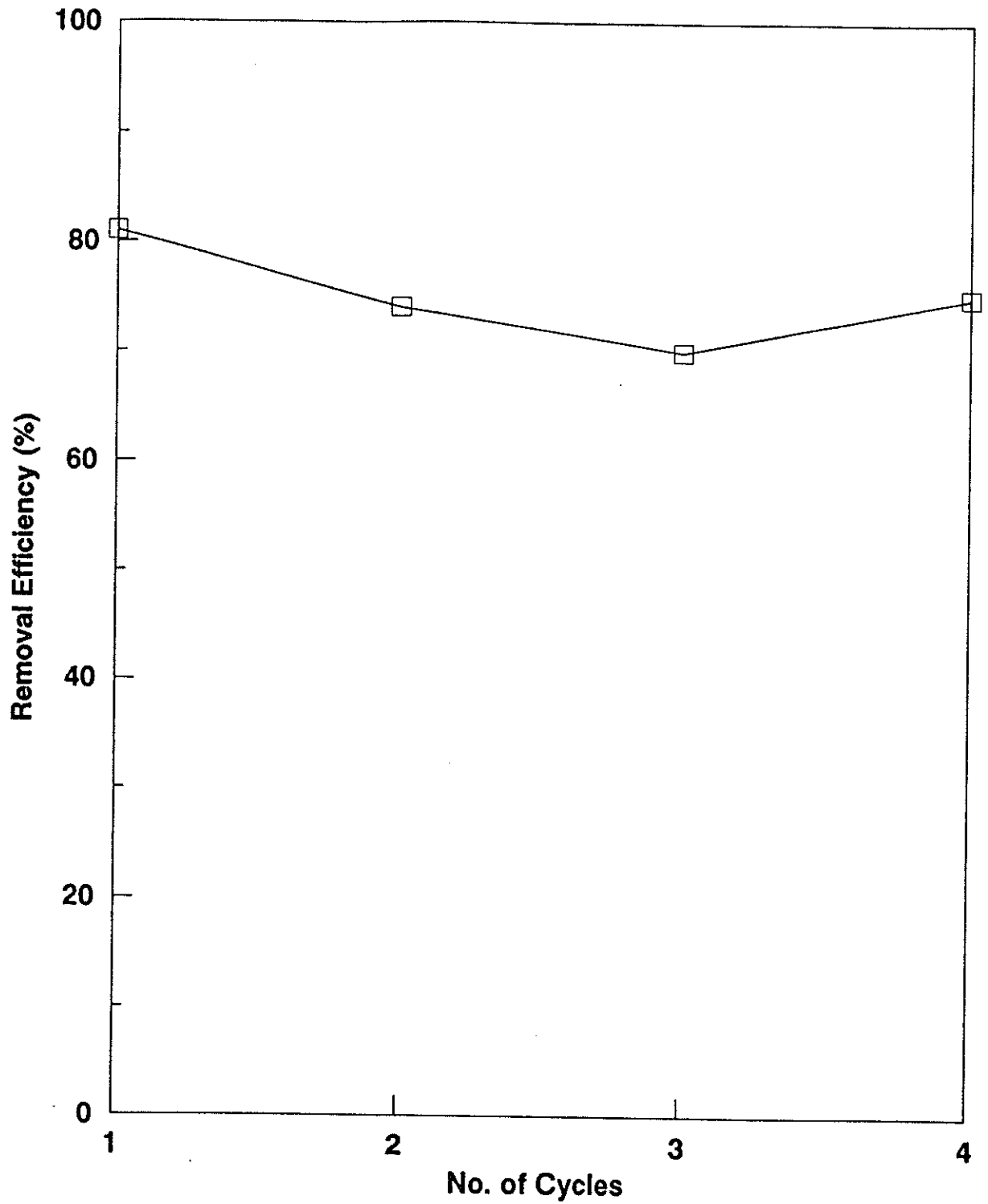


Fig. 9 Values of Removal Efficiency vs No. of Cycles for Benzene with Three Days Drying Time at 35oC Using Bentonite as Adsorbent

Further research is needed to find how the different mechanisms involved in the adsorption process affect this phenomenon. This also will yield a better understanding of the adsorption process by tailored soils. The Los Angeles soil's adsorption capacity of benzene showed no decrease with use of the soil.

The K values and the removal efficiency for each regeneration cycle for Los Angeles soil are plotted in Figures 10 and 11. The increment in this soil's adsorption capacity in the last cycle is possibly due to experimental variation rather than a real increment. The K values and the removal efficiency of benzene by the Glendale soil for each regeneration cycle are shown in Figures 12 and 13.

The Glendale soil's adsorption capacity was reduced to about 60-70% of its initial value. The resuspension of this soil was also difficult to achieve completely with the increasing number of cycles. Also in this case, the kinetics of the adsorption process may explain the decaying effect of adsorption.

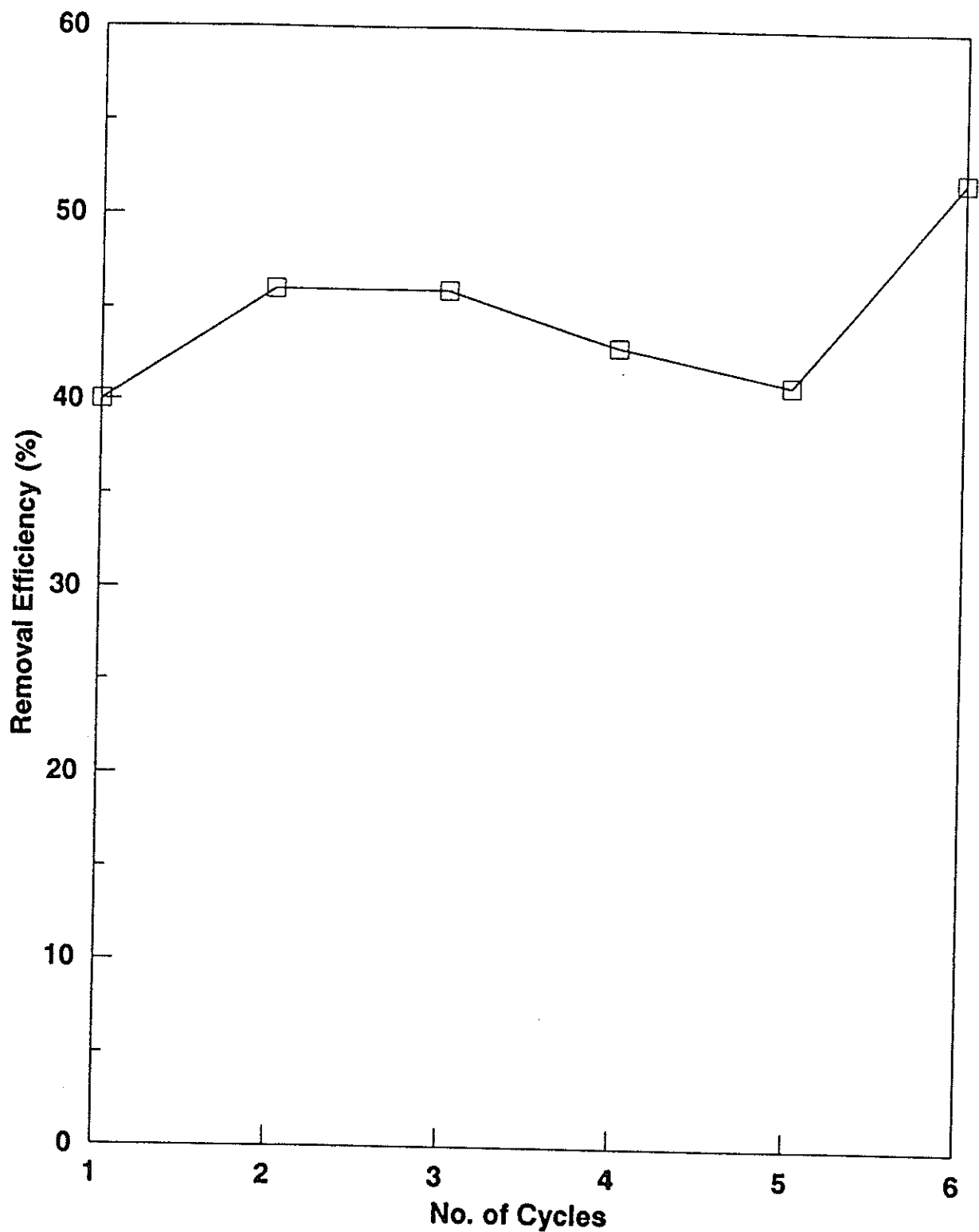


Fig. 11 Values of Removal Efficiency vs No. of Cycles for Benzene with Two Days Drying Time at 35°C Using Los Angeles Soil as Adsorbent

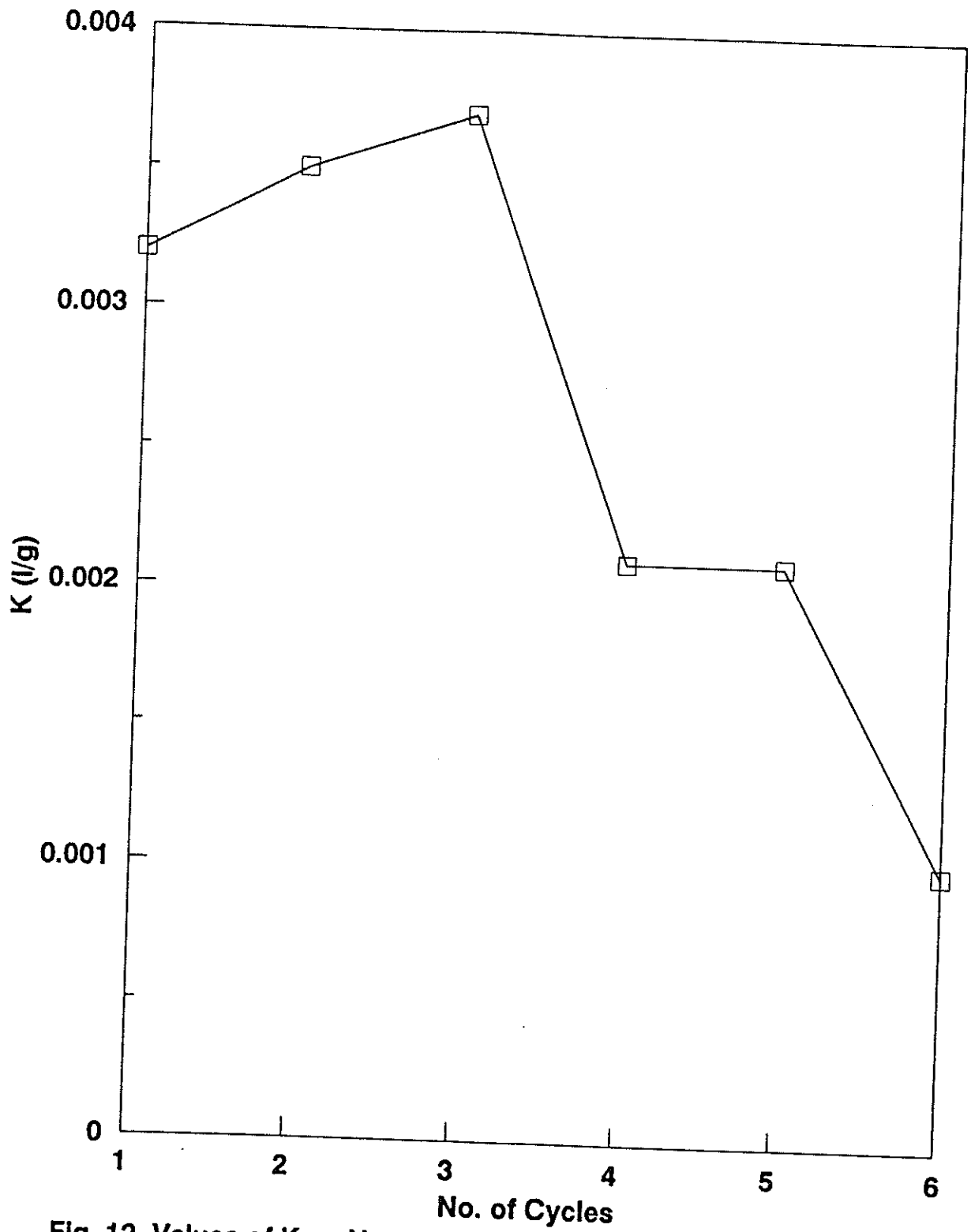


Fig. 12 Values of K vs No. of Cycles for Benzene with Two Days Drying Time at 35oC Using Glendale Soil as Adsorbent

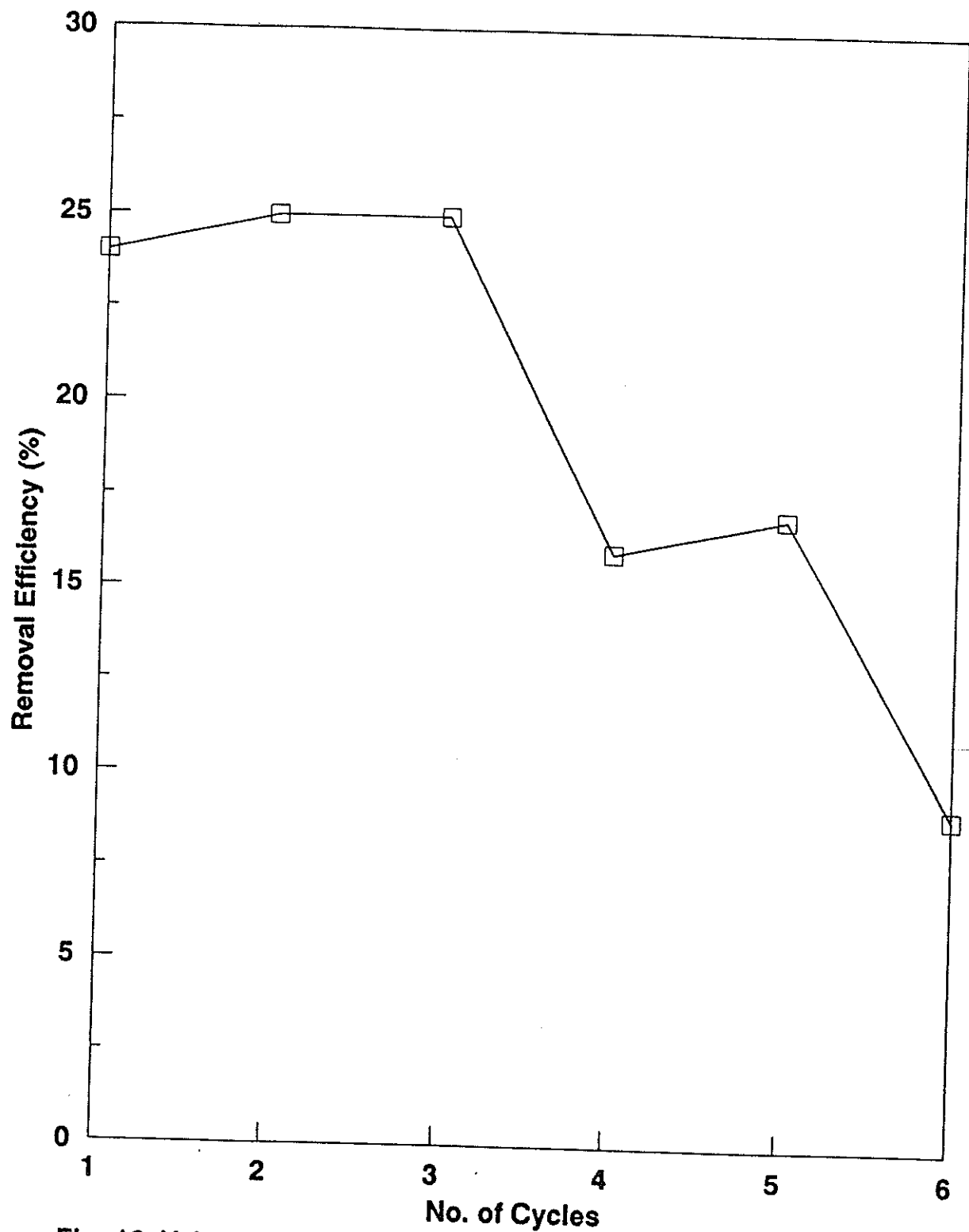


Fig. 13 Values of Removal Efficiency vs No. of Cycles for Benzene with Two Days Drying Time at 35oC Using Glendale Soil as Adsorbent

CONCLUSIONS

1. The use of TMA+ as a tailoring agent significantly improved the soils' adsorption capacity of benzene.
2. Low temperatures and short drying times permit almost total volatilization of benzene and toluene from spent soils for further adsorption of these contaminants.
3. Tailored bentonite showed moderate deterioration in its adsorption capacity for benzene after six cycles of use at 35°C using two- or three-day drying times. Technical feasibility of low temperature regeneration favors the economics of using tailored soils for the selective removal of benzene from ground water.
4. The tailored soil from Los Angeles, California showed no degradation in its adsorption capacity for benzene after being used six times at 35°C with a two-day drying time. The repetitive use of the same tailored soil and the simple conditions for regeneration make using this tailored soil an attractive alternative for benzene adsorption.
5. The Glendale soil's adsorption capacity for benzene was greatly diminished with the number of regeneration cycles. The number and size of flocs in the suspension were also notably increased with the repetitive use of this soil. This may explain the decaying effect observed in its adsorption capacity.
6. The soils' adsorption capacity for toluene was also improved by tailoring with TMA+. This improvement was more moderate

than for benzene adsorption, confirming the selective nature of this adsorption technique.

7. Tailored bentonite adsorption capacity for toluene was dramatically diminished with the number of repetitive cycles. The kinetics of the adsorption process may explain this decaying effect.

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