Kasetsart J. (Nat. Sci.) 34 : 171 - 178 (2000)

Removal of Naphthalene and 2, 4-Dinitrotoluene from Soils by Using Carboxymethyl-β-Cyclodextrin

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ABSTRACT

Spillage of petroleum and petroleum products from the underground storage tanks has caused significant contamination of groundwater aquifers by organic contaminants. These compounds are generally difficult to remove since the chemicals are hydrophobic, having a low solubility and therefore prefer to adsorb onto the soil. The ability of carboxymethyl-β-cyclodextrin (CMCD) to increase the solubilities of contaminants in soils was studied. Furthermore, studied partitioning of soil-contaminants and CMCD-contaminants were also included. Soils consisting of 7.4% clay content and 2.2% organic carbon content were used as contaminated soils. Naphthalene and 2, 4-dinitrotoluene (2, 4-DNT) were selected as the representative low polarity organic contaminants. In the batch studies, the partition coefficient between soil-naphthalene and soil-2, 4-DNT were 51.3 and 5.6 L/kg. In addition, 269.2 and 22.4 L/kg were determined from the partitioning between CMCD-naphthalene and CMCD-2, 4-DNT respectively. The results from column experiments showed that CMCD greatly enhanced the removal of naphthalene and 2, 4-DNT from soils. Using 0.01 N $NaNO_3$ as the flushing agent, 32 and 40% of naphthalene and 2, 4-DNT were removed. Meanwhile, 70 and 72% naphthalene and 2, 4-DNT were removed after 2 g/L CMCD solution was flushed through the soil columns.

Key words : CMCD, naphthalene, 2, 4-dinitrotoluene, solubility

INTRODUCTION

The remediation of subsurface (both soils and groundwater) has been the most costly and time consuming part of site cleanups. After the source of contamination has been removed and treated, contaminated soils and groundwater may still remain and require treatment. Nowadays in-situ technologies have become very attractive for treating contaminated soils and groundwater because of lower costs, less disruption to the environment, and reduced worker exposure to hazardous materials. Addition of agents such as organic cosolvents and surfactants are known to increase the transport of low polarity organics from the soils (Laha and Luthy, 1992; Edward *et al.*, 1994; Thangamani and Gina, 1994). However, it has been found that both cosolvents and surfactants have some disadvantages for soil remediation applications. Cosolvents are not effective in solubilizing the organics unless their volume-fraction concentrations are above 10%, and surfactants form high-viscosity emulsions that are difficult to remove from the soils (Wang and

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Brusseau, 1993). Furthermore, synthetic surfactants inhibit microbial activity in soils thereby reducing their natural bioremediation capability. Hence, contaminant transport-enhancing additives that do not adsorb or retain in the soil, and also do not inhibit natural soil microbial activity are desired. One such type of additives is the microbially-produced compounds, known as biosurfactants which can enhance low-polarity and nonpolar organics contaminant removal from soils without accumulating in the soil, or affecting the natural microbial activity.

Another class of microbially-produced compounds that is known to increase the aqueous solubilities of low polarity organics by forming water-soluble 1:1 inclusion complexes are called cyclodextrins. Cyclodextrins are produced from starch by bacteria, and are widely used in the pharmaceutical industry to improve the dissolution of non-polar drugs. These are cyclic oligosaccarides containing 6-8 glucose units arranged to form a hydrophobic shell, and a 5-8 °A hydrophobic cavity. It is demonstrated that carboxymethyl-β-cyclodextrin (CMCD) is a highly water soluble, anionic, non-emulsifying and non-toxic cyclodextrin. Biodegradable cyclodextrins can form complex with cationic heavy metals, significantly enhance the aqueous solubility of low polarity organic compounds, and hence enhance their removal from soils (Brusseau *et al.*, 1997). The hydrophobic cavity of β-cyclodextrin is reported to be 0.346 nm^3. Hence, low polarity organic contaminants that have molecular volume (MV) less than 0.346 nm^3 are likely to form inclusion compounds with β-cyclodextrin.

MATERIALS AND METHODS

Materials. Naphthalene and 2, 4-dinitrotoluene (2, 4-DNT) were selected as the test compounds. The physical and chemical properties of these compounds are shown in Table 1. Carboxymethyl-β-cyclodextrin (CMCD) was used as additive agent to increase the solubility of the test compounds. The soil samples were collected up to a depth of 12 inches after clearing the top 2 inches of debris and grass. The samples were brought to the laboratory for analysis in polyethylene bottles. The soils were sieved, and the fraction passing a No. 10 (2 mm) sieve was air dried and stored at room temperature in polyethylene bottles. The physical and chemical properties of these soils are shown in Table 2.

Adsorption tests. Samples for the determination of adsorption isotherms were prepared by adding a known amount of adsorbent into a series of 40 mL vials (Teflon-lined vial caps) that contained 25 mL of 0.01 N $NaNO_3$ and different amounts of contaminant. The solution was adjusted to the desired pH (4.0, 6.5 and 9.0) by adding 0.01 N HNO_3 or 0.01 N NaOH prior to adding the adsorbate. These vials were rotated in the tumbler

Table 1 Physical and chemical properties of naphthalene and 2, 4-dinitrotoluene.

Properties	Naphthalene	2,4-dinitrotoluene
Formula	$C_{10}H_8$	$CH_3C_6H_3(NO_2)_2$
Molecular weight	128.17	182.14
Density (g/cm^3)	1.145	1.321
Molecular volume (nm^3)	0.186	0.229
Solubility (mg/L)	35.5	300

Table 2 Characteristic parameters of test soil.

Soil type	I
pH	7.2
Organic matter content	4.9 %
Organic carbon content	2.2 %
Specific gravity	2.46
Clay content	7.4 %
Silt content	17.4 %
Sand content	75.2 %
pH_{zpc}	7.0
Soil type	Sandy loam

for 3 days. The samples were filtered through 0.45 mm nylon membrane filters and analyzed by the UV spectrophotometer (Perkin Elmer Lambda 3A) at wavelengths 276 and 250 nm for naphthalene and 2, 4-DNT at the end of the tests.

Contaminants-CMCD partition tests. These tests were prepared by adding a known amount of contaminant into a series of 40 mL vials (Teflon-lined vial caps) that contained 25 mL of 0.01 N $NaNO_3$ and different amounts of CMCD. The amount of contaminant added was approximately 10 times higher than the solubility limit. The solution was adjusted to the desired pH (4.0, 6.5 and 9.0) by adding 0.01 N HNO_3 or 0.01 N NaOH prior to adding the adsorbate. These vials were rotated in the tumbler for 3 days. The samples were filtered through 0.45 mm nylon membrane filter and the filtrate was analyzed by the UV spectrophotometer at the end of the test.

Column tests. Polycarbonate columns 2.54 cm in diameter and 4 cm long were used throughout the experiments. The columns were packed in incremental steps with dry soils to establish uniform bulk density. Soil was prevented from leaching out of the columns by nylon membrane filter paper supported on stainless steel screen. After packing, the columns were slowly wetted from the bottom with electrolyte (0.01 N $NaNO_3$) and contaminant solution. During this procedure the effluent from the columns was collected and determined for the contaminant. Elution experiments were conducted after the contaminant solution was pumped through the soil columns for 14 days. The effluent solution was analyzed by the UV spectrophotometer at various times to determine the amount of naphthalene and 2, 4-DNT. After 14 days of elution, the contaminated soils were extracted by placing the contaminated soils in glass containers containing methanol for 1 day. Two types of elution experiments were conducted: (1) elution with 0.01 N $NaNO_3$ solution, (2) elution with 2 and 5 g/L of CMCD and 0.01 N $NaNO_3$ solution.

RESULTS

Adsorption isotherm. Adsorption isotherm equations such as Freundlich and Langmuir equations were used to simulate the experimental data. The plot between the solid phase and aqueous phase naphthalene concentrations is shown in Figure 1. The relationship between solid phase and aqueous phase 2, 4-DNT concentrations is shown in Figure 2.

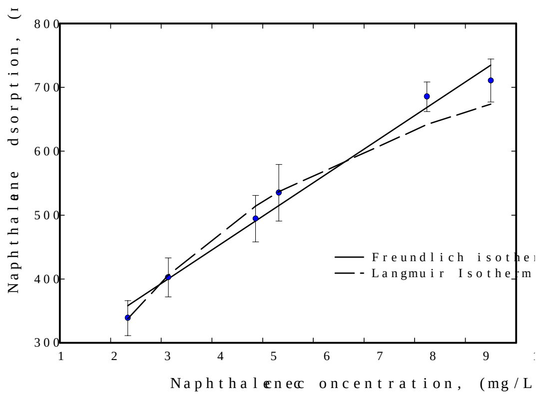

Figure 1 Adsorption isotherm of naphthalene in soil.

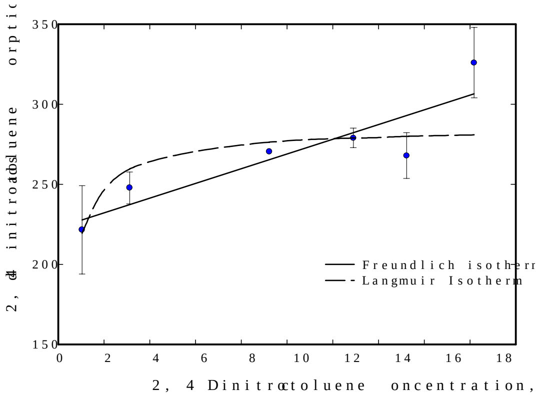

Figure 2 Adsorption isotherm of 2, 4-dinitrotoluene in soil.

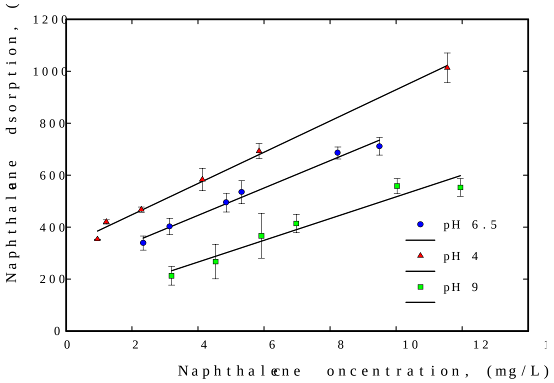

Figure 3 Adsorption isotherm for naphthalene at pH 4, 6.5 and 9.

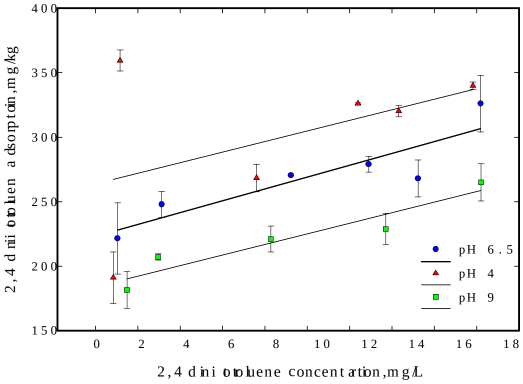

Figure 4 Adsorption isotherm for 2, 4-dinitrotoluene at pH 4, 6.5 and 9.

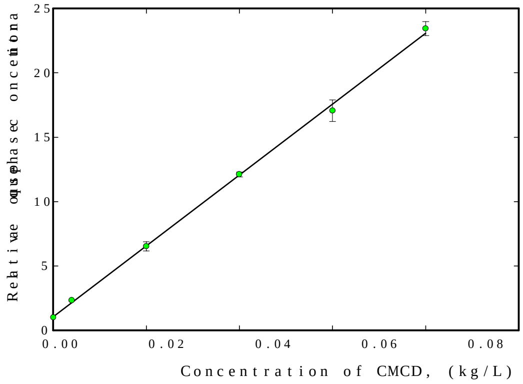

Figure 5 Plot of relative aqueous-phase naphthalene concentration versus the CMCD concentration.

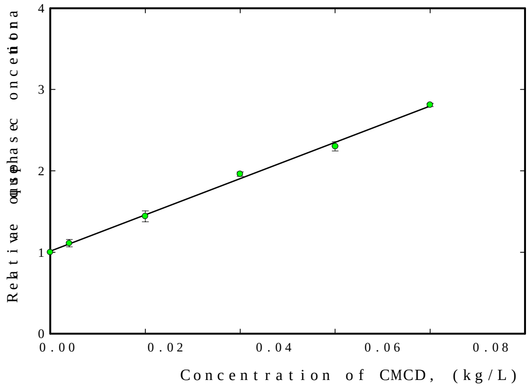

Figure 6 Plot of relative aqueous-phase 2, 4-dinitrotoluene concentration versus the CMCD concentration.

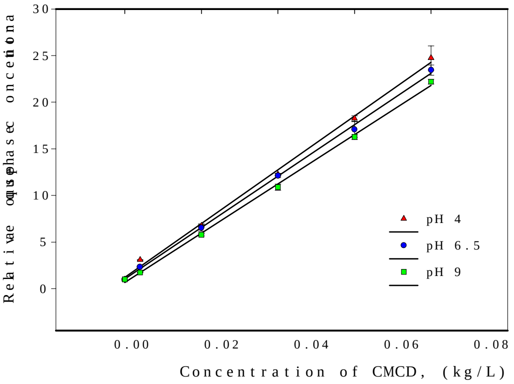

Figure 7 Plot of the relative aqueous-phase naphthalene concentration versus the CMCD concentration at pH 4, 6.5 and 9.

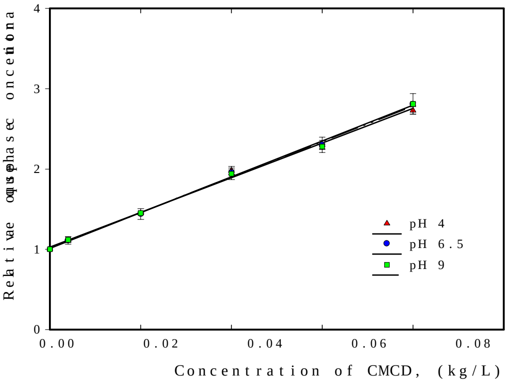

Figure 8 Plot of relative aqueous-phase 2, 4-dinitrotoluene concentration versus the CMCD concentration at pH 4.5, 6 and 9.

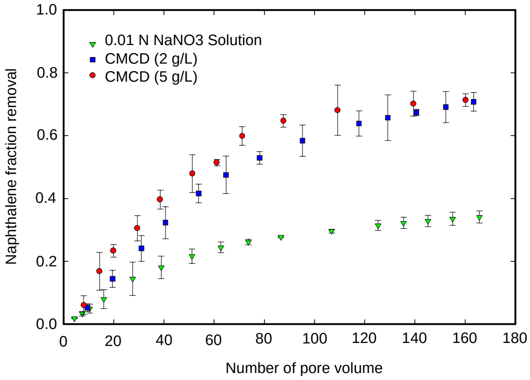

Figure 9 Elution of soil contaminated with naphthalene using CMCD and $NaNO_3$ solution.

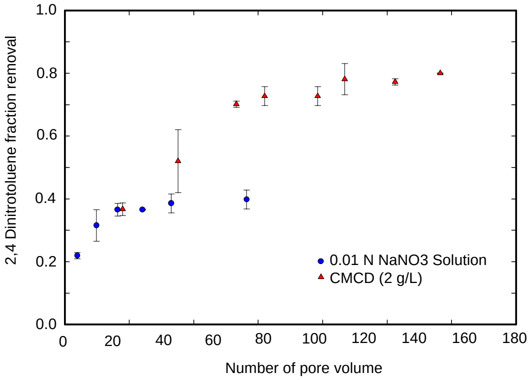

Figure 10 Elution of soil contaminated with 2, 4-dinitrotoluene using CMCD and $NaNO_3$ solution.

To understand the effect of pH on the sorption capacity of soils, three adsorption isotherms with different pH were conducted at the same time using the exact procedure. Figure 3 and 4 show the adsorption data obtained for naphthalene and 2, 4-DNT at different pH values.

Partition between contaminants and CMCD. The relative aqueous-phase concentrations (S_t/S_0) of naphthalene and 2, 4-DNT were plotted against the CMCD concentration in Figures 5 and 6 respectively. Furthermore, to determine the effect of pH on the partition of naphthalene and 2, 4-DNT to the soil, three different pH solutions were prepared simultaneously by the same procedure. The plots between the aqueous-phase concentration versus the CMCD concentration at three different pH values are shown in Figures 7 and 8 for naphthalene and 2, 4-DNT respectively.

Column tests. A comparison between the log K_d and log K_{cw} values from the above experiments reveals that both naphthalene and 2, 4-DNT have log K_{cw} values higher than log K_d values. These results suggest that CMCD has the ability to extract naphthalene and 2, 4-DNT from the soils. Column tests were conducted to confirm these results. The results from column experiments were plotted between number of pore volumes of elutant versus contaminant fraction removed. Elution curves for naphthalene and 2, 4-DNT removal from the soil are shown in Figures 9 and 10 respectively.

DISCUSSION

Adsorption isotherm. Relative to the Langmuir isotherm, the results show that the Freundlich isotherm is a better fit to the experimental data according to the sum of square error (SSE) between the experimental and model results. Freundlich partition coefficients were determined for each system by plotting the sorption capacity versus the aqueous concentrations for naphthalene and 2, 4-DNT. It has been determined for hydrophobic compounds that, if the equilibrium aqueous phase concentration is less than one half of the solute water solubility, sorption isotherms to natural sediments are linear (Karickhoff et. al., 1979). Assuming that the constant $1/n = 1$, and using only the linear portion of the curve, the partition coefficient is then the slope of the line (Roger, 1989). The log K_d values for naphthalene and 2, 4-DNT were found to be 1.71 and 0.75 respectively. Relative to the naphthalene system, the capacity of the soil for 2, 4-DNT was much smaller. This result demonstrated that naphthalene has a stronger affinity to the soil surface than 2, 4-DNT. Due to the lower solubility of naphthalene, water can cause naphthalene to sorb onto the hydrophobic surface of the soils more than 2, 4-DNT since naphthalene attempts to minimize its contact with water and migrates to the relatively hydrophobic soil organic matter.

The effect of pH on the sorption capacity of soils indicates that the log K_d values between the soils and naphthalene were 1.78, 1.76, and 1.71 at pH 4, 6.5, and 9 respectively. The log K_d values for 2, 4-DNT at pH 4, 6.5, and 9 were 0.86, 0.75, and 0.71. Using statistical t-test, there was no statistically significant difference in the log K_d values of naphthalene and 2, 4- DNT at the three different pH at the 95 percent confidence interval. The results indicate that the solution pH has no effect on the sorption capacity of naphthalene and 2, 4-DNT in soils. However, a charge-induced dipole interaction could occur between a positively charged surface and the electron-rich π system of the PAHs (Mader *et al.*,1997). At pH lower than pH_{zpc}, the soil surface becomes positively charged and tends to interact with the negative charges in the electron-rich π system of naphthalene and 2, 4-DNT. This interaction causes the affinity of the soils to increase at lower pH. From this study, it is obvious that the surface charge density does not affect sorption capacity since the dominant force is hydrophobic interaction. Meanwhile, the surface charge tends to affect the affinity of the soils by electrostatic interaction.

Partition between contaminants and CMCD. Linear regression was performed for these data following the contaminant/CMCD partition model. The linear equation fitted the observed data closely for both contaminants. The CMCD/water partition coefficient (K_{cw}) for naphthalene and 2, 4-DNT were obtained from linear regression of S_t/S_0 versus the concentration of CMCD. The log K_{cw} for naphthalene and 2, 4-DNT were found to be 2.43 and 1.35 respectively. The log K_{cw} reported by Wang and Brusseau (1993) for naphthalene/hydroxypropyl-β-cyclodextrin (HPCD) was about 2.72, which is higher than naphthalene/CMCD measured in this research. Since HPCD and CMCD are both β-cyclodextrin having 0.346 nm^3 cavity (Szejtli, 1982), the difference in the partition of the contaminants may be due to the charge of the carboxylic functional groups and the polarity of the CMCD molecules (Brusseau, 1997). Hence, HPCD having less polarity and no charge functional groups may cause larger sorption of contaminants. The results from this study indicate that CMCD can enhance the solubility of naphthalene and 2, 4-DNT due to the hydrophobic cavity of the CMCD.

The log K_{cw} for naphthalene is higher than 2, 4-DNT as naphthalene is more hydrophobic and has a smaller molecular volume. This causes the arrangement of naphthalene into the CMCD hydrophobic cavity to be easier and stronger compared to 2, 4-DNT. The molecular volumes of naphthalene and 2, 4-DNT were calculated from the density and were found to be 0.186 and 0.229 nm^3 respectively. The results from this study indicate that CMCD produces a significant increase in the apparent aqueous solubilities of naphthalene and 2, 4-DNT due to its hydrophobic cavity.

The log K_{cw} for naphthalene at pH 4, 6.5, and 9.0 were 2.46, 2.43, and 2.42 while the log K_{cw} for 2, 4-DNT were 1.34, 1.35, and 1.34 at pH 4, 6.5, and 9.0. Using statistical t-test, there was no statistically significant difference in the log K_{cw} values of naphthalene and 2, 4-DNT at the three different pH values at the 95 percent confidence interval. The results confirmed that the solution pH has no effect on the partition between the contaminants and CMCD and has little effect on the naphthalene and 2, 4-DNT solubilities. So the increase in the solubilization of naphthalene and 2, 4-DNT is strongly dependent upon the complexation between the hydrophobic cavity of CMCD and low polarity organic compounds.

The formation ratio for the naphthalene/ CMCD and 2, 4-DNT/CMCD inclusion complexes were determined from the amount of CMCD added. At pH 4 and 6.5, the formation of the naphthalene/ CMCD inclusion complexes was 1 to 0.07 (mole CMCD : mole naphthalene) while at pH 9 it was 1 to 0.06. The 1 to 0.03 (mole CMCD : mole 2, 4-DNT) 2, 4-DNT/CMCD inclusion complexes were found at pH 4, 6.5, and 9. The formation value of naphthalene inclusion complexes is higher than that of 2, 4-DNT as naphthalene has a smaller molecular size that enables easier arrangement into the CMCD cavity. However, the naphthalene and 2, 4-DNT inclusion complexes values were less than the assumed 1 to 1 inclusion complexes value as described by Blyshak *et al*., 1989.

Column tests. Clearly, CMCD greatly enhanced the removal of naphthalene and 2, 4-DNT from soils as compared to the $NaNO_3$ solution. For example, 70 percent of the initial naphthalene was removed by 2 g/L CMCD solution and 72 percent was removed by 5 g/L of CMCD solution after 160 pore volumes of flushing as compared to 32 percent using $NaNO_3$ solution. Furthermore, 73 percent of the initial 2, 4-DNT was removed after 140 pore volumes of 2g/L CMCD solution was pumped through the column while only 40 percent was removed by the $NaNO_3$ solution. Adding more CMCD did not affect the total naphthalene removal. It may be that the diffusion of the contaminants from the soils to the bulk liquid was rate limited. Furthermore, naphthalene and 2, 4-DNT could not be completely removed from the soils as the desorption of these contaminants by the hard soil organic matter domain is slow and only partially reversible (Huang, 1997). However, it can increase the removal rate of naphthalene. At 50 pore volumes of CMCD flushing, the percent naphthalene removed increased from 38 to 49 percent when CMCD solution concentration increased from 2 to 5 g/L. Since the K_{cw} value is higher than the K_d value, naphthalene and 2, 4-DNT tend to leave the soils and complex with CMCD in the aqueous solution. The total removal efficiencies for naphthalene and 2, 4-DNT are approximately equal since the K_d and K_{cw} values for naphthalene and 2, 4-DNT differs slightly.

The study of low polarity organic compounds in enhancing solubility show that CMCD greatly enhances the desorption and elution of naphthalene and 2, 4-DNT, which were used as representative low polarity organic contaminants. The partition coefficients between contaminants and CMCD (K_{cw}) were determined by using the contaminants/CMCD model. The results show that this linear equation fitted the experimental data extremely well for both naphthalene and 2, 4-DNT. Furthermore, there was no difference in K_{cw} values for naphthalene and 2, 4-DNT when the pH was changed. Further research will be focused on the removal of low polarity organic contaminants from low hydraulic conductivity soils based on cyclodextrin.

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Received date : 18/10/99
Accepted date : 30/12/99