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Extraction of Pesticides from Contaminated Soil via Cyclodextrin Complexation

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Cyclodextrins (CDs) were successfully used to extract numerous commonly used pesticides from contaminated soil via cyclodextrin complexation, a more environmentally friendly method compared to surfactants and organic solvents. A combination of five CDs (α-CD, β-CD, γ-CD, hydroxypropyl-β-CD (HP-β-CD), and methylated-β-CD (M-β-CD)) and eight pesticides (2,4-Dichlorophenoxyacetic acid (2,4-D) alachlor, acetochlor, diazinon, dicamba, dimethanamid, metalochlor and propanil) were examined in this study. It was found that a linear relationship exists between the concentrations of the M-β-CD and alachlor, which generally indicates that the amount of pesticide extracted depends on the concentration of the cyclodextrin present. With some pesticide-cyclodextrin combination, it was found that as the concentration of cyclodextrin increases the CD-pesticide inclusion complex precipitated out of solution, thus reducing the solubility of the pesticide. Overall the most effective extractants based on this study were found to be HP-β-CD and M-β-CD.
Cyclodextrins (CDs) are cyclic saccharides composed of 6-8 glucose units (α-, β-, and γ- cyclodextrin respectively (Figure 1) produced by microbial breakdown of starch\(^1\). CDs have a toroidal shape with a hydrophobic interior and a hydrophilic exterior, which give CDs the ability to interact with both polar and non-polar compounds.

![Structure of α, β, and γ cyclodextrins](image)

Figure 1: Structure of α, β, and γ cyclodextrins.\(^2\)

Depending on the size of the solute molecule and the CD cavity, CDs may form inclusion complexes with non-polar molecules, potentially allowing the complex to be more soluble than the free solute in a polar solvent (Figure 2). Due to their ability to interact with both hydrophobic and hydrophilic molecules, cyclodextrins have been widely used in the delivery of non-polar medications since the 1980s.\(^3\) Studies have also been conducted to determine whether CDs can be used to remove polycyclic aromatic hydrocarbons (PAHs) from industrial areas, and the removal of oral malodorous compounds from the mouth.\(^4\)\(^6\)

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In this study, we were interested in exploring whether CDs can be used in the agricultural industry to extract pesticides from contaminated soil. Most synthetic pesticides are designed to be non-polar, allowing them to adhere to the target product and limiting their ability to wash away with rain or irrigation water. A significant percentage of pesticides however do not reach their intended target site and instead accumulate in the soil. CDs may potentially form inclusion complexes with pesticides in the soil, increasing their solubility and allowing them to be washed away with water (Figure 2). This process could be utilized on a large controlled scale to clean up contaminated soil sites. Size selective membranes could potentially be used to isolate the pesticide solution from the soil particles.

Here, micellar capillary electrophoresis was used to separate the pesticide from the soil matrix and quantify its level in the aqueous extraction solution. Capillary electrophoresis (CE) separates molecules by applying a potential difference across a capillary, which then separates the sample molecules based on their size to charge ratio. A flow of solution due to electroosmosis allows both the negative and positive particles to reach the detection window near the end of the capillary. The introduction of a charged surfactant into the running buffer solution, allows neutral compounds to be
separated within the electric field. CE is advantageous for this study as it is capable of separating complex mixtures in small sample volumes in a short time. It is also capable of analyzing these aqueous samples directly, without an organic extraction step prior to analysis as with GC. By not using a packed LC column, we avoid any issues of soil particles clogging a chromatographic column. In this study, we examined a combination of five CDs (α-CD, β-CD, γ-CD, hydroxypropyl (HP)-β-CD and methylated (M)-β-CD) with eight widely used pesticides in the US (Figure 3).

Pesticide standards (>99% purity) obtained from Supelco (St. Louis, MO) were as follows: 2,4-D, acetochlor, alachlor, dicamba, dimethenamid, metolachlor, and propanil. α-CD, β-CD, γ-CD, sulfated-β-CD, carboxymethyl-β-CD, methyl-β-CD, hydroxypropyl-β-CD were all purchased from Sigma (St. Louis, MO). All other chemicals and buffer salts were purchased from Fisher (Fairlawn, NJ).
Pesticides were dissolved in methanol (ethanol for dicamba and 2,4-D) to make a 10mM solution. The pesticide solution was then added to 2g of soil, and left under air to evaporate the methanol for 20-24hrs. The contaminated soil was then extracted for 24 hrs with methanol, 1.0 mM pH 7 phosphate buffer, and varying concentrations of CDs dissolved in the phosphate buffer. Methanol was used to give us the approximate 100% extraction level, and the phosphate buffer was used as a baseline measurement. Phosphate buffer was used to prepare all solutions in place of water in order to prevent gradual changes in pH of the solutions and samples. 0.5 mL of the extracted pesticide solution was mixed with 0.5 mL of 5 mM phenol (internal standard, IS) in a 50/50 ratio to make a total of 1mL. The capillary was rinsed with 1 M NaOH and water for 1 minute each, then rinsed with a 50/50 mixture of methanol and 40 mM SLS (sodium lauryl sulfate), which was used as the run buffer. A Beckman P/ACE System MDQ capillary electrophoresis with 50 micron i.d. capillary (50 cm in length, 40 cm to the detector) and a Uv/Vis PDA detector was used for all the analyses.

Binding constants between these cyclodextrins and pesticides were measured in a previous study by our group, and the data indicate that moderately strong interaction exists between a majority of these pesticides and cyclodextrins. This indicates that cyclodextrins may indeed be capable of enhancing the solubility of these pesticides in aqueous solutions. In our current work, the percent of total pesticide extracted from the contaminated soil and the pesticide solubility enhancement percent (relative to 1.0 mM aqueous phosphate) when extracted using 20.0mM of cyclodextrin was measured and compared.
Figure 4: Linear increase in alachlor solubility enhancement and total extraction percent with methyl-β-CD concentration.

Hydroxypropyl- and methyl-β-CD were effective at enhancing the solubility of a majority of the pesticides, and a linear relationship was found between CD concentration and pesticide level extracted (Figure 4). This shows that the level of pesticide extracted from soil can be easily increased by using a higher concentration of CD. Generally, hydroxypropyl- and methyl-β-CD were capable of enhancing the level of soluble pesticide in aqueous solution by a factor between 175-500%, depending on the pesticide. The native cyclodextrins, however, were only capable of enhancing the solubility of certain pesticides. β-CD appeared to be the most effective of the three native cyclodextrins, enhancing the extraction of a majority of the pesticides. However, all pesticides studied, with the exception of diazinon, had a decrease or no change in solubility with γ-CD even though the binding between γ-CD and these pesticides is significant. It was found that the pesticide-γ-CD inclusion complex has a limited solubility lower than that of the free pesticide. Therefore as the concentration of γ-CD increases the complex precipitates out of solution, reducing the solubility of the pesticide (Figure 5). However, contrary to the other pesticides, the solubility of
diazinon was significantly increased by γ-CD, likely due to dazinon’s naturally low solubility (~60 mg/L).

![Graph showing the non-linear relationship between alachlor solubility enhancement and total extraction percent with γ-CD concentration.](image)

**Figure 5:** Non-linear relationship between alachlor solubility enhancement and total extraction percent with γ-CD concentration.

In addition, it is also important to note that dicamba and 2,4-D show a minimal enhancement in solubility with all the native cyclodextrins. Dicamba and 2,4-D are both anionic at neutral pH which increases their natural solubility in water. This indicates that CDs are relatively ineffective at removing dicamba and/or 2,4-D from contaminated soil. However, it is known that these pesticides accumulate far less in soils due to these same reasons.

From our data, it is evident that the most effective and versatile extractants are HP-β-CD and M-β-CD. These derivatized CDs also show significantly higher binding constant values than the other CDs. The high extraction and enhancement percentage of these CDs is clearly due to the substituted branch groups on the CD rim, which affects
the inner surface area/volume of the CD cavity and the orientation of the pesticide in the complex through steric interactions.

We have shown that CDs can be used to effectively extract pesticides from contaminated soil. Currently, in order to clean up contaminated land, farm owners must strip the top layer of soil leaving the remaining soil poor in nutrients. Alternatively, organic solvents may also be used to remove pesticides, but these solvents also extract other organic matter from the soil and disrupt valuable microorganisms in the soil. This study potentially develops a more environmental friendly method of farmland topsoil cleanup using non-toxic cyclodextrin solutions that more selectively target the toxic pesticides. In the coming weeks, we will work on determining the composition of the soil we used in this study. The results presented do not take into account the pH of the soil and the soil composition, which vary from soil to soil.

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