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# TOWARDS THE SYNTHESIS OF CYCLODEXTRINS MODIFIED WITH SILICON (Si) AND TITANIUM (Ti) BASED COMPOUNDS FOR THE REMOVAL AND DEGRADATION OF ORGANIC CONTAMINANTS IN WATER

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#### Abstract

Cyclodextrins are a class of cyclic oligosaccharides. The most common types consist of six to eight glucose units linked through  $\alpha$ -1, 4-glycosidic linkages. They are called  $\alpha$ -,  $\beta$ -, and  $\gamma$ - cyclodextrins (CDs), respectively. The use of cyclodextrin polymers has proved to be effective in the removal of organic contaminants from water. They form inclusion complexes with a wide variety of organic compounds. In this project, we synthesized cyclodextrin that possess Si and Ti pendent side chains. Polymerization of these CD derivatives with disocyanate linkers is expected to produce Si- and Tibased cyclodextrin polymers that are capable of absorption and degradation of the organic contaminants. It is envisaged that the silicon and titanium side chains will degrade organic contaminants while harboured inside the cyclodextrin cavity. The attachment of the Si and Ti pendent groups had been confirmed by the use of Fourier transform infrared (FT-IR) and Nucleic Magnetic Resonance (NMR) spectroscopic techniques. The reaction was monitored with thin layer chromatography (TLC).

Keywords: Cyclodextrin, hexamethylene diisocyanate, toluene 2,4-diisocyanate

# INTRODUCTION

# Cyclodextrins

The most common cyclodextrins (CDs) have six, seven and eight D-glucose units and are called  $\alpha$ -,  $\beta$ -, and  $\gamma$ -CDs, respectively. They are usually referred to as first generation or parent CDs. These glucose units are interlinked by  $\alpha$ -1,4 glycosidic bonds thus forming a cyclic structure (1). A characteristic feature of the CDs is that they have a toroidal shape that forms well defined cylindrical cavities of about 8Å deep and 5-10Å wide. The cone is formed by the carbon skeleton of the glucose units and the glycosidic oxygen atoms that form the glucose units (2). The primary hydroxyl (OH) group of the glucose is located at the narrow end of the cone (primary face) and the secondary OH groups are located in the wider secondary face. The primary and secondary hydroxyl groups on the outside of the CD make them water-soluble. Cyclodextrins have an interior cavity that is hydrophobic and the exterior is hydrophilic. This feature allows for the encapsulation of various organic guests to produce host-guest complexes or supramolecular species in aqueous solutions (3). **Figure 1** shows the toroidal structure of a cyclodextrin.



Figure 1: The toroidal structure of the cydodextrin

# Formation of indusion complexes

The interior cavity of the cyclodextrin provides a relatively hydrophobic environment into which an apolar pollutant can be trapped.  $\beta$ -CD based materials are known to exhibit high adsorption capacities toward phenolic molecules and dyes (4). They also form a wide variety of indusion complexes with low-molecular-weight compounds, which range from apolar

and aliphatic hydrocarbons to polar carboxylic acids, and amines (5). The CD moiety can harbour various small, suitably shaped organic compounds in its tubular cavity by shielding the bound species from the surrounding aqueous environment (6). This phenomenon is a result of the hydrophobic interaction between the host cyclodextrin and the guest organic species and is illustrated in **Scheme 1** below.



Scheme 1: The formation of the indusion complexes

# Cyclodextrin Derivatives

The presence of hydroxyl (OH) groups on the outer cavity can be exploited in order to alter the physical and chemical properties of cyclodextrins. For instance, the functionalization of CDs can decrease their solubility in water, increase their stability in the presence of light, heat and oxidizing agents and also make them more volatile (6). The primary hydroxyl groups (OH-6) are more reactive than their secondary counterparts (OH-2 and OH-3). These hydroxyl groups are shown in **Figure 1**. The OH-2 hydroxyl groups are acidic and therefore more reactive than OH-3. Also, the OH-3 hydroxyl groups are not easily accessible thereby making them even less reactive. On the other hand, the primary hydroxyl groups attached to C-6 are basic and easily accessible. As a result, OH-6 hydroxyl groups are often more reactive during nudeophilic substitution reactions (6).

Herein we report on the synthesis of  $\beta$ -cydodextrin-3-triethoxy-propyl silane **1**, a precursor for Si-and Ti-based  $\beta$ -cyclodextrin polymers. The synthetic route for this precursor is illustrated in **Scheme 2**. Reaction of this precursor with diisocyanate linkers is expected to produce the corresponding silylated  $\beta$ -cydodextrin polymer **2**. The silicon unit of the polymer is expected to participate in the degradation of the organic pollutant.



Scheme 2: The synthesis of  $\beta$ -cyclodextrin-3-triethoxy-propyl silane precursor 1 and the corresponding Si-based polymer 2.

Alternatively, nanoparticles of titanium dioxide  $(TiO_2)$  can be attached to the silylated  $\beta$ -cyclodextrin precursor to produce a compound of the type **3**. The TiO<sub>2</sub> nanoparticles have previously demonstrated catalytic, photocatalytic, and electrical properties (7). Therefore, it is envisaged that the TiO<sub>2</sub> will enhance the degradation of organic pollutants under visible light. The two Si- and Ti-based systems (**2** and **4** in **Schemes 2** and **3**, respectively) will, therefore, perform the dual role of encapsulating the organic contaminants and degrading them whilst harboured inside the cavity of the cyclodextrin polymer.



Scheme 3: The synthesis of Ti-based precursor 3 and the corresponding Ti-based polymer 4.

# EXPERIMENTAL

# <u>General</u>

NMR experiments were performed on a 300 MHz Varian Gemini 2000 spectrometer. Proton chemical shifts are reported in parts per million (ppm). The residual signal of DMSO-<sub>d6</sub> ( $\delta$  = 2.49 ppm for <sup>1</sup>H NMR) was used as the internal reference. All IR spectra were obtained from a Midac FT-IR 5000 Spectrophotometer and the IR data were listed with characteristic peaks in wavenumber (cm<sup>-1</sup>). Calcium fluoride (CaF<sub>2</sub>) was used when running samples so that the complete attachment of the 3-triethoxy-propyl isocyanate into the cyclodextrin could be confirmed.

#### The synthesis β-Cyclodextrin-3-triethoxy-propyl silane (CD-p-Si)

 $\beta$ -CD (11.35 g, 0.01 mol) was dissolved in dry dimethylformamide (DMF) under nitrogen gas at 0°C. To this stirred solution, 3-(triethoxy silyl) propyl isocyanate (4.95 ml, 0.02 mol) dissolved in DMF (20 ml) was gradually added. The reaction mixture was continued stirring at this temperature for half an hour. The reaction temperature was increased to 70°C and stirring was continued for a further 16–18 hours at this temperature. The reaction was monitored with infra-red spectroscopy. The disappearance of the isocyanate peak at 2274 cm<sup>-1</sup> confirmed the completion of the reaction. Upon addition of acetone

(40 ml) to the reaction mixture, a precipitate formed. Filtration followed by drying of the resultant precipitate led to the isolation of the product.

<sup>1</sup>**HNMR/ppm, DMSO-**<sub>d6</sub>: 5.67-5.74 (br, OH-2, OH-3), 4.82 (d, H-1), 4.46 (t, OH-6), 3.535-3.649 (m, H-6, H-3, H-5), 3.29-3.405 (m, H-2, H-2), 2.884 (t,N-H), 2.716-2.724 (m, H-8), 2.071-2.080 (m, H-9), -0.016--0.013 (t, H-10), **IR/KBr, cm<sup>-1</sup>:** 1656 (C=O), 1024 (Si-OR), 3199 (O-H). **M.pt** = 270-275°C (dec). **TLC**: Eluent: 3:2 Methanol/ Diethyl Ether, R<sub>f</sub> = 0.63. **Yield** = 10.88g, 7.97mmol, 79.7%.

# **RESULTS AND DISCUSSION**

# Infra-Red Spectroscopy and Thin Layer Chromatography Analysis

**Figure 3** shows the IR spectra of the reaction mixture at the start (t = 0, Sample A) and end (t = 18 hrs, Sample B) of the experiment. The successful incorporation of the silvl unit was confirmed by the disappearance of the isocyanate peak at 2274 cm<sup>-1</sup> (Sample B). Additionally, the IR spectrum of Sample B shows a new strong peak appearing at 1656 cm<sup>-1</sup>, which is characteristic of the C=O group of an amide. Another strong and broad band, which appears at 1024 cm<sup>-1</sup>, corresponds to the Si-OR group. It is evident from the hydroxyl groups band (3200-3550 cm<sup>-1</sup>) that the cyclodextrin unit is still in tact (8).

The  $R_f$  value of the desired product CD-3-triethoxy-propyl silane is 0.63, which is totally different from the  $R_f$  value of the starting material (0.74). Lastly, the melting point further proved the formation of a new product. While the product melted with decomposition at 270-275 °C, the melting point of the cyclodextrin is 290-300 °C.



Figure 2: FT-IR Spectroscopy of β-CD-3-triethoxy-propyl silane

# Nuclear Magnetic Resonance

<sup>1</sup>H NMR spectroscopy provided more evidence for the formation of  $\beta$ -CD-3-triethoxy-propyl silane. New peaks that correspond to N-H, N-CH<sub>2</sub> and Si-CH<sub>2</sub> were observed

(9, 10, 11). Compared to the Si-CH<sub>2</sub> triplet, which appears at -0.02 ppm, the N-CH<sub>2</sub> protons appear as a multiplet at 2.72 ppm. The electronegative nitrogen atom is obviously responsible for the deshielding of the N-CH<sub>2</sub> protons (9). The N-H triplet and the

N-CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>Si multiplet were observed at 2.88 ppm and 2.08 ppm, respectively.



Figure 3: β-Cyclodextrin-triethoxy-propyl silane

# CONCLUSION

β-Cyclodextrin-triethoxy-propyl silane, a precursor for Si- and Ti-based polymers, has been successfully synthesized. The disappearance of the isocyanate at 2274 cm<sup>-1</sup> provided evidence for the incorporation of the silyl unit onto the cyclodextrin. Other techniques such as IR, NMR, TLC and melting point provided more evidence for the formation of the silylated precursor. Polymerization of this precursor will provide access to polymers that possess the ability to absorb and degrade common organic pollutants.

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