Applications of Cyclodextrins

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Due to their unique structural, physical and chemical properties, cyclodextrins and their derivatives have been of great interest to scientists and researchers in both academia and industry for over a century. Many of the industrial applications of cyclodextrins have arisen from their ability to encapsulate, either partially or fully, other molecules, especially organic compounds. Cyclodextrins are non-toxic oligopolymers of glucose that help to increase the solubility of organic compounds with poor aqueous solubility, can mask odors from foul-smelling compounds, and have been widely studied in the area of drug delivery.

cyclodextrins applications

1. Introduction—Brief History of Cyclodextrins & Their Applications

Cyclodextrins (CDs) were formally discovered in 1891 [1] as Antoine Villers studied enzymatic degradation of potato starch in bacteria [2][3]. Villers isolated two compounds (most likely α-CD and β-CD [4]) with properties similar to those of cellulose (i.e., resistance to acid hydrolysis, and non-reducing properties) [4][5]. He consequently named them “cellulosines” [6]. Franz Schardinger, the so-called “Founding Father” of cyclodextrin chemistry, renamed these two compounds dextrins [5][6], from which the modern name of “cyclodextrins” originates. In 1939, Karl Freudenberg and his co-workers published a full description of the two separated compounds [7]. In 1954, Friedrich Cramer focused on separating and purifying CDs naturally, and studied CD-guest inclusion complexes in different states [8].

Even though CDs were discovered well over a century ago, the number of papers about cyclodextrins from 1955 to 1975 was minimal [2][9][10][11]. This low number partially due to the (erroneous) statement that CDs were toxic. Dexter French reported this in a criticical review of CDs in 1957 [5]. He and B. H. Thomas fed rats fed small quantities of highly purified β-CD, and oddly enough, all subsequently died. These results, however, were unpublished, and the authors did not explain the cause of death [5]. The methods French and Thomas used are questionable [4], and have since been proven incorrect [4]; other factors such as solubility [12][13][14], chemical modification [15][16][17][18], route of administration (oral, intravenous, topical, etc.) [19][20][21] must be taken into account when considering CDs’ toxicity, which varies even among the native CDs.

2. Applications of Cyclodextrins

Due to CDs biodegradability, biocompatibility, and versatility, their industrial applications are very varied. The applications discussed here are outlined in **Figure 1**. CDs have been used in the textile and pharmaceutical industries, as well as in agriculture, food technology, for environmental protection, chemical and biological analysis, and in dyes and cosmetics. Many of these applications are possible because of the ability of CDs to form stable complexes with many types of molecules. This will be emphasized throughout the remainder of this section.

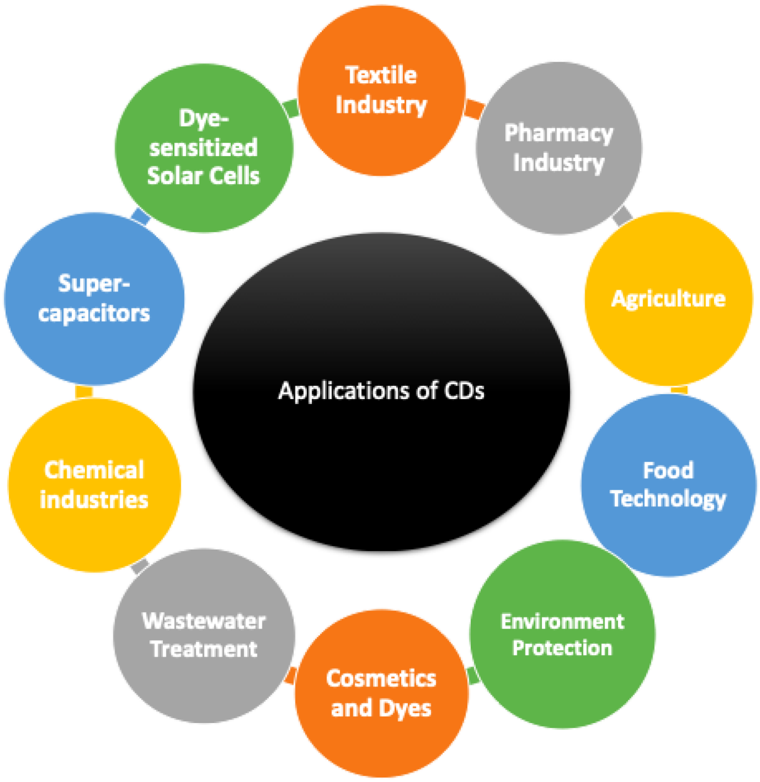

Figure 1. Various Applications of CDs.

2.1. General Applications

CDs play an important role in the textile industry, as they can be used as leveling agents in dyeing [22][23][24], in wastewater treatment [25][26][27], and in textile finishing [28][29][30][31][32]. In the dyeing process, CDs can be used as a dyeing aid, forming a complex with the dye [33], or as a chemical modification of the surface [34][35]. CDs can form a variety of inclusion complexes with textile dyes, thus influencing the quality of the dyeing.

Some researchers have grafted β-CD into insoluble solids, such as activated carbon, zeolite, magnetic materials, and silica gel, obtaining good adsorption results [36]. These adsorbent materials with cyclodextrin incorporation have considerable potential in wastewater treatment applications. This is due to their large amounts of hydroxyl groups, hydrophobic cavity, and interactions with organic and inorganic compounds.

In the cosmetic sector, CDs are distinguished by odor control, stabilization, and process improvement upon conversion of a liquid ingredient to a solid form [37]. It is used in skin creams, toothpaste, solid and liquid fabric softeners, tissues, paper towels and underarm shields [38].

CDs are also used in food formulations for flavor delivery or flavor protection [39]. Most natural and artificial flavors are volatile oils or liquids and complexation with cyclodextrins provides a favorable substitution to the conventional encapsulation technologies used for flavor protection [38].

They are also used to remove cholesterol from products such as butter, milk, and eggs [4][40]. Materials treated with CDs show 80% removal of cholesterol [38][41]. In Japan, for more than two decades, cyclodextrins have been approved as “modified starch” for food applications, serving to mask odors in fresh food and to stabilize fish oils [38][42]. Also, CDs act as molecular encapsulants, protecting the flavor [43].

CDs are able to reinforce drug delivery through biological membranes. They act as true carriers by keeping the hydrophobic drug molecules in solution and delivering them to the surface of the biological membrane. The addition of α-CD or ß-CD increases the water solubility of several poorly water-soluble substances. Furthermore, CDs can be used to reduce the effects of irritant or bitter-tasting and bad-smelling drugs [4][40][44][45].

CDs can form complexes with an enormous variety of agricultural chemicals including insecticides, herbicides, repellents, pheromones, fungicides, and growth regulators [38][43]. CDs can also be used to delay seed germination. In grain treated with β-CD, some of the amylases that degrade the starch supplies of the seeds are inhibited, yielding a 20–45% larger harvest [4].

In the chemical industry, cyclodextrins are often used to separate enantiomers and isomers, to catalyze reactions, to aid in different processes and to detoxify or remove waste materials [38]. They can be used in electrochemical chemistry to mask contaminating compounds [4]. They are also able to serve as enzyme mimics because of the molecular recognition phenomenon [4] attributed to the substituted groups on the CD.

2.2. CDs in Solar Energy

Today, energy has become one of the most significant driving forces of economic growth and manufacturing activity. Among the renewable energy resources, solar energy is an essential component of energy usage due to it being safe, easily accessible, and its unlimited nature [46]. Nevertheless, due to the high cost and low performance of some solar energy consumption systems, it is difficult to compete with conventional energy sources. Therefore, an additional priority of researchers, both now and in the near future, is to enable the efficient transfer or storage of solar energy [47]. The heat transfer fluid (HTF) in solar thermal systems plays a crucial role due to its ability to transfer heat from the collector or absorber to the heat exchanger. The brilliant heat transfer efficiency of various nanofluids have been reported [48]. Several studies have shown excellent potential of nanofluids for use mainly in solar energy devices and in the field of heat transfer fluids [49].

On the other hand, semiconductor nanocrystals have attracted enormous attention because of their strong potential for applications in various fields and their excellent physicochemical properties. Feng et al. (2005) presented a self-assembly method based on the special structure of various semiconductor/CD hybrid materials with different morphologies to produce photoactive TiO_2-cyclodextrin wires by using CDs as bifunctionals [50]. β-CD has been found to be valuable in enhancing the kinetics of charge transfer from the photoexcited semiconductor to cavity-absorbed electron acceptors [51]. A low temperature study on TiO_2-β-CD-graphene nanocomposite synthesis for energy storage and photocatalytic applications was reported by Sharavath et al. [52]. In a novel route that is a low temperature operation, the TiO_2-CD@GNS composite was synthesized. After 1000 continuous charge/discharge cycles, it exhibits high capacitance and high cyclic stability with 90 percent capacitance retention. In order to prevent agglomeration, the CD moiety loaded on graphene nanosheets acts as a stabilizing agent for the TiO_2 NPs and has served as linkers between them [52]. Obviously, in energy harvesting and storage, the advancement of nanomaterial technology plays a vital role.

In recent years, electrochemical supercapacitors have gained substantial attention because they are capable of providing high power density, rapid charging, a long cycle life, and low maintenance costs. To fabricate high performing electrochemical sensors, CDs are being combined with emerging materials. Coupling the CDs with graphene nanosheets (GNs) is one of the more exciting combinations; this method is appealing because it results in raising the remarkable electrochemical detection of drugs and biomolecules. The CD-GNs display high supramolecular recognition and enrichment properties of CDs in addition to the good electrical and large surface area properties of GNs [53]. Another motivating blend involves the combination of CDs with carbon nanotubes (CNTs). Combining the attractive properties of the CNTs with the supramolecular inclusion complexation characteristics of the CDs resulted in enhanced electron-transfer reactions at these composites. CD-CNTs displayed an outstanding capability in improving optical properties [54][55]. CDs are combined effectively within a number of conducting polymer matrices (polypyrrole (Ppy), polyaniline (PANI), and polythiophene derivatives) and used as electrochemical sensors. It has been shown that the CDs are the main players in the detection of the objective compounds. They also retain their supramolecular complexation properties [56].

In addition to the above compounds, ordered mesoporous silicas and mesoporous carbon, and 2D layered materials with good conducting properties and high surface areas have been discovered in the development of sensors, including CDs as the molecular recognition agent [57][58][59]. For a parallel connected supercapacitor and dye-sensitized solar cell, β-CD is sulfonated, thermally crosslinked with PVP, and incorporated with $MnCO_3$ nanoparticles. A sulfated composite of β-CD/PVP/$MnCO_3$ has been thought to provide renewable energy even over long periods in hot environments for a long time [60].

2.3. Environmental Application of CDs

In the field of environmental science, CDs play a key role in enhancing and removing organic pollutants and heavy metals from the soil, water and atmosphere, and in the solubility of organic contaminants. Because of their excellent physicochemical properties and their ability to boost the stabilization, encapsulation and adsorption of pollutants, CD-based adsorbents have gained worldwide attention as new-generation adsorbents for wastewater treatment [61]. CD-based adsorbent removal mechanisms partly rely on the preparation process. Singh et al. (2002) stated that after the treatment of wastewater with β-CD, the levels of all aromatic toxic hydrocarbons such as phenol, *p*-chlorophenol, and benzene present in wastewater are substantially reduced [42].

Furthermore, in environmental fields, CDs have been commonly used as adsorbents and non-toxic cyclic oligosaccharides. The use of CDs in the formulation of insecticides plays a significant role in environmental safety. CDs are integrated into the preparation of a neem seed extract insecticide by creating a water-soluble neem seed kernel extract inclusion complex, enclosing azadirachtin-A in a CD carrier molecule. In addition to all the above-mentioned uses, CDs also contribute to the photodegradation process of organophosphorus pesticides in humid water by catalyzing the reaction of reactive radical pesticides formed by the humid photosensitizer and the inclusion of complex CDs [42].

The use of silica beads, with high mechanical properties and physical strength, containing CD molecules with advantages of a complexing substrate as adsorbents has recently received a lot of attention regarding environmental problems [62][63]. These combinationsof the silica beads with the CD result in strong binding affinities toward target pollutants and relatively high pollutant adsorption capacities and are considered as an innovative and promising tool for environmental protection [64].

In short, because of their ability to form complexes with a wide variety of chemicals, CDs have immense application in many industries, and their potential applications in additional areas still deserve further study and consideration.

3. Summary and Future Perspectives

Since their discovery in 1891, CDs have attracted a wide range of research interest in both industry and academia. Among different cyclodextrins forms and their derivatives, herein focuses on the three native CDs α-CD, β-CD, γ-CD, and some of their derivatives.

The unique chemical structures of CDs is the main reason why they have such a wide variety of applications including drug delivery, wastewater treatment, and pharmaceutical industry. The different sizes of the discussed CDs, along with their wide range of chemical and physical properties such as stabilities, reactivity, and solubility, extend their medical, environmental, and industrial applications.

For example, CDs were used in different fields to address environmental problems such as the formulation of more safe insecticides creating a water-soluble carrier molecule and being utilized for the photodegradation process of organophosphorus pesticides. The CDs biodegradability and biocompatibility give them superior properties for medical applications mainly in drug delivery and the cosmetics industry. CDs are commonly utilized in conventional encapsulation technologies used for food flavor protection, to mask odors in fresh food, and to stabilize fish oils. CDs are also used to remove unwanted molecules such as cholesterol from products like milk, butter, and eggs. CDs are used in the chemical industry to remove waste materials, catalyze reactions, and to separate enantiomers and isomers. In addition to all these usages, CDs are becoming an interesting prospect for solar energy systems due to their promising features of good optical properties, suitable stability, and high thermal conductivity.

Several research areas will continue to conduct further investigation of the synthesis of new cyclodextrin derivatives, and will reveal novel applications of these important molecules. In particular, CDs will be utilized in synthesizing new nanoparticles with designed sizes, as well as fabricating nano-devices for medical applications. For example, Huang et al. (2019) used a β-CD polymer network (CPN) to synthesize various metal nanoparticles (palladium, silver, platinum, gold, and rhodium) of subnanometer size (<1 nm) [65].

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