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Water-insoluble β-cyclodextrin–epichlorohydrin polymers for removal of pollutants from aqueous solutions by sorption processes using batch studies: A review of inclusion mechanisms☆

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ABSTRACT

Although water-insoluble cyclodextrin-epichlorohydrin polymers have been known for half a century, these materials are of continued interest to the scientific community, in particular for their interesting environmental applications as sorbents in liquid-solid sorption processes. However, in spite of the abundance of literature and conclusive results obtained at the laboratory scale, interpreting the mechanisms of pollutant elimination remains an interesting source of debate and sometimes of contradiction. This review summarizes and discusses the various mechanisms proposed in the literature. A distinction was made in the description of these interactions depending on whether the polymer structures were modified or not.

Contents

Abbreviations: APs, alkylphenols; CD, cyclodextrin; CL, cross-linker; DS, degree of substitution; ECH, epichlorohydrin; ECP, cyclodextrin material cross-linked with epichlorohydrin; EP, emerging pollutants; HSAB, hard soft acid and base concept; IEC, ion-exchange capacity; K_{ass}, association constant; NSAIDs, non-steroidal anti-inflammatory drugs; PAHs, polycyclic aromatic hydrocarbons; PCBs, polychlorobiphenyls; PZC, point of zero charge; VOCs, volatile organic compounds.

☆ This review is dedicated to Giangiacomo Torri (Istituto di Chimica e Biochimica G. Ronzoni, Milan, Italy) in celebration of his retirement.

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1. Introduction

Since the end of the 1980s, cyclodextrins (CD), substances produced from the degradation of starch, one of the key polysaccharides of the planet, have been involved in numerous industrial applications in fields as varied as pharmacy, medicine, cosmetics, agro-chemistry, supramolecular chemistry, enzymology, chromatography and catalysis [1–14]. There are many reasons why CDs are used for all these different tasks [15–25]. They are non-toxic, biodegradable, produced at an industrial scale, and can be used in their dissolved or solid, native or modified forms. CDs also present a characteristic macrocyclic structure and quite particular properties due to the hydrophobic lining of the central cavity and hydrophilic outer surface. The hydrophobic cavity enables them to encapsulate other substances to form inclusion complexes presenting a host-guest type of relationship (Fig. 1). Indeed, this remarkable encapsulation property is very useful for industrial applications because the physical, chemical, and/or biological characteristics of a target molecule (the guest) can be modified and/or improved depending upon the objectives [26–29]. Moreover, due to their excellent chemical reactivity, they can also enable relatively facile synthesis of innovative materials for applications in the field of pollution removal from various compartments of the environment such as water, air, soil and sediment.

Among the various CD-based materials proposed for water treatment by liquid-solid sorption, CDs cross-linked with epichlorohydrin (abbreviated ECH) are by far the most widely studied sorbents, owing not only to their chemical efficiency at eliminating a broad range of pollutants, but also to their synthesis that is straightforward and facile. Table 1 presents several general reviews and book chapters on this subject [30–49]. The cross-linking involves creating covalent chemical bonds in all directions in space during a polymerization or co-polymerization reaction that generates a macromolecular network of larger size and with different properties than those of the initial monomer. This reaction yields the polymeric (or copolymeric) cross-linked material. The straightforward synthesis of these materials or polymers (both terms will be used in this review) is made possible by the high reactivity of the CD and of the ECH cross-linking agent in basic media. Moreover, ECH is not expensive and as it is a widely used epoxy reagent, its mode of action is well understood. ECH is the most frequently used cross-linking agent in starch chemistry, notably in pharmaceuticals where it is used to design carriers and pharmaceutical formulations involving starch [50–54].

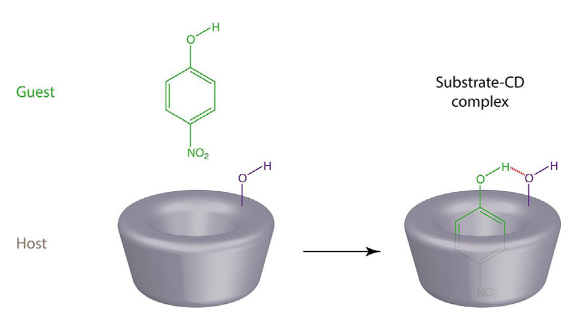

Fig. 1. Schematic representation of the association of free cyclodextrin ("host") and para-nitrophenol ("guest").

The first studies and the first patent on CD materials cross-linked with ECH (known as ECP material or ECH-cross-linked polymer in the literature) were published in 1964-65 by the Swiss group of Jürg Solms (Research Laboratory of the Nestlé Group in Vevey) [54–58]. The Dutch group of Niels Wiedenhof [59–63] (Laboratory of General Chemistry, Eindhoven) at the end of the 60s, the American group of Jerald L. Hoffman [64–66] (University of Louisville, Kentucky) in the early 70s, and the Hungarian group of József Szejtli [16,19,29,67–93] (Chinoin Chemical and Pharmaceutical Works, Budapest) in the late 70 s are also acknowledged for their numerous contributions towards cross-linking CDs with ECH. Various reviews from Crini's group can be consulted for a more detailed background concerning these materials [1,25,35,36,38,42]. The main applications of ECP materials consisted of their use in low-pressure liquid chromatography to separate vitamins, nucleic acids, and proteins or in the clarification of juice for the food industry [95–116]. In all these studies, the results were generally interpreted considering that in the presence of CD molecules, inclusion complexes would form. Szejtli was the first to demonstrate and interpret the fundamental role of CD cavities in the performance of ECP materials. He also introduced the notion of association complexes (cooperation between CD cavities) in addition to inclusion complexes [1,16,19].

At the end of the 90s, the first studies appeared on the use of these materials to complex and remove drugs and also pollutants from the environment, mainly aromatics or phenolics of varying complexity [19,33,35]. Several interesting patents [117,118] and papers [119–139] can be consulted concerning these applications. Here again, the results stressed the essential role of the cavities in the CDs. Just as a consensus of opinion, the main force involved in the proposed sorption mechanisms was chemisorption through the formation of an inclusion complex. Recent studies have led to reports demonstrating that inclusion alone cannot explain the whole range of sorption results. It was suggested that other phenomena occurred, especially mechanisms involving the polymer network (external to the inclusion sites). Other interactions were then proposed: complexes involving association (cooperative effect of the grid of the polymer network), surface sorption, van der Waals forces, hydrophobic interactions, hydrogen bonding, electrostatic interactions, Yoshida forces, etc. It was the beginning of a debate in the literature on how much importance to give to each of these interactions.

In the early 2000s, new chemically modified ECP were proposed for applications in water and wastewater treatment [36,94,120,121]. The aim of the modifications was, for instance, to enlarge the range of use of the materials to cover the removal of pollutants such as metals and dyes, by introducing particular ionic functions into the polymer network through reactions well-known in the field of polysaccharide chemistry [36,140–143]. Here again, the literature stressed the importance of the moieties at the surface of the ECP material rather than inclusion to explain the mechanisms. Inclusion aside, various mechanisms are proposed depending on the type of function or ligand grafted, for instance ion exchange, electrostatic attraction, chelation, and precipitation (or microprecipitation). The mechanisms then become more difficult to explain, particularly considering which interaction will play a greater role.

Although the cross-linking of CDs with ECH has been known for half a century, it continues to be of interest to the scientific commu-