Chapter 8
Water-Insoluble Cyclodextrin-Epichlorohydrin Polymers

Grégorio Crini

Contents

8.1 Introduction 347
8.2 Synthesis of Water-Insoluble Cyclodextrin-Epichlorohydrin Polymers 349
    8.2.1 Cross-Linking Reaction 349
    8.2.2 NMR Characterization 353
    8.2.3 Swelling Properties of Cyclodextrin-Epichlorohydrin Polymers 356
    8.2.4 Chemical Modification of Cyclodextrin-Epichlorohydrin Polymers 357
8.3 A Brief History of Water-Insoluble Cyclodextrin-Epichlorohydrin Polymers for Environmental Applications 360
8.4 Elimination of Environmental Contaminants Using Cross-Linked Cyclodextrin Polymers as Adsorbents 363
    8.4.1 Early Works 363
    8.4.2 Organics and Dye Removal 363
    8.4.3 Pollutant Removal Using Modified Cyclodextrin Polymers 366
    8.4.4 Treatment of Organic Substances and Metals Present in Industrial Discharge Waters 368
    8.4.5 Mechanisms of Sorption 370
8.5 Conclusions 373
References 386

Abstract Proposed and studied in the mid-1960s, water-insoluble cyclodextrin-epichlorohydrin polymers are of continued interest to the scientific community, particularly for their environmental applications. The most characteristic feature of these materials is their ability to form inclusion complexes with various contaminants through host-guest interactions. This leads to many environmental applications, including water and wastewater treatment, soil remediation, air purification, and the concentration or elimination of target substances such as cholesterol.

In the early 1990s, our group began working on the synthesis of water-insoluble cyclodextrin-based materials, their structural characterization, and their application

---

G. Crini (✉)
Chrono-environnement, UMR 6249, UFR Sciences et Techniques,
Université Bourgogne Franche-Comté, Besançon, France
e-mail: gregorio.crini@univ-fcomte.fr

G. Crini et al. (eds.), *The History of Cyclodextrins*, Environmental Chemistry
for a Sustainable World 52, https://doi.org/10.1007/978-3-030-49308-0_8

in the removal of pollutants present in wastewater. One of the first results published in 1995 concerned the fact that this material was not a true polymer but a copolymer with a particular structure with two different molecular mobilities. In 1997, this was demonstrated for the first time by solid-state NMR spectroscopy. These materials were composed of a relatively dense, rigid, and hydrophobic cross-linked core and a more hydrophilic surface, less cross-linked containing long and highly mobile hydroxyalkylated polymer chains through the homopolymerization of the cross-linking agent. In 1998, cyclodextrin-based materials were used as adsorbents to efficiently remove organic contaminants from contaminated water. One year later, a more surprising result showed that a high proportion of cyclodextrin was not necessary to have useful performance in terms of pollutant removal. In 2000, using cross-polarization magic angle spinning with dipolar decoupling and high-resolution magic angle spinning spectra, we concluded that the mechanism of adsorption can be explained by the presence of two main interactions: the formation of an inclusion complex due to the cyclodextrin molecules and the physical adsorption in the polymer network. In 2005, a patent was filed on a process for the synthesis of cross-linked polysaccharides with ionic functional groups for the simultaneous removal of metals and organic contaminants present at low trace levels in polycontaminated effluents. At the end of the 2000s, we carried out the first pilot studies demonstrating that a single cyclodextrin material with amphoteric and ion-exchange properties could replace two conventional adsorbents to effectively treat multi-contaminated effluent. In the early 2010s, our group proposed for the first time biomonitoring tests using plants as bioindicators to determine and compare the toxicity of industrial effluent from wood, pulp and paper, textile, and surface treatment industries before and after treatment with a cyclodextrin material. In the mid-2010s, we confirmed the feasibility of implementing materials for the treatment of discharge waters from surface treatment industries on an industrial scale.

The purpose of this chapter is to summarize the research conducted over the past 30 years by our research group on water-insoluble cyclodextrin-epichlorohydrin polymers used as complexing materials to remove contaminants present in aqueous solutions. It shows the progress of our work and our contribution to a better understanding of these materials. These years were devoted to the synthesis of a series of water-insoluble materials with different functionalities in the form of gels or beads, their characterization by innovative solid-state NMR techniques, the demonstration of their effectiveness as adsorbents in wastewater treatment, and the explanation of contaminant removal mechanisms according to the type of material used.

Keywords History · Cyclodextrin polymers · Synthesis · Characterization · Complexation · Adsorption · Industry

Abbreviations

CPMAS	Cross-polarization magic angle spinning with dipolar decoupling
ECP	Cyclodextrin-epichlorohydrin polymers
HRMAS	High-resolution magic angle spinning
NMR	Nuclear magnetic resonance

8.1 Introduction

In 1990, I was a young student in organic chemistry and macromolecular chemistry at the *Laboratoire de Chimie Organique et Macromoléculaire* (University of Lille 1, France) under the supervision of Professor Michel Morcellet.

In the same year, a French company (Roquette Frères, Lestrem) asked Morcellet's group to produce a series of cross-linked cyclodextrin gels using epichlorohydrin as cross-linking agent for applications in chromatography at industrial scale. The main objective was to verify if the polymer cyclodextrins were suitable chromatographic supports for gel inclusion chromatography, e.g., for the separation of caffeine, phenylalanine, naphthols and derivatives, benzaldehyde, nucleic acids, etc. This project was also carried out in collaboration with Professor Yahya Lekchiri of the University of Mohamed 1st, Oujda (Morocco).

Our first approach was to review the literature, an activity that we have been doing continuously since then (Crini et al. 2001; Crini and Morcellet 2002; Crini 2005a, 2006, 2014, 2015a, b; Badot et al. 2007; Sancey and Crini 2012; Morin-Crini and Crini 2013; Euvrard et al. 2015; Fourmentin et al. 2015; Crini et al. 2018a, b, 2019a; Morin-Crini et al. 2018a, b, 2019a). In 2002, we published a first comprehensive review on the synthesis, characterization, and applications of cross-linked cyclodextrin-based materials (Crini and Morcellet 2002). This review was updated 11 years later (Morin-Crini and Crini 2013).

Then we started working on the synthesis of water-insoluble cyclodextrin-based materials, thanks to industrial and European grants. With the first results obtained, I supported a Master of Science in Organic Chemistry in 1990, a Master of Science in Macromolecular Chemistry in 1992, and then a PhD in Organic Chemistry and Macromolecular Chemistry in 1995 (Crini 1995).

In 1994, my interest extended to solid-state nuclear magnetic resonance (NMR) characterization of these cyclodextrin polymers with a 1-year visit to the NMR Department of the G. Ronzoni Institute for Chemical and Biochemical Research (Milan, Italy), invited by the Research Director Giangiacomo Torri. Interesting results have been obtained both from the point of view of synthesis and characterization and applications in chromatography and oil removal and petroleum industry (Crini et al. 1995a, b, 1996, 1998a, b; Shao et al. 1996; Vecchi et al. 1998). However, for several reasons, such as the variability of polymer characteristics, the difficulty of producing materials with the same cross-linking density, lack of porosity, lack of reproducibility of the chromatographic results, etc., the industrial project initiated in the early 1990s on cyclodextrin-based polymers for chromatographic applications was abandoned 1 year later.

At the same period, Professor Gerhard Wenz asked Professor Morcellet and Professor Casu to participate in the implementation of a European project on cyclodextrin polymers. In 1995, the project, focusing on the "Development from cyclodextrin derivatives to polymeric materials for selective transport, separation and detection of active substances" (FAIR Program 1995–1999, European Commission DGXII, contract no. CT 95-0300), was accepted. This was my entrance to the world of oligosaccharides and polysaccharides for environmental applications. As part of this project, after obtaining my PhD in 1995, I spent 2 years as a postdoctoral fellow at the Chemical Unit of G. Ronzoni Institute, under the direction of Dr. Torri and Professor Benito Casu, to work on the synthesis and NMR characterization of cyclodextrin-epichlorohydrin polymers, two of the objectives of the FAIR Program. At that time, the Institute's internationally recognized chemistry unit played a leading role in the pure and applied chemistry of carbohydrates and biopolymers. During the FAIR project, I had the opportunity to work with academics, including Dr. Anna-Maria Naggi, Dr. Carmen Vecchi, Dr. Marco Guerrini, Dr. Cesare Cosentino, Dr. Edwin Yates, Dr. Bernard Martel, Professor Wenz, Professor Wilfried König (Fig. 8.1), Dr. Bruno Perly, Professor Jacques Defaye, and Professor David Reinhoudt, and industrialists, e.g., Wacker Chemie, Bruker Italy, Chiesi Pharmaceutical, and *Stazione Sperimentale per i Combustibili*.

In September 1995, "after a long evening of fruitful exchanges at the *Galleria Vittorio Emanuelle II* in the Centre of Milan" with Giangiacomo Torri on the problems of the textile and paper industries, I had the idea to use cyclodextrin-based materials to remove dyes from aqueous solutions. Back at the Ronzoni Institute, I started working on the subject under the supervision of Dr. Torri, Professor Casu, and Professor Morcellet. The first results were presented at the Eight International Cyclodextrin Symposium in Budapest, March 31–April 2, 1996 (Fig. 8.1). At this Symposium, we first introduced the term "cyclodextrin microsponges" and proposed these materials as non-conventional adsorbents for the removal of target contaminants such as dyes and aromatic and phenolic compounds. However, this term

Fig. 8.1 Left: An evening organized by Professor König (with the red sweater) in Hamburg in 1996 during the FAIR project; Right: G. Crini with Professor M. Morcellet and Dr. G. Torri at the Eighth International Symposium on Cyclodextrins, Budapest, Hungary, March 31–April 2, 1996, where we introduced for the first time the term "cyclodextrin microsponges"

has generated much negative debate and criticism, although Professor József Szejtli, one of the prestigious researchers who contributed to the development of cyclodextrins, accepted it and congratulated our work. At the time, we abandoned it and then used the terms cyclodextrin polymer, cyclodextrin material, or simply gel/hydrogel. A few years later, the term "microsponges" was adopted over by other researchers.

In 1996, my interest also extended to starch, cellulose, and chitosan biopolymers, after two fruitful meetings in Milano, the first with Dr. Torri, Dr. Carmen Vecchi, and Professor Piero Sozzani organized at the *Stazione Sperimentale per i Combustibili* and the second with Professor Casu, Professor Bonaventura Focher, and Professor Kjell Vårum at the *Stazione Sperimentale per la Cellulosa, Carta e Fibre Tessili*. A year later, I joined the University of Franche-Comté where, with Professor Joël Vebrel, I created a research group working on adsorption processes based on oligosaccharides and polysaccharides for pollutant removal. At that time, our work focused mainly on the use of cyclodextrin-epichlorohydrin polymers and chitosan-based materials used as adsorbents for the removal of dyes from industrial effluents. Our current research focuses on the design of new functionalized macromolecular networks based on oligosaccharides (linear or cyclic dextrins), polysaccharides (starch, chitosan, cellulose), or agricultural fibers (hemp) for applied research for environmental purposes.

The purpose of this chapter is to present a review of some 30 years of research within my team as part of a scientific and industrial strategy. Our main area of research focused on the design and use of cyclodextrin-based materials for the removal of trace contaminants from polycontaminated industrial effluents from the textile, pulp and paper, wood, and surface treatment industries. The work involved the production of a series of water-insoluble cyclodextrin-epichlorohydrin polymers with different physical and textural properties, their chemical modification and solid-state NMR characterization, and their use as complexing agents in wastewater treatment. An important part of the work has also focused on explaining the contaminant removal mechanisms according to the type of cross-linked material used.

8.2 Synthesis of Water-Insoluble Cyclodextrin-Epichlorohydrin Polymers

8.2.1 Cross-Linking Reaction

Chemical cross-linking using epichlorohydrin as cross-linking agent is the most straightforward method to produce water-insoluble cyclodextrin-based polymers. These cyclodextrin-epichlorohydrin polymers known as ECP materials were first proposed in 1964 by the Swiss chemist Jürg Solms (Research Laboratory of the Nestlé Group, Vevey), who patented their chemical synthesis by block polymerization and their analytical applications as "inclusion resins" in chromatography and separation science (Solms and Egli 1964, 1965; Solms 1966, 1967, 1969).

The Dutch group of Niels Wiedenhof (Laboratory of General Chemistry, Eindhoven) at the end of the 1960s (Wiedenhof 1969; Wiedenhof et al. 1969, 1971; Wiedenhof and Trieling 1971), the American group of Jerald L. Hoffman (University of Louisville, Kentucky) in the early 1970s (Hoffman 1970, 1972, 1973), and the Hungarian group of József Szejtli (Chinoin Chemical and Pharmaceutical Works, Budapest) in the late 1970s (Szejtli et al. 1978; Szejtli 1980, 1982, 1984, 1988; Szemán et al. 1987) are also known for their many contributions to the cross-linking of cyclodextrins with epichlorohydrin. In the late 1990s, our group also studied ECP polymers and contributed to a better understanding of their synthesis. We used the same the procedure as described by Solms and improved by Hoffman but with some modifications, in particular in the molar ratios of the reagents.

The reaction that leads to the cross-linking of cyclodextrin molecules by epichlorohydrin, 1-chloro-2,3-epoxypropane (Fig. 8.2), is an easy method for preparing cyclodextrin-based materials (Solms and Egli 1964; Wiedenhof 1969; Hoffman 1970). Their one-step synthesis in water is simple and easy to set up in a lab and only requires mild reaction conditions (water-based chemistry, mild temperatures between 50° and 80 °C, and at atmospheric pressure). However, to obtain beads with porosity, it is necessary to use organic solvents. Figure 8.3 shows the reactor used in our laboratory to prepare up to 50 kg of material in a single step. The reagents involved are easy to find and inexpensive. The only compounds are water, caustic soda, and epichlorohydrin.

Cyclodextrin molecules are cross-linked by direct reaction between their hydroxyl groups with epichlorohydrin (abbreviated ECH or EPI in the literature) in an alkaline medium to form polymeric structures or ECP materials. Depending on the experimental conditions, in particular the degree of cross-linking, the ECP materials may be cross-linked polymers that are soluble or insoluble in water (Shao et al. 1996; Crini et al. 1998a). Due to its high reactivity in basic medium, the cross-linking agent can form bonds with cyclodextrin molecules (cross-linking step) and/

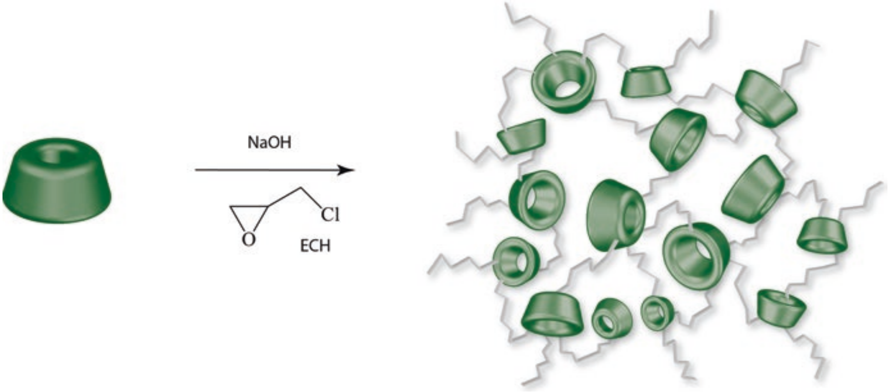

Fig. 8.2 Chemical reaction between a cyclodextrin molecule and epichlorohydrin (ECH) in basic medium to give a cyclodextrin-epichlorohydrin polymer

Fig. 8.3 Pilot used for the synthesis of cyclodextrin-epichlorohydrin polymers in our lab

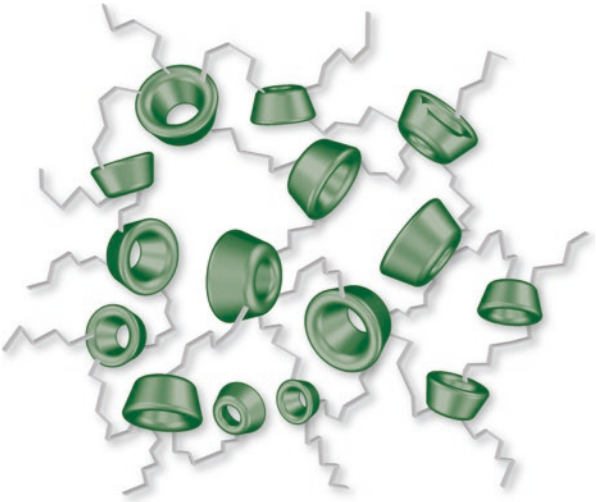

Fig. 8.4 Structure of a cyclodextrin-epichlorohydrin polymer known as ECP material in the literature

or itself (polymerization step). A number of cyclodextrin rings are interconnected, and a three-dimensional polymer network is formed. In 2002, our group proposed the structure of an ECP material described in Fig. 8.4, inspired on the 1972 Hofmann structure.

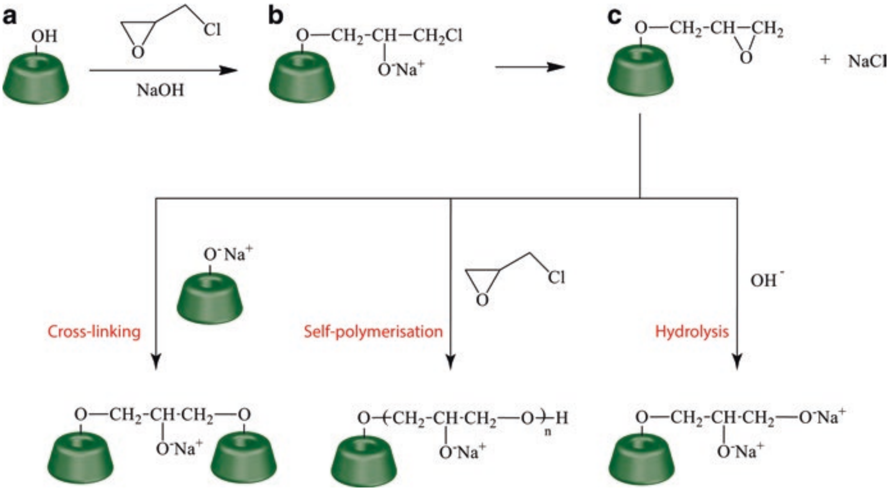

Fig. 8.5 Possible reactions between a cyclodextrin molecule and epichlorohydrin: (**a**) cross-linking to form a polymer; (**b**) self-polymerization of the cross-linker, and (**c**) formation of a glycerol monoether derivative by hydrolysis

To explain the cross-linking reaction (Fig. 8.2), Professor Szejtli adopted the mechanism described in Fig. 8.5, first proposed in the 1960s by Professor Hofmann, in the 1980s. This mechanism is divided into three main steps that take place simultaneously. The first step, cross-linking, consists in creating a three-dimensional structure using the bridging agent that binds the cyclodextrin molecules by strong covalent bonds. This is the main reaction and is responsible for creating a macromolecular network with a variable proportion of cross-links. The second step is the polymerization of the cross-linking agent, due to the high reactivity of epichlorohydrin, which allows it to polymerize with itself in basic medium, particularly with an excessive concentration of epichlorohydrin. This results long hydroxyalkyl macromolecular chains that function both as bridges and as side chains in the network. This is why some authors consider these materials as copolymers with two distinct components. In the last reaction (hydrolysis in Fig. 8.5), glycerol monoether polymer subunits are considered undesirable by-products. This reaction is not easy to control, which is why epichlorohydrin is often used in the synthesis in excess, usually 10 mol/mol cyclodextrin (Morin-Crini et al. 2013, 2018a).

A cyclodextrin-epichlorohydrin polymer, in water-insoluble or water-soluble form, is an O-alkylated polymeric resin. However, this is not a true polymer but a copolymer, first suggested in the 1970s by Professor Hoffman and taken up by Professor Szejtli in the 1980s. The concept is to consider cyclodextrin as a first monomer and epichlorohydrin as a second monomer in the synthesis. By modifying the molar ratio of the two monomers, the resulting copolymer is richer in one or the other of the monomers. In 1998, our group demonstrated that changes in the relative mole ratio of cyclodextrin (monomer A) to epichlorohydrin (monomer B) modify the repetitive structure of monomer units from an A-B-type copolymer to an

A-B$_n$-type copolymer; the latter type contains epichlorohydrin-rich domains that are hydrophilic by nature with an amorphous structure. This was demonstrated using NMR data (Crini et al. 1998b; Bertini et al. 1999) and later confirmed by the Spanish group of Professor José Ramon Isasi at Navarra University (Romo et al. 2004, 2006, 2008; García-Zubiri et al. 2006; Vélaz et al. 2007).

At the time, in accordance with Szejtli's results, our group also reported that it was important to select the optimal synthesis conditions to obtain the desired product characteristics, such as the degree of swelling and cyclodextrin content (Shao et al. 1996; Vecchi et al. 1998; Crini et al. 1998a). By varying the synthesis conditions, for example, the amounts of the different reagents, the molar ratio of cyclodextrin to epichlorohydrin, the NaOH concentration, the reaction temperature, and the reaction time, it was possible to induce structural modifications in the hydrogel networks in terms of surface area and porosity and also to obtain gels or beads with different cyclodextrin contents (Crini et al. 1998a, b). We have reported that a high polymerization temperature promoted a high degree of polymer swelling. The introduction of rigid structures into a material has been beneficial to create porosity and has increased the surface area, as well as the co-presence of an organic solvent during synthesis. Later, similar conclusions were reported by Professor Isasi (Romo et al. 2004, 2006, 2008; García-Zubiri et al. 2006; Vélaz et al. 2007), by the Turkish group of Professor Mustafa Yilmaz at Selçuk University (Yilmaz Ozmen and Yilmaz 2007, 2008), and by the Canadian group of Professor Lee D. Wilson at the University of Saskatchewan (Mohamed et al. 2010, 2012; Pratt et al. 2010; Wilson et al. 2010).

The cross-linking step has always been the subject of debate in the literature. Two "schools of thought" have been established (Crini 2005a; Morin-Crini and Crini 2013): one promoting a low cross-linking leading to hydrogel-type products and the other promoting a high cross-linking leading to organic bead-type products. However, as Professor Szejtli has pointed out, this distinction may result from different end uses. For wastewater treatment, gel-type systems are appropriate but not for use in high-pressure chromatography, as the particles must have some mechanical resistance (Szejtli 1982, 1988).

8.2.2 NMR Characterization

The mechanism described in Fig. 8.5 was studied in detail by Professor Bernard Sébille (*Université de Paris XII*, France) in 1997 for water-soluble epichlorohydrin-cross-linked cyclodextrin polymers (Renard et al. 1997). The same year, our group demonstrated for the first time the structure of water-insoluble ECP polymers by NMR spectroscopy. These results were presented at the IXth European Carbohydrate Symposium at Utrecht (The Netherlands, 6–11 July 1997) and published 1 year later in the journal *Carbohydrate Research* (Crini et al. 1998b). Using cross-polarization magic angle spinning with dipolar decoupling (CPMAS) and high-resolution magic angle spinning (HRMAS) spectra, we demonstrated that, in the materials, two kinds of structures existed with different molecular mobility: cyclodextrin cross-linked by epichlorohydrin due to the cross-linking reaction between the cyclodextrin molecules and epoxide and polymerized epichlorohydrin due to the homopolymerization of epichlorohydrin with itself. These two components were analyzed in terms of relaxation parameters, i.e., ^{13}C spin lattice relaxation and ^{1}H spin lattice relaxation in the rotating frame (Crini et al. 1998a, b, 2000).

In spite of the facile synthetic conditions for the preparation of ECP-based polymers, the polymer networks may adopt variable structural variability. Since cyclodextrin molecules contain several glucose units and hydroxyalkyl groups present at positions 2, 3, and 6 in each glucose unit, the structure of the polymer network is complicated because, during synthesis, many units can be interconnected as shown in Fig. 8.2. This structure has been demonstrated by solid-state NMR experiments and relaxation time techniques (Crini et al. 1998a, 2000). Figure 8.6 shows the CPMAS spectra of a β-cyclodextrin sample and a water-insoluble β-cyclodextrin-epichlorohydrin polymer. The CPMAS spectrum of a polymer is typical of a solid with an amorphous structure, but it resembles to a classical β-cyclodextrin spectrum. However, this spectrum permits only one well-defined signal, i.e., the resonance at 100 ppm due to the anomeric C-1, to be assigned because there is a large degree of signal overlap in the range 55–85 ppm (Crini et al. 1998a). The signals of polymerized epichlorohydrin are completely hidden by the C-2, C-3, C-4, and C-5 β-cyclodextrin peaks. Our group was the first to overcome this overlap problem with a comprehensive NMR study, including CPMAS, MAS, and HRMAS experiments and relaxation parameter measurements. These NMR data made it possible to assign

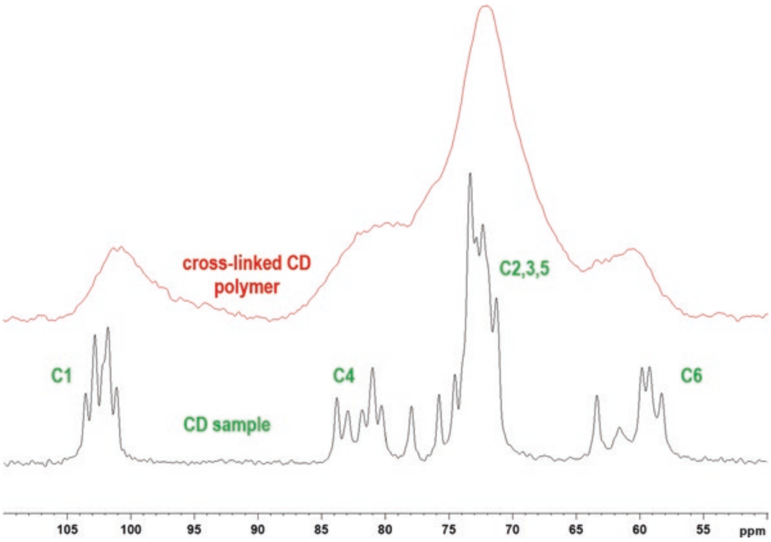

Fig. 8.6 Comparison of CPMAS spectra of a β-cyclodextrin sample and a water-insoluble β-cyclodextrin-epichlorohydrin polymer recorded by our team in 1994 on a Bruker AC-300 spectrometer and CXP-300 NMR spectrometer, respectively

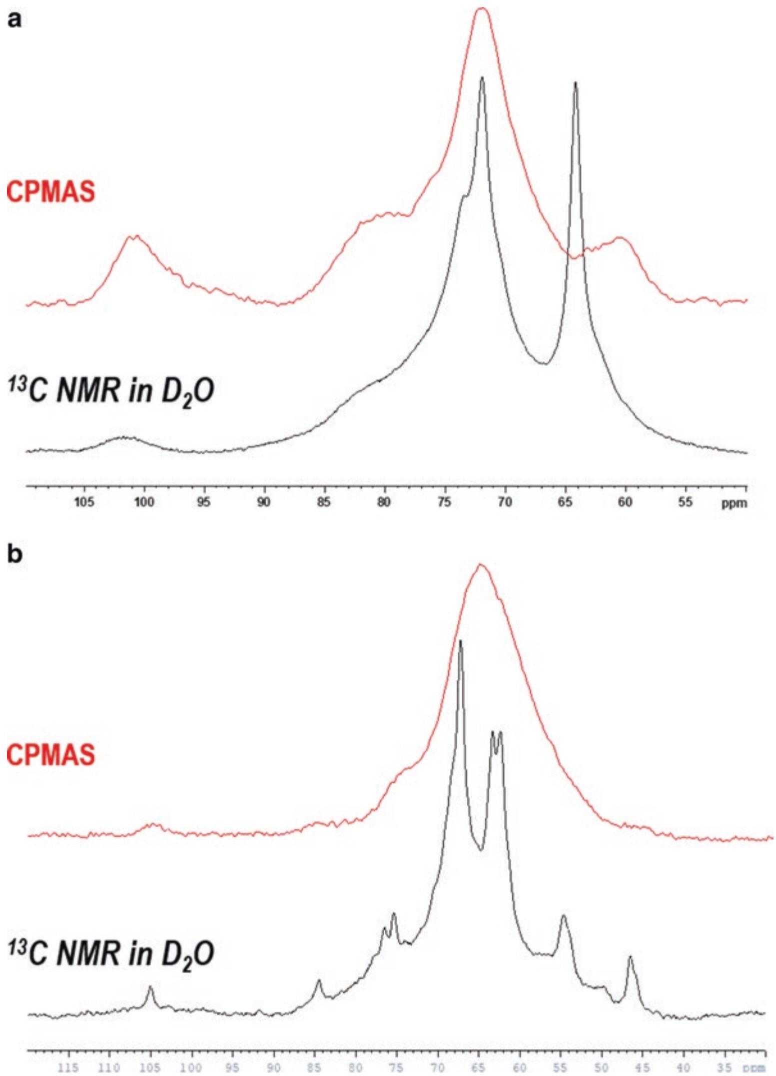

Fig. 8.7 Influence of the degree of cross-linking on CPMAS and ^{13}C NMR spectra of a water-insoluble β-cyclodextrin-epichlorohydrin polymer. (**a**) cross-linked polymer. (**b**) highly cross-linked polymer

the main ^1H and ^{13}C signals and to demonstrate the presence of two distinct components in the materials with different mobility.

As the degree of cross-linking increases, the resolution decreases in the CPMAS spectra as shown in Fig. 8.7; however, the resolution increases in the ^{13}C NMR spectra recorded in solution as revealed by the number of resonances. This highlights the mobility of the polymerized epichlorohydrin grafted onto the surface of the cross-linked polymer (Crini et al. 1998a). When the degree of cross-linking is high, the sample is mostly amorphous, and cross-linking is not homogeneous. The amorphous character is caused by the loss of cyclodextrin crystallinity during the cross-linking reaction. The structure is heterogeneous and presents different regions with different mobility properties. For the first time, NMR studies have shown cyclodextrin gels are composed of a relatively dense, rigid, and hydrophobic cross-linked core and a more hydrophilic surface, less cross-linked containing long and highly mobile hydroxyalkylated polymer chains through the homopolymerization of the cross-linking agent (Crini et al. 1998a). Two years later, these conclusions were confirmed by HRMAS experiments (Crini et al. 2000). In 2012, Wilson's group reported similar interpretations using NMR experiments (Mohamed et al. 2012).

8.2.3 Swelling Properties of Cyclodextrin-Epichlorohydrin Polymers

Various types of materials can be obtained with physical textures and mechanical properties that can be varied by giving different shapes, such as gels/hydrogels or "small balls" (beads, resins). At the end of the 1960s, Professor Wiedenhof was the first to demonstrate that materials can easily be prepared as irregularly shaped particles or regular "balls" and that they had a remarkably high swelling capacity in water, depending on the conditions of synthesis, especially the degree of cross-linking. Under particular synthesis conditions, such as heterogeneous two-phase synthesis in the presence of a blowing agent, it is possible to obtain a well-defined spherical size and shape and a uniform and controlled distribution (Bertini et al. 1999; Vecchi et al. 1998). Other forms of such sponges or foams insoluble in water and in many other solvents can also be obtained, depending on the intended application (Crini and Morcellet 2002; Crini 2005a).

Among the most studied materials are gel polymers that can swell in water and absorb up to several times their weight. They simultaneously have properties characteristic of both liquids and solids. Their swelling properties become useful for the complexation of contaminants because they promote diffusion processes in the polymer network (Crini et al. 1998a). The macromolecular network also has a structure that is mainly amorphous with very few or complete absence of crystalline zone (Crini et al. 1998b, 2000; Vecchi et al. 1998). This amorphous character represents an additional advantage in wastewater treatment as it favors adsorption processes (Crini 2005a). Indeed, it is also important to note that the flexibility of the molecular chains makes them easily entangled with each other, resulting in a non-porous structure with a very low specific surface area (Crini and Morcellet 2002; Crini 2005a). Professor Szejtli was the first to study in detail the precise role of the solvent (water, organic solvents, or a mixture of both) in the formation of non-porous or porous gels and beads (Szejtli 1982). Since then, all highly porous cyclodextrin polymers have been synthetized in organic phase using customized cross-linkers, including epichlorohydrin (Morin-Crini et al. 2013, 2018a). Literature methods to produce porous cyclodextrins polymers can require long reaction times, and the type of cross-linking agent strongly influences the pore diameter. Nevertheless, synthesis in aqueous media is generally preferred because of their simplicity and their more ecological nature (Crini and Morcellet 2002; Crini 2005a; Morin-Crini et al. 2013, 2018a). Xu et al. (2019) recently proposed for the first time the synthesis of an ultraporous polymer in aqueous phase.

Nowadays, several materials with different characteristics in terms of cross-link density, surface area, pore structure, and physical and chemical properties can be obtained. They can be precisely tailored to have desired architectures and functionalities. This explains the fact that, although the cross-linking of cyclodextrin molecules with epichlorohydrin has been known for more than half a century, it continues to be of interest to the scientific community (Euvrard et al. 2017; Crini et al. 2018a, b; Morin-Crini et al. 2018a). Ongoing work is proposing innovative macromolecular architectures in the form of foams, nanoparticles, nanosponges, fibers (nanofibers/nanowebs), felts, membranes/nanomembranes, "intelligent" hydrogels, composites, or film-based products. These materials are developed for various applications not only in the environmental field, for example, the elimination of the so-called emergent pollutants (pesticides, drugs, endocrine disruptors, etc.) present in polluted water or soil and air filtration, but also in the pharmaceutical or medical fields (drug delivery, biomedicine) or in innovative fields (medical textiles, composites for packaging, encapsulation of essential oils and volatiles, nanocatalysis, nanoelectronics) (Crini et al. 2019a).

8.2.4 Chemical Modification of Cyclodextrin-Epichlorohydrin Polymers

The chemical modification of a cyclodextrin-based material is an interesting step to introduce specific properties in order to broaden the scope of its potential applications. This was first suggested by Professor French in the 1950s and then studied by Professor Casu in the 1960s (Crini 2014). In general, the objectives are to improve pollutant adsorption properties, to increase selectivity for target pollutants, and to prepare amphoteric polymers. For example, the functionalization of ECP materials can modify characteristics of this class of gel such as selectivity when forming inclusion complexes. By replacing one or more OH groups at a "desired" position and with an appositely designed substitution group, multisite recognition systems can be obtained (Crini and Morcellet 2002). The preparation of homogeneous, selectively derivatized ECP is, however, not an easy task, as reported by Professor Szejtli in the 1980s.

The literature suggests two main methods for modifying ECP materials. The first method was introduced by Professor French in the 1950s and adopted by Professor Wiedenhof in the 1960s and Professor Szejtli in the 1980s (Crini 2014; Morin-Crini et al. 2018a). It consists in grafting specific moieties onto the materials after cross-linking using conventional modification reactions such as carboxymethylation and aminoalkylation. The main aim is to modify the surface chemistry of cross-linked materials by grafting ionic ligands (cationic and/or anionic) or neutral ligands (amine functions). These new ligands will then also behave as active binding sites and participate in the adsorption process (Crini and Morcellet 2002; Crini 2005b). These grafting reactions, which occur in heterogeneous media, are derived from the chemistry of polysaccharides such as cellulose. The second uses polymers such as carboxymethylcellulose or neutral or ionic reagents such as ammonia, glycidyl trimethylammonium chloride, etc. at the same time as epichlorohydrin in the cross-linking step of the same synthesis reactor. In this approach, the main objective is to control the structure of the materials (porosity, specific surface area, mechanical properties, etc.) while modifying the surface chemistry of the material (Crini and Morcellet 2002; Crini 2005b). Figure 8.8 shows that NMR techniques are also an interesting tool for demonstrating chemical grafting of carboxylic groups on an ECP material.

We have reported ECP materials with both cationic and anionic groups (Fig. 8.9), synthetized in two steps: cross-linking with epichlorohydrin in the presence of 2,3-epoxypropyltrimethylammonium chloride and carboxymethylation reaction (Crini 2005b). The degree of substitution (number of substituents in a cyclodextrin unit, DS) of hydroxyl groups by ionic functions was relatively low (DS < 0.2) but sufficient to exhibit chemisorption properties to remove pollutants from real poly-contaminated effluents (Euvrard et al. 2015, 2017). When the cross-linked polymer

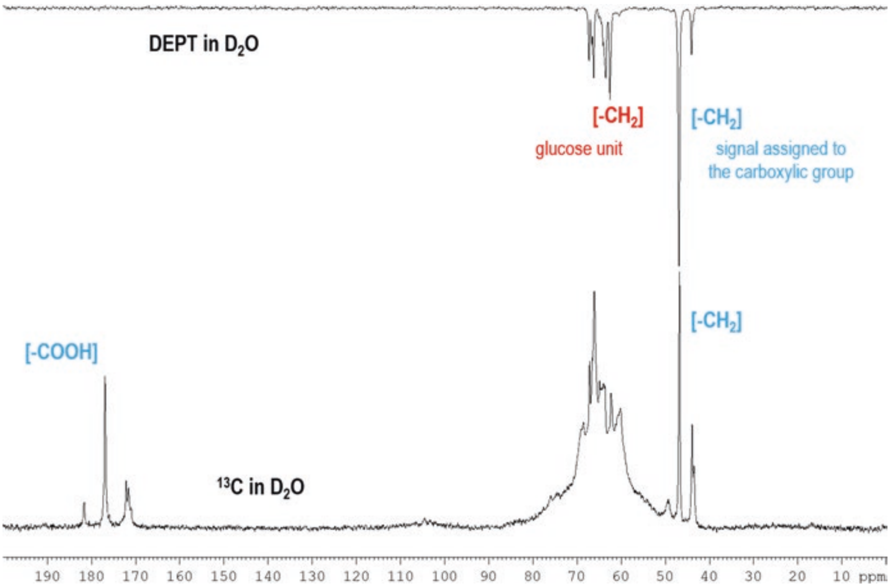

Fig. 8.8 ^{13}C NMR and DEPT spectra in D_2O showing the grafting of carboxylic groups onto the surface of a cross-linked polymer. The presence of two additional peaks at 48 and 180 ppm demonstrates carboxymethylation reaction

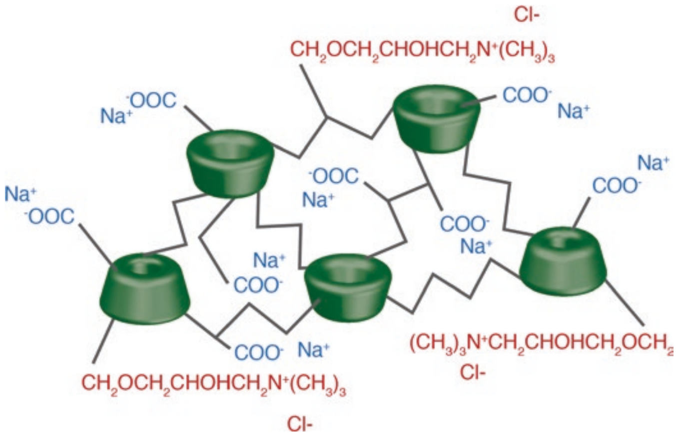

Fig. 8.9 A possible structure of a water-insoluble cyclodextrin-epichlorohydrin polymer containing both cationic and anionic groups

is modified or the cross-linking and modification are carried out simultaneously, the ionic substituents can then be located both on the rims of the cyclodextrins and on the network. This can be explained by the fact that the hydroxyl groups on the glyceryl bridges and on the side chains of the glyceryl monoether polymer are reactive (Szejtli 1982, 1988). Therefore, instead of degree of substitution, it is better to characterize the polymer by the concentration of substituents (mM)/g of the polymer adsorbent (Morin-Crini and Crini 2013). Modification by charged functional units can improve the binding affinity of cyclodextrin molecules for oppositely charged guests. This can be explained by the fact that, because one of the main driving forces for the formation of inclusion complexes by the cyclodextrin molecule in solution is hydrophobic interaction (Szejtli 1982, 1988), a more hydrophobic guest is apt to be accommodated in the cyclodextrin cavity and any hydrophobic functional groups on the guests tend to reduce the binding affinity (Crini and Morcellet 2002; Crini 2003). Other approaches proposed by our group focused on the reaction of epichlorohydrin in the presence of a chemical such as NH_4OH: this method is a convenient and inexpensive way to introduce weakly basic anion-exchange groups into the polymer network (Delval et al. 2005).

The main problem of epichlorohydrin is its toxicity. Other more environmentally and health-friendly cross-linking agents have been proposed. Recently, in collaboration with Professor Martel (University of Lille, France), we have demonstrated that polycarboxylic acids (cross-linking agents considered safe and environmentally friendly) can also be used to prepare bifunctionalized cyclodextrin-based materials, even if their performance is lower than polymers obtained with epichlorohydrin (Euvrard et al. 2016, 2017).

8.3 A Brief History of Water-Insoluble Cyclodextrin-Epichlorohydrin Polymers for Environmental Applications

The idea of preparing ECP materials for analytical purposes, such as gel chromatography, inclusion chromatography, and target substance complexation, has been the focus of attention of scientists worldwide for the past 60 years, but the most intensive studies on their use as adsorbents in wastewater treatment to remove toxic contaminants have only begun in the past two decades.

In the mid-1960s, Professor Solms was the first to demonstrate that α-, β-, and γ-cyclodextrin molecules have the ability to easily form cross-linked networks that could have industrial applications in the field of separation sciences such as chromatography (Solms 1966, 1967, 1969; Solms and Egli 1964, 1965). He has shown that cyclodextrin polymers exhibited strong adsorptive properties as inclusion resins for the separation of various molecules such as aniline, nitrophenols, benzaldehyde, pyridine, iodine, Congo red, and methylene blue and as chromatographic supports for the separation of phenylalanine, tryptophan, vitamins, and perfumes. To demonstrate the fundamental role of cyclodextrin cavities in the performance of ECP materials, Professor Solms compared the results with those obtained with a commercial cross-linking epichlorohydrin-dextran polymer, SEPHADEX®, which did not have inclusion properties. The results were interpreted in terms of the formation of inclusion complex or more simply complexation. Professor Solms also used the concept of "molecular encapsulation," introduced by Professor Cramer about 12 years earlier.

Professor Wiedenhof showed that α-cyclodextrin and β-cyclodextrin gels had a chromatographic behavior comparable to that of SEPHADEX G-25 resin in terms of swelling characteristics and heat resistance but with more interesting performances in terms of complexation. The results confirmed that ECP materials were suitable chromatographic supports for gel inclusion chromatography. Different separations using phenol, benzoic acid, aniline, chlorobenzoic acids, and tyrosine were obtained, and again the results were mainly interpreted using the complexation phenomenon. Professor Wiedenhof pointed out the fact that the ability of the cyclodextrin-based resins to separate different molecules was due to the fact that "each resin contained cyclodextrin voids which were able to form inclusion compounds." He introduced the term "inclusion isotherm" instead of adsorption isotherm.

Professor Wiedenhof was also the first to characterize ECP materials using infrared and NMR data (Wiedenhof 1969; Wiedenhof et al. 1969, 1971; Wiedenhof and Trieling 1971). Figure 8.10 shows the infrared spectrum of an ECP material with the following main bands: OH stretching, 3444 cm^{-1}; CH stretching, 2928 cm^{-1}; CH stretching, 2865 cm^{-1}; CH deformations, 1360 cm^{-1}; OH bending (water), 1629 cm^{-1}; OH bending, 1223 cm^{-1}; bending of COH group/CO stretching glycosidic bond, 1070–1150 cm^{-1}; CO/CC stretching, 1026 cm^{-1}; anomeric CH

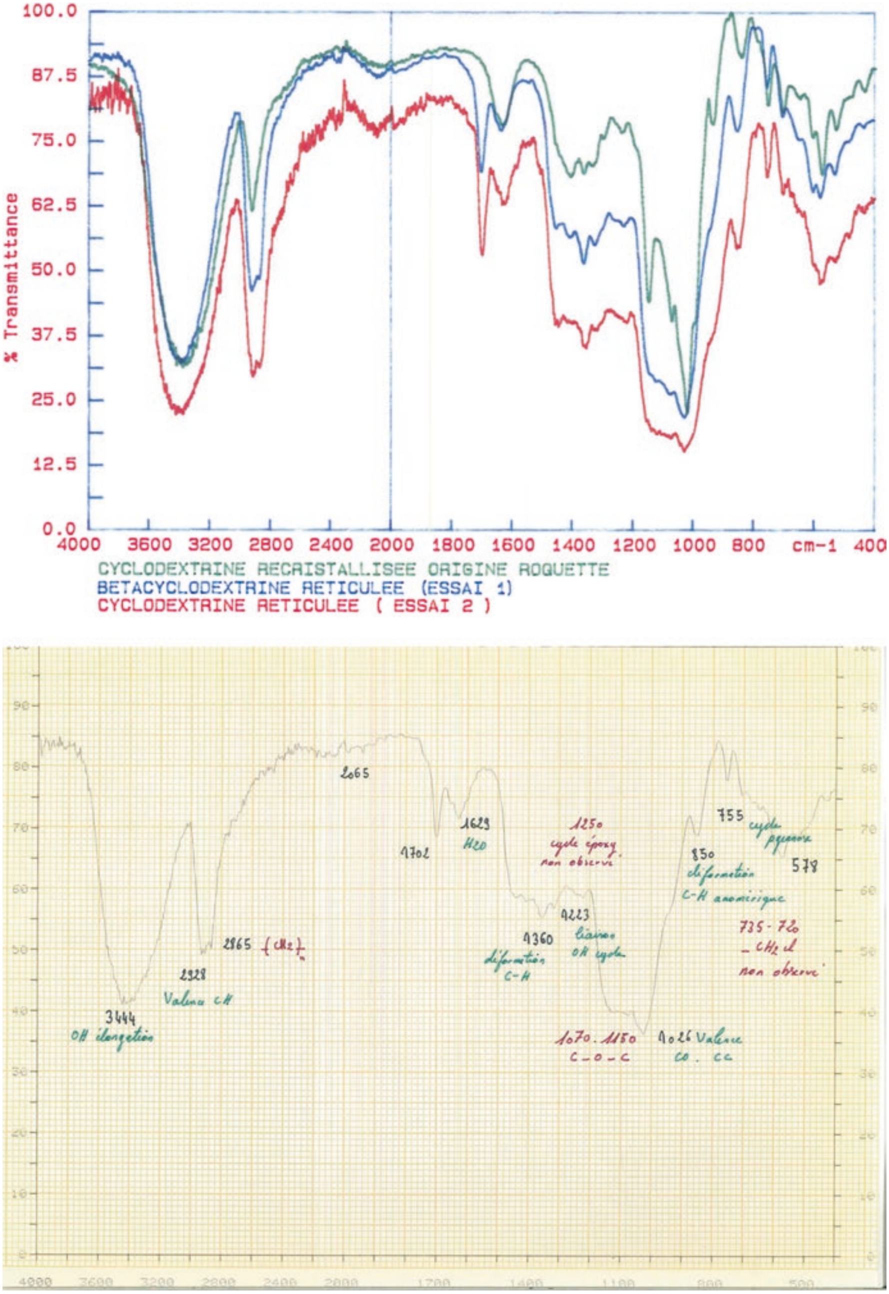

Fig. 8.10 Infrared spectra of a β-cyclodextrin sample and a water-insoluble β-cyclodextrin-epichlorohydrin polymer (above) recorded by our team in 1991 on a Perkin-Elmer spectrophotometer (powder sample using KBr pellet method) and the main assignments for the polymer spectrum (below)

deformation, 850 cm^{-1}; and pyranose ring vibrations, 755 cm^{-1}. This assignment of bands was in accordance with that of Professor Wiedenhof.

In 1970, Professor Hoffman proposed materials with high cyclodextrin contents in bead form for column chromatography. The materials were suitable chromatographic supports for the separation of nucleic acids, nucleotides, nucleosides, and oligonucleotides. Professor Hoffman also demonstrated that ECP materials were useful for separating various positional and optical isomers. The results were interpreted not only in terms of inclusion complexation but also by the presence of anion-exchange interactions, depending on the polymer structure (Hoffman 1970, 1972, 1973).

In the early 1980s, the Hungarian group of Professor Szejtli became very active in the field of ECP polymers for extraction, concentration, and purification of substances. Many significant results on chromatographic, environmental, and pharmaceutical applications have also been obtained (Szejtli 1980, 1982, 1984, 1988). Professor Szejtli has clearly demonstrated that cyclodextrin cavities retain their complexing properties despite the cross-linking reaction. In polymerized form, cyclodextrin molecules are enclosed in a network with loss of mobility, which, to some extent, “exacerbated steric hindrance at the entrance to cavities” (Szejtli 1988). However, this steric effect was “less important when the guest molecule was too large to be fully inserted into a single cavity because a second cyclodextrin molecule in the polymer network can then encapsulate its other extremity.” This was the first time that this concept had appeared in the literature (Crini 2014). Professor Szejtli demonstrated that porous polymers had a high adsorption capacity due to their adsorption strength and large high surface area. The introduction of micro- and mesopores offered both abundant adsorption sites and open diffusion pathways for pollutants and thus contributed to improving the adsorption rate. Professor Szejtli was also the first to demonstrate that the presence of unreacted free epichlorohydrin (this cross-linking agent is toxic and far from being “green”) in the materials was unlikely because epichlorohydrin was a highly reactive substance and underwent hydrolysis under alkaline reaction conditions. This was important for potential applications in the pharmaceutical field (Szemán et al. 1987; Fenyvesi 1988).

At the end of the 1980s, the main applications of the cyclodextrin polymers consisted of their use in low-pressure liquid chromatography to separate proteins, nucleic acids, mandelic acid derivatives, aromatic amino acids, vitamins, and perfumes (Szejtli 1980, 1982, 1988; Zsadon et al. 1981; Smolkova-Keulemansova 1982), in gas chromatography (Cserháti et al. 1983), in food industry to remove bitter substances from filtered orange and grapefruit juices using batch and column debittering procedures (Shaw and Wilson 1983, 1985; Wagner et al. 1988; Shaw 1990), and also in pharmacy (Szejtli et al. 1978; Szemán et al. 1987; Fenyvesi 1988). From the late 1990s onward, many patents and publications on environmental applications began to appear (Friedman and West 1988; Vanzo 1991; Cserháti and Forgács 1994). Over the past two decades, cyclodextrin polymers have gained considerable attention for their performance in environmental remediation-based applications. In an industry dominated by activated carbons and organic resins, in which the main barrier of their use lies in the difficulty associated with their regeneration and rapid saturation, respectively, a large interdisciplinary effort has been devoted to the study of new materials including cyclodextrin-based products with unique adsorption and desorption mechanisms. In 2013, we published a historical review of this subject covering the last 50 years (Morin-Crini and Crini 2013).

8.4 Elimination of Environmental Contaminants Using Cross-Linked Cyclodextrin Polymers as Adsorbents

8.4.1 Early Works

As already mentioned, in the mid-1990s, thanks to a collaboration between the University of Lille (Professor Morcellet and Dr. Martel) and the G. Ronzoni Institute (Dr. Torri, Dr. Vecchi and Dr. Crini), our group has begun to focus on ECP materials. This Franco-Italian research program has been supported by several French and Italian industrialists. The objectives were to produce a series of ECP materials with the desired characteristics (e.g., a well-defined spherical size and shape, degree of swelling, cyclodextrin content) and to find applications in gel inclusion chromatography (separation of various natural products), the oil industry (complexation of aromatic pollutants), and textile (complexation of dyes), paper (incorporation in the pulp), tobacco (incorporation in the filters), and personal care and hygiene (superabsorbent polymers to treat odors) sectors (Shao et al. 1996; Crini et al. 1998a, b, 2000; Vecchi et al. 1998; Bertini et al. 1999). At the end of the 1990s, this work was continued at the University of Besançon (France) by Dr. Crini, and a friendly and fruitful collaboration was then established between the three research groups. In the mid-2000s, our research focused on the use of ECP materials in water treatment.

8.4.2 Organics and Dye Removal

For nearly 30 years, our group has been studying the use of ECP materials as adsorbents for the elimination of target contaminants (e.g., aromatic and phenolic substances, dye molecules, metals, anions, pesticides) from synthetic solutions or real effluents, for the treatment of multi-contaminated waters produced by industries such as textile, paper, wood, and surface finishing treatment and more recently for the cleanup of domestic waters and groundwater contaminated by so-called emerging chemicals such as endocrine disruptors.

Our first paper was published in 1996 (Shao et al. 1996) and presented the same year at the Eight International Cyclodextrin Symposium in Budapest. This work was the result of a collaboration between the G. Ronzoni Institute, the University of Lille, and the Textile Technology Center (Canada). We have shown that ECP materials, mainly in the form of weakly cross-linked gels, can be used as complexing agents to interact with many dyes, e.g., acid, direct, mordant, and reactive dye molecules. The performance in terms of adsorption capacity, evaluated using batch experiments, depended mainly on the range of dye concentrations used in the experiments. Hydroxypropyl-β-cyclodextrin gels had a lower adsorption capacity than β-cyclodextrin gels. No correlation was observed between the performance of the gels and their respective degree of cross-linking. The presence of additives such as NaCl could improve the complexation of the dye, while sodium dodecyl sulfate had the opposite effect. Like Professors Solms and Wiedenhof, we explained these early results mainly by the formation of inclusion complexes and thus by the presence in the materials of cyclodextrin molecules' cavities. We used the notion of complexation by chemisorption and assumed that, in this mechanism, no covalent bonding occurred between the cyclodextrin and the dye. The reaction was a dissociation-association equilibrium, as in the case of the formation of inclusion complexes involving native cyclodextrin molecules in solution, in accordance with the conclusions published by Professor Szejtli (1982, 1988). The cross-linking did not change this property (Shao et al. 1996).

Two years later, in collaboration with an Italian institute, *Stazione Sperimentale per i Combustibili*, we proposed several materials with different cyclodextrin contents, ranging from 20% to 80% w/w (Crini et al. 1998a, b; Vecchi et al. 1998). We have modified the protocol of Professor Solms by increasing the amount of epichlorohydrin to obtain mechanically stable materials but with different mobility in terms of swelling properties and cyclodextrin content. The results demonstrated that ECP materials (particles of irregular shape or regular beads) could also be used as adsorbents to efficiently remove organic contaminants from contaminated water, whatever the quantity of cyclodextrin present in the gels (Crini et al. 1998b; Vecchi et al. 1998). ECP materials were able to interact with contaminants such as chlorophenols, nitrophenols, naphthols, and benzoic acids, in complex solutions, particularly those with hydrophilic properties. They were effective not only at trace levels of contaminants but also at high concentrations. Kinetics of contaminant adsorption were rapid: 2 h was sufficient for reaching the maximum adsorption capacity. The adsorption was much greater in the case of organic molecules which presented compatible size, steric arrangement, and hydrophobicity with the β-cyclodextrin molecules such as β-naphthol, p-nitrophenol, and 4-tert-butylbenzoic acid. However, small molecules such as phenol, known to be too small for the cyclodextrin cavity, were also complexed by the materials (Crini et al. 1998b; Vecchi et al. 1998; Bertini et al. 1999). Comparison with conventional adsorbents such as activated carbons and organic resins showed that ECP gels and beads were more selective and led to better results in terms of elimination, especially at trace levels. A more surprising and interesting result also showed that a high proportion of cyclodextrin was not necessary to have useful performance in terms of pollutant removal (Bertini et al. 1999). In the mid-2000s, Professor Isasi and Professor Christopher H. Evans (Ryerson University, Ontario) reported similar conclusions (Orprecio and Evans 2003; Romo et al. 2004, 2006; Zohrehvand and Evans 2005; García-Zubiri et al. 2006).

The performance of materials in terms of their ability to complex contaminants was strongly related to their structure and swelling properties and therefore to the experimental conditions used during cross-linking, notably the reaction temperature, the amount of caustic soda added, the epichlorohydrin dosage, the volume of water, and the use of a blowing agent or not. The stronger the cross-linking, the lower the swelling properties, and the less interesting the adsorption performance, whatever the quantity of cyclodextrin present in the gels. We also observed in our experiments that performance was independent of the concentration of the pollutant present in the solutions, as well as, more surprisingly, of the amount of cyclodextrin. As ECP did not alter the pH of the solutions to be depolluted (no variation during adsorption), it was not necessary to maintain the initial pH of the solutions during batch tests. However, performance depended on the pH used. Results obtained at pH 2 and pH 6 were similar but were different from those obtained at pH 11, suggesting that the inclusion complexes with cyclodextrin and aromatic and phenolic guests were less stable in basic than in neutral or acidic medium. The results were explained by the different ionization degree of the guest upon the various pH used (Crini et al. 1998b; Vecchi et al. 1998).

One of our objectives was to highlight a correlation between the structure of polymers and their adsorption properties. To do this, we used solid-state ^{13}C NMR spectroscopy techniques such as cross-polarization magic angle spinning with dipolar decoupling (CPMAS), magic angle spinning both with and without dipolar decoupling (DD-MAS and MAS, respectively) and CPMAS with dipolar dephasing (dd-CPMAS), and relaxation parameter measurements. Two components have been found, cross-linked cyclodextrin molecules and polymerized epichlorohydrin. We demonstrated that solid-state NMR techniques were useful to characterize insoluble cross-linked gels with a limited mobility (Crini et al. 1998a). Two years later, we confirmed these results by using high-resolution magic angle spinning with gradients (HRMAS) spectroscopy (Crini et al. 2000). ^{1}H spectra, ^{13}C CPMAS spectra at high temperature, and NOESY, TOCSY, HOHAHA, and $^{1}H/^{13}C$ HSQC spectra are published for the first time. The HRMAS experiments clearly demonstrated the presence of two types of structures in ECP materials, in accordance with the results obtained by CPMAS techniques. The NOESY experiments also demonstrated the interaction between the β-cyclodextrin molecules present in an ECP material and the pollutant adsorbed.

Adsorption results were then explained by taking into account just two important parameters: the presence of cyclodextrin molecules and their degree of cross-linking. The formation of inclusion complexes played the most important role in the mechanism. HRMAS experiments demonstrated not only the presence of two types of structures in ECP materials but also the adsorption mechanism by complexation due to the β-cyclodextrin molecules. NOESY and HOHAHA experiments clearly demonstrated the interaction between the β-cyclodextrin molecules present in an ECP material and the contaminant adsorbed. Our results also highlighted the importance of the structure of the 3D network (Crini et al. 1998b; Vecchi et al. 1998; Bertini et al. 1999). Using solid-state NMR data, we concluded that the mechanism of adsorption can be explained by the presence of two main interactions: the formation of an inclusion complex due to the β-cyclodextrin molecules and the physical adsorption in the polymer network. In the mid-2000s, Professor Isasi's work also confirmed that the presence of cyclodextrin cavities cannot alone explain the adsorption results and stressed the importance of the polymer network structure and thus of the degree of cross-linking (Romo et al. 2004, 2006, 2008; García-Zubiri et al. 2006; Vélaz et al. 2007).

As the materials were relatively highly cross-linked, they could be used both in batch and column studies (Crini et al. 1998b; Vecchi et al. 1998; Bertini et al. 1999). The method proposed extended the potential applications of these materials because the use of cyclodextrin cross-linked gels in adsorption columns in general had limitations due to hydrodynamic problems and column fouling. Another advantage that has been mentioned was the regeneration of adsorbents after use (Vecchi et al. 1998; Janus et al. 1999). In the 1980s, Professor Szejtli stressed that the reversible nature of complex formation was essential in the case of water treatment (Szejtli et al. 1978; Szejtli 1980, 1982) since it enabled the ECP materials to be regenerated after use as first suggested by Professors Solms, Wiedenhof, and Hoffman. Our group has also confirmed this subsequently (Crini 2003; Crini and Peindy 2006; Crini et al. 2007). The ECP polymers could be easily regenerated, and column adsorption and desorption tests showed that the contaminants adsorbed on cross-linked polymers were successfully released by different types of aqueous alcohol solutions. Unlike for active carbons, the regeneration of these systems is simple and straightforward, which makes them more attractive (Crini et al. 2007, 2019b).

8.4.3 Pollutant Removal Using Modified Cyclodextrin Polymers

It is known that ECP polymers without modification had a low affinity for cationic dyes. An improvement can be obtained by introducing groups such as carboxyl or amino groups onto ECP materials able to complex target dyes. Some materials were prepared by reticulation in the presence of carboxymethyl cellulose. Due to the –OH and –COOH groups in the polymer network, the material was hydrophilic and easily swollen by water, but above all it had ion-exchange properties. Indeed, the gels exhibited more specific and higher adsorption of contaminants from water samples than other traditional ECP materials (Crini et al. 2002, 2003; Crini 2003). The presence of carboxymethyl cellulose also enhanced both accessibility and mobility of the cyclodextrin in the polymer by promoting the swelling of the material in water. However, the results confirmed that, despite identical experimental conditions, as for the performance of unmodified materials, the performances of two batches of modified ECP material may be different, mainly due to the exothermic nature of the cross-linking reaction, which makes it difficult to maintain the temperature in the reaction medium during the synthesis of the material. This last conclusion had previously been reported by Professor Szejtli (Szejtli et al. 1978; Szejtli

1980, 1982). To explain the adsorption results, the mechanisms integrated not only the presence of inclusion due to cyclodextrin cavities but also the effects of electrostatic interactions and van der Waals forces due to the presence of new reactive groups on the surface particles. We have also introduced the presence of pollutant-pollutant hydrophobic interactions that could explain the adsorption properties. However, depending on the experimental conditions used in the batch method, the mechanisms are more complex because other interactions such as ion exchange and chemical microprecipitation may also play a role (Crini 2005a, 2006). All these interactions have been discussed in two comprehensive reviews published in the journal *Progress in Polymer Science* (Morin-Crini and Crini 2013; Morin-Crini et al. 2018a).

In 2005, our group patented a process for the synthesis of cross-linked polysaccharides with ionic functional groups for the simultaneous removal of metals and organic contaminants present at low trace levels in polycontaminated effluents (Crini 2005b). The oligomer (cyclodextrin, linear dextrin) or polymer (starch) was mixed with an epoxy cross-linking agent (1,4-butanediol diglycidyle ether) and 2,3-epoxypropyltrimethylammonium chloride in the presence of NH_4OH at moderate temperature. During the cross-linking step with 1,4-butanediol diglycidyl ether, polymer chains were cationized with 2,3-epoxypropyltrimethylammonium chloride. The cross-linked polymer had both hydroxyl, tertiary amino, and quaternary ammonium groups with different degrees of substitution. The procedure gave beads with excellent physical (e.g., high surface area, 100–150 $m^2\ g^{-1}$) and chemical properties (amphoteric in nature) and uniform and regular shape. The beads were easily wettable, insoluble in water and in organic solvents, and stable in aqueous alkaline or acidic solution. The modified materials possessed a remarkably high swelling capacity in water due to the hydrophilic nature of its cross-linked units. Some porous polymers were capable of swelling in both acidic and basic media, without requiring modification of the pH. All these features were interesting for environmental applications (Crini 2005a, b; Delval et al. 2005; Renault et al. 2008; Charles et al. 2010; Sancey et al. 2010).

The aminoethylation and carboxymethylation of cationic cross-linked materials also enabled the preparation of amphoteric derivatives for possible use in the treatment of wastewater containing metals from surface treatment industries, dyes from textile industries, or organic matter from the paper industry (Renault et al. 2008; Charles et al. 2010; Sancey et al. 2010). The gels possessed typical amphoteric characteristics, due to the protonation and deprotonation of the backbone tertiary amine and pendant carboxyl groups in the polymer network. We proposed these new amphiphilic polymers as complexing resins for the removal of organic matter, turbidity, metals, and boron and fluoride ions from industrial wastewater. The gels could be used over a wide pH range due to their particular electrical character. The comparison with similarly prepared starch-based materials demonstrated the higher capacity for organic compound adsorption, due to the formation of inclusion complexes between cyclodextrins and pollutants.

8.4.4 Treatment of Organic Substances and Metals Present in Industrial Discharge Waters

It is extremely difficult to remove pollutants present at low concentrations in industrial discharge waters (Badot et al. 2007; Crini and Badot 2008). For this purpose, a sequential dual approach can be considered: firstly, adsorption onto commercial activated carbon to remove organics, e.g., oils, solvents, and organic load, combined with ion exchange by means of commercial organic resins to remove inorganic pollutants, e.g., metals and anions such as fluorides (Sancey et al. 2010, 2012; Crini 2015a). At the industrial scale, this type of sequence is acknowledged for its efficiency. However, it is an approach to water treatment that combines two methods of separation using two distinct commercial materials. Materials capable of combining the two functions are not yet available (Morin-Crini et al. 2019b).

With the exception of a few works, studies of real applications using cyclodextrin polymers are rare (Vélaz et al. 2007; Romo et al. 2008; Jurecska et al. 2014; Nagy et al. 2014; Crini et al. 2019b; Fenyvesi et al. 2020). Thanks to industrial grants and a French-Romanian research program, at the end of the 2000s, our group carried out the first pilot studies demonstrating that a single ECP with amphoteric and ion-exchange properties material could replace two conventional adsorbents (activated carbon and resins) to effectively treat multi-contaminated effluent (Sancey et al. 2010, 2011a, b, 2012; Sancey and Crini 2012). Coupled with an advanced oxidation preliminary step, adsorption on ECP materials was efficient for the treatment of water with multiple inorganic (e.g., metals, boron, fluoride) and organic (e.g., polycyclic aromatic hydrocarbons, volatile organic compounds, chlorophenols, and alkylphenols) contaminants both from a chemical and from an environmental point of view. The proposed process combined the advantages of oxidation (i.e., mineralization and/or degradation of part of the organic substances) with those of adsorption (i.e., physisorption and chemisorption of the pollutants by the crosslinked framework of the cyclodextrins). After use, the materials could be eliminated by incineration, thus avoiding the need for fastidious and expensive regeneration. This is the first time that such systems were able to treat both so-called emerging pollutants such as chlorophenols and alkylphenols and conventional pollutants such as metals, present in trace amounts in industrial effluents. We were talking about two-in-one materials (Sancey and Crini 2012), a term coined by Professor French in the 1950s and taken up by Professors Casu and Szejtli in the 1960s and 1980s, respectively (Crini 2014).

In the early 2010s, our group proposed biomonitoring tests with plants or animals used as bioindicators to determine and compare the toxicity of industrial effluent from wood, pulp and paper, textile, and surface treatment industries before and after treatment with an ECP material (Sancey et al. 2010, 2011a, b, c, 2012; Charles et al. 2010). For example, to evaluate the usefulness of this process, bioassays based on lettuce seed germination (*Lactuca sativa* L.) were proposed for the first time. The results showed that, after treatment, the impact on lettuce germination was significantly reduced, thanks to the reduction in effluent toxicity. These phytotoxicty tests using plants such as *Lactuca sativa* were indeed good indicators of contaminant concentrations in wastewater before and after treatment. They were simple, quick, and reliable, being inexpensive and not requiring major equipment (Sancey et al. 2010, 2011a). Later, we also used another short-term bioassay based on the immobilization of a freshwater crustacean, *Daphnia magna*, for the ecotoxicological assessment of industrial discharge waters untreated or treated with ECP materials (Euvrard et al. 2015, 2017; Morin-Crini et al. 2019b). The two bioindicators, *Lactuca sativa* and *Daphnia magna*, were proved to be pertinent to assess the ecotoxicity of polycontaminated discharge waters.

In the mid-2010s, two European and international projects involving French, Italian, Romanian, and Canadian colleagues began on the possibility of using cyclodextrin polymers in water treatment on a semi-industrial scale. In a series of pilot-scale experiments, we confirmed the possible feasibility of its implementation on an industrial scale for the treatment of discharge waters from surface treatment industries (Charles et al. 2014, 2016; Euvrard et al. 2015, 2016, 2017). Chemical results in terms of pollutant abatement have confirmed that the combined use of oxidation and adsorption on a single bifunctionalized ECP material can achieve high levels of pollutant removal, well below regulatory values. Biological tests also demonstrated the efficiency of the adsorption process to radically decrease the effluent toxicity. From all these studies, we concluded that the removal of trace pollutants by an ECP polymer was an efficient tool to significantly decrease pollutant concentrations and water toxicity (Crini et al. 2019b).

Fenyvesi et al. (2020) recently reported a similar conclusion. Their study demonstrates the feasibility of ECP materials for the removal of dissolved micro-pollutants as a tertiary treatment of wastewater in a pilot-scale experiment using real municipal wastewater effluent in the adsorptive post-step of the investigated technology. For example, the measured removal efficiencies were >99% for hormones and bisphenol A and ~85% for ibuprofen and diclofenac in a few minutes of contact time. Bioassays also confirmed the environmental benefits obtained after ECP polymer treatment. The decrease in pollutant concentrations in wastewaters has resulted in a significant reduction in their impact on bioindicators. Their pilot-scale results in removing emerging pollutants such as pharmaceuticals and endocrine disruptors are very encouraging. Now it will be necessary to convince industry to use these materials in their wastewater treatment plants.

Currently, we are working on the treatment of certain industrial baths containing high loads of multiple organic and metallic contaminants through two national and European projects. These complex baths are difficult to treat. In general, they are eliminated by dilution in less loaded effluents and then by physicochemical treatment. A promising solution would be to pre-treat the baths with ECP particles of known size in order to decomplex the contaminants and insolubilize them more effectively. Another challenging application might be the removal of endocrine disruptors such as alkylphenols, alkylphenol polyethoxylates (Priac et al. 2017), and pesticides (Crini et al. 2017) from industrial and municipal discharges. These substances, which appear on a European priority list of potentially hazardous pollutants, are the subject of much research and policy debate. Results of adsorption in batch mode showed that ECP materials are efficient adsorbents for the removal of fungicides present in polycontaminated solutions (Crini et al. 2017). Interesting affinities were found toward the mixture propiconazole + tebuconazole + epoxiconazole + bromuconazole + difenoconazole, five triazole fungicides. These contaminants are commonly used in the wood industry, vegetable cultivation, horticulture, and agriculture to protect various products against fungal decay.

8.4.5 Mechanisms of Sorption

In spite of the abundance of literature and conclusive results, interpreting the mechanisms of pollutant removal by ECP materials remains a source of debate and sometimes contradiction (Morin-Crini and Crini 2013; Gidwani and Vyas 2014; Cova et al. 2018; Morin-Crini et al. 2018a; Sikder et al. 2019; Liu et al. 2020). Recently, we published a review summarizing the different mechanisms proposed in the literature (Morin-Crini et al. 2018a).

Mechanisms are still being debated because they involve various interactions that can occur simultaneously, making it difficult to interpret the results. Until the 2000s, the literature reported a consensus on the adsorption/sorption mechanism which was mainly a chemical mechanism (chemisorption) via the formation of inclusion complexes (complexation concept introduced by Professor Cramer in the 1950s), as first suggested by Professor Solms in the 1960s to interpret its adsorption results, particularly the adsorption mechanism. At the same time, this concept was also taken up by Professors Wiedenhof and Hoffman. It was only demonstrated in the 1980s by Professor Szejtli (Crini 2005a; Morin-Crini and Crini 2013). Professor Szejtli also used the notion of association complexes (also suggested by Professor Cramer in the 1950s), i.e., the cooperation effect between cyclodextrin cavities during the adsorption process, in addition to the formation of inclusion complexes to interpret the adsorption mechanism (Crini 2014). Since the mid-2000s, studies have also highlighted the role played by the macromolecular network formed by the cross-linking agent. The performance of an ECP material depended not only on the presence of cyclodextrin units but also on its structure and therefore on the cross-linking step.

Since the 1980s, to explain the chemical effectiveness of ECP materials in water treatment, the concept of inclusion complex or more simply complexation was used by all researchers working on this subject, demonstrating the predominant role of the cyclodextrin molecules in the performance of an ECP material. This concept is mainly the formation of inclusion complexes between cyclodextrin and pollutant molecules. Our first studies also confirmed it (Crini et al. 1998b; Bertini et al. 1999; Janus et al. 1999). Kinetic studies have indicated longer contact times required to achieve equilibrium independently of polymer structure, suggesting chemisorption mechanism such as molecular encapsulation or complexation. During synthesis, the parameter that must be followed the most closely to obtain a material efficient for forming complexes was the quantity of cyclodextrin present per gram of material used. The greater this quantity (for a constant amount of adsorbent), the greater the complexing capacity of the material (Bertini et al. 1999). This first led to an important notion, namely, that a molecule of cyclodextrin corresponds to a guest molecule. The complexation reaction depended also on the polarity of the guest molecule, stressing the major role played by the cyclodextrin in the mechanism (Crini et al. 2002, 2003; Crini 2003). It was the most hydrophobic part of the host molecule that was preferentially included in the cavity. The more hydrophobic the guest molecule, the greater the stability of the complex, and the more efficient the decontamination performance. Similar conclusions were previously reported by Professor Szejtli.

Later, studying the formation of complexes with low molecular weight model organic molecules such as phenol, benzene, and naphthol derivatives, up to more complicated chemical structures with higher molecular weights (dyes, polycyclic aromatic hydrocarbons), we have obtained four surprising results regarding the adsorption of bulky molecules (Crini and Peindy 2006; Crini et al. 2007; Crini 2008; Charles et al. 2010). The first showed that, even if the guest dye was too large, it could be complexed by the ECP polymers, irrespective of the size of the cyclodextrin ring. Even if the pollutant is too bulky, it could be immobilized in a complex, thanks to the cooperative effect of the cyclodextrin molecules of the macromolecular network. Several different cyclodextrin cavities could encapsulate different parts of a pollutant. This conclusion was in accordance with the notion of association complexes introduced by Professor Cramer for soluble native cyclodextrins in solution or solid state and demonstrated by Professor Szejtli for insoluble cyclodextrin polymers (Crini 2014). Two types of complexes are distinguished: complexes with simple model molecules for which inclusion is total – these they called inclusion complexes – and complexes with larger molecules for which inclusion would only be partial, which they called association complexes, and which can be the preponderant form of interaction or simply occur alongside inclusion complexes. This is why some bulky molecules are adsorbed by ECP polymers (Crini 2003, 2008; Crini and Peindy 2006; Crini et al. 2007; Charles et al. 2010; Sancey et al. 2010, 2011a). This was previously demonstrated using HRMAS experiments (Crini et al. 2000). Later, we also reported that there may be a cooperative effect not only between the cavities but also between the cyclodextrin cavities and the 3D polymer network, as shown in Fig. 8.11 (Euvrard et al. 2015, 2016, 2017).

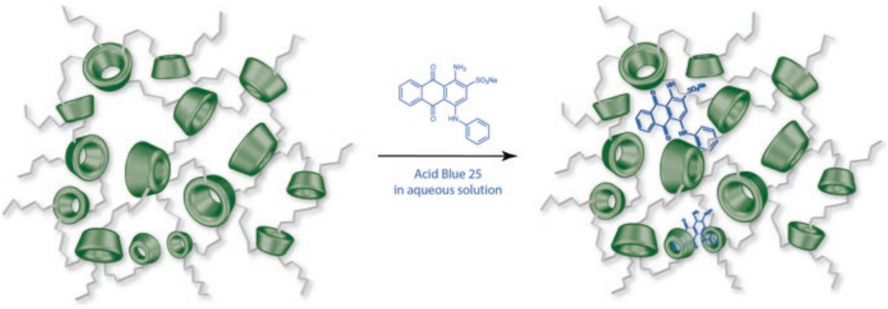

Fig. 8.11 Schematic illustration of the cooperative effect between cyclodextrin cavities and/or the role of the 3D polymer network during the removal of the Acid Blue 25 dye present in aqueous solution by an ECP material

The second result indicated that for polymers containing only a small proportion of cyclodextrin, the quantity of pollutant bound by the material was often much greater than the quantity of cyclodextrin present in the material, contradicting the notion that one molecule of cyclodextrin traps one pollutant molecule. For contaminants containing aromatic groups, we also introduced the occurrence of hydrophobic interactions leading to pollutant stacking (π–π interactions) and/or the formation of multilayers of contaminants at the surface of the polymers, in agreement with Freundlich's model. In the presence of phenolic derivatives with high dipole moments, electrostatic interactions of the dipole-dipole type between pollutant molecules were also possible, in particular at high concentrations (Crini and Peindy 2006; Crini et al. 2007). Another surprising result was the type of cyclodextrin incorporated into the gel. We prepared materials based on α-, β-, and γ-cyclodextrin using the same experimental conditions during the synthesis. The results showed that contaminants could be removed regardless of the type of cyclodextrin polymer used. For example, the cross-linked α-cyclodextrin polymer can adsorb Acid Blue 25 dye, which is too large to be a guest. For the three types of polymers (with a close cyclodextrin content but with different swelling properties), the performance could be comparable (Crini 2005a, b). A response was found in the structure of each macromolecular network. Similar conclusions have been published by Professor Yilmaz (Yilmaz Ozmen and Yilmaz 2007, 2008). The last result was related to the shape of the materials. As expected, the more regular the structure and spherical distribution of the beads, the higher their performance. However, the results were independent of the amount of cyclodextrin but dependent on the degree of cross-linking. With the beads, kinetic studies have indicated short contact times necessary to reach equilibrium, suggesting rapid adsorption surface. This led us to highlight the importance of physisorption in the process of pollutant removal by ECP polymers. This physisorption mechanism acts as a complement to chemisorption by complexation (Crini and Peindy 2006; Crini 2008).

We explained these four results mainly by the network structure of the materials and their shape and swelling properties, closely related to the degree of cross-linking, and also by the presence of cyclodextrin units (Morin-Crini and Crini 2012, 2013; Morin-Crini et al. 2015). For ECP materials, the question arises as to the predominance of inclusion complexes due to the cyclodextrin molecules or association complexes due to the polymer network. Currently, the consensus is rather for the latter, with the results being mainly due to the structure of the macromolecular network independent of the quantity of cyclodextrin actually present (Morin-Crini et al. 2018a).

The concept of association complexes is less simple since there can be a cooperative effect, not only between the cyclodextrin cavities themselves (particularly for large guest molecules) but also between the cyclodextrin cavities and those of the polymer network. To demonstrate this conclusion, we synthetized materials composed of non-cyclic oligosaccharides (linear dextrins, sugars such as sucrose which has similar dimensions and chemical composition to cyclodextrin moieties) and polysaccharides (starch fractions rich in amylose or amylopectin components, chitosan) under the same experimental conditions as the ECP polymers (Badot et al.

2007; Crini et al. 2007; Crini 2008; Sancey et al. 2010, 2011a, b, 2012). These cross-linked materials have been studied in pollutant complexing experiments, and their different performances were compared. It was found that, in some cases, cross-linked starches and cross-linked dextrins had higher adsorption capacities than cross-linked cyclodextrin polymers even if they did not have the type of cavity that participates in the inclusion complexes. The density of the cross-linking mainly explained these results. The cross-linking reaction creates a particular 3D macromolecular structure (recognized as difficult to control) forming a mesh that is also susceptible to bind pollutants (Fig. 8.11). The polymer network therefore offers cross-linked oligosaccharide and polysaccharide materials the possibility to sequester contaminants through effects of cooperation not only between cyclodextrin molecules but also via additional interactions in the mesh with diffusion into the network (Morin-Crini et al. 2013, 2015, 2018a). These mesh interactions have a greater role when the degree of cross-linking is lower, enabling the polymer to swell in water and thus enhance diffusion of the contaminants through the network. Professors Isasi and Yilmaz have carried out similar studies, which have led to similar conclusions.

8.5 Conclusions

This chapter reviews the research conducted over the past 30 years by our research group on water-insoluble cyclodextrin-epichlorohydrin polymers. It shows the progress of our work and our contribution to a better understanding of these materials. Table 8.1 summarizes all our contributions on cyclodextrin polymers during the period 1996–2019. Table 8.2 reports the ten most cited papers in the ISI Web of Science and Scopus databases since 1998 with “cyclodextrin polymer” and “pollutant removal” in the topic of our works.

Cyclodextrin-epichlorohydrin polymers can be used as complexing adsorbents to remove contaminants from polycontaminated effluents. They have several advantages: technological simplicity in their use, efficiency in the elimination of substances even at trace levels, easily recyclable (regeneration) or disposable (incineration), and beneficial to the environment to reduce the impact/toxicity of an effluent. However, as industrial production of cyclodextrin-epichlorohydrin polymers has not started, the materials produced at lab scale suffer from variability in their characteristics. There is also a non-negligible cost difference with conventional materials such as activated carbon used in wastewater treatment. Therefore, cyclodextrin polymer materials are basically at the laboratory study stage, and there is still a lot of work to be done to demonstrate their potential on an industrial scale.

On this subject, the first study on the industrial-scale use of cyclodextrin-epichlorohydrin polymers to remove emerging pollutants such as endocrine disrupters from wastewater treatment plant effluents has just been published (Fenyvesi et al. 2020). Chemical abatement and toxicity mitigation of wastewater have shown that adsorption on modified ECP materials can be an interesting additional

Table 8.1 Recap of the main results published by our group on water-insoluble cyclodextrin-epichlorohydrin polymers, from 1996 to 2019

Year	Result	Reference(s)
1996	The first paper on the complexation of dye molecules by ECP materials. β-cyclodextrin- and hydroxypropyl-β-cyclodextrin-based gels are able to adsorb acid, direct, mordant, and reactive textile dyes without specificity. Performance depends on the concentration range of the dye molecules in the experiments. The influence of pH is rather low, while that of ionic strength is important on their performance. The performance depends on the type of anionic surfactants and the salts present in the solution. Hydroxypropyl-β-cyclodextrin gels have a lower adsorption capacity than β-cyclodextrin gels. The results highlight not only the essential role of the cavities of cyclodextrin molecules but also of the macromolecular network of the gel. No correlation was observed between the performance of the gels and their respective degree of cross-linking	Shao et al. (1996)
1998	The synthesis of ECP materials is straightforward and facile; this is made possible by the high reactivity of cyclodextrin and of the cross-linking agent in basic media. The materials obtained are in the form of high molecular weight networks, without porosity and with a very low specific surface area. The 3D macromolecular network is composed of areas of cross-linked cyclodextrin units and areas of macromolecules corresponding to long chains of polymerized epichlorohydrin, with different molecular mobility: this structure is demonstrated for the first time using solid-state NMR measurements	Crini et al. (1998a)
	CPMAS technique and relaxation measurements are useful to characterize cross-linked gels with a limited mobility. The ^{13}C spin lattice relaxation values of the materials are very similar to those of the crystalline β-cyclodextrin form. The β-cyclodextrin trapped inside the network does not seem to change its mobility whatever the amount of epichlorohydrin. The addition of water to polymers results in better resolution in the NMR spectra and significantly increases the ^{13}C spin lattice relaxation values reflecting strong interactions between cyclodextrin molecules and water. The ^{1}H spin lattice relaxation values in the rotating frame are equivalent, indicating the homogenous nature of samples	
	Although the synthesis conditions that determine the properties of the ECP material are closely controlled, the cross-linking density remains difficult to predict. The structure of a macromolecular network depends directly on the degree of cross-linking: the higher the degree, the more the cross-linking increases, making the material rigid, which reduces both the ability of the material to swell in water and the concentration and accessibility of the CD cavities. The materials are amphiphilic, with both hydrophilic properties (owing to the presence of carbohydrate units and especially of their hydroxyl groups) and hydrophobic properties (due notably to the methyl groups of the cross-linking agent and to the ether bonds of cyclodextrin-glyceryl bonds)	

1998	For water treatment, especially in batch methods, particles that are not spherical and do not have regular shapes and sizes are sufficient to achieve satisfactory results in pollutant removal. ECP materials are effective materials for adsorbing aromatic compounds, particularly phenolic pollutants. Kinetics of pollutant adsorption on ECP materials are rapid: 2 h is sufficient for reaching the maximum adsorption capacity. The adsorption is much greater in the case of contaminants which present compatible size, steric arrangement, and hydrophobicity with the β-cyclodextrin molecules such as β-naphthol, p-nitrophenol, and 4-tert-butylbenzoic acid. The quantity of the retained compound depends on the concentration of the aqueous solution	Crini et al. (1998b) and Vecchi et al. (1998)
	Adsorption capacities obtained at pH 2 and pH 6 are similar but are different from those obtained at pH 11, suggesting that the inclusion complexes with cyclodextrin and aromatic and phenolic guests are less stable in basic than in neutral or acidic medium: the results can be explained by the different ionization degrees of the guest upon the various pH used. There is a close relationship between the degree of cross-linking and the complexation performance of the polymers, independent of the amount of cyclodextrin. A high proportion of cyclodextrin is not necessary to have useful adsorption results. The quantity of pollutant adsorbed is always higher than the content of cyclodextrin, suggesting that the macromolecular network participates in the complexation, independent of the method used (batch method or column setup). The mechanism of adsorption is physical adsorption in the polymer network and/or the formation of an inclusion complex and/or the formation of hydrophobic pollutant-pollutant interactions. ECP materials are chemically, thermally, and even mechanically stable when the degree of crosslinking is sufficient. For the complete regeneration of the material, it is necessary to use a mixture of water and ethanol	

(continued)

Table 8.1 (continued)

Year	Result	Reference(s)
1999	The presence of numerous hydroxyl groups gives ECP materials hydration properties of varying intensities depending on the degree of cross-linking. The macromolecular network is both hydrophilic and hydrophobic, a property that can be very useful for applications in aqueous media and that ECP materials can be used to efficiently remove pollutants, notably organics, from contaminated water, whatever the quantity of cyclodextrin present in the materials. Even for polymers containing few cyclodextrin units, the amount of pollutant retained by the adsorbent may be much greater than the amount of cyclodextrin present	Bertini et al. (1999) and Janus et al. (1999)
	β-Cyclodextrin polymers more effectively sequester pollutants, particularly those with hydrophilic properties. They have excellent performance even if they have specific surface areas that are much smaller than carbons. Contaminants with complex structures and high molecular weights are more easily complexed. It is much more advantageous to prepare materials in the form of regular, spherical beads with controlled swelling properties, especially for column setup	
	The increase of the β-cyclodextrin content increases the performance of the materials toward the aromatic compounds tested. A hydrophobic pollutant has a greater affinity for the ECP polymer with a higher cyclodextrin content, while the opposite behavior can be observed with a hydrophilic pollutant. However, a high proportion of cyclodextrin is not necessary to have useful adsorption results, and there is a relationship between the performance of the ECP materials and their molecular structure. When the degree of cross-linking is too high, the quantity of contaminants adsorbed decreases. Performances varies considerably from one batch of gels to another although the experimental conditions used in their synthesis are the same, due to their different degrees of swelling. The results obtained at basic pH are more in agreement with the association constants between β-cyclodextrin and the contaminants than those obtained in acidic conditions or in water. ECP materials can be regenerated without significant loss of adsorption capacity	
2000	HRMAS spectroscopy is useful to characterize insoluble cross-linked materials (gels or beads) with a limited mobility. ^{1}H spectra, ^{13}C CPMAS spectra at high temperature, and NOESY, TOCSY, HOHAHA, and HSQC ^{1}H/^{13}C spectra are published for the first time. HRMAS experiments demonstrate not only the presence of two types of structures in ECP materials but also the adsorption mechanism by complexation due to the β-cyclodextrin molecules. With the help of NOESY and HOHAHA experiments, it is possible to highlight the formation of an inclusion complex	Crini et al. (2000)
2001	Adsorption using ECP materials is a procedure of choice for the removal of organic compounds from wastewater. Cyclodextrin polymers exhibit high adsorption capacities toward phenolic compounds and dyes and high selectivity	Crini et al. (2001)
	The mechanism of adsorption can be explained by the presence of several interactions: the formation of an inclusion complex due to the β-cyclodextrin molecules, and/or the physical adsorption in the polymer network, and/or the formation of hydrophobic-hydrophobic pollutant-pollutant interactions	

2002	The first review on water-insoluble cyclodextrin-epichlorohydrin polymers published by our group. ECP materials are by far the most studied adsorbents due to their chemical effectiveness in removing a wide range of pollutants. These polymers are a versatile tool in separation science and for environmental purposes because cyclodextrin chemistry and polyfunctional character offer various possibilities for preparing different types of materials. However, it is difficult to find commercial sources of ECP materials with guaranteed reproducible properties. Although the role of the cyclodextrin is essential, a compromise must be found between the amount of cyclodextrin and the degree of cross-linking to obtain useful results in low-pressure chromatography and in adsorption-oriented processes	Crini and Morcellet (2002)
2002	ECP materials containing carboxylic groups are synthetized; these modified materials exhibit better adsorption capacities toward the same contaminants tested, pointing out the important role of the carboxylic groups. Grafting ionic or chelating groups on ECP materials can result in the modification of the polymer surface chemistry, which can then give rise to new interactions, in addition to inclusion in the cyclodextrin cavities during adsorption experiments. We also confirm the presence of pollutant-pollutant hydrophobic interactions which can explain the adsorption properties. For the first time, the notion of association complexes, i.e., cooperation between cyclodextrin cavities, introduced by Professor Szejtli, in addition to inclusion complexes, is proposed to explain the performance of the materials	Crini et al. (2002)
2003	The results confirm that, despite identical experimental conditions, the performances of two batches of ECP material can be different due to the exothermic nature of the cross-linking reaction which makes difficult to maintain the temperature within the reaction medium during the synthesis of the material. The particular macromolecular structure of the non-modified ECP polymers is composed of units that can also bind pollutants. Adsorption mechanism is also due to the presence of dye-dye interactions	Crini (2003)
2003	Grafting cationic groups on an ECP gel in well-controlled experimental conditions yields excellent adsorbents of acid, reactive, and direct dyes. Again the presence of cyclodextrin cavities cannot alone explain the adsorption results; we also stress the importance of the polymer network (the degree of cross-linking) and the chemical interactions via acid-base interactions, ion exchange, and hydrogen bonding due to the carboxylic groups. For modified ECP materials, the results are strongly dependent on the pH but independent on the cyclodextrin content	Crini et al. (2003)

(continued)

Table 8.1 (continued)

Year	Result	Reference(s)
2005	The complexation process results from a multitude of interactions between the three components of the adsorption system, i.e., the cyclodextrin molecules of the material, the contaminants, and the effluent to be treated. The role of cyclodextrins fundamentally occurs through the formation of inclusion and/or association complexes. We note the importance of the moieties at the surface of the ECP material rather than inclusion to explain the mechanisms	Crini (2005a, 2005b) and Delval et al. (2005)
	Materials composed of oligosaccharides (linear dextrins, sugars) or polysaccharides such as starches, prepared in the same cross-linking conditions as ECP materials, were studied in pollutant complexing experiments, and their different performances were compared. The results demonstrate that the most important parameter is the degree of cross-linking: the higher the degree of cross-linking, the lower the performance of the material. Cross-linked starches and cross-linked linear dextrins show adsorption capacities that are higher than those of ECP materials even though they do not possess the type of cavity that participates in inclusion complexes. Very high adsorption properties are described with respect to the same contaminants studied for several years. The materials are also capable of treating real effluents. For modified polymers, the mechanism is mainly due to electrostatic interactions, surface adsorption, and dye-dye interactions, which explain the rapid contact times	
	To obtain adsorbents able to efficiently process both minerals (including metals) and organics, it is necessary to modify or activate the networks by grafting different types of moieties (neutral or ionic): new bifunctionalized ECP materials with high porosity and surface area are synthetized	
2006	Contaminants with a complex structure and a high molecular weight are more easily complexed, due to an effect of cooperation between cyclodextrin molecules and the polymer network. The performance of the materials is strictly linked to the conditions of their synthesis: the degree of cross-linking is a key element in the same way as the presence of the cyclodextrin molecules. Adsorption kinetics are strongly dependent on the degree of cross-linking	Crini (2006) and Crini and Peindy (2006)
	Inclusion aside, various mechanisms are proposed depending on the type of function or ligand grafted, e.g., ion exchange, electrostatic attraction, chelation, and/or precipitation	
2007	The structure and the polarity of the contaminants studied as well as the experimental conditions (e.g., dosage of material, contaminant concentration, pH, ionic strength, etc.) of the batch used can contribute to complicating the interpretations on the adsorption mechanism. The reproducibility of the performances of cyclodextrin polymers used as adsorbents for the removal of dyes and the regeneration of the materials after saturation is reported	Crini et al. (2007)

2008	For non-modified materials, the cross-linking step not only influences the concentration and accessibility of the cyclodextrin molecules (the greater the accessibility of the cyclodextrin sites, the higher the adsorption properties) but also the swelling, which determines the diffusional properties of the gels. For modified ECP materials, the results also depend on the density of the cross-linking	Crini (2008), Gimbert et al. (2008), and Renault et al. (2008)
2010	A novel material, presenting amino, hydroxyl, and carboxylic groups coupled with the incorporation of cyclodextrins, ensures the simultaneous adsorption of different contaminants onto the surface material. The comparison with a similarly prepared starch-based material demonstrates the higher capacity for organic compound adsorption, due to the formation of inclusion complexes between cyclodextrins and pollutants	Charles et al. (2010) and Sancey et al. (2010)
	Our group proposes biomonitoring tests with plants or animals to determine and compare the toxicity of industrial effluent from wood, pulp and paper, textile, and surface treatment industries before and after treatment with an ECP material. The first study on the evaluation of the phytotoxicity of polycontaminated industrial effluents using the lettuce plant *Lactuca sativa* as a bioindicator is published. Both the chemical abatement and toxicity mitigation of wastewater show that adsorption on modified ECP materials can be an interesting additional treatment step for the detoxification of industrial effluents	
2011	The results confirm that the adsorption using an ECP material is a viable alternative for treating industrial wastewaters. Biological tests demonstrate the efficiency of the adsorption process to radically decrease the effluent toxicity. A modified ECP material can also interact with metals and anions such as fluoride ions present both in synthetic solutions and in real effluents. The comparison of its adsorption capacity with that of a similarly prepared starch material shows superior efficiency toward organic compounds, though maintaining the same efficiency toward inorganic species. Metal removal is dependent on the mass of material and contact time but independent of the pollutant load. Adsorption reaches equilibrium in 60 min irrespective of the metal considered	Sancey et al. (2011a, b, c)
2012	ECP materials remove residual turbidity and leads to a significant decrease in the residual chemical oxygen demand present in industrial water discharge. Adsorption on ECP materials represents an interesting tool for preventing or decreasing the environmental impact of industrial effluent: pilot-scale experiments confirm the possible feasibility of its implementation on an industrial scale. Plant biomonitoring tests are useful tools to evaluate and compare the toxicity of real effluents, presenting trace metal polycontamination. We indicate for the first time that the coupling of oxidation with adsorption on an ECP material allows the efficient removal of organic pollutant present in polycontaminated effluents. The proposed process combines the advantages of oxidation (i.e., mineralization and/or degradation of part of the organic substances) with those of adsorption (i.e., physisorption and chemisorption of the contaminants by the cross-linked framework of the cyclodextrins)	Sancey and Crini (2012) and Sancey et al. (2012)

(continued)

Table 8.1 (continued)

Year	Result	Reference(s)
2013	A comprehensive historical review on the ECP materials. The exact role of the cross-linking agent on the properties of the materials is still a matter of debate, and many contradictions have been published in the literature. Some works suggest that the quantity of epichlorohydrin should be limited, while others advise that it should be increased	Morin-Crini and Crini (2013)
2014	There is a relationship between the chemical structure of the organic pollutant and the performance of the materials. Synthesis of bifunctionalized ECP materials containing ionic ligands and able to simultaneously remove organics, metals, and anions: the greater the number of grafted ligands, the higher the material's performance. A single material with both cationic and anionic charges is capable of removing multi-contaminants present at concentrations close to a few milligrams per liter but also at trace concentrations in synthetic solutions and in real discharge waters. The materials have amphoteric properties and can therefore be used over a wide range of pH values. The pre-treatment of a real effluent by an oxidation step significantly improves the efficiency of the subsequent adsorption	Crini (2014) and Charles et al. (2014)
2015	Amphoteric ECP materials are promising in wastewater treatment: they are able to decontaminate effluent with multiple contaminants present as traces in complex mixtures. Pilot-scale experiments demonstrate that ECP treatment alone or in combination with advanced oxidation pre-treatment can remove polycyclic aromatic hydrocarbons, volatile organic compounds, chlorophenols, and alkylphenols. In real effluents, competition effects appear, especially because of the presence of calcium at high concentrations, which can compete with other contaminants for the adsorption sires of the ECP materials	Crini (2015a, b) and Euvrard et al. (2015)
2015	The first book on cyclodextrins published by our group	Morin-Crini et al. (2015)
2016	Results confirm that the combined use of oxidation and adsorption on a bifunctionalized ECP material achieves high levels of pollutant removal. The complexing of contaminants with an ECP material is a possible decontamination process on an industrial scale for several reasons: efficiency in the elimination of contaminants even at trace levels, simple from a technological point of view, easily recyclable (regeneration) or disposable (incineration), interesting from an environmental point of view (to reduce the impact/toxicity of a effluent)	Charles et al. (2016) and Euvrard et al. (2016)
	Although host-guest inclusion, on the one hand, and surface adsorption and ion exchange on the other hand are the main phenomena interacting between modified ECP materials and contaminants, the interpretation of the results is difficult due to the wide diversity of polluting species present in real effluents, involving numerous other interactions in the adsorption process	

2017	Solid-state NMR and X-ray diffraction analysis are interesting techniques to characterize modified ECP materials	Crini et al. (2017), Euvrard et al. (2017), and Priac et al. (2017)
	The first study on the use of cyclodextrin-based materials to remove a mixture of five fungicides. Significant affinities are found with the mixture propiconazole + tebuconazole + epoxiconazole + bromuconazole + difenoconazole, five pesticides listed as priority substances in Europe. Multilayer adsorption due to π–π bonds and steric effects can be advanced to explain the differences of adsorption observed	
	ECP materials can also remove significantly endocrine disruptors such as alkylphenols and alkylphenol polyethoxylates	
2018	An updated review on the applications of ECP materials. Non-modified and modified ECP materials have proved to be efficient and more advantageous than conventional systems in water and wastewater treatment	Crini et al. (2018a)
2018	The first review on the adsorption mechanisms described during the complexation of contaminants by ECP materials. The mechanisms are still being debated because they involve various interactions that can occur simultaneously. There is nevertheless a consensus on the fundamental role of cyclodextrin units	Morin-Crini et al. (2018a)
2018	Two other books published on cyclodextrins	Fourmentin et al. (2018a, b)
2019	The last review on non-conventional sorbents for wastewater treatment	Crini et al. (2019b)

Table 8.2 The ten most cited papers in the ISI Web of Science and Scopus databases since 1998 with "cyclodextrin polymer" and "pollutant removal" in the topic of our works, July 02, 2020

		ISI Web of Science	Scopus	
Journal	Article title	Times cited	Times cited	References
Bioresource Technology	Non-conventional low-cost adsorbents for dye removal: a review	2777	2872	Crini (2006)
Progress in Polymer Science	Recent developments in polysaccharide-based materials used as adsorbents in wastewater treatment	1382	1396	Crini (2005a)
Separation and Purification Technology	Removal of C.I. Basic Green 4 (Malachite Green) from aqueous solutions by adsorption using cyclodextrin-based adsorbent: kinetic and equilibrium studies	674	688	Crini et al. (2007)
Chemical Reviews	Review: a history of cyclodextrins	599	604	Crini (2014)
Dyes and Pigments	Kinetic and equilibrium studies on the removal of cationic dyes from aqueous solution by adsorption onto a cyclodextrin polymer	307	317	Crini (2008)
Journal of Separation Science	Synthesis, characterization, and applications of adsorbents containing cyclodextrins	238	247	Crini and Morcellet (2002)
Progress in Polymer Science	Environmental applications of water-insoluble beta-cyclodextrin-epichlorohydrin polymers	216	212	Morin-Crini and Crini (2013)
Bioresource Technology	Studies on adsorption of dyes on beta-cyclodextrin polymers	175	190	Crini (2003)
Journal of Applied Polymer Science	Sorption of aromatic compounds in water using insoluble cyclodextrin polymers	137	132	Crini et al. (1998b)
Journal of Hazardous Materials	Adsorption of C.I. Basic Blue 9 on cyclodextrin-based material containing carboxylic groups	120	127	Crini and Peindy (2006)

treatment step for the detoxification of municipal effluents. Their results clearly indicated that ECP materials are efficient as non-conventional adsorbents to treat complex mixtures. Bioassays also confirmed the environmental benefits obtained after ECP polymer treatment: the decrease in pollutant concentrations in effluents resulted in a significant reduction of toxicity water. The authors also showed that both inclusion complex formation of pollutants with cyclodextrin and physisorption due to the polymer network played a role in the adsorption mechanism. These chemical and biological results are very encouraging. Now, the industry should be convinced to use these materials in their wastewater treatment plants as we mentioned in our last review (Morin-Crini et al. 2018a).

Table 8.3 Authors of recent research on pollutant removal by insoluble cyclodextrin-epichlorohydrin materials (selected papers)

Corresponding author	Country	Pollutants(s)	Experimental protocol	Effluents^{a,b}	Mechanism(s)	References
Wilson L.D.	Canada	P-nitrophenol, trinitrophenol	Batch	SS	Inclusion complexation, interstitial binding sites, hydrogen bonds	Danquah et al. (2018)
Hao X.K.	China	Nitrophenols	Batch	SS	Inclusion complexation	Li and Hao (2019)
Ji H.	China	2,4,6-Trichlorophenyl, bisphenol A	Batch	SS	π-π interactions, host-guest interactions	Huang et al. (2020)
Li X.	China	Erochrome black T	Batch	SS	Electrostratic interactions, inclusion complexation, π-π interactions, intraparticle diffusion	Li et al. (2019)
Lü Q.	China	Bisphenol S	Batch	SS	Inclusion complexation, hydrogen bonds, hydrophobic interactions	Lü et al. (2018)
Luo J	China	Phenol	Batch	SS	Inclusion complexation	Cai et al. (2017)
Tsai F.C.	China	Acid orange 7	Batch	SS	Intraparticle diffusion, inclusion complexation, hydrophobic interactions	Zhang et al. (2017)
Xie X.C.	China	Bisphenol A, 3-phenylphenol, ethinyl estradiol	Batch	SS	Inclusion complexation, hydrogen bonds, hydrophobic interactions, association complexes due to the polymer network	Xu et al. (2019)
Zhao H.	China	Lead, cadmium	Batch	SS	Chemisorption	Zheng et al. (2019)
Zhang Y.	China	Methylene blue, methyl purple, Congo red	Batch	SS	Inclusion complexation, hydrogen bonds, hydrophobic interactions	Zhang et al. (2019)
Zhu L.P.	China	Bisphenol A, 2-naphthol, 2,4-dichlorophenol, propranolol hydrochloride	Batch	SS	Inclusion complexation, specific interactions	Wang et al. (2017)

(continued)

Table 8.3 (continued)

Corresponding author	Country	Pollutants(s)	Experimental protocol	Effluents^{a,b}	Mechanism(s)	References
Fenyvesi É.	Hungary	Estradiol, ethinyl estradiol, estriol, diclofenac, ibuprofen, bisphenol A	Column, batch	RE, SS	Inclusion complexation, hydrogen bonds, hydrophobic interactions, association complexes due to the polymer network	Fenyvesi et al. (2020)
Nagy Z.M.	Hungary	Bisphenol A, hormones, ibuprofen, ketoprofen, naproxen, diclofenac	Column, batch	SS, RE	Inclusion complexation	Nagy et al. (2014)
Vyas A.	India	Drugs	Batch	SS	Inclusion complexation, specific interactions	Gidwani and Vyas (2014)
Doostan F.	Iran	Cobalt, zinc, copper	Batch	SS, RE	Chemisorption, electrostatic interactions	Heydari et al. (2017)
Nojavan S.	Iran	Benzene, toluene, ethylbenzene, xylenes	Solid-phase extraction	SS	Inclusion complexation	Nojavan and Yazdanpanah (2017)
Sheibani H.	Iran	Methylene blue, phenol, 1-naphthol, 2-naphthol	Batch	SS	Inclusion complexation, adsorption surface, specific interactions	Heydari et al. (2018)
Mishael Y.G.	Israel	Bisphenol A	Batch, column	SS, RE	Hydrophobic size inclusion, electrostatic interactions	Shabtai and Mishael (2018)
Cosma P.	Italy	Atrazine	Batch	SS	Inclusion complexation, complex surface adsorption, association complexes	Romita et al. (2019)
Kurasaki M.	Japan	Metals, phenols, aromatics	Batch	SS	Inclusion complexation, surface adsorption, association complexes, electrostatic interactions	Sikder et al. (2019)
Ogawa K.	Japan	Bisphenol A, 4-nonylphenol, methyl orange	Batch	SS	Inclusion complexation	Ogawa and Hiromi (2015)
Sikder M.T.	Japan	Cadmium	Batch	SS	Chemisorption	Sikder et al. (2017)

Kwak S.Y.	Korea	Bisphenol A	Batch	SS	Inclusion complexation	Lee and Kwak (2020)
Valente A.J.M.	Portugal	Metals, phenols, aromatics, dyes, pharmaceuticals	Batch, column	SS, RE	Inclusion complexation, surface adsorption, association complexes, specific interactions	Cova et al. (2018)
Isasi J.R.	Spain	1-Naphthol, 2-acetanaphthalene, tannic acid	Batch	SS	Inclusion complexation, specific interactions	Fujiyoshi et al. (2019)
Gabaldón J.A.	Spain	Direct blue 78	Batch	SS	Inclusion complexation, hydrogen bonds, hydrophobic interactions	Murcia-Salvador et al. (2019)
Uyar T.	Turkey	Phenolphthalein, phenanthrene	Filtration, batch	SS	Inclusion complexation	Celebioglu et al. (2019)
Dichtel W.R.	USA	Perfluorooctanoic acid	Batch	SS	Inclusion complexation, hydrophobic interactions	Xiao et al. (2019)
Suri R.P.S.	USA	Steroid hormones, perfluorooctanoic acid, bisphenol A	Batch	SS	Inclusion complexation	Bhattarai et al. (2014)

[a] *SS* synthetic solutions
[b] *RE* real effluents

Finally, from a fundamental point of view, cross-linking cyclodextrin polymers continue to be of interest to the scientific community, as evidenced by the many publications on the subject that are published each year (Table 8.3), and I am sure it will last for years.

Acknowledgments The solid-state NMR spectroscopy of cyclodextrins was my entrance to the world of oligosaccharides and polysaccharides, and a lot of what I know I owe to my two scientific mentors Professor Michel Morcellet (*Laboratoire de Chimie Macromoléculaire*, Lille, France) and Research Director Giangiacomo Torri (*Istituto di Chimica e Biochimica G. Ronzoni*, Milan, Italy), to whom I would like to express my immense gratitude. This chapter is dedicated to them in recognition of their constant inspiration and for their excellent spirit of cooperation, unlimited enthusiasm, and great friendship.

I am also particularly grateful to all those who have contributed to this work through several friendly and fruitful national, European, and international collaborations, with particular attention to Dr. Nadia Morin-Crini (Besançon, France), Pr. Benito Casu (Milan, Italy), Pr. Yahya Lekchiri (Oudja, Morocco), Pr. Bernard Martel (Lille, France), Mr. Cesare Cosentino (Milan, Italy), Dr. Carmen Vecchi (Milan, Italy), Dr. Marco Guerrini (Milan, Italy), Dr. Anna-Maria Naggi (Milan, Italy), Pr. Edwin Yates (Liverpool, UK), Dr. Marcella Chiari (Milan, Italy), Dr. Peter Winterton (Toulouse, France), Dr. Corina Bradu (Bucharest, Romania), Dr. Bruno Perly (Gif-sur-Yvette, France), Pr. Joëlle Morcellet (Lille, France), Dr. Ludovic Janus (Lille, France), Pr. Joël Vebrel (Besançon, France), Pr. Pierre-Marie Badot (Besançon, France), Dr. Sophie Gavoille (Besançon, France), Mr. Xavier Hutinet (Champlitte, France), Mr. Jean-François Minary (Devecey, France), Dr. Danielle Bonenfant (Montréal, Canada), Pr. Elena Vismara (Milan, Italy), Dr. Giuseppe Trunfio (Messina, Italy), Pr. Robert Haussler (Montréal, Canada), Pr. Sophie Fourmentin (Dunkerque, France), Dr. Marc Fourmentin (Dunkerque, France), Pr. Eric Lichtfouse (Aix-Marseille, France), Pr. Lee D. Wilson (Saskatchewan, Canada), Dr. Éva Fenyvesi (Budapest, Hungary), Dr. Vincent Placet (Besançon, France), and Pr. Andrei Sarbu (Bucharest, Romania).

I would also like to thank all the PhD students (Sabrina Bertini, Davide Sforzini, Angelo Cambiaghi, Yvan Lunghi, Angelo Ficaro, Roberta Suardi, Alessandro Ficarra, Nadia Morin, Mustapha Quendouchen, Frank Delval, Olivier Adam, François Renault, Bertrand Sancey, Jérémie Charles, Anne Priac, Elise Euvrard) and postdoctoral fellows (Harmel N. Peindy, Capucine Robert, Trann Phan, Giuseppe Trunfio, Lucian Staicu, Sonia Loiacono, Chiara Mongiovi) who have worked on this topic.

Finally, I would like to sincerely thank the industrialists (*SILAC Industrie*, *Papeterie du Doubs*, *GEMDOUBS*, *Minoterie Pont*, *Altadis-Seita*, *Papeterie de Mandeure*, *Incotex Textile*, *Electrolyse Abbaye d'Acey*, *VMC Pêche*, *Zindel, Galvanoplast*, *Roquette*, CycloLab) and the various financial contributors to our projects (*Agence de l'eau Rhône Méditerranée Corse*, *FEDER*, *Europe*, *INRA Transfert*, *Région Franche-Comté*, *Ville de Besançon*, *OSEO/ANVAR*, *Incubateur de Franche-Comté*, *Agence de l'Environnement et de la Maîtrise de l'Energie*, *Université de Franche-Comté*).

References

Badot PM, Comte E, Gravier E, Bernard-Brunel P, Fahys B, Crini G (2007) Chapter 5: De l'amidon pour adsorber des colorants. In: Crini G (ed) Traitement et épuration des eaux industrielles polluées: procédés membranaires, bioadsorption et oxydation chimique. Presses Universitaires de Franche-Comté, Besançon, pp 187–234. ISBN:978-2-84867-197-0

Bertini S, Crini G, Naggi AM, Suardi R, Torri G, Vecchi C, Janus L, Martel B, Morcellet M (1999) In: Labandeira T, Vila Jato JL (eds) Insoluble polymers with high amounts of β-CD: characterization and adsorption capacity. Proceedings of the IX international symposium on cyclodextrins, Saint-Jacques-de-Compostelle, pp 175–178

Bhattarai B, Muruganandham M, Suri RPS (2014) Development of high efficiency silica coated beta-cyclodextrin polymeric adsorbent for the removal of emerging contaminants of concern from water. J Hazard Mater 273:146–154. https://doi.org/10.1016/j.jhazmat.2014.03.044

Cai S, Luo J, Liu H (2017) Preparation of β-cyclodextrin polymer by inverse-phase suspension polymerization ant its capability for phenol removal. Key Eng Mater 730:195–199. https://doi.org/10.4028/www.scientific.net/KEM.730.195

Celebioglu A, Topuz F, Uyar T (2019) Water-insoluble hydrophilic electrospun fibrous mat of cyclodextrin-epichlorohydrin polymer as highly effective sorbent. Appl Polym Mater 1:54–62. https://doi.org/10.1021/acsapm.8b00034

Charles J, Sancey B, Trunfio G, Badot PM, De Carvalho M, Colin A, Rietmann M, Minary JF, Grosjean E, Crini G (2010) Chapter 12: Pollutant removal from surface-treatment industry wastewaters by starch-based sorbents: chemical abatement and impact on water toxicity. In: Sorption process and pollution – conventional and non-conventional sorbents for pollutant removal from wastewaters. Presses Universitaires de Franche-Comté, Besançon, pp 313–334. ISBN:978-2-84867-304-2

Charles J, Crini G, Morin-Crini N, Badot PM, Trunfio G, Sancey B, de Carvalho M, Bradu C, Avramescu S, Winterton P, Gavoille S, Torri G (2014) Advanced oxidation (UV-ozone) and cyclodextrin sorption: effects of individual and combined action on the chemical abatement of organic pollutants in industrial effluents. J Taiwan Inst Chem Eng 45:603–608. https://doi.org/10.1016/j.jtice.2013.06.023

Charles J, Bradu C, Morin-Crini N, Sancey B, Winterton P, Torri G, Badot PM, Crini G (2016) Pollutant removal from industrial discharge water using individual and combined effects of adsorption and ion-exchange processes: chemical abatement. J Saudi Chem Soc 20:185–194. https://doi.org/10.1016/j.jscs.2013.03.007

Cova TFGG, Murthino D, Pais AACC, Valente AJM (2018) Cyclodextrin-based materials for removing micropollutants from wastewater. Current Org Chem 22:2146–2177. https://doi.org/10.2174/1385272822666181019125315

Crini G (1995) Nouvelles phases stationnaires à base de cyclodextrine: applications à différentes séparations en chromatographie liquide haute performance. PhD, Université de Lille 1

Crini G (2003) Studies on adsorption of dyes on beta-cyclodextrin polymer. Bioresour Technol 90:193–198. https://doi.org/10.1016/S0960-8524(03)00111-1

Crini (2005a) Recent developments in polysaccharide-based materials used as adsorbents in wastewater treatment. Prog Polym Sci 30:38–70. https://doi.org/10.1016/j.progpolymsci.2004.11.002

Crini (2005b) Method for making a gel-type compound for treating effluent. French Patent PCT/FR2006/050549, WO2006/134299

Crini G (2006) Non-conventional low-cost adsorbents for dye removal. Bioresour Technol 97:1061–1085. https://doi.org/10.1016/j.biortech.2005.05.001

Crini G (2008) Kinetic and equilibrium studies on the removal of cationic dyes from aqueous solution by adsorption onto a cyclodextrin polymer. Dyes Pigments 77:415–426. https://doi.org/10.1016/j.dyepig.2007.07.001

Crini G (2014) Review: a history of cyclodextrins. Chem Rev 114:10940–10975. https://doi.org/10.1021/cr500081p

Crini G (2015a) Chapter 10: Non-conventional adsorbents for dye removal. In: Sharma SK (ed) Green chemistry for dyes removal form wastewater. Scrivener Publishing LLC, Beverly, pp 359–407. ISBN:978-1-118-72099-8

Crini G (2015b) Chapter 1: Histoire des cyclodextrines. In: Morin-Crini N, Fourmentin S, Crini G (eds) Cyclodextrines – histoire, propriétés, chimie et applications. Presses Universitaires de Franche-Comté, Besançon, pp 19–56. ISBN:978-2-84867-520-6

Crini G, Badot PM (2008) Application of chitosan, a natural aminopolysaccharide, for dye removal from aqueous solutions by adsorption processes using batch studies: a review of recent literature. Prog Polym Sci 33:399–447. https://doi.org/10.1016/j.progpolymsci.2007.11.001

Crini G, Morcellet M (2002) Synthesis and applications of adsorbents containing cyclodextrins. J Sep Sci 25:789–813. https://doi.org/10.1002/1615-9314(20020901)25:13<789::AID-JSSC789>3.0.CO;2-J

Crini G, Peindy HN (2006) Adsorption of C.I. Basic Blue 9 on cyclodextrin-based material containing carboxylic groups. Dyes Pigments 70:204–211. https://doi.org/10.1016/j.dyepig.2005.05.004

Crini G, Lekchiri Y, Morcellet M (1995a) Separation of structural isomers on cyclodextrin-polymers coated on silica beads. Chromatographia 40:296–302. https://doi.org/10.1007/BF02290360

Crini G, Torri G, Lekchiri Y, Martel B, Janus L, Morcellet M (1995b) High performance liquid chromatography of structural isomers using a cyclodextrin-poly(allylamine) coated silica column. Chromatographia 41:424–430. https://doi.org/10.1007/BF02318617

Crini G, Martel B, Torri G, Morcellet M (1996) HPLC of structural isomers using cyclodextrin systems coated on silica bead. In: Szejtli J, Szente L (eds) Proceedings of the VIII international symposium on cyclodextrins, Budapest, Hungary, March 31–April 2, 1996. Springer, pp 667–670

Crini G, Cosentino C, Bertini S, Naggi AM, Torri G, Vecchi C, Janus L, Morcellet M (1998a) Solid state NMR study of molecular motions in cyclomaltoheptaoses (β-cyclodextrins) crosslinked with epichlorohydrin. Carbohydr Res 308:37–45. https://doi.org/10.1016/S0008-6215(98)00077-9

Crini G, Bertini S, Torri G, Naggi AM, Sforzini D, Vecchi C, Janus L, Lekchiri Y, Morcellet M (1998b) Sorption of aromatic compounds in water using insoluble cyclodextrin polymers. J Appl Polym Sci 68:1973–1978. https://doi.org/10.1002/(SICI)1097-4628(19980620)68:12<1973::AID-APP11>3.0.CO;2-T

Crini G, Bourdonneau M, Martel B, Piotto M, Morcellet M, Richert T, Vebrel J, Torri G, Morin N (2000) Solid state NMR characterisation of cyclomaltoheptaose (beta-cyclodextrin) polymers using high resolution magic angle spinning with gradients. J Appl Polym Sci 75:1288–1295. https://doi.org/10.1002/(SICI)1097-4628(20000307)75:10<1288::AID-APP10>3.0.CO;2-J

Crini G, Morcellet M, Morin N (2001) Quelques applications des complexes d'inclusion cyclodextrine/substrat. Act Chim 11:18–25

Crini G, Morin N, Rouland JC, Janus L, Morcellet M, Bertini S (2002) Adsorption de béta-naphtol sur des gels de cyclodextrines-carboxyméthylcelluloses réticulés. Eur Polym J 38:1095–1103. https://doi.org/10.1016/S0014-3057(01)00298-1

Crini G, Morin-Crini N, Badot PM (2003) Adsorption de dérivés aromatiques par des gels de cyclodextrines. Hydrosciences 8:58–61

Crini G, Peindy HN, Gimbert F, Robert C (2007) Removal of C.I. Basic Green 4 (Malachite Green) from aqueous solutions by adsorption using cyclodextrin-based adsorbent: kinetic and equilibrium studies. Sep Purif Technol 53:97–110. https://doi.org/10.1016/j.seppur.2006.06.018

Crini G, Exposito AS, Rocchi S, Jeanvoine A, Fourmentin M, Millon L, Morin-Crini N (2017) Simultaneous removal of five triazole fungicides from synthetic solutions on activated carbons and cyclodextrin-based adsorbents. Heliyon 3:e00380. https://doi.org/10.1016/j.heliyon.2017.e00380

Crini G, Fourmentin S, Fenyvesi É, Torri G, Fourmentin M, Morin-Crini N (2018a) Chapter 1: Fundamentals and applications of cyclodextrins. In: Fourmentin F, Crini G, Lichtfouse É (eds) Cyclodextrins fundamentals, reactivity and analysis. Environmental chemistry for a sustainable world, vol 1. Springer, pp 1–55. https://doi.org/10.1007/978-3-319-76159-6_1

Crini G, Fourmentin S, Fenyvesi É, Torri G, Fourmentin M, Morin-Crini N (2018b) Cyclodextrins – from molecules to applications. Environ Chem Lett:1361–1375. https://doi.org/10.1007/s10311-018-0763-2

Crini G, Fourmentin S, Morin-Crini N, Fourmentin M (2019a) Principales applications des complexes d'inclusion cyclodextrine-substrat. In: Techniques de l'ingénieur, collection recherché et innovation, ref. IN232v1, pp 1–16

Crini G, Lichtfouse E, Wilson LD, Morin-Crini N (2019b) Conventional and non-conventional adsorbents for wastewater treatment. Environ Chem Lett 17:145–155. https://doi.org/10.1007/s10311-018-0785-9

Cserháti T, Forgács E (1994) Retention of 4-cyanophenyl herbicides on water-insoluble β-cyclodextrin support. J Chromatogr A 685:295–302. https://doi.org/10.1016/0021-9673(94)00642-3

Cserháti T, Dobrovolszky A, Fenyvesi É, Szejtli J (1983) Beta-cyclodextrin polymer beads as GC packings. J High Res Chromatogr 6:442–443

Danquah MK, Aruei RC, Wilson LD (2018) Phenolic pollutant uptake properties of molecular templated polymers containing beta-cyclodextrin. J Phys Chem B 122:4748–4757. https://doi.org/10.1021/acs.jpcb.8b01819

Delval F, Crini G, Bertini S, Filiatre C, Torri G (2005) Preparation, characterization and sorption properties of crosslinking starch-based exchangers. Carbohydr Polym 60:67–75. https://doi.org/10.1016/j.carbpol.2004.11.025

Euvrard É, Morin-Crini N, Bradu C, Gavoille S, Winterton P, Lagarrigue C, Hutinet X, Trunfio G, Torri G, Druart C, Poupeney A, Avramescu S, Fourmentin S, Crini G (2015) Chapter 13: Polymères réticulés de cyclodextrine: complexation de substances émergentes et mécanismes d'adsorption. In: Morin-Crini, Fourmentin S, Crini (eds) Cyclodextrines – histoire, propriétés, chimie et applications. PUFC, Besançon, pp 279–300. ISBN:978-2-84867-520-6

Euvrard É, Morin-Crini N, Druart C, Bugnet J, Martel B, Cosentino C, Moutarlier V, Crini G (2016) Cross-linked cyclodextrin-based material for treatment of metals and organic substances present in industrial discharge waters. Beilstein J Org Chem 12:1826–1838. https://doi.org/10.3762/bjoc.12.172

Euvrard É, Morin-Crini N, Martel B, Cosentino C, Crini G (2017) Chapter 12: Cyclodextrines réticulées pour traiter des eaux contaminées. In: Morin-Crini, Crini G (eds) Eaux industrielles contaminées. PUFC, Besançon, pp 341–371. ISBN:978-2-84867-589-3

Fenyvesi É (1988) Cyclodextrin polymers in the pharmaceutical industry. J Incl Phenomena 6:537–545. https://doi.org/10.1007/BF00660751

Fenyvesi É, Barkács K, Gruiz K, Varga E, Kenyeres I, Záray G, Szente L (2020) Removal of hazardous micropollutants from treated wastewater using cyclodextrin bead polymer – a pilot demonstration case. J Hazard Mater 383:121181. https://doi.org/10.1016/j.jhazmat.2019.121181

Fourmentin S, Morin-Crini N, Crini G (2015) Chapter 2: Cyclodextrines et complexes d'inclusion. In: Morin-Crini N, Fourmentin S, Crini G (eds) cyclodextrines – histoire, propriétés, chimie et applications. Presses Universitaires de Franche-Comté, Besançon, pp 57–84. ISBN:978-2-84867-520-6

Fourmentin S, Crini G, Lichtfouse É (eds) (2018a) Cyclodextrin fundamentals, reactivity and analysis. Springer: environmental chemistry for a sustainable world, 255 p. https://doi.org/10.1007/978-3-319-76159-6

Fourmentin S, Crini G, Lichtfouse É (eds) (2018b) Cyclodextrin applications in medicine, food, environment and liquid crystals. Environmental chemistry for a sustainable world. Springer, 240 p. https://doi.org/10.1007/978-3-319-76162-6

Friedman RB, West IR (1988) Method for removing polychlorinated biphenyl compounds from water US Patent 4,726,905

Fujiyoshi T, Carrez O, Imizcoz M, Zornoza A, Isasi JR (2019) Interpenetrated polymer networks of poly(beta-cyclodextrin) and polyvinylpyrrolidone with synergistic and selective sorption capacities. Carbohydr Polym 219:105–112. https://doi.org/10.1016/j.carbpol.2019.05.027

García-Zubiri IX, González-Gaitano G, Isasi JR (2006) Thermal stability of solid dispersions of naphthalene derivatives with β-cyclodextrin and β-cyclodextrin polymers. Thermochim Acta 444:57–64. https://doi.org/10.1016/j.tca.2006.02.024

Gidwani B, Vyas A (2014) Synthesis, characterization and application of epichlorohydrin-β-cyclodextrin polymer. Colloids Surf B Biointerfaces 114:130–137. https://doi.org/10.1016/j.colsurfb.2013.09.035

Gimbert F, Morin-Crini N, Renault F, Badot PM, Crini G (2008) Adsorption isotherm models for dye removal by cationized starch-based material in a single component system: error analysis. J Hazard Mater 157:34–46. https://doi.org/10.1016/j.jhazmat.2007.12.072

Heydari A, Khoshnood H, Sheibani H, Doostan F (2017) Polymerization of cyclodextrin in the presence of bentonite clay to produce polymer nanocomposites for removal of heavy metals from drinking water. Polymers Adv Technol 28:524–532. https://doi.org/10.1002/pat.3951

Heydari A, Sheibani H, Hronsky V, Janigova I, Slouf M, Siffalovic P, Chodak I (2018) Beta-Cyclodextrin-epichlorohydrin polymer/graphene oxide nanocomposite: preparation and characterization. Chem Papers 72:1299–1313. https://doi.org/10.1007/s11696-017-0371-9

Hoffman JL (1970) Chromatography of nucleic acid components on cyclodextrin gels. Anal Biochem 3:209–217. https://doi.org/10.1016/0003-2697(70)90288-5

Hoffman JL (1972) Chromatography of nucleic acids on cross-linked cyclodextrin gels having inclusion-forming capacity. Abstr Paper Am Chem Soc 164:47–47

Hoffman JL (1973) Chromatography of nucleic acids on cross-linked cyclodextrin gels having inclusion-forming capacity. J Macromol Sci Chem A7:1147–1157. https://doi.org/10.1080/10601327308060488

Huang Q, Chai K, Zhou L, Ji H (2020) A phenyl-rich β-cyclodextrin porous crosslinked polymer for efficient removal of aromatic pollutants: insight into adsorption performance and mechanism. Chem Eng J 387:124020. https://doi.org/10.1016/j.cej.2020.124020

Janus L, Crini G, El-Rezzi V, Morcellet M, Cambiaghi A, Torri G, Naggi AM, Vecchi C (1999) New sorbents containing beta-cyclodextrin. Synthesis, NMR characterization and preliminary sorption properties. React Funct Polym 42:173–180

Jurecska L, Dobosy P, Barkács K, Fenyvesi É, Záray G (2014) Characterization of cyclodextrin containing nanofilters for removal of pharmaceutical residues. J Pharm Biomed Anal 98:90–93. https://doi.org/10.1016/j.jpba.2014.05.007

Lee JH, Kwak SY (2020) Branched polyethylenimine-polyethylene glycol-*β*-cyclodextrin polymers for efficient removal of bisphenol A and copper from wastewater. J Appl Polym Sci 137:48475. https://doi-org.inee.bib.cnrs.fr/10.1002/app.48475

Li XH, Hao XK (2019) Study of adsorption of nitrophenols from aqueous solution using ECDMZ. Adv Energy Sci Environ Eng III 2106:020007. https://doi.org/10.1063/1.5109330

Li X, Nie XJ, Zhu YN, Ye WC, Jiang YL, Su SL, Yan BT (2019) Adsorption behaviour of Eriochrome Black T from water onto a cross-linked beta-cyclodextrin polymer. Colloids Surf A Physicochem Eng Aspects 578:123582. https://doi.org/10.1016/j.colsurfa.2019.123582

Liu Q, Zhou Y, Lu J, Zhou Y (2020) Novel cyclodextrin-based adsorbents for removing pollutants from wastewater: a critical review. Chemosphere 241:125043. https://doi.org/10.1016/j.chemosphere.2019.125043

Lü Q, Gong H, Wang R (2018) Synthesis of β-cyclodextrin/epichlorohydrin polymer and its adsorption properties for bisphenol S. Res Environ Sci 31:1933–1939. https://doi.org/10.13198/j.issn.1001-6929.2018.07.03

Mohamed MH, Wilson LD, Headley JV (2010) Estimation of the surface accessible inclusion sites of β-cyclodextrin based copolymer materials. Carbohydr Polym 80:186–196. https://doi.org/10.1016/j.carbpol.2009.11.014

Mohamed MH, Wilson LD, Pratt DY, Guo R, Wu C, Headley JV (2012) Evaluation of the accessible inclusion sites in copolymer materials containing beta-cyclodextrin. Carbohydr Polym 87:1241–1248. https://doi.org/10.1016/j.carbpol.2011.09.011

Morin-Crini N, Crini G (2012) Review of current physical and chemical technologies for the decontamination of industrial wastewater. Int J Chem Eng 5:143–186

Morin-Crini N, Crini G (2013) Environmental applications of water-insoluble β-cyclodextrin-epichlorohydrin polymers. Prog Polym Sci 38:344–368. https://doi.org/10.1016/j.progpolymsci.2012.06.005

Morin-Crini N, Fourmentin S, Crini G (eds) (2015) Cyclodextrines. PUFC, Besançon, p 370. ISBN:978-2-84867-520-6

Morin-Crini N, Winterton P, Fourmentin S, Wilson LD, Fenyvesi É, Crini G (2018a) Water-insoluble β-cyclodextrin-epichlorohydrin polymers for removal of pollutants from aqueous solutions by sorption processes using batch studies: a review of inclusion mechanism. Prog Polym Sci 78:1–23. https://doi.org/10.1016/j.progpolymsci.2017.07.004

Morin-Crini N, Fourmentin M, Fourmentin S, Torri G, Crini G (2018b) Chapter 6: Silica materials containing cyclodextrin for pollutant removal. In: Fourmentin F, Crini G, Lichtfouse É (eds) Cyclodextrins applications in medicine, food, environment and liquid crystals. Environmental chemistry for a sustainable world, vol 2. Springer, pp 149–182. https://doi.org/10.1007/978-3-319-76162-6

Morin-Crini N, Fourmentin M, Fourmentin S, Torri G, Crini G (2019a) Synthesis of silica materials containing cyclodextrin and their applications in wastewater treatment. Environ Chem Lett. https://doi.org/10.1007/s10311-018-00818-0

Morin-Crini N, Badot PM, Crini G (2019b) Complémentarité des outils scientifiques pour évaluer la toxicité de rejets industriels. Techniques de l'Ingénieur, Collection Recherche et Innovation, RE184v1, pp 1–17

Murcia-Salvador A, Pellicer JA, Fortea MI, Gomez-Lopez VM, Rodriguez-Lopez MI, Nunez-Delicado E, Gabaldon JA (2019) Adsorption of Direct Blue 78 using chitosan and cyclodextrins as adsorbents. Polymers 11:1003. https://doi.org/10.3390/polym11061003

Nagy ZM, Molnár M, Fekete-Kertész I, Molnár-Perl I, Fenyvensi E, Gruiz K (2014) Removal of emerging micropollutants from water using cyclodextrin. Sci Total Environ 485–486:711–719. https://doi.org/10.1016/j.scitotenv.2014.04.003

Nojavan S, Yazdanpanah M (2017) Micro-solid phase extraction of benzene, toluene, ethylbenzene and xylenes from aqueous solutions using water-insoluble beta-cyclodextrin polymer as sorbent. J Chromatogr A 1525:51–59. https://doi.org/10.1016/j.chroma.2017.10.027

Ogawa K, Hiromi Y (2015) Preparation of water-insoluble beta-cyclodextrin polymer cross-linked with (waste) glycerin and epichlorohydrin. Kobunshi Ronbunshu 72:64–70. https://doi.org/10.1295/koron.2014-0032

Orprecio R, Evans CH (2003) Polymer-immobilized cyclodextrin trapping of model organic pollutants in flowing water streams. J Appl Polym Sci 90:2103–2110. https://doi.org/10.1002/app.12818

Pratt DY, Wilson LD, Kozinski JA, Mohart AM (2010) Preparation and sorption studies of β-cyclodextrin/epichlorohydrin copolymers. J Appl Polym Sci 116:2982–2989. https://doi.org/10.1002/app.31824

Priac A, Morin-Crini N, Druart C, Gavoille S, Bradu C, Lagarrigue C, Torri G, Winterton P, Crini G (2017) Alkylphenol and alkylphenol polyethoxylates in water and wastewater: a review of their options for their elimination. Arab J Chem 10:S3749–S3773. https://doi.org/10.1016/j.arabjc.2014.05.011

Renard E, Deratani A, Volet G, Sébille B (1997) Preparation and characterization of water soluble high molecular beta-cyclodextrin-epichlorohydrin polymers. Eur Polym J 33:49–57. https://doi.org/10.1016/S0014-3057(96)00123-1

Renault F, Morin-Crini N, Gimbert F, Badot PM, Crini G (2008) Cationized starch-based material as a new ion-exchanger adsorbent for the removal of C.I. Acid Blue 25 from aqueous solutions. Bioresour Technol 99:7573–7586. https://doi.org/10.1016/j.biortech.2008.02.011

Romita R, Rizzi V, Semeraro P, Gubitosa J, Gabaldón JA, Gorbe MIF, López VMG, Cosma P, Fini P (2019) Operational parameters affecting the atrazine removal from water by using cyclodextrin based polymers as efficient adsorbents for cleaner technologies. Environ Technol Innov 16:100454. https://doi.org/10.1016/j.eti.2019.100454

Romo A, Peñas FJ, Isasi JR (2004) Sorption of dibenzofuran derivatives from aqueous solutions by β-cyclodextrin polymers: an isosteric heat approach. J Colloid Interface Sci 279:55–60. https://doi.org/10.1016/j.jcis.2004.06.043

Romo A, Peñas FJ, Sevillano X, Isasi JR (2006) Application of factorial experimental design to the study of the suspension polymerization of β-cyclodextrin and epichlorohydrin. J Appl Polym Sci 100:3393–3402. https://doi.org/10.1002/app.23778

Romo A, Peñas FJ, Isasi JR, Garcia-Zubiri IX, Gonzalez-Gaitano G (2008) Extraction of phenols from aqueous solutions by β-cyclodextrin polymer. Comparison of sorptive capacities with other sorbents. React Funct Polym 68:406–413. https://doi.org/10.1016/j.reactfunctpolym.2007.07.005

Sancey B, Crini G (2012) Décontamination des effluents de traitement de surface par oxydation/bioadsorption sur cyclodextrine. In: Techniques de l'Ingénieur, Collection Recherche & Innovation, pp 8–12

Sancey B, Crini G, Trunfio G, Morin-Crini N, Torri G (2010) Chapter 15: Cross-linked cyclodextrins for pollutant removal. In: Crini G, Badot PM (eds) Sorption process and pollution – conventional and non-conventional sorbents for pollutant removal from wastewaters. PUFC, Besançon, pp 387–400. ISBN:978-2-84867-304-2

Sancey B, Trunfio G, Charles J, Badot PM, Crini G (2011a) Sorption onto crosslinked cyclodextrin polymers for industrial pollutants removal: an interesting environmental approach. J Incl Phenom Macrocycl Chem 70:315–320. https://doi.org/10.1007/s10847-010-9841-1

Sancey B, Charles J, Trunfio G, Badot PM, Jacquot M, Hutinet X, Gavoille S, Crini G (2011b) Effects of additional sorption treatment of industrial water discharge by cross-linked starch. Ind Eng Chem Res 50:1749–1756. https://doi.org/10.1021/ie1010492

Sancey B, Trunfio G, Charles J, Minary JF, Gavoille S, Badot PM, Crini G (2011c) Heavy metals removal from industrial effluents by adsorption on crosslinked starch: chemical study and impact on water toxicity. J Environ Manage 92:765–772. https://doi.org/10.1016/j.jenvman.2010.10.033

Sancey B, Bradu C, Torri G, Crini G (2012) Cross-linked polysaccharides as adsorbents for industrial pollutant removal (2012). Proceedings of the 5th European symposium biopolymers diversity and industrial applications perspectives, Rennes, pp 36–41

Shabtai IA, Mishael YG (2018) Polycyclodextrin-clay composites: regenerable dual-site sorbents for Bisphenol A removal from treated wastewater. Appl Mater Interf 10:27088–27097. https://doi.org/10.1021/acsami.8b09715

Shao Y, Martel B, Morcellet M, Weltrowski M, Crini G (1996) Sorption of textile dyes on beta-cyclodextrin-epichlorohydrin gels. J Incl Phenom Mol Recognition Chem 25:209–212

Shaw PE (1990) Cyclodextrin polymers in the removal of bitter components from citrus juice. In: Rouseff RL (ed) Bitterness in foods and beverages. Elsevier, Amsterdam, pp 309–324

Shaw PE, Wilson CW III (1983) Debittering citrus with β-cyclodextrin polymer. J Food Sci 48:646–647. https://doi.org/10.1111/j.1365-2621.1983.tb10811.x

Shaw PE, Wilson CW III (1985) Reduction of bitterness in grapefruit juice with β-cyclodextrin polymer in a continuous-flow process. J Food Sci 50:1205–1207. https://doi.org/10.1111/j.1365-2621.1985.tb13054.x

Sikder MT, Jakariya M, Rahman MM, Fujita S, Saito T, Kurasaki M (2017) Facile synthesis, characterization, and adsorption properties of Cd (II) from aqueous solution using beta-cyclodextrin polymer impregnated in functionalized chitosan beads as a novel adsorbent. J Environ Chem Eng 5:3395–3404. https://doi.org/10.1016/j.jece.2017.06.007

Sikder MT, Rahman MM, Jakariya M, Hosokawa T, Kurasaki M, Saito T (2019) Remediation of water pollution with native cyclodextrins and modified cyclodextrins: a comparative overview and perspectives. Chem Eng J 355:920–941. https://doi.org/10.1016/j.cej.2018.08.218

Smolkova-Keulemansova E (1982) Cyclodextrins as stationary phases in chromatography. J Chromatogr 251:17–34. https://doi.org/10.1016/S0021-9673(00)98506-6

Solms J (1966) Société des Produits Nestlé S.A. Chem Abstr 64:16687. Netherlands patent 6,505,361; 1964/1965; British patent 1,091,637; 1967

Solms J (1967) Inclusion resins. Nestle's Prod. Ltd. British Patent 1,091,637

Solms J (1969) Inclusion resins of cyclodextrin and methods of use. US patent 3,420,788

Solms J, Egli RH (1964) Abstracts Sixth International Congress of Biochemistry, New York, p 180

Solms J, Egli RH (1965) Harze mit einschlusshohlräumen von cyclodextrin-struktur. Helv Chim Acta 48:1225–1228

Szejtli J (1980) Complexing properties of substituted cyclodextrins and cyclodextrin polymers in aqueous-solutions. Abstr Paper Am Chem Soc 179:65–66

Szejtli J (1982) Cyclodextrins and their inclusion complexes. Akadémiai Kiadó, Budapest, p 296. ISBN:963-05-2850-9

Szejtli J (1984) Highly soluble β-cyclodextrin derivatives. Starch/Stärke 36:429–432. https://doi.org/10.1002/star.19840361207

Szejtli J (1988) Cyclodextrin technology. Kluwer Academic Publishers, Dordrecht, p 450. ISBN:90-277-2314-1

Szejtli J, Fenyvesi É, Zsadon B (1978) Cyclodextrinpolymere. Starch/Stärke 30:127–131. https://doi.org/10.1002/star.19780300407

Szemán J, Fenyvesi É, Szejtli J, Ueda H, Machida Y, Nagai T (1987) Water-soluble cyclodextrin polymers – their interaction with drugs. J Incl Phenom 5:427–431. https://doi.org/10.1007/BF00664098

Vanzo E (1991) Spherical cyclodextrin polymer beads. US patent 5,075,432

Vecchi C, Bertini S, Crini G, Naggi AM, Torri G (1998) Polymers of cyclodextrins can adsorb pollutants: evaluation of their adsorption capacity and characterization. Rivista dei Combustibili 52:231–236

Vélaz I, Isasi JR, Sanchez M, Uzqueda M, Ponchel G (2007) Structural characteristics of some soluble and insoluble β-cyclodextrin polymers. J Incl Phenom Macrocyclic Chem 57:65–68. https://doi.org/10.1007/s10847-006-9221-z

Wagner CJ, Wilson CW III, Shaw PE (1988) Reduction of grapefruit bitter components in a fluidized β-cyclodextrin polymer bed. J Food Sci 53:516–518. https://doi.org/10.1111/j.1365-2621.1988.tb07745.x

Wang ZH, Zhang PB, Hu F, Zhao YF, Zhu LP (2017) A crosslinked beta-cyclodextrin polymer used for rapid removal of a broad-spectrum of organic micropollutants from water. Carbohydr Polym 177:224–231. https://doi.org/10.1016/j.carbpol.2017.08.059

Wiedenhof N (1969) Properties of cyclodextrins. Part IV: Features and use of insoluble cyclodextrin-epichlorohydrin-resins. Starch/Stärke 21:163–166. https://doi.org/10.1002/star.19690210606

Wiedenhof N, Trieling RG (1971) Properties of cyclodextrins. Part V. Inclusion isotherms and kinetics of inclusion of benzoic acid and m-chlorobenzoic acid on β-E25 cyclodextrin-epichlorohydrin resin. Die Stärke 23:129–132. https://doi.org/10.1002/star.19710230405

Wiedenhof N, Lammers JNJJ, van Panthaleon van Eck CL (1969) Properties of cyclodextrins. Part III. Cyclodextrin-epichlorohydrin resins: preparation and analysis. Die Stärke 21:119–123. https://doi.org/10.1002/star.19690210504

Wiedenhof N, van Panthaleon van Eck CL, Lammers JNJJ (1971) Cyclodextrins derivatives. British patent 1,244,990

Wilson LD, Mohamed MH, Guo R, Pratt DY, Kwon JH, Mahmud ST (2010) Sorption of agrochemical model compounds by sorbent materials containing beta-cyclodextrin. J Agromedicine 15:105–116. https://doi.org/10.1080/10599241003618770

Xiao LL, Ching C, Ling YH, Nasiri M, Klemes MJ, Reineke TM, Helbling DE, Dichtel WR (2019) Cross-linker chemistry determines the uptake potential of perfluorinated alkyl substances by beta-cyclodextrin polymers. Macromolecules 52:3747–3752. https://doi.org/10.1021/acs.macromol.9b00417

Xu GH, Xie XC, Qin L, Hu XJ, Zhang D, Xu J, Li D, Ji XW, Huang Y, Tu Y, Jiang L, Wei DY (2019) Simple synthesis of a swellable porous β-cyclodextrin-based polymer in the aqueous phase for the rapid removal of organic micro-pollutants from water. Green Chem. https://doi.org/10.1039/c9gc02422k

Yilmaz Ozmen E, Yilmaz M (2007) Use of beta-cyclodextrin and starch based polymers for sorption of Congo red from aqueous solutions. J Hazard Mater 148:303–310. https://doi.org/10.1016/j.jhazmat.2007.02.042

Yilmaz Ozmen E, Sezgin M, Yilmaz A, Yilmaz M (2008) Synthesis of beta-cyclodextrin and starch based polymers for sorption of azo dyes from aqueous solutions. Bioresour Technol 99:526–531. https://doi.org/10.1016/j.biortech.2007.01.023

Zhang KD, Tsai FC, Ma N, Xia Y, Liu HL, Guo X, Yu XY, Jiang T, Chiang TC, Chang CJ (2017) Removal of azo dye from aqueous solution by host-guest interaction with beta-cyclodextrin. Des Water Treatment 86:174–182. https://doi.org/10.5004/dwt.2017.21187

Zhang H, Zhang Y, Cheng BW, Li YX, Zhou S (2019) Preparing gamma-cyclodextrin-immobilized starch and the study of its removal properties to dyestuff from wastewater. Polish J Environ Studies 28:1701–1711. https://doi.org/10.15244/pjoes/90028

Zheng S, Xia S, Han S, Yao F, Zhao H, Huang M (2019) β-Cyclodextrin-loaded minerals as novel sorbents for enhanced adsorption of Cd and Pb from aqueous solutions. Sci Total Environ 693:133676. https://doi.org/10.1016/j.scitotenv.2019.133676

Zohrehvand S, Evans CH (2005) 2-Naphthol-containing β-cyclodextrin-epichlorohydrin copolymers: synthesis, characterization and fluorescence studies. Polym Int 54:744–753. https://doi.org/10.1002/pi.1747

Zsadon B, Szilasi M, Tüdős F (1981) Inclusion chromatography of alkaloids on cyclodextrin polymer gel beds. J Chromatogr 208:109–112