



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



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ABSTRACT

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

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

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

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1. Introduction

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

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

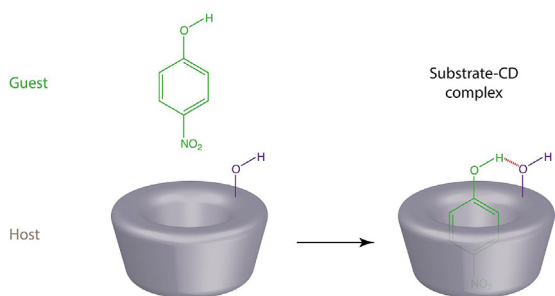


Fig. 1. Schematic representation of the association of free cyclodextrin ("host") and para-nitrophenol ("guest").

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

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

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

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

Table 1
Examples of general reviews and book chapters on epichlorohydrin-cross-linked CD-based materials for environmental applications.

Year	Corresponding Author	Title	Topic(s)	Reference
1982	Smolkova-Keulemansova, E.	Cyclodextrins as stationary phases in chromatography.	Applications	[30]
1984	Atwood, J. L.	Industrial applications of cyclodextrins.	Applications	[17]
1987	Sébille, B.	Cyclodextrin derivatives.	Synthesis, applications	[31]
1991	Szejtli, J.	The use of cyclodextrins in biotechnological operations.	Applications	[32]
1998	Szejtli, J.	Introduction and general overview of cyclodextrin chemistry.	Applications	[29]
2001	Crini, G.	<i>Quelques applications des complexes d'inclusion cyclodextrine/soluté</i> (in French).	Applications	[33]
2001	Mocanu, G.	Cyclodextrins polymers.	Synthesis, applications	[34]
2002	Crini, G.	Synthesis and applications of adsorbents containing cyclodextrins.	Synthesis, characterization, applications	[35]
2005	Crini, G.	Recent developments in polysaccharide-based materials used as adsorbents in wastewater treatment.	Synthesis, characterization, applications	[36]
2010	Kozlowski, C. A.	Use of cyclodextrin polymers in separation of organic species.	Synthesis, applications	[37]
2010	Crini, G.	Cross-linked cyclodextrins for pollutant removal.	Synthesis, applications	[38]
2011	Rath, G.	Nanotechnology for water treatment.	Applications	[39]
2012	Fourmentin, S.	Cyclodextrins for remediation technologies.	Applications	[40]
2012	Slavik, R.	Removal of phthalates from aqueous solution by different adsorbents: A short review.	Applications	[41]
2013	Crini, G.	Environmental applications of water-insoluble β -cyclodextrin-epichlorohydrin polymers.	Applications, mechanisms	[42]
2013	Nesic, A. R.	Sorption of azo dyes on polymer materials.	Applications	[43]
2013	Yang, J. S.	Preparation and application of cyclodextrin immobilized polysaccharides.	Synthesis, applications	[44]
2013	Wilson, L. D.	Cyclodextrin-based microcapsule materials – Their preparation and physicochemical properties.	Synthesis, applications	[45]
2014	Vyas, A.	Synthesis, characterization and application of epichlorohydrin-beta-cyclodextrin polymer.	Synthesis, characterization, applications	[47]
2014	Wilson, L. D.	Novel materials for environmental remediation of oil sand contaminants.	Applications	[46]
2015	Crini, G.	<i>Polymères réticulés de β-cyclodextrine: complexation de substances émergentes et mécanismes d'adsorption</i> (in French)	Applications, complexation	[48]
2016	Shen, H. M.	Progress in the immobilization of beta-cyclodextrin and their application in sorption of environmental pollutants.	Synthesis, applications	[49]

nity. For example, the development of innovative macromolecular architectures (e.g. hydrogels, nanoparticles, nanosponges, foams, fibres, felts, membranes or composites) was proposed for environmental applications, especially the elimination of the so-called emergent chemicals (pesticides, drugs, endocrine disruptors, etc.) in polluted waters or soils. These innovative materials are also studied for their potential applications in pharmacy and medicine [144–150]. Also, interest is focused on understanding and explaining the sorption mechanisms themselves. Indeed, in spite of the abundance of literature and conclusive results obtained at the industrial scale, interpreting the mechanisms of pollutant elimination remains an interesting source of debate and sometimes of contradiction.

The main aim of this review is to summarize and discuss the various mechanisms of pollutant elimination proposed in the literature to explain the performance of ECH-cross-linked CD polymers used as sorbents in liquid-solid sorption processes. Abundant data on the synthesis, analysis (microscopic, spectroscopic, etc.), and applications of these materials exists (Table 1). After a brief description of the cross-linking reaction used to produce these materials and an overview of their advantages and disadvantages, we mainly discuss the interactions and the forces involved in sorption processes. A distinction is made in the description of these interactions depending on whether the ECP structures are modified or not.

2. Insoluble epichlorohydrin-cross-linked cyclodextrin polymer

2.1. Cross-linking reaction

The reaction that leads to the cross-linking of CDs by ECH (1-chloro-2,3-epoxypropane) is well documented in the literature [19,33,35,36,42,151]. Figs. 2 and 3 describe this reaction and the schematic structure of the polymers obtained, respectively. It

should be noted that certain authors speak of insoluble polymers or copolymers, considering CD as the first monomer and ECH as the 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 [36,42,151–153].

To explain the reaction in Fig. 2, the mechanism described in Fig. 4 and proposed by Hofmann [1,64,66] in the 60s was adopted by Szejtli [1,67–72] in the 80s and described in detail for the first time by Sébille [1,31,151–153] in 1997 for water-soluble cross-linked polymers. Crini demonstrated the structure of insoluble polymers or materials by NMR spectroscopy in 1998 [1,36,42,154,155].

Following his NMR studies, Crini proposed the structure reported in Fig. 3 to describe the water-insoluble ECP polymers [154,155]. The mechanism can be divided into three major stages, that occur simultaneously: A) cross-linking, B) polymerization of the cross-linking agent, C) formation of the glycerol monoether derivative of the CD. Cross-linking (stage A) consists of creating a large three-dimensional structure using the bridging agent (ECH) that joins the CD molecules together with strong covalent bonds. This is the principal reaction and is responsible for the creation of a 3D macromolecular system with a variable proportion of cross-links. Depending on the experimental conditions used for the synthesis, and in particular on the degree of cross-linking (or the level or density of cross-linking, depending on the authors) the modified CDs can be soluble or water insoluble cross-linked polymers [55,59,64]. In the latter case, different types and sizes can be obtained depending on the intended application: gels or hydrogels, particles, or small balls (resins) insoluble in water and in many other solvents, sponges or foams. It can be noted that, owing to their three-dimensional structure, these materials are very stable (chemically, thermally, and even mechanically) [16,19]. The macromolecular network is composed of areas of cross-linked CD units and areas of macromolecules corresponding to long chains of poly-

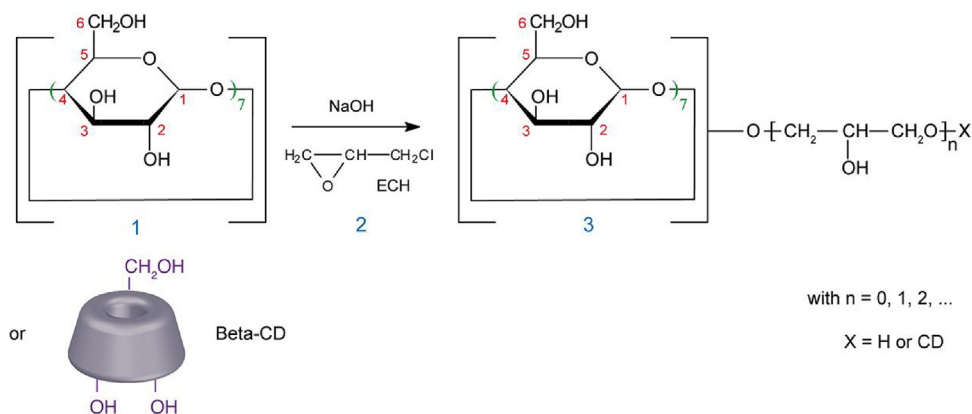


Fig. 2. Chemical reaction between cyclodextrin (Beta-CD) and epichlorohydrin (ECH) in basic medium.

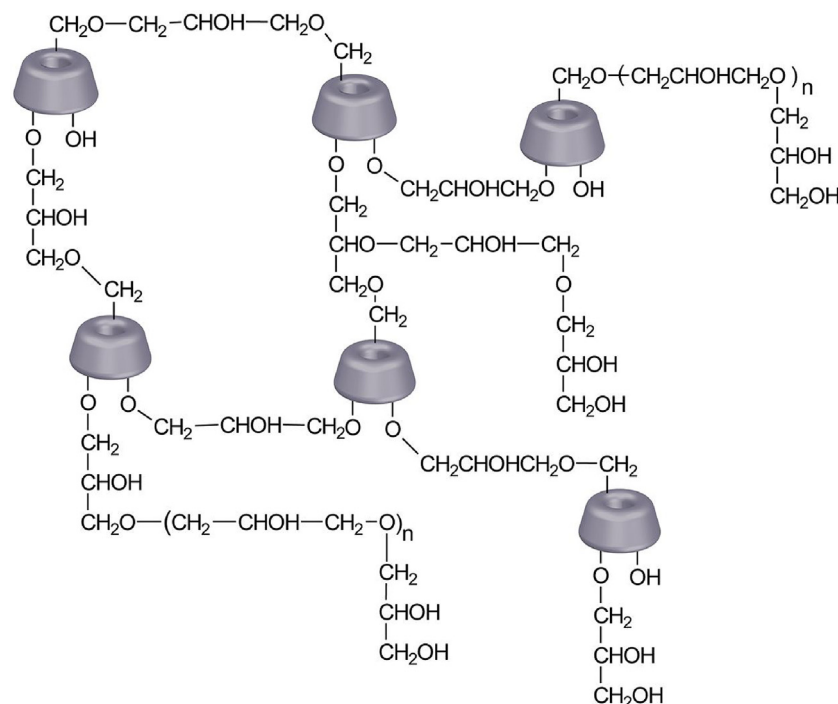


Fig. 3. Structure of a water insoluble ECH-cross-linked CD material (this scheme, based on that of Hofmann, was reported by Crini [35] in 2002).

merized ECH. The polymerization of the cross-linking agent (stage B) is due to ECH strong reactivity enabling it to polymerize with itself in basic medium (especially at excess ECH concentration) and thus create long hydroxyalkyl macromolecular chains functioning both as bridges and as side chains within the network. This is why some authors consider these materials as copolymers with two distinct components with different molecular mobilities. The glycerol monoether polymer subunits are nevertheless considered as an unwanted by-product (stage C). This is because ECH should be used in the synthesis in excess (usually 10 mol/mol CD) [16,19,42].

2.2. Chemical modification of the polymers

The ECH-cross-linked polymers can be easily modified [36–42]. For use as sorbents in applications concerning water treatment, the chemical modifications can be carried out (i) to fine-tune the hydrophilic/hydrophobic balance, (ii) to modify the surface chemistry and enhance their binding and selectivity performance, (iii) to control the transfer kinetics, (iv) to broaden the range of pH for their use and (v) to increase their mechanical resistance. The lit-

erature proposes two methods to modify the ECP [16,19,34–36]. The first consists of using polymers such as carboxymethylcellulose or neutral or ionic reagents such as ammonia, glycidyl trimethylammonium chloride, etc. at the same time as ECH in the cross-linking step in the same synthesis reactor. The aim is to control the structure of the materials (porosity, specific surface area, mechanical properties, etc.) while modifying the surface chemistry of the material. The second method consists of grafting specific moieties onto the materials after cross-linking (concept introduced by French [1,26] in the 1950s, and adopted by Wiedenhof [1,61,62] in the 1960s and Szejtli [1] in the 1980s). With this approach, the main aim is to modify the surface chemistry of the cross-linked materials by grafting ionic ligands (cationic and/or anionic) or neutral ligands (amine functions). These new ligands will then behave as active “binding” sites and participate in the chemisorption mechanism. The grafting reactions, that take place in heterogeneous media, are classic modification reactions (carboxymethylation, aminoalkylation, etc.) and are well understood in oligosaccharide and polysaccharide chemistry [19,36,50–54]. Fig. 5 presents examples of frequently used cationic, anionic and

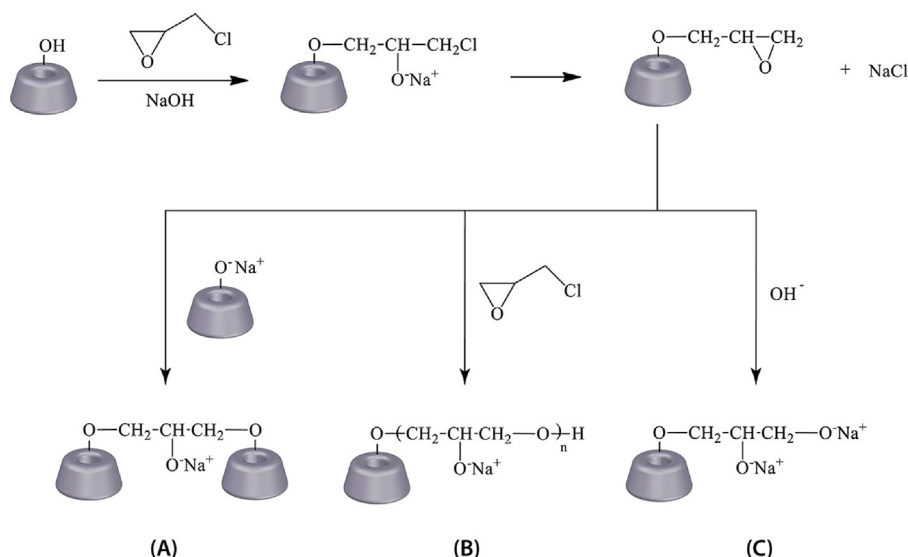


Fig. 4. Reaction mechanism for the cross-linking of CD by ECH (reaction A) which also shows the self-polymerisation of the cross-linker (reaction B) and the formation of a glycerol monoether derivative by hydrolysis (reaction C).

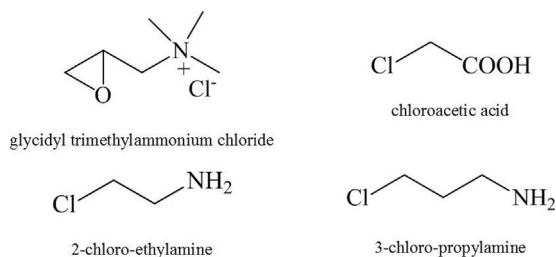


Fig. 5. Examples of ligands frequently used to functionalize ECP polymers.

neutral ligands. Solid-state NMR is used to study these added functions. Fig. 6 reports an example of the NMR spectral results of a carboxymethylated (or not) ECP material [36]. Fig. 7 shows a possible structure of an ECH-cross-linked-CD polymer containing both cationic and anionic groups. Note that the degree of substitution (the number of substituents in a CD unit, DS) of the hydroxyl groups by ionic functions described in the literature is usually relatively low (DS < 0.2) but sufficient to present chemisorption properties [16,19,26,27]. When the polymer is modified or the crosslinking and modification are carried out simultaneously the hydroxyl groups on the glyceryl bridges and on glyceryl monoether polymer side chains are also reactive. Consequently, the ionic substituents can be located both on the CD rims and on the network (Fig. 7). Therefore instead of DS, it is better to characterize the polymer by the concentration of substituents (mM)/g of the polymer sorbent. It should also be noted that modified ECP polymers can make the wastewater that they are used to treat either acidic or basic depending on the moiety grafted (in the former case, for example, polymers that contains basic carboxylate groups). This form of modification explains why the pH of the solution can vary during the sorption process [42].

2.3. Main advantages and disadvantages of cross-linked and/or modified materials

Considering synthesis, cross-linked CD materials are interesting for several reasons [16,19,22,77,78,116,117,157]. Their one-step synthesis in water is simple, easy to set up in a lab (standard lab equipment, reaction that can be easily scaled up for industrial sized reactors), only requires mild reaction conditions (green, water-

based chemistry, mild temperatures generally between 50° and 80 °C and at atmospheric pressure), where the reagents involved are easy to find and inexpensive. The ease of preparation of these materials was stressed early on in the 60s by the research groups of Solms [54,55] and of Wiedenhof [59,60]. In addition to the CD, the only compounds used in the synthesis are water, caustic soda and the cross-linking agent. The cross-linking agent must however be used with caution owing to its toxicity. As already mentioned, various types of materials can be obtained with physical textures and mechanical properties that can be varied giving different forms: hydrogels/gels, powders/particles, beads/resins and or nanoparticles/nanobeads [16,19]. In particular conditions of synthesis (two-phase heterogeneous synthesis, use of a blowing agent, etc.), a well-defined spherical size and shape with controlled distribution can be obtained for particular applications [22,23,37,40,48]. However, for water treatment, particles that are not spherical and that do not have regular shapes and sizes are sufficient to obtain satisfactory results (as demonstrated by Wiedenhof [1,60] in the 1960s). Moreover, the production costs of these rough powders are much less than those of nanobeads for instance. The materials obtained occur in the form of high-molecular-weight networks, that are generally non-porous (except for nanoparticles and nanobeads). They present a very low specific surface area (generally between 0.5 and 10 m² g⁻¹) [36,42] compared to that of carbonaceous materials (> 1500 m² g⁻¹). They 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 CD-glyceryl bonds). The 3D macromolecular network is thus both hydrophilic and hydrophobic, a property that can be very useful for applications in aqueous media. The presence of numerous hydroxyl groups also confers hydration properties to the ECP materials, varying its intensity depending on the degree of cross-linking. Some forms (gels and hydrogels) can swell in water absorbing up to several times their weight [211]. These gel/hydrogel materials simultaneously present properties characteristic of both liquids and solids. Their properties are strictly linked to their molecular structure and to the concepts of connectivity and networks. Owing to their ability to swell in water these materials also present the cohesive properties of a solid and the diffusion characteristics of a liquid. The swelling properties become useful for the complexation of pollutants and more gener-

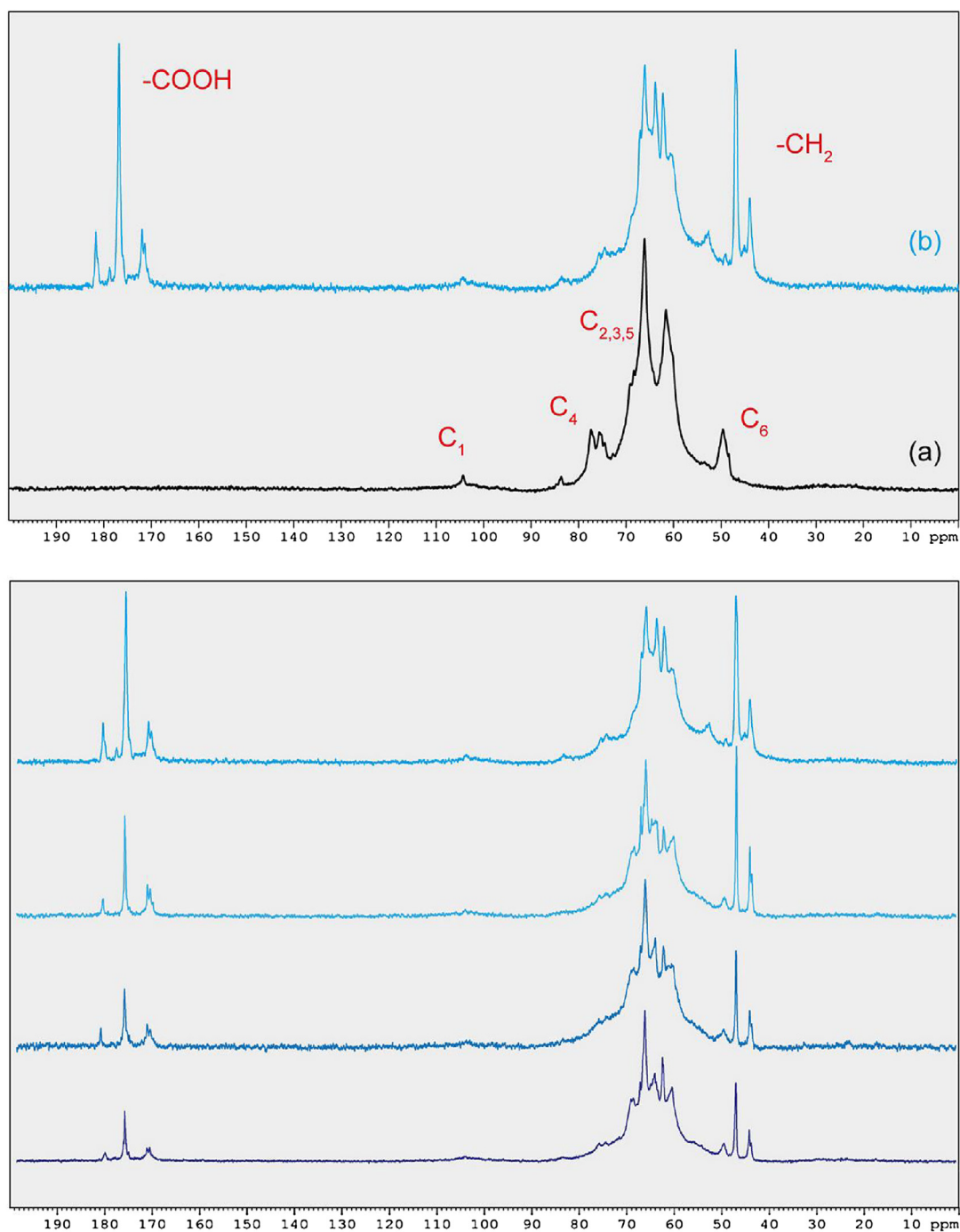


Fig. 6. ^{13}C NMR spectra of cyclodextrin-epichlorohydrin polymer – Top: a) after cross-linking and b) after cross-linking and carboxymethylation; Bottom: influence of the degree of carboxymethylation reaction.

ally in sorption processes involving natural substances (chitosan, alginate...), as they favour processes involving diffusion within the polymer network. The macromolecular networks also have a structure that is mainly amorphous, with very few or complete absence of crystalline zones, as shown by solid state NMR and relaxation-time techniques, X-ray diffraction, and differential scanning calorimetry [1,16,19,22,36]. The amorphous character, caused by the loss of CD crystallinity during the cross-linking reaction, represents an additional advantage as it favors sorption processes.

The physical, microscopic, and spectroscopic characterization of macromolecular networks is well documented and provides a set of useful information: size distribution of the particles, mobil-

ity/rigidity of the macromolecular network, percentage swelling, pH at the point of zero charge (pH_{PZC}), etc. [19,36,42]. From the point of view of the properties involved in the sorption of pollutants, these materials present certain advantages. The most remarkable property of ECP polymers is their ability to generate inclusion complexes: the term used is molecular encapsulation or more simply complexation [15–17,157–167]. CDs preserve their complexation properties in spite of the cross-linking reaction that locks the CDs into a network (loss of mobility) and that can, to a certain extent, exacerbate a steric hindrance at the entrance to the CD cavities [16,19]. However, this steric effect is less important when the guest molecule is too large to be totally inserted into a single

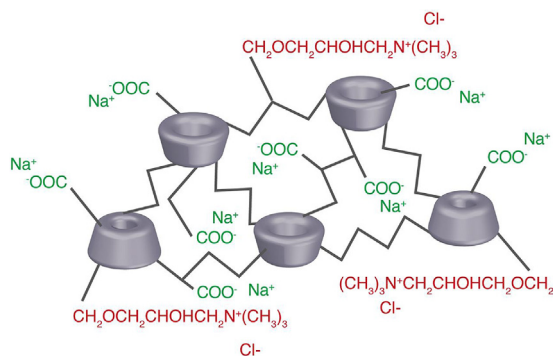


Fig. 7. A possible structure of an ECH-cross-linked β -cyclodextrin polymer containing both cationic and anionic groups (this material was prepared in two steps: cross-linking with ECH in the presence of 2,3-epoxypropyltrimethylammonium chloride and carboxymethylation reaction).

cavity as its other extremity can then be encapsulated by a second molecule of CD in the polymer network (Fig. 8).

Native, water soluble CDs can form several types of host/guest inclusion complex [15,19], not only with a 1/1 stoichiometric ratio but also 2/1, 2/2, 3/1, 3/2 or 4/5. These multi-component complexes can also be found with ECP. When the guest molecule has a complex structure, it is always the apolar (hydrophobic) part that interacts with the CD cavity while the rest of the molecule interacts either with another molecule of CD (cooperative effect occurring through the presence of another cavity nearby), or with any of the numerous hydroxyl functions (stabilization of the complex via hydrogen bonding, for instance). The reference works of Bergeron [140], Bender [15], Atwood [17] and of Szejtli [16,19] can provide further information on these phenomena. Two types of complexes can be distinguished: if inclusion is complete and is the majority contribution to the complex, we speak of an inclusion complex. If the inclusion is only partial, we speak of an association complex. This distinction was introduced by Cramer [1,17] in the 50s and confirmed by Szejtli [1,16] in the 80s. However, there can also be

an effect of cooperation not only between cavities (especially for large molecules, Fig. 8) but also between the CD cavities and the 3D polymer network. It should not be forgotten that the 3D network also enables the ECP polymer to trap pollutants through additional interactions that supplement the inclusion complexes. Owing to this additional binding, it has been demonstrated that the stability constants of these pollutant complexes are often greater than those of native CD-pollutant interactions. This explains why it is not always essential to have materials containing a high proportion of CDs to obtain useful levels of sorption [42]. However, as discussed further in this paper, this point is still being debated. Another advantage of these polymers is that compared to conventional sorbents such as active carbon or ion exchange resins, ECPs are able to interact specifically with pollutants present as traces in complex solutions. Pollutants, particularly those with hydrophilic properties, are more efficiently sequestered by CD polymers than by native CDs. Pollutants with a complex structure and a high molecular weight such as dyes and polycyclic aromatic hydrocarbons are more easily complexed – again due to an effect of cooperation between CDs and/or the polymer network. There now exist materials that are cross-linked and functionalized by chemical ligands (ionic or neutral) able to simultaneously remove organic and mineral (including metals and anions) pollutant species [40,42,47]. Some materials bearing both cationic and anionic charges have amphoteric properties and can thus be used over a wide range of pH values (2–11).

The synthesis of these polymers does have disadvantages [16,19,21–23,40,42]. Firstly, the ECH reagent used for the cross-linking (obtained through fossil-based resource) is toxic and far from being “green”. Handling it is a delicate operation. However, as the cross-linker is highly reactive under the alkaline conditions of the synthesis and as the resulting ECP is rinsed several times during the synthesis steps, the likelihood of unbound ECH occurring in the final material is minimal. It can be noted that, a new bio-based ECH (under the commercial name Epicerol[®]) obtained from glycerol with the same physico-chemical properties but with

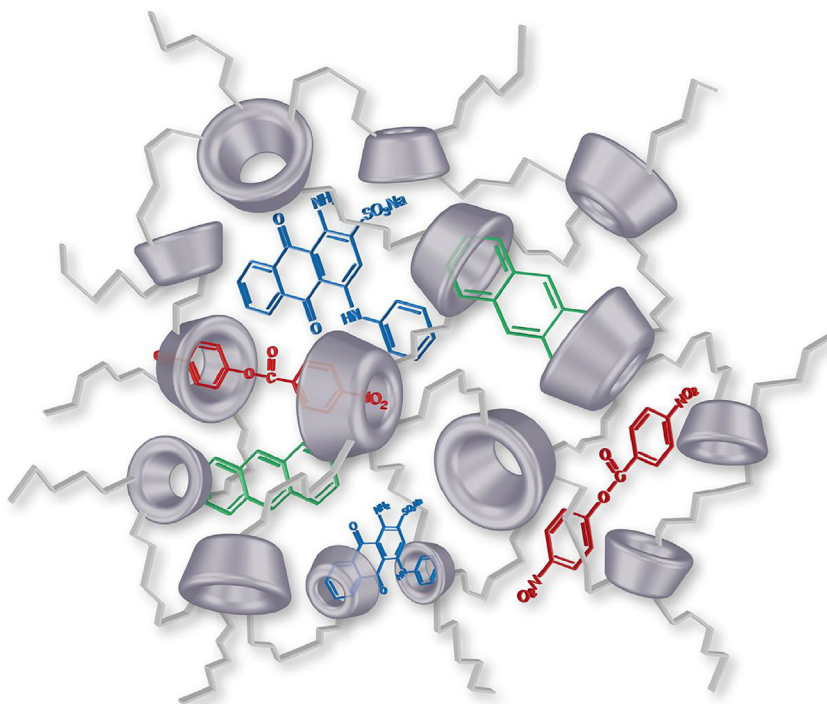


Fig. 8. Schematic illustration of the cooperative effect between CD cavities (complexation of three organic solutes: anthracene, acid blue 25 and *p*-nitrophenyl *p*-nitrobenzoate).

environmental advantages compared to ECH from propylene is proposed. It is also very difficult to find sources of cross-linked CD materials with guaranteed reproducible properties. The only commercially available material for which reproducibility is confirmed is a beta-cyclodextrin cross-linked with ECH produced by the Hungarian company Cyclolab Ltd. [42]. The performance of materials in complexing other substances is strongly linked to the experimental conditions used during cross-linking, notably the reaction temperature, the amount of caustic soda added, the ECH dosage, the volume of water, and the use of a blowing agent or not. Although the synthesis conditions that determine the properties of the cross-linked material are now closely controlled, the cross-linking density remains difficult to predict. This issue was reported as early as the 1960s by Wiedenhof [59,60] and Hoffmann [64–66]. This means that in spite of identical experimental conditions, the properties of two batches of ECP material can thus be different due to the exothermic nature of the cross-linking reaction that makes difficult to maintain the temperature within the reaction medium. The cross-linking step has always been at the focus of debate in the literature. Two “schools of thought” have become established [36,42]: that favoring a low proportion of cross-linking yielding hydrogel type products, and that favoring strong cross-linking making organic bead type products. However, as stressed by Szejtli [16,19,68,72,77], this distinction can result from different end uses. For use in high-pressure chromatography, gel-type systems are not suitable, as the particles must present a certain mechanical resistance [78,80,86]. The structure of a macromolecular network is actually directly dependent on the degree of cross-linking: the higher the degree, the greater the proportion of cross-links, making the material rigid. This will decrease both the ability of the material to swell in water and the concentration and the accessibility of the CD cavities [16,19,42]. Thus, the properties of the materials and hence their performance can vary so that they can only be used for specific applications. To obtain systems 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). The repeated steps involved can be arduous and more particularly, added cost.

3. Mechanisms of sorption

3.1. Interactions involved

In general, the sorption properties of cross-linked CD materials are studied using batch techniques [36,42,94]. Indeed liquid/solid sorption is one of the most frequently used techniques for the decontamination of aqueous media worldwide [94,168–181]. To compare and determine the sorption capacity of any two given cross-linked CD polymers used as sorbents, reference is often made to the differences in their intrinsic characteristics (type of material, chemical type and structure) [36,40,42,47]. It is acknowledged that sorption depends mainly on the characteristics of the solid material used. The process of sorption is the consequence of specific interactions between the material and the species to be adsorbed, where these interactions are highly correlated to the texture and the physical and chemical structure of the material. The interactions occurring between the sorbent and the pollutant to be eliminated may involve both physical and chemical mechanisms [36,42,94].

Before describing the mechanisms of sorption and the different interactions involved in the processes that use ECP polymers, it is important to distinguish the two broad categories of materials currently studied: non-modified ECP polymers (chemically neutral) and modified ECP polymers (neutral, ionic or amphoteric) in the form of gels, particles, beads or nanobeads [19,22,40,42,94]. The importance of this distinction is that the complexity of the

Table 2

Interactions reported in the literature to explain the mechanisms of sorption depending on the type of ECP polymer.

Non-modified polymers	Modified polymers
– Complexation (inclusion complex)	– Complexation (inclusion complex)
– Physical	– Physical
– Hydrogen bonding	– Hydrogen bonding
– Hydrophobic interactions	– Hydrophobic interactions
– van der Waals interactions	– van der Waals interactions
– Electrostatic interactions	– Electrostatic interactions
– Yoshida interactions	– Yoshida interactions
	– Ion-exchange
	– Chelation
	– Acid-base interactions
	– Precipitation

polymers and their specific individual characteristics adds complexity to the mechanisms. For instance, grafting ionic or chelating groups on these materials can result in the modification of the polymer surface chemistry, that can then give rise to new interactions, in addition to inclusion in the CD cavities during sorption experiments [40–47]. Also, the structure and the polarity of the pollutants studied as well as the experimental conditions (dosage of material, pollutant concentration, pH, ionic strength, etc.) of the batch used can also contribute to complicating the interpretations [36,94]. Table 2 presents interactions reported in the literature to explain the sorption mechanisms depending on the two types of ECP polymers, modified and non-modified [34–36,42,94]. A question remains: Must all these interactions be taken into account to explain the sorption mechanisms? The answer to this question is not so easy.

3.2. Case of non-modified cross-linked polymers

Based on the analysis and discussion of 277 bibliographic references, Morin-Crini and Crini [42] found that most sorption results obtained using non-modified ECP materials are explained by just two important parameters: the presence of cyclodextrins and their degree of cross-linking. CD molecules retain their ability to form complexes after the cross-linking reaction. With the exception of certain nanoparticles (developed in recent years), these materials are known for their lack of porosity and very low specific surface areas [33,35,94,214]. Hence, physisorption mechanisms can be ignored and chemisorption is the major process [40,42,47]. In this case, it is often inclusion (complexation) that is put forward to explain the sorption. Moreover, as ECP do not alter the pH of the solutions, it is not necessary to maintain the initial pH of the solutions during batch tests [40,42,94].

From the end of the 60s, Solms' group [55–59], followed by that of Wiedenhof [59–62] suggested that, in ECP polymers, CDs can behave like refuges able to accept molecules in their inner space, leading to the formation of inclusion complexes independently of pH. Comparison with gels that do not have cavities (for instance Sephadex[®] gels) [16,19] indeed shows much less sorption capacities compared to cross-linked CDs. On this particular point, further details can be obtained in the reviews of Mocanu et al. [34], and Crini and Morcellet [35]. Solms and Wiedenhof explained all of their results in terms of the complexation load of ECP materials [54–62], solely by the formation of inclusion complexes and thus by the presence of cavities of CD molecules in the polymer network. They introduced the notion of complexation by chemisorption, and assumed that, no covalent bonding occurred between the CD and the guest molecule (the pollutant). The reaction is a dissociation-association equilibrium, as in the case of the formation of inclusion complexes involving native CDs in solution [16,19]. The cross-linking does not change this property. In the 1970s, similar conclusions were published by Hoffmann [64–66].

In the 80s, Szejtli [16,19,67–74] was the first to explain this mechanism in detail with the aid of experiments carried out on polymers either soluble or insoluble in water. He demonstrated that the complexation process results from a multitude of interactions between the three components of the system, i.e. the CD molecules of the polymer, the guest molecules and water, leading to a more stable thermodynamic state [16,19]. In aqueous solution, the cavities of the CD molecules of the polymer are occupied by water molecules, that are then in an unfavorable energy state owing to polar-apolar interactions and that can therefore be easily replaced by an appropriate guest less polar than water. Moreover, the organic pollutants dissolved in the water have a preference for hydrophobic environments. They are thus maintained within the cavities by non-covalent forces. To account for the complexation, Szejtli proposed four types of force [16,19]: i) van der Waals forces (forces of orientation, induction and/or dispersion), ii) electrostatic interactions, iii) hydrogen bonding, and iv) hydrophobic interactions, where the different interactions contribute toward complex stability in a variable manner. Some authors include van der Waals forces (forces of repulsion and attraction) among the electrostatic interactions [40–47,94]. The van der Waals forces or dipole–dipole interactions are short distance induction forces between a dipole and an induced dipole [22,25,40]. Although often debated, according to Szejtli, these forces play a role in the stabilization of the complex [19]. Electrostatic interactions (ion–ion, ion–dipole and dipole–dipole) occur between the electric charges present in the approaching molecules and provoke attraction between opposite charges (or repulsion between charges of the same sign). Although non-modified ECP materials are not ionic [16,19], Szejtli indicates that electrostatic interactions with the guest molecule are possible since CDs present a dipolar moment. Hydrogen bonds result from the forces existing between hydrogen bound to an electronegative atom that acts as an electron donor and an electronegative acceptor atom [15–17,168]. It is an electrostatic interaction. A distinction should be made between the bonds caused by the pollutant and those caused by the solvent (water) [168]. Szejtli considers the hydrogen bonds to have a stabilizing effect, contributing additional forces [16,19]. The role of the hydrophobic interactions is rather controversial due to the very way they are defined. Hydrophobicity leads to variable entropy states of water molecules in the vicinity of non-polar molecules, that favors apolar aggregation in such a way as to minimize the excess of energy required for the formation of a structured hydration shell. Hydrophobic forces are fundamental in stabilizing inclusion complexes [19]. All of these noncovalent forces are also weak, making the complexes reversible. Szejtli stresses that the reversible nature of complex formation is essential for water treatment because it enables the ECP materials to be regenerated after use [36,42].

Also, the complexation reaction depends on the polarity of the guest molecule and on the pH of the solution to be treated, again stressing the major role played by the CD in the sorption process. It is the most hydrophobic part of the host molecule that is preferentially included in the cavity [42,47]. In other words, the most hydrophobic molecules present the greatest affinity for the CD cavity and are oriented in such a way as to optimize contact between their hydrophobic parts and the apolar cavity of the CD. Similarly, the more hydrophobic the guest molecule, the greater the stability of the complex and the more efficient the decontamination performance. The following is an interesting example [42]: sodium *p*-nitrophenolate forms a more stable complex than *p*-nitrophenol. This can be accounted for the fact that the delocalization of the resonance charge accentuates the electron density and the polarizability of the substrate, thus increasing the van der Waals forces and thus the stability of the complex. Szejtli also demonstrated that the more complex the structure of a molecule the greater its sorption [16,19]. In the case of azo dyes, it is the sulfonate moiety, even

though it is rather bulky, that is inserted into the cavity. The van der Waals forces are enhanced and thus the stability of the azo dye-CD complex [17]. It was shown that the Freundlich model provides a better representation of these experimental results, suggesting that sorption to ECP materials occurs on a heterogeneous surface and is not limited to a monolayer (as in the case of Langmuir sorption isotherms) [169,180,181].

In the 80s and 90s, many studies continued to confirm the essential role of CD molecules in the formation of complexes [96–108,121–123,157–164]. The kinetic studies indicated short contact times are required to reach equilibrium independently of the structure of the polymers rather suggesting chemisorption mechanisms. During synthesis, the most important for obtaining a material efficient for forming complexes is the quantity of CD present per gram of sorbent used [16,19,55,62,64,88]. The greater this quantity (for a constant amount of sorbent), the greater the complexing capacity of the material. This led to an important notion, namely that one molecule of CD corresponds to one molecule of guest [68,71].

Other studies published two surprising results with respect to the sorption of bulky pollutant molecules [33–47,94]. One of the studies showed that even if the guest pollutant is too large, it can be complexed by the ECP polymers, irrespective of the size of the CD ring (alpha-, beta- or gamma-CD). Another study showed that for polymers containing only a small proportion of CD, the quantity of pollutant bound by the material is often much greater than the quantity of CD present, contradicting the notion that one molecule of CD traps one pollutant molecule. These two results were mainly explained by the network structure of the materials, their shape, and their swelling properties, closely related to the degree of cross-linking. As early as the 70s, the studies of Hoffmann [64–66] already showed that even though the role of the CD is essential, a compromise must be found between the quantity of CD and the degree of cross-linking to obtain useful results in low-pressure chromatography. Hoffman showed that the performance varied greatly between different batches of material. He attributed this variability to the different degrees of swelling of the gels, i.e. their degree of cross-linking. A few years later, Szejtli confirmed this relationship [67,68,79]. In order to demonstrate the phenomenon, he synthesized ECP polymers with different types of CD (alpha-, beta-, and gamma-CD) changing the reaction conditions to prepare materials in different forms. He obtained gels and particles with different degrees of cross-linking and with irregular sizes obtained by block polymerization, spherical beads of controlled size and distribution obtained by cross-linking in heterogeneous phase in the presence or absence of blowing agents, all with variable quantities of CD [69,70]. Szejtli then studied the formation of complexes with low molecular weight model organic molecules, such as benzene and phenol derivatives, up to more complicated chemical structures with higher molecular weights (e.g. polycyclic aromatic hydrocarbons PAHs, complex aromatic dyes, polymers, steroids) [79]. He found that the more the beads had a regular spherical structure and distribution, the more they showed useful properties, independently of the quantity of CD but following the degree of cross-linking. This led him to point out the importance of surface sorption by physisorption. The physisorption mechanisms acted in addition to the chemisorption. It was noted that a further advantage of the bead systems was their greater mechanical and thermal stability and easier regeneration, use them in high-pressure chromatography systems. Another important result, that was unexpected at the time, was reported [1,42,79]. When naphthalene and anthracene are the molecules to be eliminated, they can be removed irrespective of the type of CD polymer used. For instance, a cross-linked α -CD can adsorb naphthalene, too large to be a guest, and cross-linked β -CD can complex anthracene that can only be taken in by a γ -CD host [15]. In other words, even

if the guest is too bulky, it can still be immobilized in a complex through the cooperative effect of the CD molecules of the polymer network. Several different CD cavities can encapsulate different parts of a pollutant. This is where Szejtli introduced the notion of association complex for ECP materials, in accordance with the notions previously introduced by Cramer [1]. Indeed he distinguished two types of complex, complexes with simple model molecules for which inclusion is total – these he called inclusion complexes – and complexes with larger molecules for which inclusion would only be partial – that he called association complexes – and that can be the preponderant form of interaction or simply occur alongside inclusion complexes. This is why some bulky molecules (e.g. dyes, macrocycles or steroids) are adsorbed by ECP polymers. Szejtli finally observed that even for polymers containing few CD motifs, the amount of pollutant retained by the material can be much greater than the amount of CD present. For aromatic compounds such as PAHs, he proposed the occurrence of hydrophobic interactions leading to pollutant stacking (π - π interactions) and/or the formation of multilayers of pollutants at the surface of the polymers, in agreement with Freundlich's model. Szejtli's cumulative work came to the following conclusions: i) the role of CDs fundamentally occurs through the formation of inclusion and/or association complexes; ii) the mechanisms are more complex than they may appear; iii) unlike dissolved CD molecules, ECP polymers are less sensitive to steric hindrance effects that play a less important role in the complexation process, and iv) 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 early 2000s, studies casted doubt on the notion that it is only the presence of CD molecules in the polymers that accounts for the sorption results [124,126–129,134,136,137,139,154–156]. Materials composed of oligosaccharides (starches, dextrans, sugars...), prepared in the same cross-linking conditions as ECP polymers, were studied in pollutant complexing experiments and their different performance was compared [36,42]. The starch-based systems did not contain the type of cavity occurring in CD but the results were greatly superior to those of ECP polymers. These results had to be explained. A response was found in the structure of the macromolecular network. For ECP materials, the question arises as to the predominance of inclusion complexes or association complexes due to the CDs or association complexes due to the polymer network. Currently, the consensus is for the latter. The concept of association complexes is less simple since there can be a cooperative effect, not only between the CD cavities themselves (particularly for large guest molecules) but also between the CD cavities and those of the polymer network. Indeed, 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. The polymer network therefore offers ECP materials the possibility to sequester pollutants through effects of cooperation between CDs and/or via additional interactions in the mesh with diffusion into the network. 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 pollutants through the network.

Over the last two decades, Crini's group has been focusing on cross-linked CD materials, not only from the point of view of their synthesis and characterization (especially by NMR), but also for their environment-oriented applications, i.e. for the treatment of polycontaminated industrial waste water [154–156,182–197]. Towards the end of the 90s, Crini's group used the works of Solms, Wiedenhof and Hoffman and especially the conclusions of Szejtli, to demonstrate that firstly there is a close relationship between the degree of cross-linking and the complexation performance of the polymers, independently of the amount of CD. Moreover, a high proportion of CD is not required to have useful sorption results

[154,155]. Their studies showed 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. Indeed, when the degree of cross-linking is too high, the quantity of pollutants adsorbed decreases. This has been explained by the strong increase of the connections between polymer chains, leading to a decrease of their flexibility and mobility and also of their swelling properties (network hydration reduced), leading to a diminished accessibility of the network, i.e. the pollutant finds it increasingly difficult to diffuse within the network. The cross-linking step not only influences the concentration and accessibility of the CDs (the greater the accessibility of the CD sites, the higher the sorption properties) but also the swelling, that determines the diffusional properties of the gels. Moreover, it should be noted that introducing new bonds with the cross-linking agent alters the hydrophobicity of the polymer [42,154]. The sorption kinetics is also strongly dependent on the level of cross-linking. It is therefore essential to select optimal synthesis conditions to obtain the characteristics required, in agreement with the conclusions of Szejtli [67–71]. They described longer time was required to reach equilibrium (a few hours) for dyes depending on the conditions for cross-linking, demonstrating a kinetic diffusion mechanism (due to the structure of the polymer network) [42,154,155]. By varying the conditions such as the quantity of the different reagents, the CD/ECH mole ratio, the NaOH concentration, the reaction temperature and/or the reaction time, it is possible to cause different structural modifications in the hydrogel network and obtain gels that not only have different quantities of CD but that also present differences in terms of rigidity or mobility of the polymer networks. For instance, by modifying the ratio between the CD (monomer A) and ECH (monomer B), it becomes possible to alter the structure of the repeat motif of the monomer units from an A-B structure to an A-B_n structure (where n indicates the degree of polymerization of polymer B) [155]. As this copolymer is richer in ECH units, the material will be more hydrophilic. Similarly, a higher temperature enhances the swelling of the polymer. Overall, conclusions arising from the analysis of carbon-13 nuclear magnetic resonance spectra indicated that the cross-linking led to the formation of amorphous and crystalline regions in the gel structures. Amorphous regions were by far the most abundant. By comparing relaxation times, it was confirmed that the structures were heterogeneous and presented different regions with different mobility properties. For the first time, the solid-state NMR studies demonstrated that the gels are composed of a relatively densely cross-linked core that is rigid and hydrophobic, and a less cross-linked more hydrophilic surface that is much more mobile including long, but very mobile hydroxyalkylated polymer chains due to the homopolymerization of the ECH [155,156].

Other studies [45,46,119,125–127,197–235] also demonstrated the importance of cross-linking on the physico-chemical properties of the materials. For instance, to explain the sorption results, Iasi's group introduced a significant proportion of interactions between the polymer network and the pollutant, the polymer and the water to be treated, the pollutant and the water, and finally, the pollutant molecules with each other [203–208]. They showed that the interactions depend on the intrinsic characteristics of the cross-linked materials used and the pollutants to be complexed (e.g. structure, size, polarity, hydrophobicity). They concluded that the presence of CD cavities cannot alone explain the sorption results and stressed the importance of the polymer network structure and thus of the degree of cross-linking. A hydrophobic guest shows higher affinity for the polymer of higher CD content, while opposite behavior can be observed with a hydrophilic guest. The former favors inclusion interactions while the latter interacts with the glycerol crosslinking bridges and glycerol monoether polymer side chains [256]. However, the exact role of the cross-linking agent on the properties of the materials is debated. Some authors suggest that the quan-

Table 3The main interactions involved during the sorption of metal cations (Me^{n+}) on the ECH-cross-linked polymers containing carboxylic/carboxylate groups.

Interaction	Schematic representation
Ion-exchange	
Electrostatic interaction	
Chelate formation	
Cation-dipole attraction	
Microprecipitation	

tity of ECH should be limited while others advise that it should be increased. In reality, it seems to depend on the type of application considered [33,35,36,42,47].

3.3. Case of modified cross-linked polymers

For modified ECP polymers, the mechanisms are somewhat more complex because the processes of sorption and particularly the type of reaction (chemisorption, physisorption or both at the same time) depend not only on the network structure characteristics of the solid material and its texture, but especially on its chemical properties [42,94]. As in the case of non-modified ECP materials, textural characteristics are the shape of the particle, its size distribution and the proportion of water it contains when swollen as well as its porosity and its specific surface area (nanobeads). Also, materials cross-linked in the presence of carboxymethylcellulose and/or modified by grafting functional (carboxymethylation reaction) groups present very different chemical properties. These properties depend on the surface of the materials (presence of active sites, type and number of the ligands), chemical properties (acidic, basic, neutral, amphoteric and/or amphiphilic) and point of zero charge. In addition to the interactions described for non-modified materials (Table 2), it is therefore necessary to add interactions, such as electrostatic attraction, ion exchange, chelation, acid-base interactions and precipitation (microprecipitation) depending on the functions grafted. For instance, the presence of moieties, such as carboxylic functions, on ECP materials can be useful for the treatment of water co-contaminated with a number of pollutants [126,127,156,185,189]. The free functions are initially acids ($-\text{COOH}$ form) and can be converted into the basic form (carboxylate, $-\text{COO}^- \text{Na}^+$ form) when the cross-linked functionalized polymer is subjected to treatment with a weak base. In this case, the so-called activated material is in its basic form. The sodium carboxylate functions have a pronounced ionic character much more favorable towards ion exchange reactions, for instance. When in the presence of cations such as metals,

the basic form will sequester them by ion exchange with its sodium ions. Table 3 sums up the main interactions involved during, for example, the sorption of metal cations (Me^{n+}) on the cross-linked cyclodextrin polymers containing carboxylic groups.

As ion exchange capacity (IEC) increases, the electrostatic attractions become stronger. By adjusting the synthesis parameters, it is possible to vary the number of carboxylate groups. By varying the IEC of the material, it is seen that the higher it is, the greater the quantity of cationic dyes and metals that are complexed. This again stresses the importance of the carboxylate groups. Similar conclusions have been reported for urethane-type CD polymers [218–223]. Other interactions were also invoked such as electrostatic attraction, cation-dipole interactions by the carboxylate groups or processes of pollutant microprecipitation. Indeed, during sorption, the pH can, for instance, rise leading to metals or dyes becoming insoluble (Table 3). This is one of the reasons for which the quantities of pollutants eliminated can be greater than that calculated from CD content in the sorbents. However, it should be noted that in the large majority of studies published, the initial pH of the solutions is left unadjusted during sorption [36,94]. As the pH varies, the microprecipitation phenomenon can then occur. Modified ECP materials thus present all the characteristics required to treat wastewater contaminated by both metals, via the carboxylic groups, and organic compounds, through the action of the CD and the 3D polymer network. These unique and versatile sequestering action on both cationic species and organic molecules is useful for the treatment of wastewater contaminated by a range of pollutants.

The surface reactivity of the ECP polymers also allows the preparation of materials with amphoteric properties that can then be used over a much wider pH range. Among the various types of moiety that can be grafted, it would indeed seem that amphoteric materials, having both an anionic and a cationic charge, are the most promising [194–196]. In 2006, Crini [156] patented a novel cross-linked CD material presenting high sorption capacities, due not only to its chemical structure, obtained by controlled cross-linking, and physical properties, with its high porosity, but also to its

amphoteric behavior. The material is prepared in two main steps: the first consists of cross-linking the CD molecules with ECH in the presence of a second, cationic, cross-linking agent. The second step is the carboxymethylation of the surface of the cross-linked particles (Fig. 7). The usefulness of these materials arises from their ability to complex not only organic molecules through the formation of inclusion and/or association complexes, but also to chelate ions, in particular metal ions, via the carboxymethyl groups and the amine functional groups that lead to further chemical interactions (electrostatic, ion exchange, etc.). The pH range over which the amphoteric polymers can fulfil their role is from pH 2 to pH 10. These materials are also able to decontaminate effluent with multiple contaminants. Yilmaz's group have been reported similar conclusions for urethane-type CD polymers [218–223].

4. Complexation of environmental pollutants using cross-linked cyclodextrin materials

In 2013, Morin-Crini and Crini [42] published a historical review of ECH-cross-linked CDs covering the past 50 years. A similar review has been recently compiled by Gidwani and Vyas [47]. These reviews also gave abundant information on the use of these materials in environmental applications (for other reviews, see Table 1). The behavior of numerous molecules when interacting with ECP gels has been widely studied, especially using synthetic solutions containing a single contaminant. Few studies have been carried out on typical industrial effluent containing multiple contaminants [94]. The list of molecules that can occur in these effluents is quite vast, covering benzene- and phenol-based pollutants to PAHs, volatile organic compounds (VOCs), polychlorobiphenyls (PCBs), pesticides, drugs and pharmaceutical molecules, non-ionic or ionic surfactants, detergents and a whole array of metals. Almost all the results reported were obtained using batch techniques [42,47,94].

This section gives a summary of the main conclusions published on the proposed mechanisms of sorption and the optimization of the synthesis parameters to obtain efficient sorbents. Table 4 summarizes the main research groups currently working on ECH-cross-linked β -cyclodextrin for environment-related applications and whose studies will be reviewed.

In the early 2000s, the Spanish group of José Ramon Isasi at Navarra University became very active in the field of ECP polymers for environmental and pharmaceutical applications [203–208]. Isasi showed that ECP gels (non-modified, particles of irregular shape or as regular beads) participated in the efficient complexation of numerous organic molecules, irrespective of their concentration. Comparison with conventional sorbents (activated carbons, organic resins) used in batch or column experiments showed that ECP gels and beads are more selective and more effective. His group published the first pilot study on effluents with a single contaminant (phenol). The results were very interesting from the point of view of extraction capacity, and were promising for forthcoming industrial applications. Isasi also interpreted his results via the formation of inclusion complexes. However, he did show that in three-component systems (ECP polymer/pollutant/solution), specific interactions other than inclusion complexes can occur, related to the structure of the polymeric material (degree of cross-linking and size of the particles) and to the substances to be eliminated. He showed that cross-linked CD gels present heterogeneous structures and demonstrated the very important role, not only of the CD cavities in the sorption phenomena but also the role of cross-linking during the synthesis of the materials, confirming the conclusions of Crini. The amphiphilic properties of the gels were also pointed out as being a crucial characteristic in explaining the sorption results, introducing the possibility of hydrogen bonding, better diffusion of the pollutants

through the network by adjusting the properties of hydration and swelling of the systems, etc. These strongly suggested that the structure of the polymer is a key element in the same way as the presence of the CD cavities to explain the sorption mechanisms. Finally, Isasi proposed a simple dual mode sorption consisting of inclusion and non-inclusion phenomena. He claimed that sorption by ECP material through CD complexation was the most effective decontamination technique (efficiency in pollutant removal, economically feasible, easily recyclable).

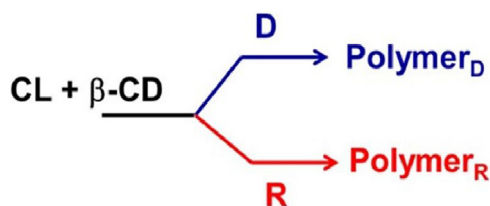
During the same period, three Canadian groups also investigated ECP polymers and contributed to a better understanding of the sorption mechanisms, stressing the importance of the cross-linking step. In the mid-2000s, Christopher H. Evans [201,202] of Ryerson University, Ontario, demonstrated that ECP materials can be used to efficiently remove pollutants, notably organics, from contaminated water, whatever the quantity of CD present in the materials. It was shown that it is much more advantageous to prepare sorbents in the form of regular, spherical beads with controlled swelling properties. He pointed out that the method of polymerization (homogenous or heterogeneous solution during the synthesis) was important. Owing to the macromolecular structure of the material and its physical characteristics (no porosity, very small specific surface area) the sorption process mainly involves a chemisorption mechanism of the inclusion complex type. Evans accounts for their results mainly through the presence of cavities in the CD molecules. He also stresses the importance of the 3D network's structure. His studies showed that, unlike for active carbons, the regeneration of these systems is simple and straightforward, enhancing their attractiveness for industrial applications.

Lee D. Wilson [45,46,209–217] of the University of Saskatchewan, compared the efficiency of commercial activated carbons to that of ECP gels tested in similar conditions. Wilson demonstrated the excellent performance of ECP polymers even though they presented much smaller specific surface areas than carbons, according to nitrogen sorption BET results. The performances were independent of the concentration of the pollutant present in the solutions (ECPs are also efficient for the treatment of organic molecules present as traces), independent of the quantity of CD present in the materials, and independent of the initial pH of the solutions. Moreover, another advantage mentioned is the ease of regenerating the sorbents by solvent extraction. Wilson's team then compared materials obtained by the use of epoxy cross-linkers (such as ECH) and isocyanate cross-linkers [211,215]. They showed that ECP gels were more efficient than those obtained using diisocyanate bridging agents. The results can be explained by different mobility of the polymer network and hydrophobic properties. Wilson stressed the importance of the cavities in the CD molecules in the performance of the materials, notably their mobility and accessibility. He showed the fundamental role of the polymer network (hydration, swelling) were in agreement with the interpretations of Szejtli and Crini. The sorption capacity and the properties of these materials result from their behavior in water, that in turn depends on the synthetic conditions. Wilson's group concluded that the ECP absorbents are particularly useful and efficient for the treatment of wastewater containing phenolic species [212].

In spite of the facile synthetic conditions for the preparation of ECP-based polymers, the polymer networks may adopt structural variability, as illustrated in Fig. 4. The synthetic conditions were shown to favour reaction A over B, depending on the relative ratio of ECH and β -CD, along with the mode of addition of the cross-linker unit via drop-wise or rapid addition. According to [211], reaction A was favoured during drop-wise addition of ECH, while rapid addition of ECH yielded a mixture of cross-linked (reaction A) and self-polymerized (reaction B) forms of ECH, in accordance with stoichiometric considerations for such hetero- vs. homo-

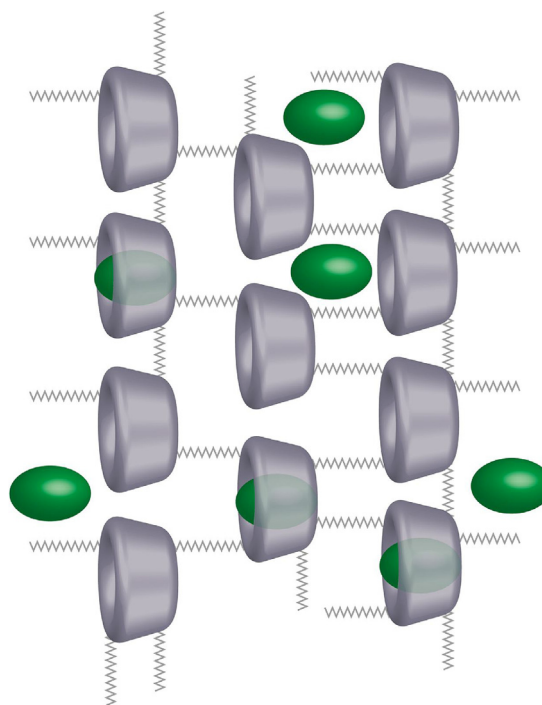
Table 4The main research groups currently working on ECH-cross-linked β -cyclodextrin polymers designed for environment-related applications.

Country	Research group	University/Company	Reference(s)
Canada	Christopher H. Evans	Ryerson University, Ontario	[201,202]
Canada	Robert Hausler	École de Technologie Supérieure, Montréal	[126,127]
Canada	Lee D. Wilson	University of Saskatchewan, Saskatoon	[45,46,209,211,212,214,215]
China	Xiyun Cai	Dalian University of Technology, Dalian	[235,236]
China	Yanxiang Fang	Guangdong University of Technology, Guangzhou	[237]
China	Hongbing Ji	School of Chemistry and Chemical Engineering, Guangzhou	[238,239]
China	Ning Li	College of Environmental and Biological Engineering, Chongqing	[231–235]
China	Haimin Chen	Zhejiang University of Technology, Hangzhou	[240]
China	Xiao Mei Zhang	Anhui University of Science and Technology, Anhui	[241]
China	Liang Zhao	Henan Academy of Sciences, Zhengzhou	[242]
France	Grégorio Crini	University of Bourgogne-Franche-Comté, Besançon	[34–36,38,42,48,94,156,183–196,230]
France	Sophie Fourmentin	University of Littoral Côte d'Opale, Dunkerque	[40,224–229,243]
France	Bernard Martel	University of Lille 1, Lille	[120]
Hong Kong	Jimmy C. Yu	Chinese University of Hong Kong, Hong Kong	[244]
Hungary	Éva Fenyvesi	CycloLab Cyclodextrin Research & Development Ltd., Budapest	[119,197–200]
Hungary	Katalin Gruiz	Budapest University of Technology and Economics, Budapest	[245,246]
Hungary	Gyula Záray	Eötvös Loránd University, Budapest	[247]
India	Amber Vyas	University Institute of Pharmacy, Raipur	[47]
Italy	Giangiaco Torri	G. Ronzoni Institute for Chemical and Biochemical Research	[124,154,155]
Japan	Motomitsu Kitaoka	National Food Research Institute, Ibaraki	[248]
Japan	Shoji Murai	Kanagawa Industrial Technology Research Institute, Kanagawa	[121–123]
Korea	Man Ho Choi	Korea Institute of Science and Technology	[249–251]
Korea	Jin-Chul Kim	Kangwon National University, Chunchon	[252]
Spain	José Ramon Isasi	Navarra University, Pamplona	[203–208,253–266]
Turkey	Mustafa Yilmaz	Selçuk University	[218–223]
USA	Ali K. Oskouie	Institute of Technology, Chicago	[136]

**Fig. 9.** The formation of cross-linked polymers containing β -CD under equilibrium and kinetically controlled conditions, according to drop-wise (D) and rapid (R) addition of cross-linker (CL).

polymerization processes. A detailed study concerning the role of cross-linking under drop-wise *versus* rapid addition of reagents was carried out in [267], where evidence was presented concerning the structure and morphology of the cross-linked polymers containing β -CD. The subtle variation in the morphology of the polymers was shown using dye based sorption methods under equilibrium and kinetic conditions. It was concluded that materials revealed variable accessibility of the inclusion sites due to cross-linking at variable mole ratios and reaction conditions governed by thermodynamic *versus* kinetically controlled polymerization (Fig. 9). Polymers that were prepared at the 1:2 (CD/linker) mole ratio revealed variable structure and textural properties because product branching was noted via thermodynamic *versus* kinetic controlled conditions using drop-wise *versus* rapid addition of cross-linker. The contribution of this study revealed that tunable polymer materials with variable structure and physicochemical properties can be prepared for diverse sorption-based applications.

The preparation of cross-linked CD polymers can be carried out at variable cross-linker ratios and conditions to afford materials with variable sorption properties due to two key factors; i) site accessibility of the sorption sites and ii) tunability of the surface chemistry of the polymer framework. The accessibility of the inclusions sites of CD in the polymer framework was demonstrated using phenolphthalein as a dye probe for polymers with incremental levels of cross-linking [211,268]. Remarkable variation in the site accessibility was shown across a relatively narrow range of cross-linking that illustrates the importance of inclusion bid-

**Fig. 10.** The extended framework structure of a cross-linked polymer containing an adsorbed guest molecule (sphere) within the β -CD inclusion sites (tori interior) and the interstitial sites (tori exterior) of the polymeric framework (adapted from [211]). The line segments connecting the β -CD tori represent the cross-linker (ECH).

ing contributions that are modified according to steric effects of the cross-linking within the polymer network. The occurrence of secondary binding sites from the cross-linker domains (referred as associative complexation) was shown clearly in the case of *p*-nitrophenol sorption with urethane-based polymers containing CD, where associative complexation was evidenced by the onset of multilayer sorption that cannot be accounted for by inclusion binding alone [268]. Fig. 10 provides a schematic illustration of the

potential location of an adsorbate at two types of sites in an ECH cross-linked polymer.

A systematic sorption study of cross-linked polymers with naphthenates and dyes was carried out to further understand the role of inclusion and non-inclusion sites within such cross-linked polymer materials [268]. Crini's group studies are in good agreement with the general conclusions reported by Isasi's group [208], where Wilson's group report that the sorption properties of cross-linked polymers containing CD can be understood on the basis of a two-site model. The two sorption sites are represented by β -CD inclusion sites and interstitial domains of the polymer network through the quantitative results obtained by the spectral displacement technique [269]. The sorption results are well described by a model reported by Mohamed et al. [270] (see Eq. 10 therein) and in close agreement with the dual mode approach presented by Isasi's group. The thermodynamic sorption model describing the uptake of low to medium molecular weight pollutants is inferred to apply across a range of sorption results for ECH polymers that have variable accessibility of the CD inclusion sites and cross-linker domains according to an apparent sorption affinity constant (K_s), where $K_s = f(X_\alpha K_\alpha + X_\beta K_\beta)$, and the respective binding affinity values (K_i) are weighted according to the mole fraction of bound species (X_i) at each site (α and β) in accordance with the two site model described above (see also Scheme 1 in Ref. [211]). The sorptive uptake of such cross-linked polymers depend on the textural properties and surface chemistry of the sorption sites. This was clearly shown in the case of polymers prepared at kinetic and thermodynamically controlled conditions (Fig. 9 above) [267].

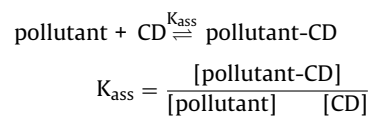
Finally, in 2009, Robert Hausler's group [125–127] at the *École de Technologie Supérieure* in Montréal, showed the efficiency of ECP gels for the elimination of alkylphenols (APs) in the form of ethoxylates, known to act as endocrine disruptors. The abatement performance of the gels was high, between 1.1 and 6.8 mg of pollutant adsorbed per mass of sorbent, whatever the initial concentration of pollutant. The kinetics was, however, relatively slow (a few hours). The sorption results were mainly explained by the formation of inclusion complexes and were found to be dependent on the steric hindrance of the APs being studied. Hausler also showed that the polymer structure of the material is a key element in the interpretation of the data obtained and stressed the importance of both the inclusion and the physical-chemical interactions (hydrogen bonding, partition in the polymer network, etc.). Furthermore, he showed that with ionic ECP gels, the sorption mechanisms are more complex and variable depending on the batch conditions and that it is difficult to indicate which interaction is preponderant in the mechanism. For instance, CD materials (modified or not) bear hydroxyl and carboxyl groups, able to interact via hydrogen bonding, that they can do with phenolics and aromatics. These interactions are particularly important and must not be neglected. They can be studied by altering the ionic strength of the solutions. Hydrophobic interactions and van der Waals forces are also possible: the center of the materials present hydrophobic properties owing to the presence of numerous ether-oxide groups between each of the glucose units. This electron density can play a fundamental role in the mechanism of AP sorption. Finally, Hausler indicated a relationship between the chemical structure of the organic pollutant and the performance of the materials. Similar conclusions on APs had been previously published by the Japanese group of Shoji Murai [121–123] (Tokyo Institute of Polytechnics, Kanagawa) and more recently by Crini [194–196].

Fourmentin's group [40,224–229] (University of Littoral Côte d'Opale, France) also reported that ECP materials can retain target organic molecules by mainly forming inclusion complexes with CDs. However, this group pointed out the role of both molecular inclusion and physical and chemical interactions (hydrogen

bonding, partition in the polymer network, etc.), depending on the chemical structure of the pollutant. They concluded that the mechanism of the interaction between the pollutants and the material was a combined effect of inclusion and (physical and chemical) sorption, in accordance with the dual mechanism proposed by the groups of Isasi and Wilson. Cai's group [236,237] (Dalian University of Technology, China), studying the sorption of pesticides on ECP materials, recently reported similar interpretations. In addition, their multivariate regression analysis permitted analysis of the role of polymer and pesticide. The apparent sorption potential of the polymer was related mainly to CD content, swelling ratio and pore size.

Another group in China, Ning Li's group [231–235] (College of Environmental and Biological Engineering, Chongqing) was very active in the field of ECP polymers for organic pollutant removal with particular attention on sorption mechanisms. Li reported that ECP materials have a particular structure with a less rigid hydrophobic core composed of strongly cross-linked glucose residues and a hydrophilic surface due to the presence of long mobile hydroxyalkyl chains. This structure can help explain the sequestration of chlorinated phenol derivatives (*p*-chlorophenol, 2,4-dichlorophenol, etc.) present as traces (ppb levels) in aqueous solutions. Dual mechanisms were also proposed although hydrogen bonding and physical sorption played some important roles. Li's group not only stresses the chemical efficiency of ECP gels independently of the quantity of CD, but also rapid sorption/desorption kinetics, suggesting a rapid inclusion mechanism, and straightforward regeneration of the materials (made possible due to the high degree of cross-linking). Li's group also showed that ECP materials with regular beads and controlled swelling properties can be used advantageously in industrial applications because they can be readily packed and settled. The beads were also mechanically stable even after repeated sorption/desorption cycles.

The Turkish group of Mustafa Yilmaz [218–223] (Selçuk University, Konya) prepared highly cross-linked materials (both ECP- and urethane-type) that were non-modified or modified (by grafting on cationic ligands). Yilmaz studied the sorption-desorption process and showed that the incorporation of CD into non-modified polymeric systems can influence the mechanisms by which pollutant is released. The complexation of pollutant with material can be defined by an association constant K_{ass} given the following formula (where [pollutant] and [CD] represent the free concentration of pollutant and cyclodextrin and [pollutant-CD] is the concentration of the complex):



In modified polymer compared to the unmodified, Yilmaz systematically observed an increase in the K_{ass} of the complex formed between pollutant (dye molecules) and material, suggesting the presence of strong interactions. Pollutant removal was a function of the CD-pollutant binding constants with the exception of larger molecules that did not form inclusion complexes. Anomalies to this removal behavior were observed and they were attributed to different interactions of the pollutant with the various cross-linkages. In addition, thermodynamic data can vary with the guest species. For non-modified polymers, the forces driving complexation have been attributed to the exclusion of high energy water (due to the inclusion complex formation), the release of ring strain, van der Waals interactions (combination of induction and dispersion forces), hydrogen and hydrophobic binding. van der Waals interactions were important because they provided large negative enthalpy: they were a driving force of the complexation, in accor-

dance with the interpretations published by Casu [1,271,272] in the 1960s. This was explained by the hydrophobic interaction between two non-polar systems (sorber and pollutant) with a positive enthalpy change, the observation of a negative enthalpy change in CD-based complexation phenomenon was considered to indicate the dominance of van der Waals interactions [16,19,22]. Yilmaz also used molecular modeling to demonstrate the involvement of van der Waals interaction. This subject remains controversial because the total negative enthalpy and entropy did not indicate that the van der Waals interaction was more important than the hydrophobic interaction. This was explained by other interactions such as the exclusion of high-energy water from CD cavities could contribute negative entropy and enthalpy to the complexation. In addition, a major source of large negative enthalpy changes, in particular with temperature, were not only van der Waals interactions but also intermolecular hydrogen bonds, as demonstrated by Irwin et al. for beta-CD complex of chlorogenic acid [273].

Yilmaz's group also showed that the modifications of the polymers led to new products that presented their own strong complexing powers in addition to those of the non-modified materials [222,223]. They also reported the role of both the CD cavities and those of the cationic sites in the performance of the materials (localized and homogeneous sorption). The group showed that, as with active carbon sorbents, the characteristics of a grafted ECP sorber depends on its structure and its physical-chemical properties, in particular its surface chemistry. For cationic ECP polymers, although all the results in terms of sorption capacity reported to date indicate a high capacity, they are strongly dependent on the cationic nature of the grafted ligands, and their quantity in addition to the experimental conditions (pH, temperature). The greater the number of grafted ligands, the higher the performance of the material. For Yilmaz's group, the presence of these functional groups plays a fundamental role. This is because these functions are susceptible to become protonated or deprotonated depending on the pH of the solution, creating charges that can alter the interaction in the tertiary system and hence the sorption mechanisms. The ionic character of the material and sorption behavior can be analyzed by the pH_{PZC} , the pH at which the net charge of the surface is zero. If the pH of the solution is below pH_{PZC} , the surface of the material will have an overall positive charge and vice versa. Studies have shown that the pH is an important factor in understanding sorption involving modified polymers. The variation of pH during sorption is also a factor that should be taken into account although it is most often ignored. But, an increase of pH can lead to microprecipitation of metal ion pollutants. Yilmaz's team also showed that other factors can influence sorption such as the characteristics of the pollutant (solubility, structure molecular weight, pK_a , charge, polarity) and the experimental characteristics of the analytical system that is used, as pointed out by Shaw [109–112], Crini [154,155], Isasi [203–205] and Wilson [209–211].

For over 20 years, Crini's group has investigated the development of ECP materials mainly in the form of weakly cross-linked gels for the elimination of model pollutants present in synthetic solutions or for treatment of multi-contaminated water produced by industries such as textiles, wood, paper and surface finishing [154–156,183–196]. To explain the sorption mechanisms at the end of the 1990s, Crini, working on the hypotheses of Szejtli's group, showed that in the case of ECP gels, sorption is due to physisorption processes (presence of hydrogen bonds, van der Waals forces and electrostatic interactions) via the structure of the polymer network, to chemisorption (ion exchange, formation of inclusion complexes) through the active sites (CDs and/or charged ligands), to diffusion through the polymer network (association complexes) and to the presence of various other interactions (processes involving aggregation or precipitation, the presence of hydrophobic bonds Yoshida [274] interactions) through the structure of the pollutants

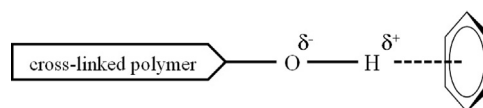


Fig. 11. Schematic representation of intermolecular interaction between π electrons from aromatic pollutant molecule and hydroxyl group of polymer (this interaction is known as Yoshida interaction [274]).

[154,155]. In addition, Crini demonstrated that the amphiphilic properties of the gels must be taken into account to explain the results obtained. The hydrophilic properties of a hydrogel allow it to firstly interact with water, not only leading to better hydration (with the possibility to form hydrogen bonds) but also better swelling of the network (thus a greater potential for diffusion). Likewise, the hydrophobic character of the gel (hydrophobic cavity of the CDs and cage structures formed by the cross-linker rich in ethylene oxide groups) attracts hydrophobic pollutants. These various hypotheses were confirmed in the mid-2000s by the use of mathematical models, that, although empirical, enabled the experimental data to be interpreted. The data were also validated at the end of the 2000s by the groups of Isasi [203–208], Evans [201,202] and Wilson [209–214] and more recently by those of Hausler [125–127] and Li [231–235].

To pursue validation of these interpretations on CD gels, Crini's group also prepared materials using starch (fractions that were either rich in amylose or in amylopectin), dextrans and non-cyclic oligosaccharides under the same synthesis conditions [94,182,188]. The performance of these materials was then compared using model pollutants such as phenol, nitrophenols, cresols and dyes. In certain cases, cross-linked starches and dextrans showed sorption capacities that were higher than those of cross-linked CDs even though they did not possess the type of cavity that participates in inclusion complexes. These results were mainly explained by the density of the cross-linking. Similar studies were carried out by Isasi and Yilmaz's groups and they led to similar results [218–223]. In addition, they showed that it is important not only to take into account the characteristics of the ECP materials but also the interactions between the three components of the sorption system (i.e. the polymer, the pollutant and the water to be decontaminated), as indicated by Szejtli [67–72] in the 80s. Yet, these interactions are often ignored in the literature and it is the characteristics of the cross-linked polymer that are considered foremost. In the presence of phenolic derivatives with high dipole moments, electrostatic interactions of the dipole–dipole type between pollutant molecules are also possible, in particular at high concentrations. Other forces can also participate. For instance, ECP materials are formed of cross-linked oligosaccharides bearing numerous hydroxyl functions that can form specific interactions (Yoshida interactions [274]) with the aromatic rings of pollutants (Fig. 11). Decreasing the number of hydroxyls, for instance through methylation, leads to a drop in performance, most probably related to a decrease in the Yoshida interactions. It could also be due to both an increased hydrophobicity of the materials and greater steric hindrance restricting the access to the CD cavities. González-Gaitano [253–255], Wilson [275,276] and Li [231–233] published similar conclusions.

Besides the Yoshida interactions [274], other types of interactions between a dye molecule and the material occur, such as hydrogen bonding (the dye can be a proton donor while the material can accept the lone pairs), dipolar interactions between the functions of the dye and the hydroxyl groups of the ECP gels, van der Waals forces occur between the benzene rings of the dye and the sorber (dispersion forces or London forces between the electron clouds of the molecules). This is the case, for instance, during the sorption of PAHs, the greater their hydrophobicity, the more efficiently they will be adsorbed [35].

Each pollutant has a particular chemical structure and can therefore interact differently with the sorbent. For instance, acid dyes generally contain ionisable groups such as sulfonates, carboxylates or sulfates to enhance their water solubility. These groups are strongly influenced by the pH. When the aim is to complex these dyes, the occurrence of strong interactions between the molecules due to concentration-related processes, pH or ionic strength can lead to the overestimation of sorption results. Such dyes can simply precipitate out, dimerize or aggregate depending on the conditions. Yilmaz reported the occurrence of aggregation [221]. It should not be forgotten that all the experimental conditions can play an important role and should all be taken into account to adequately account for the activity of the solvent and pollutant species [277]. In particular, the dosage of polymer used (often in excess in laboratory experiments) must be indicated. Overall, these parameters and their variability during the sorption process explain why it is difficult to compare results that are obtained in different conditions and to clearly identify the underlying sorption mechanisms and the respective binding affinity between polymer and pollutant (see Eq. (1) in Ref. [277]).

In order to promote the application of ECP polymers to treat metals, carboxymethylation of the materials has been proposed [42,156]. Here, complexation plays an important role, but it is not to be confused with inclusion complexation, because it involves the sharing of a pair of electrons between a metal cation and a complexing agent, the ligand, such as a carboxylate function. For these modified ECPs, the process is more precisely electrostatic attraction that occurs spontaneously between the positive charges of the cationic species (such as metal cations) and the negative charges of two neighboring atoms on carboxylate functions (non-directional bonding, where each species is subjected to the field from its neighbors). The species adsorbed, mainly at the surface of the materials, keep the water molecules with which they are associated. The energies involved in this type of interaction, are in fact relatively weak, that can be an advantage for the regeneration of the materials.

Generally, for the materials studied, the results agree with Pearson's acid-base concept (HSAB: hard/soft/acid/base) [278–284]. This theory indicated that, firstly, metal species called hard (mostly) and intermediate metal species become preferentially bound to hard bases (such as carboxylate functions) and secondly that the mutual affinity is mainly of an ionic nature (short-distance low-energy interactions). The results do show that it is the hard acids that tend to have the shortest ionic radii, the highest oxidation states, the lowest polarizability (small orbitals), strong electropositivity and a very localized electronic charge, that interacts most easily with the carboxylate functions tending towards preponderance of electrostatic interactions. The other mechanism proposed is ion exchange. During the sorption phenomenon, the metal ions can be exchanged (bound) in the place of the original cationic counter ions, i.e. the Na^+ ions originally paired with the carboxylic anions on the polymeric sorbent, that are released into the solution. A systematic increase in the concentration of Na^+ ions in the supernatant after sorption, coupled with a decrease in the concentration of the heavier metal ions present as contaminants, is generally taken as an indication of the occurrence of ion exchange [195,196,222].

These materials, however, do have a disadvantage: the ionization states and the sorption properties of the functional groups towards metal cations are strongly dependent on the pH. Altering the pH can lead to competition between the metal cations and the protons of the solution particularly when the pH is acidic. It is therefore important to check the initial pH. Furthermore, studies have shown that the quantity of metal cations retained by the polymer was significantly greater than the polymer's IEC indicating that the electrostatic and/or ion exchange interactions, via the carboxylate functions, are not the only mechanisms leading to the

retention of cations. Other reactions have been suggested: i) the non-protonated carboxyl functions can form cation-dipole type attractions with metals; ii) metals can diffuse and become adsorbed in the bulk of the macromolecular network, the materials can then play the role of electron donors for certain metal cations that have a higher redox potential than they do themselves; iii) the CD cavities can also host some metals such as copper (as proposed by Szejtli [16,19] in the 80s). Several research groups [285–289] have shown that CD molecules are able to interact with metal cations to form complexes following two types of mechanism involving inclusion complexes ions (CDs act as second sphere coordination ligands and the cavity includes metal ion complexes forming adducts) and cation-dipole attractions owing to the numerous hydroxyl functions present on the glucosidic units; iv) microprecipitation of metals is also possible through the change in pH brought about by the behavior of the basic polymer in water; the colloids of metal hydroxide formed can then in turn act as sorbents able to interact with metal cations still free in solution. The phenomenon of microprecipitation is complex and can occur during sorption bringing numerous parameters into play (pH, metal concentration, redox potential of the elements studied, presence of anions, etc.) [168,282–284]. Table 3 shows the main interactions proposed in the literature to explain the removal of metals by ECP polymers involving carboxylic groups and/or hydroxyl groups. All these interpretations show that, although the roles of the CD cavities and the structure of the macromolecular network and the carboxylic functions are well documented, the mechanisms of sorption are more complex than they might at first appear.

Crini's group also demonstrated that the mechanisms involved in the formation of dye complexes by cationic ECP gels is not that straightforward. Grafting cations on an ECP gel in well-controlled experimental conditions can yield excellent sorbents of acid, reactive and direct dyes. The mechanism is mainly due to electrostatic interactions and surface sorption, that explain the rapid contact times [185–188]. Here again, the greater the ion exchange capacity, the more sorption occurs. This was confirmed by Yilmaz using identical sorbents and using urethane-type polymers [218–223]. Yet, it must not be forgotten that both the CD cavities and the polymer network play an important role. We noted that the distribution of the cationic sites on the cross-linked molecular chains and the ionic strength of the water to be processed are both crucial factors. These dye complexing studies using cationic ECP also showed that the diffusion properties of the materials, and hence their retention properties, are closely dependent on the quantity of ECH and on the mobility of the macromolecular chains independently of the quantity of ligand. Although the polymer's IEC is high, if the degree of crosslinking is also high, performance will suffer, stressing the complexity of the mechanisms [94,187]. The results are also strongly dependent on the pH, in relation with the IEC. The chemical modification of ECP gels in fact presents a disadvantage that should be mentioned: the presence of cationic (or neutral or anionic) ligands makes the gel properties pH-dependent. In addition, cationic ECP material cannot be used to bind cationic or basic dyes. To overcome these disadvantages, various authors propose either to use amphoteric ECPs obtained by double grafting (Fig. 7), anionic and cationic, or to use other cross-linking agents (such as diisocyanate derivatives). Crini's group [48,196] showed that the sorption capacity of gels and beads of amphoteric ECP with respect to dyes is independent of the pH over a pH range of 2–10. Their results showed that the double modification (anionic through carboxylic functions and cationic through quaternary ammoniums) of cross-linked CD particles was a means to obtain materials with both high sorption capacities and rapid kinetics while remaining independent of the pH. Note however, that almost all the results were obtained with solutions containing a single contaminant.

5. Comments

We have shown that although a number of sorption mechanisms are still open to debate, with the literature reporting often contradictory data, ECP polymers do present interesting sorption properties for environmental purposes. However, unlike cross-linked and/or grafted starch, used in the treatment of wastewater as flocculants or precipitation enhancers for over 30 years, materials made from cross-linked CDs are having a hard time finding industrial applications for the environment. Several reasons can be mentioned. Firstly, the cost, as these materials are relatively more expensive than conventional sorbents. Although cyclodextrins are obtained from starch, one of the most abundant and cheapest polysaccharides on the planet, there is a non-negligible cost difference with active carbons. To be used in the treatment of water by sorption, the CDs must be cross-linked and often modified, all adding to the cost. ECP materials can be found on the market although it would not be possible to talk of an ECP industry. Various laboratories and a few companies, especially a private Hungarian company, synthesize these materials to order. As industrial production of ECP has not started, the sorbents produced at lab-scale suffer from variability in their characteristics (problems of particle size and its distribution, lack of porosity, low specific surface area), lack of reproducibility (difficulty to produce materials of the same cross-linking density, etc.). In addition, the requirement for different types of chemical modification to optimize sorption, and problems related to insufficient swelling in solution when they are used in column reactors, explain why it is difficult to transfer the ECP-mediated water purification processes to the industrial scale. With the exception of a few very recent works, studies of real applications are rare. Moreover, there are no technical-economic studies on these materials in the literature. Similarly, there is a total lack of studies of their life cycle. However, as shown by many researchers, there is no lack of interest in developing this type of sorbent, that will be increasingly the case if pollution laws change. In Europe, the tightening of regulations concerning effluent implies a better level of treatment of waste to tend towards zero pollution. With most types of conventional water treatment, it is difficult to remove pollutants present at low or very low levels in heterogeneous and variable effluents. ECP materials are able to remove pollution present solely as traces. Therefore their application for the purified wastewater was suggested. The costs can be reduced if sorption by ECP is used not for heavily contaminated industrial wastewater but only as a third step following the physical (filtration) and biological purification steps to remove the micro-contaminants still present [246]. Another challenging application might be the removal of emerging pollutants (EP) from drinking water. As the presence of pharmaceuticals, hormones, pesticides, etc. in drinking water is still not regulated household water purification systems are used to remove them. The efficiency of such filters can be improved by replacing the usual activated carbon filter by ECP. Similarly, but at the other extremity, certain industrial solutions containing high loads of multiple contaminants that can already be present as complexes are difficult to process. Generally, these effluents are disposed after dilution in less loaded effluent for more efficient physical-chemical treatment (e.g. precipitation). A very promising solution recently proposed in the literature is to pre-treat the solutions with ECP particles of known size in order to decomplex the pollutants and insolubilize them more efficiently [196,230].

Currently, there are no materials available that can act as single sorbents able to bind all the mineral and organic substances present in complex industrial effluents. To reach this goal, a combination of two materials is often used, for instance coupling of active carbon and ion exchange on a polymer resin generally with a prior filtration step to protect the subsequent extractions. In this

two-step decontamination technology, the active carbon removes the residual organic load, protecting the resins in the next step, and the resins then sequester the minerals (including metals) dissolved in the water to be treated, by chelation. So, these filtering materials, especially carbons, present performance problems when they have to eliminate substances present as traces in water with multiple contamination. They must be regularly renewed, either by changing them for fresh material (active carbons) or by regenerating them (ion-exchange resins). The aim would therefore be to find new sorbents able to eliminate all the different types of substances present in the effluent in a single operation.

For the last ten years, ECP materials have been proposed to eliminate both the organic molecules and the minerals. We speak of *two-in-one* materials, a term coined by French [26] in the 1950s. More recently, Crini's group demonstrated that amphoteric sorbent containing CDs are efficient for the decontamination of industrial effluent containing multiple contaminants [94,195,196]. This is the first time that such systems are able to process both EP, VOCs and PAHs and the metals present as traces in the effluent. Coupled with an advanced oxidation preliminary step, sorption on ECP materials is efficient for the treatment of water with multiple contaminants both from a chemical and an environmental point of view [196]. The first pilot studies have been reported recently showing that a single material could replace two conventional sorbents (carbon and resins) to efficiently treat multi-contaminated effluent [260,291]. For example, 1 kg of ECP material was applied to 300 L purified waste water spiked with 9 micropollutants including non-steroidal anti-inflammatory drugs (NSAIDs), estrogen hormones, bisphenol-A and cholesterol [291]. These micropollutants, especially estradiol, ethinylestradiol and bisphenol A (>99%), estriol (>96%) were effectively removed. Two of the four NSAIDs were also sorbed in a high extent (>80%). Now it will be necessary to convince industry to use these materials in their wastewater treatment plants.

6. Conclusions

In this review, we have summarized and discussed the various mechanisms of pollution elimination proposed in the literature to explain the performance of ECH-cross-linked CD polymers used as sorbents in liquid-solid sorption processes. The different comments were illustrated by examples from selected studies.

Numerous studies have actually demonstrated the potential of cross-linked CD materials in the complexation of environmental pollutants. These macromolecular systems have proved to be efficient and more advantageous than conventional systems. The advantages often cited are: the materials are straightforward to synthesize, their chemistry is based on aqueous systems (in a single step for ECP materials, several steps for amphoteric), they present high sorption capacities and are efficient in the removal of just traces, the kinetics are relatively rapid, and in addition they can be regenerated without significant loss of sorption capacity, unlike carbons and more easily than resins.

The difficulty with these materials however is that the sorption mechanisms are still being debated [290] because they involve various interactions that can occur simultaneously, complicating the interpretation of the results. In the present review, among the various interactions introduced, we can mention the formation of inclusion complexes, association complexes, electrostatic interactions, ion exchange, chelation, and other phenomena involving forces such as microprecipitation or hydrogen bonding. Each of these playing a role of varying importance depending not only on the type of material used (ECP polymer modified or not) but also on the experimental conditions (pH, etc.) used in the batch process. What importance should be given to each contribution? The answer is far from simple. For non-modified ECP polymers,

until the 2000s, the literature reported a consensus emerging on the mechanism of sorption that was mainly a chemical mechanism via the formation of inclusion complexes in addition to stabilizing forces (van der Waals, electrostatic interactions, hydrophobic interactions, hydrogen bonding, etc.). In spite of the numerous results reported demonstrating the existence of this interaction (chemisorption by inclusion), in recent years another mechanism is becoming generally acknowledged. Studies have stressed the role played by the macromolecular network formed by the cross-linking agent. The performance of the ECP material depends mainly on its chemical structure, and thus on the cross-linking step. To explain this performance, the concept of association complex has been introduced and demonstrates both the role of the CD molecules and of the 3D macromolecular network of the materials. Research on synthesis and characterization (especially through solid state NMR studies) and applications of cross-linked cyclodextrins continue to interest the scientific community as illustrated by the numerous publications on the subject that appear each year [291–316]. Other cross-linking agents that may be more ecologically friendly such as citric acid, have been proposed just like other shapes of ECP particle such as nanoparticles. For these new materials, the sorption mechanisms remain to be explained to understand their performance better.

Notes

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