

# Bio-Inspired Materials for Environmental Remediation



Sayaka Fujita and Nobuo Sakairi

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S. Fujita

National Institute of Technology, Tomakomai College, Tomakomai, Hokkaido, Japan  
e-mail: [fujita@tomakomai-ct.ac.jp](mailto:fujita@tomakomai-ct.ac.jp)

N. Sakairi (✉)

Hokkaido University, Sapporo, Hokkaido, Japan  
e-mail: [nsaka@ees.hokudai.ac.jp](mailto:nsaka@ees.hokudai.ac.jp)

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**Abstract** Highly organized structures and functions in living organisms have been a source of inspiration of new materials, of which properties are beyond the artificially synthesized materials. This chapter describes the development of design and synthesis of new adsorbents mimicking remarkable biological system of molecular recognition. These adsorbents are expected to apply to selective and efficient removal of organic micropollutants.

Cyclodextrin (CD), a cyclic oligosaccharide, with unique property to form inclusion complex, was utilized as recognition site in the new adsorbent. Coupling with CD derivatives and polysaccharide, chitosan, provided CD-based adsorbents, which had a high affinity toward various organic and hydrophobic pollutants with appropriate molecular sizes. Furthermore, importance of soft, flexible, and swelling polymer support of CD such as polysaccharides was revealed to demonstrate their high selectivity and high adsorption capacity. The importance of the soft scaffold was also shown in the preparation of biomass-immobilized adsorbents. Their bio-compatible nature of polysaccharide hydrogel beads was useful for the growth of various bacteria and fungi with pollutant degradation ability, and their multifunctionality was useful for structural modification such as introducing molecular recognition sites and cross-linking.

Furthermore, adsorbents having intercalation and chelation ability are also received much attention. DNA-immobilized materials inspired by interaction between DNA and genotoxins are shown to be useful for the removal and the detoxification of water containing various polycyclic aromatic pollutants. Chitosan derivative with pendant EDTA showed potential chelation ability toward various metal ions, and its zwitterionic property resulted in pH dependent dynamic morphology change, which could apply to the removal of heavy metals by flocculation.

Furthermore, this chapter also highlights recent advances in these biomimetic adsorbents for the selective and efficient removal of target pollutants.

**Keywords** Biomass-immobilized adsorbents, Biomimetic adsorbents, Chelation, Genotoxins, Inclusion, Intercalation, Micropollutants

## 1 Background

### 1.1 Micropollutants

Contamination of water has been one of the major concerns of global environment. The problems of water contamination of toxic heavy metals and harmful organic chemicals from a point source such as a factory or a mine have been existed since before. Nowadays, non-point source pollution is the leading course of water pollution. Development of microanalytical technology reveals that water resources contain a variety of organic substances at extreme low concentration ranging from ppb (parts per billion,  $\mu\text{g}/\text{kg}$ ) level to ppt (parts per trillion,  $\text{ng}/\text{kg}$ ) level, and that the

**Table 1** Examples of micropollutants (MPs)

Source	Chemicals
Industrial products	Chlorinated alkane, polycyclic aromatics, bisphenol A (BPA), phthalates, PCB
Pesticides	Atrazine, DDT
Pharmaceuticals	Acetaminophen, codeine, antibiotics, ibuprofen
Steroid hormones	Estradiol (E2), ethynilestradiol (EE2)

pollution spreads through the world. These pollutants are called micropollutants (MPs) or emerging pollutants. Although there is a little toxicological data of MPs, they are becoming serious threat of ecosystem and human health due to their undesirable developmental, reproductive, and endocrine disrupting effects [1, 2] (Table 1).

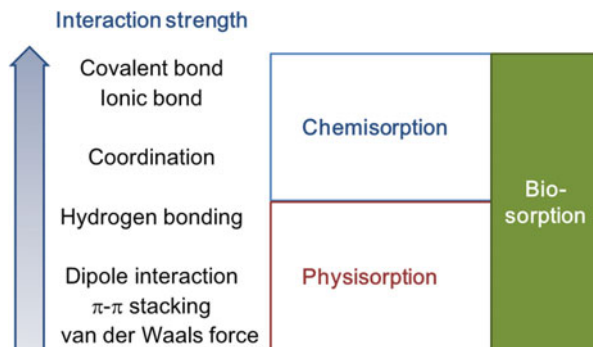
A most intractable problem concerning MPs is their bio-accumulation and bio-magnification. MPs are hydrophobic organic compounds. Because MPs have a nature of persistent and biological inefficiency, MPs captured by an organism tend not to be eliminated by catabolism or excretion. Therefore, MPs are accumulated in tissue of the organism. Moreover, in the ecosystem, the system of food web transfers the MPs accumulated in an organism to that of higher level with increasing MPs concentration. It means that higher level animals on the food chain build up greater and more dangerous amounts of toxic materials than animals in lower level.

## 1.2 Adsorbents for Removing Contaminants

In order to remove harmful contaminants from water, various technologies, e.g., adsorption, chemical precipitation, flocculation, membrane filtration, biological treatment, and photocatalytic degradation, have been extensively investigated. Some of them are contributing in the actual process of water purification. Among these removal technologies, an adsorption process has been the most widely employed due to its low cost and easy operation, as well as a little production of undesired secondary pollutants.

Adsorption is generally classified into three categories, chemisorption, physisorption, and biosorption. Chemisorption process occurs by a specific reaction between an adsorbent surface and adsorbate, and creates such a strong electronic linkage as covalent bond and ionic bond. Although its selectivity is extremely high, the adsorption process is irreversible. On the other hand, physisorption is caused by weaker interactions such as van der Waals interactions and dipole–dipole interaction between the adsorbate and the surface. Activated carbon (AC) is a typical example of physisorption, and is regarded as the most widely used adsorbent to remove organic pollutants. AC has high surface areas and nanostructured pores, and attracts the adsorbate through van der Waals force in the surrounding medium [3]. Since AC has various advantages such as low cost and decent absorption capacity, AC has been the

**Fig. 1** Three categories of adsorbents used for environmental remediation



most widely used adsorbents for water treatment. However, AC based approaches are subject to limitations including slow uptake kinetics, low affinities for many relatively hydrophilic pollutants and low selectivity (Fig. 1).

Living organisms synthesize a large number of polymer materials such as proteins, polysaccharides, lignin, and humic acid. *Biosorption* is a property of certain bio-material to bind and concentrate organic and inorganic chemical substances from aqueous solution through physico-chemical process. For example, bacteria produce extracellular polymeric substances, a complex mixture of bio-materials, which aid in resistance to harmful exogenous materials [4]. Bio-materials have extremely complicated structures and many functional groups, which bind the adsorbates through non-covalent multivalent interactions.

Biosorption, especially using biomass waste, is currently considered to be one of the most promising environmentally benign techniques for removing various pollutants from aqueous solutions [5]. Biosorption-based processes are expected to have a number of advantages including low production cost of adsorbents, simple operation, high efficiency, as well as improved selectivity for specific pollutants of interest.

### 1.3 Designing Biomimetic Adsorbents

In living organisms, biomaterials play essential biological roles including structural support, signal transduction, sensing, catalysis, light-harvesting, molecular recognition, and self-organization. These highly sophisticated and well-organized biological functions basically rely on non-covalent and multivalent interactions. This is important for not only understanding many biological processes but also designing novel artificial materials and systems. The remarkable phenomena such as self-assembly, molecular recognition, and molecular complexation frequently seen in biological processes have stimulated chemists to mimic in artificial systems. Extensive studies are performed to create new bio-inspired materials, and some examples are seen in

construction of artificial self-assembly system [6], synthesis and application of hybrid materials [7], and inorganic materials [8].

Molecular recognition plays an important role in biological systems, such as highly specific binding between enzyme–substrate, receptor–ligand, lectin–sugar, and antibody–antigen. Two or more molecules specifically interact with each other by non-covalent bonding, such as van der Waals force,  $\pi$ – $\pi$  stacking, hydrogen bonding, and metal coordination to form a complex. In a typical enzymatic reaction, an enzyme recognizes its substrate, specifically forms an enzyme–substrate complex, and subsequently displays an excellent catalytic efficiency. This process has been encouraged us to develop. Since the 1990s, key applications of mimicking biological molecular recognition and complex formation have been the construction of artificial molecular sensors and artificial enzymes [9, 10]. Macrocyclic compounds are very useful for synthesis of artificial enzyme, because they provide appropriate cavities that can surround the substrate molecules to form host–guest complex. Cyclodextrins, calixarenes, and crown ethers have been used for constructing the artificial systems [11]. In order to solve the problem of organic MPs, the development of novel adsorbents having molecular recognition ability has been expected. An adsorbent having highly selective molecular recognition site would be useful for environmental remediation.

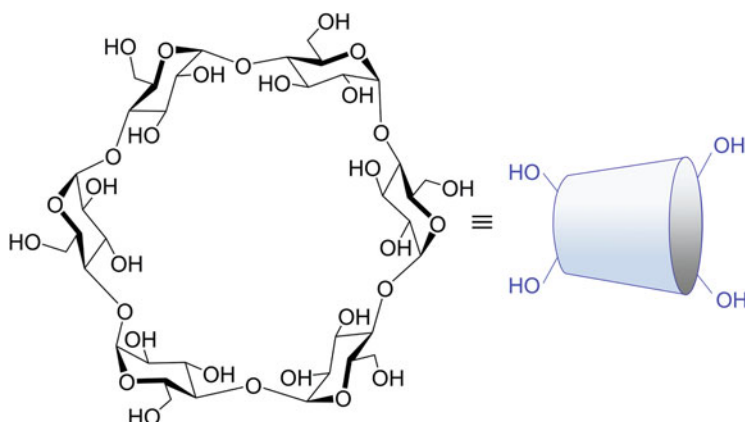
Another approach to efficient adsorbents is thought to be biomimetic design of the structure surrounding the adsorption site. Cell membranes are complex and highly dynamic systems, which consist of amphipathic lipids and polymeric substances such as protein and polysaccharides. Their major function is to protect the cell, to transport various materials in and out through a passive or an active way, and to communicate with its surroundings. These biopolymers have soft, flexible, and highly swelling properties. The investigations of cell surface mimics are performed with biomedical interest. Since the biosorption is involved in these biological function [12], novel adsorbents with soft and flexible constituents mimicking cell surface would be expected to improve their adsorption ability.

This chapter describes important consideration in designing and synthesizing new adsorbents mimicking remarkable biological system such as molecular recognition and cell surface structure, and also highlights recent advances in biomimetic adsorbents for the selective and efficient removal of target pollutants.

## 2 Cyclodextrin Linked Chitosan

### 2.1 Cyclodextrin

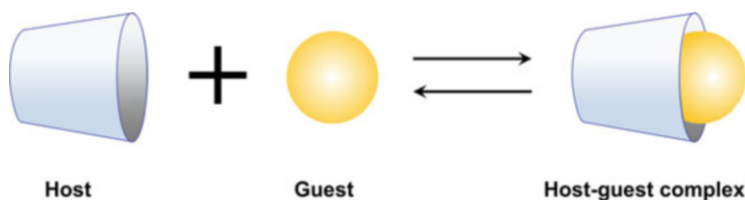
Cyclodextrins (CDs), cyclic oligosaccharides, are produced by enzymatic degradation (cyclodextrin glucanotransferase) of starch in an industrial scale. CDs mainly consist of six, seven, and eight  $\alpha$ -linked D-glucopyranose units, which are called  $\alpha$ -,  $\beta$ -, and  $\gamma$ -CD, respectively. The most remarkable feature of CDs is to form inclusion complex with various hydrophobic compounds [13]. As shown in Fig. 2, CDs have



**Fig. 2** Chemical structure and schematic representation of  $\alpha$ -CD

**Table 2** Physical property of CDs

CDs	$\alpha$	$\beta$	$\gamma$
Number of Glc units	6	7	8
Molecular weight	972	1,135	1,297
Outer diameter (nm)	1.37	1.53	1.69
Inner diameter (nm)	0.53	0.65	0.83
Height (nm)	0.79	0.79	0.79
Cavity volume (nm <sup>3</sup> )	0.174	0.267	0.427



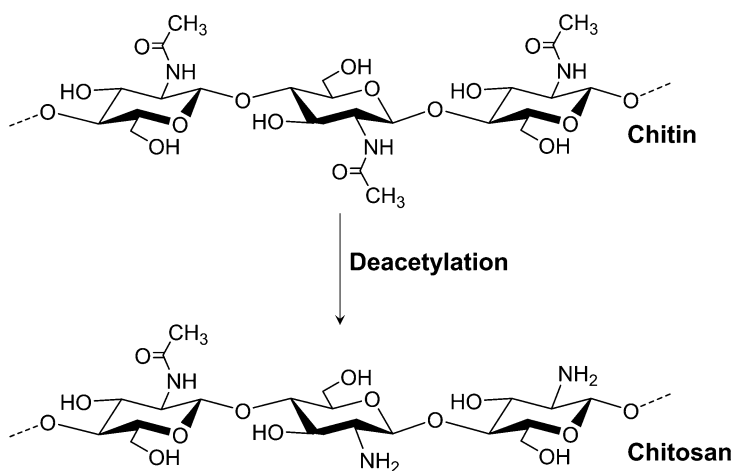
**Fig. 3** Schematic drawing of the host-guest inclusion complexation on the more favorable wider rim of CD molecule

cone-shape structures, where the secondary hydroxyl groups and the primary hydroxyl groups are located on wider rim and narrow rim, respectively. Physical properties of three kinds of CDs are summarized in Table 2. The interior of CD cavity is less hydrophilic than the exterior because of the absence of hydrophilic functional groups. Consequently, in aqueous media, CDs can interact with appropriately sized hydrophobic guest molecules to result in the formation of inclusion complexes (Fig. 3). Removal of water molecules from the cavity of the CDs to make room for the guest molecule for accommodation while formation of inclusion complex, increases entropy of the process. Estimating from the diameters of inner cavities of  $\alpha$ -,  $\beta$ -, and  $\gamma$ -CD (0.53, 0.65, and 0.83 nm, respectively), appropriate sizes

of the guests are similar to benzene, naphthalene, and anthracene, respectively. Due to this unique property, CDs have been singled out for studies on host–guest chemistry. Numerous investigations have been carried out to construct artificial enzymes and receptors and to apply in pharmaceutical, cosmetic, and food industries [14]. Moreover, CDs have also been investigated for the removal of toxic substances from industrial effluent. For example, toxicity of an insecticide, tetramethrin, was reduced by formation of inclusion complex with  $\beta$ -CD [15], and CD oligomers and polymers prepared by cross-linking with epichlorohydrin have been investigated as encapsulation materials [16]. The unique inclusion ability of CDs attracted us to create new CD-based adsorbents for the pollutant removal.

## 2.2 Characteristics of Chitosan

In order to synthesize biomimetic adsorbents bearing CDs, chitosan was first chosen as a polymer scaffold. Cellulose and chitin are the most abundant extracellular polysaccharides found in cell wall or extracellular matrix of various organisms. Chitin is isolated from several sources including cuticles of arthropods such as crab, shrimps, and insects, and fungal biomass. Chitin of  $\beta$ -*N*-acetylglucosamine residues and its basic hydrolysis affords chitosan, a linear polymer of  $\beta$ (1 $\rightarrow$ 4) linked 2-amino-2-deoxyglucopyranose (Fig. 4). Since the amino groups of chitosan are protonated in numerous dilute mineral and organic acids, it shows polycationic character and high solubility. Chitosan has been extensively studied as an adsorbent of heavy metals, as an ion exchanger, as an antifungal agent, and so on. Furthermore, these properties of chitosan make it possible to introduce various functional groups by chemical modifications [17]. Chitosan-based hydrogel beads can be easily



**Fig. 4** Chemical structure and transformation of chitin to chitosan

prepared by dropping chitosan solution in aqueous acetic acid into an alkaline solution. They have been extensively studied as micro- or nano-particulate carriers in the pharmaceutical and medical fields such as drug delivery and as adsorbent for pollutants such as heavy metal ions and dyes [18, 19]. Considering the versatility of chitosan, it seemed to be a promising candidate of the supporting material of CD-based adsorbent.

### 2.3 Pioneering Researches on CD Linked Chitosan

Among three kinds of functional group in chitosan, the amino group at 2-position is the most reactive, and a large number of chitosan derivatives have been synthesized mainly by chemical modifications of this group [17]. Furusaki et al. synthesized for the first time  $\beta$ -CD-linked chitosan ( $\beta$ -CD-ch-A) through formation of amido bond (Fig. 5) [20]. Water-soluble low molecular weight chitosan ( $M_w = 7,300$ ) was coupled with carboxymethylated  $\beta$ -CD in the presence of water-soluble carbodiimide (WSC) as a condensation reagent in water. The degree of substitution

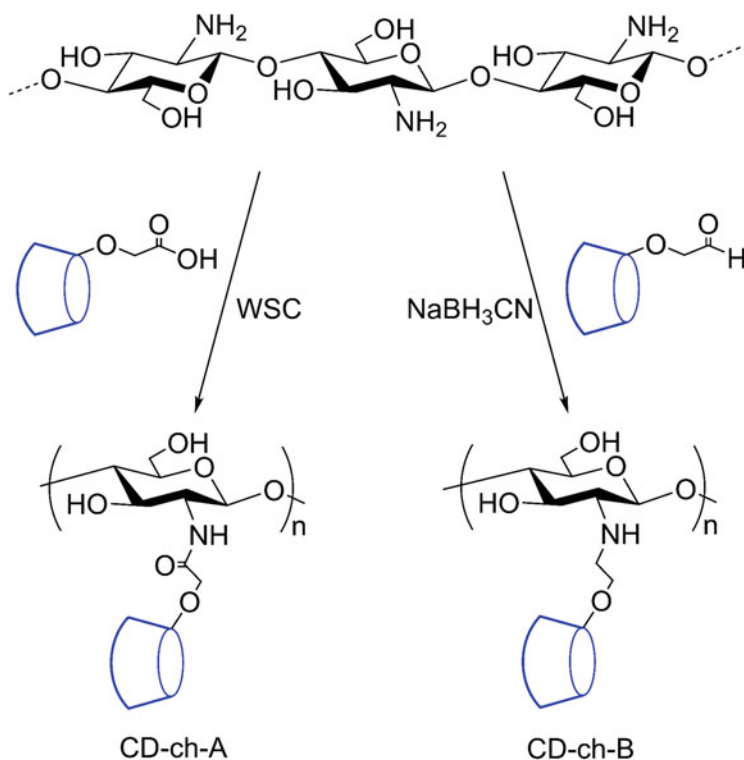


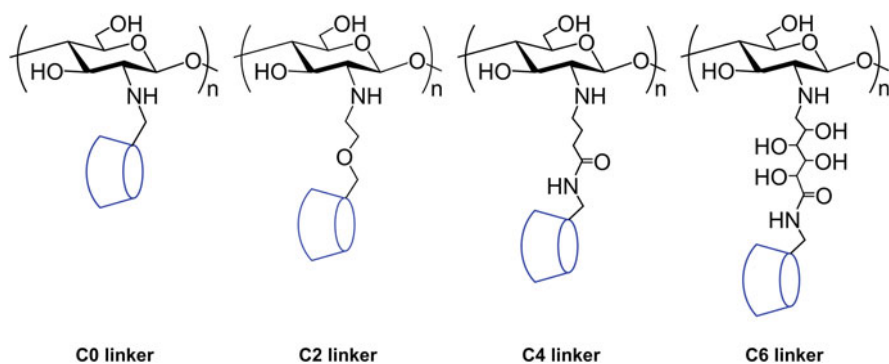
Fig. 5 Two possible routes for the synthesis of CD pendant chitosan derivatives



(DS) of the product ( $\beta$ -CD-ch-A) estimated by  $^1\text{H}$  NMR spectrum was 20%. Inclusion ability of  $\beta$ -CD-chitosan-A with 1:1 stoichiometry was determined by spectroscopic titration using a fluorescent dye, 6-(*p*-toluidino)-2-naphthalene-6-sulfonate (TNS). Association constants ( $K_a$ ) of  $\beta$ -CD-ch-A and TNS complex was  $1.13 \times 10^3 \text{ mol}^{-1} \text{ L}$  at pH 7.0 and that of  $\beta$ -CD was  $2.54 \times 10^3 \text{ mol}^{-1} \text{ L}$ , showing that the inclusion ability of  $\beta$ -CD is maintained after coupling with chitosan.

Another major route of chitosan modification is to use reductive amination, which involves Schiff's base formation between the amino group of chitosan and carbonyl reagents and subsequent reduction of the C=N double bond [21]. An advantage of this route is that the reaction proceeds in aqueous acidic solution, which is suitable to perform the reaction under homogeneous conditions and without isolation of any intermediates. Tojima et al. described synthesis of  $\alpha$ -CD-linked chitosan ( $\alpha$ -CD-ch-B) by this route [22]. Thus, mono-*O*-allyl- $\alpha$ -CD was oxidized with ozone to generate 2-*O*-(formylmethyl)- $\alpha$ -CD having an aldehyde function, which was subjected to Schiff's base formation with medium molecular weight chitosan (Mw = 40,000) in acetate buffer at pH 4.4 and subsequent to reduction with  $\text{NaBH}_3\text{CN}$ . Purification by dialysis afforded  $\alpha$ -CD-ch-B with D.S. from 15 to 60%. The product was soluble in water even under neutral and alkaline conditions. Inclusion property of  $\alpha$ -CD-ch-B determined by UV-visible and circular dichroism spectroscopic titration using *p*-nitrophenolate confirmed that it had the almost similar ability of original  $\alpha$ -CD [22].

The reductive amination route can be applicable to various CD derivatives having an aldehyde function to convert into the corresponding CD-chitosan-B derivatives. In a similar way as above,  $\beta$ -CD-ch-B having different length of cross-linker moieties,  $\beta$ -CD-ch-B C0, C2, and C4 (Fig. 6) were synthesized [23, 24]. Their inclusion properties of  $\beta$ -CD-ch-B C4 (D.S. 18%),  $\beta$ -CD-ch-B C2, and  $\beta$ -CD-ch-B C0 (D.S. 17%) with TNS were investigated in acetate buffer (pH 4.3) at 25°C. Job's continuous variation plot showed the stoichiometry of inclusion complex of C2 and C4 cross-linker derivatives and TNS was 1:1, whereas that of C0 derivatives was not

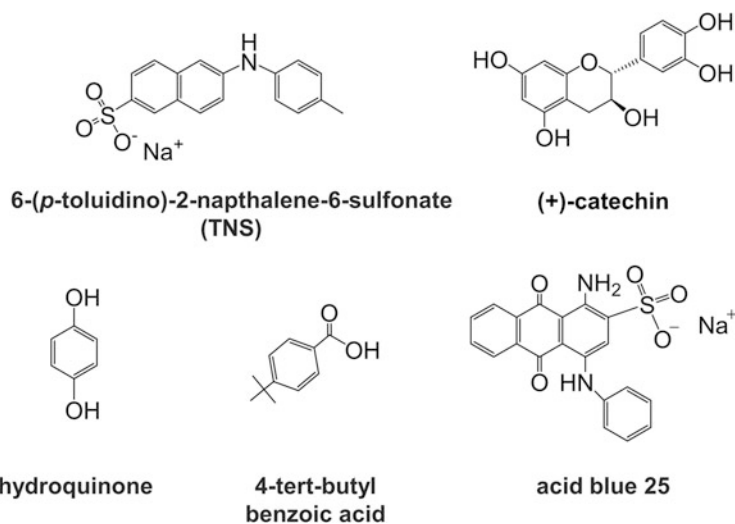


**Fig. 6** Partial structures of  $\beta$ -CD-ch-B with various cross-linkers synthesized via reductive amination route

fit 1:1 stoichiometry. Furthermore, a viscose solution was formed when  $\beta$ -CD-ch-B C0 and TNS were mixed. The association constants of  $\beta$ -CD-ch-B C2 and C4 determined by Benesi–Hildebrand plot were almost same as that of native  $\beta$ -CD, suggesting the inclusion ability of CD is maintained after immobilized on polysaccharide backbone [24]. The distance between CD moiety and polymer main chain is influenced on their inclusion property. The unusual inclusion property of directly linked C0 derivative is probably due to lack of flexibility of the  $\beta$ -CD residue. The constrained conformation around the CD residue may interfere the guest molecule approaching from the wider rim of the CD cavity as shown in Fig. 3.

Since hemiacetal group of a reducing sugar is a potential aldehyde function, reducing sugars are used as starting materials for the reductive amination reaction. Therefore, chitosan and CD residue can be linked with hydrophilic group. Thus, 6-amino- $\beta$ -CD was coupled with a galacturonic acid derivative, and then underwent similar reductive amination with chitosan. The product ( $\alpha$ -CD-ch-B C6) had a polyol-type cross-linker, and showed inclusion ability toward 4-tert-butylbenzoic acid and (+)-catechin (Fig. 7) as model guests [25]. In case of such a large guest as catechin, CD grafting on chitosan left its inclusion ability unaffected relative to the original CD.

Using reductive amination, various CD derivatives found to be efficiently grafted on chitosan, yielding highly water-soluble CD-polymers, which exhibit the same inclusion properties toward hydrophobic guests as the native CD (Fig. 7).



**Fig. 7** Chemical structures of guest molecules for CD-based adsorbents

**Fig. 8** Flowchart for the preparation of CD-linked chitosan beads

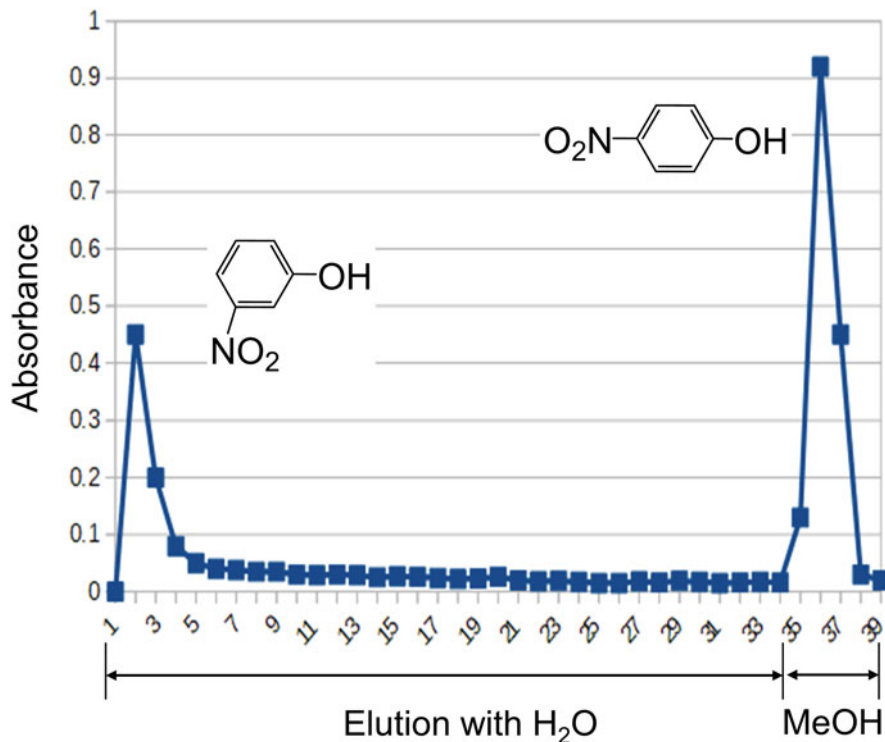


## 2.4 CD-Linked Chitosan Gel Beads

In order to apply CD-chitosan to adsorbent for pollutant removal, similar reductive amination of water-insoluble chitosan beads was examined. Chitosan gel beads were prepared according to the flowchart shown in Fig. 8. An aqueous acetic acid solution of chitosan was dropped into a coagulating liquid such as ethanolic aqueous sodium hydroxide. The spherical chitosan gel was subsequently undergone cross-linking with hexamethylene diisocyanate. Glutaraldehyde, epichlorohydrin, ethylene glycol diglycidyl ether, and molybdate salt are also reported as the useful cross-linking reagents. Formation of chitosan beads provides solid material with high porosity and large surface area [26]. The beads were converted into  $\alpha$ -CD chitosan beads ( $\alpha$ -CD@ch) by reductive amination with 2-*O*-formylmethyl- $\alpha$ -CD in the presence of NaBH<sub>3</sub>CN in acetate buffer at pH 4.4 [27].

As a preliminary experiment for the utilization of  $\alpha$ -CD@ch as adsorbent, column chromatographic adsorption–desorption was examined by use of a mixed aqueous solution of 4-nitrophenol and 3-methyl-4-nitrophenol. The former is a preferable guest for  $\alpha$ -CD, while the latter has a bulky methyl group that inhibits formation of the inclusion complex with  $\alpha$ -CD. The chromatogram (Fig. 9) showed 3-methyl-4-nitrophenol was quickly eluted with water, while 4-nitrophenol was adsorbed by  $\alpha$ -CD@ch during elution with water. 4-Nitrophenol was readily recovered by eluting the  $\alpha$ -CD@ch column with methanol, less hydrophobic solvent [27]. This experiment shows that CD@ch has an ability of size selective adsorption of guests and desorption.

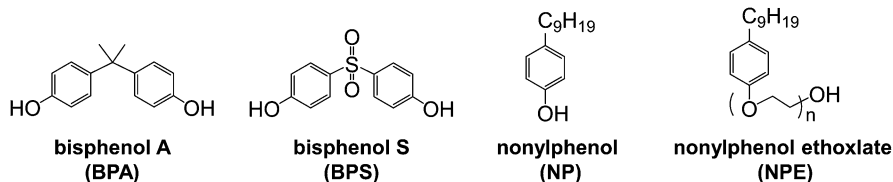
Furthermore, other type of insoluble CD@ch was synthesized and its adsorption behavior was examined by several groups. Martel et al. prepared different types of insoluble  $\beta$ -CD-chitosan with triazinyl cross-linker ( $\beta$ -CD-TZ@ch), which exhibited adsorption ability toward such textile azo dyes as acid blue 15 and acid blue 25 (Fig. 7). The adsorption capacity was superior to a conventional CD-polymer prepared from chitosan and CD-epichlorohydrin [28]. Zha et al. introduced  $\beta$ -CD into chitosan beads by subsequent treatment with hexamethylene isocyanate and  $\beta$ -CD, giving insoluble  $\beta$ -CD linked chitosan beads ( $\beta$ -CD-HMC@ch), and its adsorption behavior was examined with hydroquinone. This adsorption process was found to be a spontaneous, endothermic, and a random process [29].



**Fig. 9** Chromatogram of nitrophenols separation with  $\beta$ -CD-chitosan beads ( $\beta$ -CD@ch) observed at 400 nm

## 2.5 Adsorbents for MPs Removal

Adsorption behavior of these CD-based adsorbents was also examined for the purpose of MPs removal. Nishiki et al. prepared water-insoluble and highly porous  $\beta$ -CD linked chitosan beads ( $\beta$ -CD@ch) in a similar way as above, and preliminary experiments for its application to removal of bisphenol A (BPA), an endocrine disrupting chemical (Fig. 10), was carried out using  $\beta$ -CD@ch gel beads. More than 90% removal of BPA from aqueous solution was successful by the use of  $\beta$ -CD@ch column, and washing the column with methanol recovered BPA. Furthermore, this procedure was applicable to the removal of BPA at concentrations <1 ppm [30]. Aoki et al. reported coupling 6-amino- $\beta$ -CD with succinylated chitosan gave insoluble  $\beta$ -CD linked SU-chitosan ( $\beta$ -CD-SU@ch). Adsorption experiments with  $\beta$ -CD-SU@ch showed excellent adsorption ability toward BPA and NP and initial adsorption rates with BPA and NP were 40 and 1.3 times larger than those of AC, respectively [31]. Removal of non-ionic surfactants, 4-nonylphenol ethoxylates (NPEs), was compared with three kinds of adsorbents ( $\alpha$ -,  $\beta$ -, and  $\gamma$ -CD@ch), and found that  $\beta$ -CD@ch was the most suitable for the



**Fig. 10** Structures of MPs captured by CD-based adsorbents

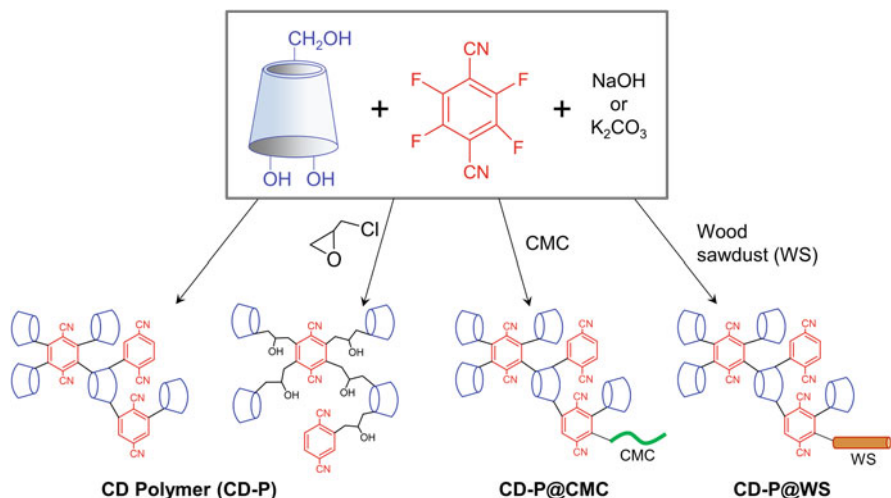
adsorption of the phenol derivatives (Fig. 10). Most of the NPE adsorbed on  $\beta$ -CD@ch was successfully released by the treatment of  $\beta$ -CD@ch with aqueous alcohol solutions and its adsorption ability was maintained after 20 cycles of the adsorption–desorption [32]. Other examples of CD-chitosan based adsorbents and CD-polymer are mentioned in several reviews [33, 34].

## 2.6 Recent Progress in CD-Based Adsorbents for MPs Removal

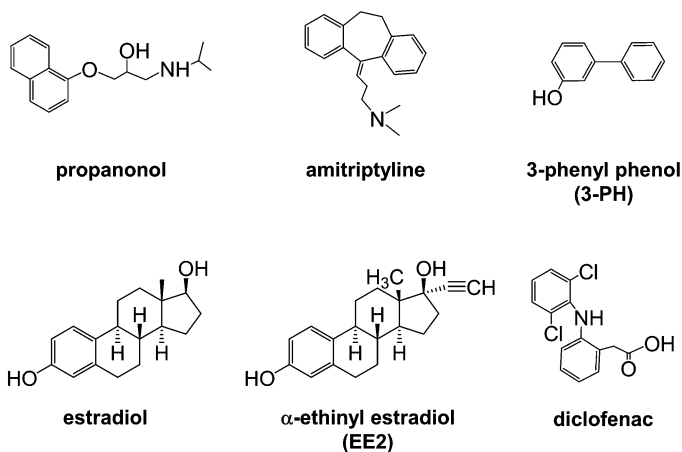
Based on the fundamental investigations mentioned above, various CD-based adsorbents were synthesized and applied to MPs removal. Orelma et al. reported that surface modification of cellulose fiber yarns with CD-chitosan gave a new adsorbent for removal of 17 $\alpha$ -ethinyl estradiol (EE2) [35]. A deep eutectic solution of cellulose was subjected to dry jet spinning in choline chloride-urea to give cellulose fiber yarns. The yarns were immersed in a chitosan solution in acetate buffer, and then treated with a TEMPO-oxidized  $\beta$ -CD derivative in the presence of WSC as a condensation agent. Surface plasmon resonance (SPR) experiments showed the EE2 adsorption capacity of the  $\beta$ -CD modified fiber yarn was 2.5 mg g<sup>-1</sup>.

Very recently, porous  $\beta$ -CD polymer ( $\beta$ -CD@P) with rigid aromatic cross-linker was synthesized by aromatic nucleophilic substitution, and it rapidly adsorbed various MPs. The co-polymerization was performed by  $\beta$ -CD, tetrafluoroterephthalonitrile (TFN), and K<sub>2</sub>CO<sub>3</sub> in aprotic solvents (Fig. 11).  $\beta$ -CD@P showed an excellent property to adsorb various MPs, e.g., BPA, bisphenol S (BPA-S), EE2, propranolol with adsorption rate constants 15 to 200 times greater than those of AC [36].

Furthermore, the property of  $\beta$ -CD@P was found to be remarkably changed by the property of cross-linker group. When the polymerization was carried out using two cross-linking reagents, TFN and flexible cross-linker (epichlorohydrin), the product  $\beta$ -CD@P showed highly swellable property [37]. Owing to the porous structure and easy access of adsorption sites, these  $\beta$ -CD@P exhibited ultra-rapid adsorption of organic micropollutants, such as bisphenol A (BPA), 3-phenylphenol (3-PH), and ethinyl estradiol (EE2). The polymer adsorbent could be easily regenerated by methanol at room temperature and reused many times without a



**Fig. 11** Schematic representations for the synthesis of cross-linked CD polymers for MPs removal



**Fig. 12** Chemical structures of pharmaceuticals captured by CD-polymer adsorbents

significant decrease in the adsorption performance. Thus,  $\beta$ -CD-P could effectively remove many organic pollutants (Fig. 12) from water at environmentally relevant concentrations and without being affected by the pH level, ionic strength, and humic acid concentration, indicating that it is very suitable for application in practical water treatment [37].

Versatility of this polymerization procedure of  $\beta$ -CD-P was applicable to surface modification of various materials. Alzate-Sánchez et al. synthesized an adsorbent with a core/shell structure by incorporation of  $\beta$ -CD-P onto cellulose microcrystals

(CMC) [38]. Batch adsorption experiments using  $\beta$ -CD-P@CMC demonstrated rapid pollutant uptake and high accessibility of the CD on the adsorbent. Similarly, column experiments demonstrate rapid uptake of a model pollutant with minimal back-pressure, demonstrating potential for use in packed-bed adsorption processes. Furthermore, the pollutant-saturated columns were regenerated using methanol and reused three times with almost no change in performance [38]. Similarly, Guo et al. incorporated  $\beta$ -CD@P onto wood sawdust (WS), a byproduct of the wood-processing industry, and applied  $\beta$ -CD-P@WS to cross-flow filtration to remove some pharmaceutical pollutants. Consequently, the  $\beta$ -CD-P@WS filter device shows a high removal efficiency of over 97.5% within 90 s for various pharmaceutical contaminants including propranolol, amitriptyline, chlortetracycline, diclofenac, and levofloxacin, and a high saturation uptake capacity of 170, 156, 257, 159, and 185 mg/g, respectively [39].

Utilizing the unique inclusion property of cyclodextrins, new type of adsorbents have been synthesized and shown to have a high affinity toward various organic and hydrophobic pollutants with appropriate molecular sizes. In addition to CD residue, consideration of structure and property of the polymer support and/or the cross-linker is also important for designing. Selection of soft, flexible, and swelling polymer such as polysaccharide scaffolds of CD is found to demonstrate their high selectivity and high adsorption capacity of CD-based adsorbents.

### 3 Encapsulated Biomass for MPs Removal

#### 3.1 Immobilized Biomass

Various living and dead biomass obtained from bacteria, algae, fungi, and yeast have been used for remediation of polluted water through adsorption, biosorption, biodegradation, and bioprecipitation [40]. However, there are some drawbacks to use biomass, such as low stability (storage, pH, and temperature), high price of production, poor reusability, and difficult separation from reaction media.

Immobilized biomass on various supporting materials has been extensively investigated to overcome these problems [41]. Swelling and porous polysaccharide gel beads are a candidate of supporting materials for environmental remediation [42]. Enzyme immobilization can improve these problems. Fixing the enzymes in solid supports makes it easier to separate them from solutions, and improves the reusability. However, in some of the cases, activity of the immobilized enzyme decreases probably due to undesired interactions between the support and the enzyme, lower movement of the enzymes, or inhibited interaction between the enzyme and substrate.

### 3.2 Nonyl Phenol Removal by Immobilized Biomass

Lang et al. reported introduction of a fungal biomass into chitosan beads and utilization for biosorption of NP [43]. The beads were prepared by a modified procedure shown in Fig. 8. Spore of *Rhizopus arrhizus* TISTR 3606, a fungal strain, was mixed with an autoclaved acetic acid solution of chitosan. It was dropped into a sterilized coagulating liquid containing sodium tri-polyphosphate, which forms polyion complex with chitosan to yield stable beads without any affection of the living spores. The resulting beads were incubated in TGY medium for 5 days, inactivated by autoclaving at 121°C, filtered, washed with water, and vacuum dried to give the beads encapsulating dead fungal biomass inside (fungus@ch). During the 5-days incubation, the diameter of dried *R. arrhizus*@ch was increased from 1 to 1.5 mm (original beads) to 4 mm, and the whole bead surface was homogeneously covered with outward growing mycelia. The dry weight of immobilized fungus was 0.97 mg/bead.

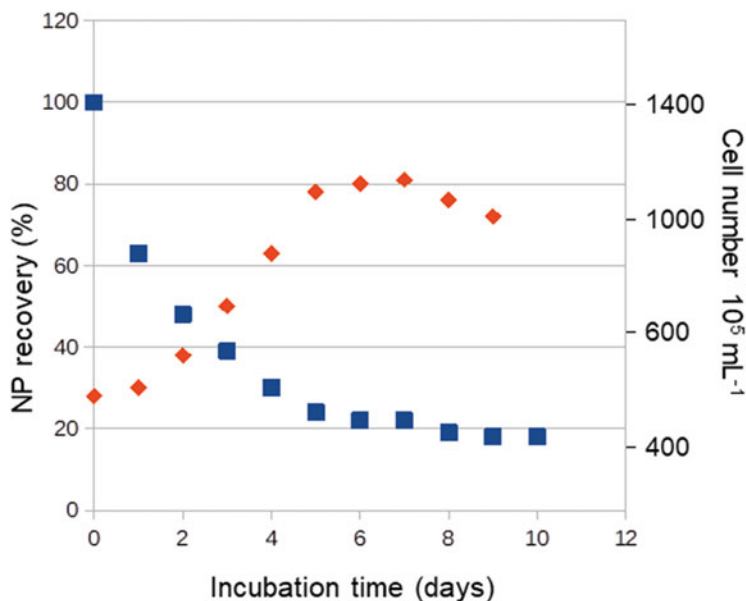
Adsorption and desorption experiments of NP using *R. arrhizus*@ch were performed by batch method. It was found that Fritz–Schluender model was the best fit with the experimental data and the adsorption capacity was 30.25 mg/g. The entrapped NP on the beads could be released by washing with methanol, and the regenerated dead beads were reusable for NP uptake. Table 3 shows the usefulness repeated adsorption–desorption of NP. However, by the end of the fifth batch use, the recovery of NP was decreased to 38% of the first batch and the weight loss of dead beads was 43% probably due to physical decomposition of fine mycelia immobilized on the beads.

*Sphingomonas cloacae*, which has a degradation ability of NP, was immobilized in calcium alginate beads covalently linked with  $\alpha$ -cyclodextrin (*S. cloacae*@CD-alg). Column chromatographic experiment using *S. cloacae*@CD-alg beads showed a strong affinity for NP adsorption. Incubation of *S. cloacae*@CD-alg in NP containing medium at 25°C in a shallow incubation tube for 10 days showed 83% NP removal. Furthermore, cell numbers of the bacteria in the beads were increased from 400 to 1,200 during the incubation (Fig. 13). Scanning electron microscopic photographs revealed that multiplied bacteria were present both on the surface and inside the beads [44].

**Table 3** Sorption–desorption of nonyl phenol by repeated use of *R. arrhizus*@ch

Cycle	Recovery of NP (%)	Beads weight (%)
1	100	100
2	78	63
3	77	61
4	76	60
5	38	43





**Fig. 13** Time-course of NP degradation and bacterial growth with *S. cloacae*@CD-alg. Percentage of NP remaining unchanged (blue square) and cell number (orange diamond)

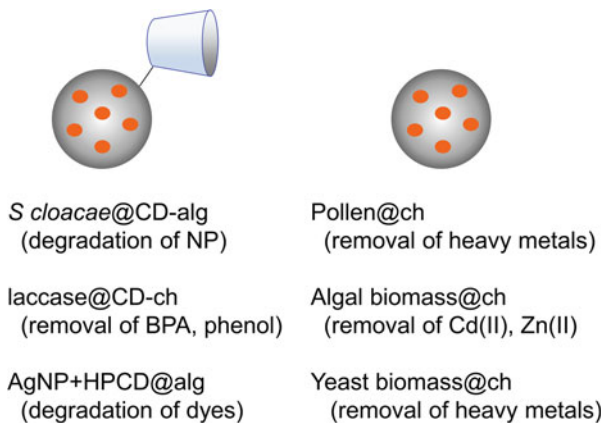
### 3.3 Recent Applications to Removal of MPs

A large number of biomass encapsulated polysaccharide beads have been prepared and evaluated mainly their ability of heavy metal removal (Fig. 14), e.g., pollens containing chitosan micro capsule (pollen@ch) [45], chitosan–algal biomass composite (algal@ch) [46], and yeast immobilized in chitosan/lignosulphonate matrix (yeast@ch) [47]. Application to the removal of micropollutants has also been extensively investigated.

Tarasi et al. reported synthesis of CD-chitosan conjugated with  $\text{Fe}_3\text{O}_4$  magnetic nanoparticle (laccase@CD-ch) is useful for laccase immobilization and degradation of some phenolic compounds [48]. Laccase is known to catalyze one-electron oxidation of phenolic compounds. The immobilized enzyme maintained 70% of its initial activity up to 12 days, and showed maximal removal with 96.4 and 85.5% for phenol and BPA, respectively. One of the advantages of the magnetic beads is that they could be collected or transported by an external magnetic field at specific positions. Furthermore, laccase immobilization on chitosan beads using WSC resulted in significant improvement of the enzyme activity [49]. Removal experiment of indigo carmine as a model micropollutant showed the activity remained almost constant of up to 80% during 10-cycle of reuse and that the residual activities were 85% after 32 days of storage.

Similarly horseradish peroxidase catalyzed oxidation of various organic compounds by hydrogen peroxide. Bilal et al. immobilized this enzyme onto the self-

**Fig. 14** Some examples of living or dead biomass encapsulated polysaccharide gel beads for the removal of MPs and metal ions



fabricated polyvinyl alcohol-alginate (peroxidase@alg-PVA) beads using sodium nitrate as a cross-linker. They reported simple and shorter time for preparation method, high reusability, and minimum enzyme leakage. They applied it to the degradation of an azo dye, ethyl orange [50].

Reduction of 2-hydroxypropyl- $\beta$ -CD (HPCD) and Ag(I) encapsulated calcium alginate gel using aqueous extract of *Jasminum subtriplinerve* leaves as a reducing agent gave Ag nanoparticles and HPCD containing nanocomposites (AgNP + HPCD@alg). The AgNP + HPCD@alg showed excellent catalytic performance for degradation of pollutants within industrial effluents including 4-nitrophenol, methyl orange, and rhodamine B [51] (Fig. 14).

Furthermore, Zhang et al. synthesized magnetic chitosan beads immobilized *Aspergillus sydowii* (*A. sydowii*@ch), and examined simultaneous removal of Cd (II) and trichlorfon, an insecticide [52]. The beads were prepared from a chitosan solution of aqueous citric acid containing Fe<sub>2</sub>O<sub>3</sub> and the fungal spore and incubated at 28°C for 24 h. During the incubation, the surface area of the beads was significantly increased to 55.38 m<sup>2</sup> g<sup>-1</sup>. Using *A. sydowii*@ch, simultaneously removal of both organic pollutant and heavy metal ion was examined. The equilibrium removal capacities of TCF and Cd(II) were 135.43 and 56.40 mg g<sup>-1</sup>, respectively. *A. sydowii*@ch exhibited excellent recyclability up to four cycles.

Chitosan and calcium alginate hydrogel beads are flexible and highly swelling scaffold of a large number of living or dead biomass, which have an ability of pollutant accumulation and degradation. Their biocompatible nature helps the growth of various bacteria and fungi with pollutant degradation ability, and their multi-functionality is useful for structural modification such as introducing molecular recognition sites and cross-linking.

## 4 DNA Based Adsorbent

### 4.1 DNA Intercalation

Deoxyribonucleic acid (DNA) carrying genetic instructions is a biopolymer, which has a unique three-dimensional structure. A combination of hydrogen bonding and  $\pi$ - $\pi$  stacking between the nucleobases constituting DNA makes a double-helical ladder structure. Double-helical DNA most commonly has B-form, in which distance between nucleobase pairs is 0.34 nm and 10 base pairs makes one turn in 3.4 nm. Large amounts of DNA-enriched materials can be available from the waste of food industry such as salmon milts and shellfish gonads. DNA is highly water-soluble and biochemically unstable, which have been making it difficult to utilize as a functional material. Immobilization of DNA on solid supports such as cellulose powder or gold nanoparticle, or by making a stable complex with other polymers, such as cationic amphiphilic lipids or acrylamide has been reported [53]. Conjugation of DNA with alginic acid [54], chitosan, or collagen was also attempted [55] to expand the scope of DNA material for medical use.

Intercalation is a phenomenon that a guest molecule or ion is inserted into a material with layered structure. In biochemistry, intercalation mainly means the insertion of guest molecules between the ladder structure of double-helical DNA (Fig. 15). The DNA intercalator has an appropriate size and chemical nature to fit between the base pairs of DNA through sharing of the  $\pi$ -electrons. The suitable structures of intercalators are mostly polycyclic, aromatic, and planar compounds (Fig. 16). DNA intercalators are often carcinogenic, which leads structural change of DNA and often to inhibition of transcription and replication. Inspiring this biological process, harmful DNA intercalating pollutants uptake of immobilization of double-stranded DNA was investigated as follows.

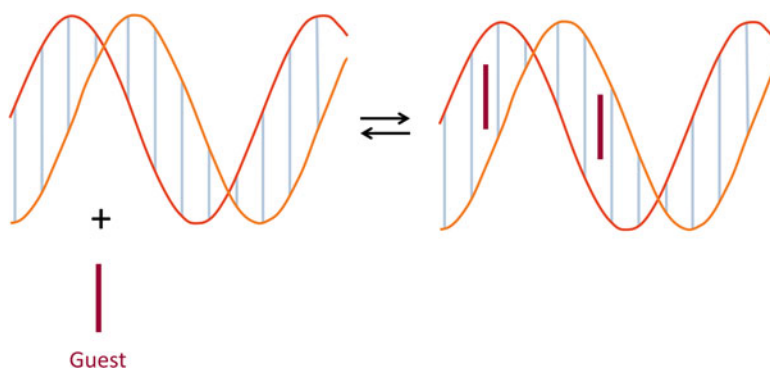
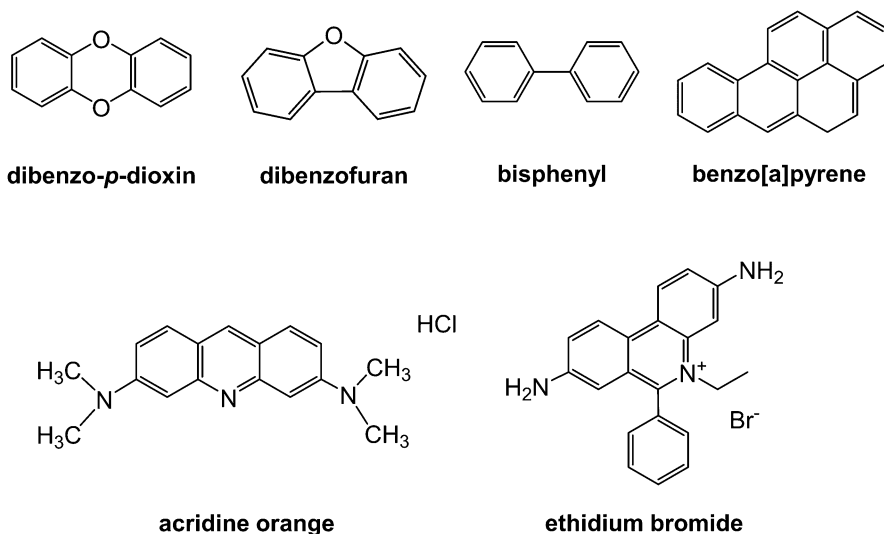


Fig. 15 Schematic representation of double-stranded DNA and its intercalation complex



**Fig. 16** Chemical structures of DNA intercalators

## 4.2 DNA Based Adsorbents

Immobilized DNA film was first investigated as an accumulator of intercalating substances [56]. Although native DNA is a high water-soluble biopolymer, exposure of DNA to UV light makes irreversible change to give insoluble material. The mechanism is explained by [2 + 2] cycloaddition reaction between two adjacent pyrimidine bases to form cyclobutane pyrimidine dimer, which crosslinks between two DNA chains [57]. The starting DNA film was prepared by casting an aqueous double-stranded DNA ( $M_w = 5 \times 10^3$  kDa) solution onto glass plates, and dried at room temperature. The film was irradiated with UV light at 254 nm for several times, giving a water-insoluble film. Since addition of a radical scavenger, galvinoxyl, inhibited this change, the reaction is revealed to proceed through a radical reaction mechanism. Agarose gel electrophoresis of the short UV-irradiated product showed significant increase of the molecular weight of DNA. The longer irradiated DNA film showed both physical and biological stability because it did not dissolve in water even after incubation for a long time and the UV-irradiated DNA films showed resistance to hydrolysis by nuclease. Circular dichroism spectra of the DNA film, which have a maximum peak at 280 nm and a minimum peak at 240 nm, revealed it has the B-form structure, which suggested native double-stranded DNA structure in water was maintained.

Intercalation property of the UV-irradiated DNA film was examined by UV-vis spectroscopy using ethidium bromide and acridine orange. When the UV-irradiated DNA film was incubated with a dilute aqueous ethidium bromide solution for 24 h, the color of DNA film changed from clear to red, and the absorption peak of the solution at 480 nm disappeared completely. The binding constant for ethidium

bromide was calculated to be  $6.8 \times 10^4 \text{ mol}^{-1} \text{ L}$ , which was consistent with the data of native double-stranded DNA [56]. The UV-irradiated DNA films have potential uses as a bio-material filter for the removal of harmful DNA intercalating compounds.

### 4.3 Application to MPs Uptake

Immobilization of double-stranded DNA onto nonwoven cellulose fabric by UV irradiation and utilization of DNA-immobilized cloth were examined. The immobilized DNA was found to be stable in water, with the maximum amount of fabric-immobilized DNA being approximately  $20 \text{ mg}\cdot\text{g}^{-1}$  of nonwoven fabric. The DNA-immobilized cloth could effectively accumulate endocrine disruptors and harmful DNA intercalating pollutants, such as dibenzo-p-dioxin, dibenzofuran, biphenyl, benzo[a]pyrene, and ethidium bromide [58]. Additionally, DNA-immobilized cloth was found to bind metal ions such as Ag(I), Cu(II), and Zn(II) due to the polyanionic property of DNA.

Furthermore, DNA was immobilized on a glassy carbon electrode by UV irradiation, and the electrochemical oxidation of tetracycline (TC) was detected by cyclic voltammetry. The applicability of the DNA modified electrode was demonstrated by detection of TC in such complicated samples as pharmaceutical formulations and milk [59].

Polycyclic aromatic hydrocarbons (PAHs) are combustion related pollutants and are also members of micropollutant. Some carcinogenic PAHs are genotoxic and induce mutations. Since PAHs are planar molecule, intercalation of PAHs with DNA occurs through physical interaction with the hydrophobic spaces between adjacent base pairs of DNA strands. Upon contact with DNA, stable PAH–DNA adducts form rapidly as the first step toward their toxic effects. Topuz et al. prepared by cross-linking of inverse miniemulsion of double-stranded DNA molecules using poly(ethylene oxide) diglycidyl ether [60]. Their biomimetic approach relies on interaction between PAHs and the complete network that constitutes the water swelling DNA nanogels. PAH adsorption capacity of the DNA nano gel  $720 \text{ }\mu\text{g}\cdot\text{g}^{-1}$ , which means that 1 mg of DNA nanogel is sufficient to purify a liter of water containing the critical PAH concentration for cancer risk ( $600 \text{ ng}\cdot\text{L}^{-1}$ ). Double-stranded DNA nanogels showed larger phenanthrene uptake than that of single-stranded ones. As a result of short diffusion pathways, PAH uptake is rapid, reaching 50% loading after 15 min.

DNA-immobilized materials have been developed on the basis of mechanistic study of interaction between DNA and genotoxins. They are expected to be useful for the removal and the detoxification of water containing various polycyclic aromatic pollutants.

## 5 EDTA-Chitosan

### 5.1 Chelation

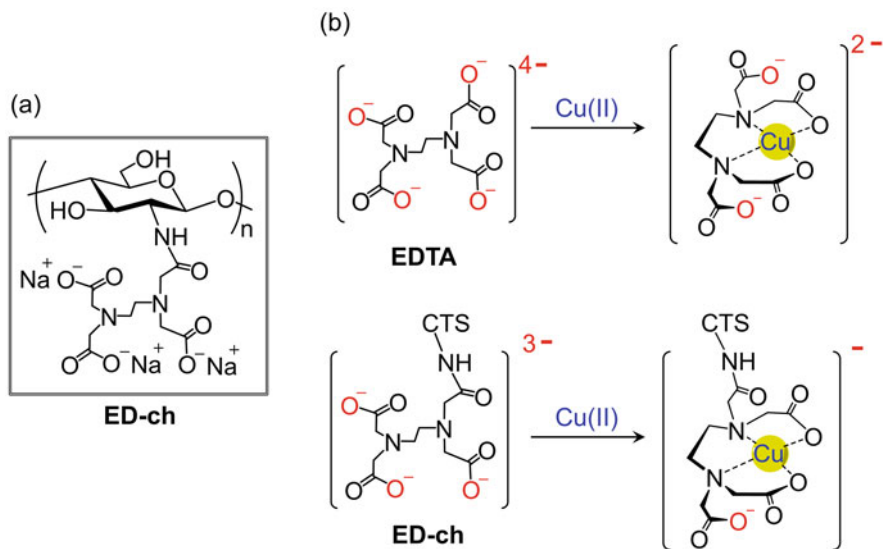
Metal ions play important roles of many natural proteins, providing structural, catalytic, and electron transfer functions. Some metalloproteins act as such important biological roles as oxygen transfer, metabolism, and signal transduction, and have transition metal ions through a coordination bonds with nitrogen, oxygen, or sulfur atoms of side-chains of constituted amino acid residues or their cofactors. Although some bio-materials have an ability to bind various metal ions, introduction of a chelation site is expected to enhance the ability. Chelation involves the formation or presence of two or more separate coordinate bonds between a polydentate (multiple bonded) ligand and a single central metal atom. Focusing on the coordination ability of amino group with transition metals, chitosan-based materials have been extensively investigated to remove heavy metal ions [61].

### 5.2 Preparation of Water-Soluble EDTA-Linked Chitosan

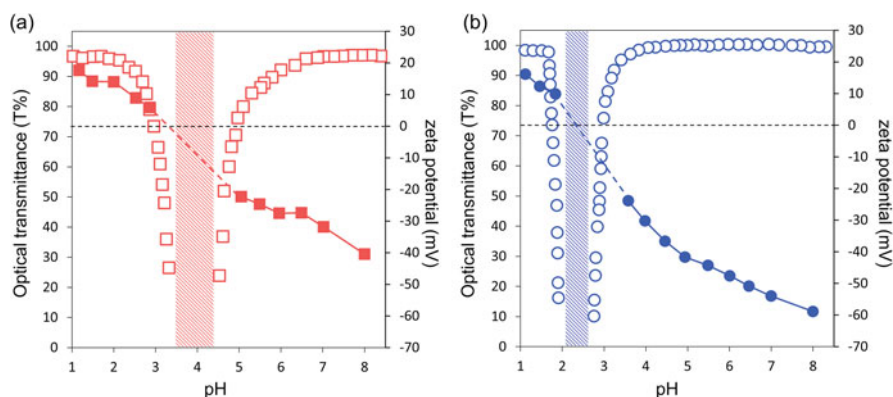
Ethylenediaminetetraacetic acid (EDTA) is the most useful hexadentate ligand and chelating agent, which is used for sequestering metal ions, reducing water hardness, removing metal ions, and so on. In order to enhance the metal binding ability of chitosan, introduction of EDTA residue was investigated. In the previous work, solid EDTA-linked chitosan (ED-ch) was synthesized and evaluated its heavy metal ions uptake [62]. Fujita et al. reported the synthesis and property of the corresponding water-soluble derivative [63]. Behavior of metal ion chelation and property of polyelectrolyte in water have received much attention. Since chitosan skeleton has positive charge and EDTA residue has negative charge, the water-soluble ED-ch was expected to have a zwitterionic property. The charge density is changeable by pH of the solution and amount of chelated metal ions (Fig. 17), which is useful to apply to metal ion removal by flocculation.

In the previous study, introduction of EDTA residue was simply performed by a reaction between chitosan amino group and EDTA dianhydride underwent cross-linking reaction to give insoluble ED-ch. In order to avoid the cross-linking, an acetic acid solution of high molecular weight chitosan ( $M_w = 50\text{--}100$  kDa) was treated with EDTA monoanhydride. This reaction proceeded smoothly and homogeneously by addition of aqueous  $\text{NaHCO}_3$  to control the pH of the reaction mixture to slightly basic. The degree of substitution (DS) of EDTA residues in the product was changeable from 20 to 80% by the amount of the acylation reagent used. ED-ch thus obtained was highly soluble in water and it was purified by dialysis or ultrafiltration.

ED-ch is a polyelectride having amino groups and carboxylic acid, and positive charge and negative charge should present predominantly under acidic and basic

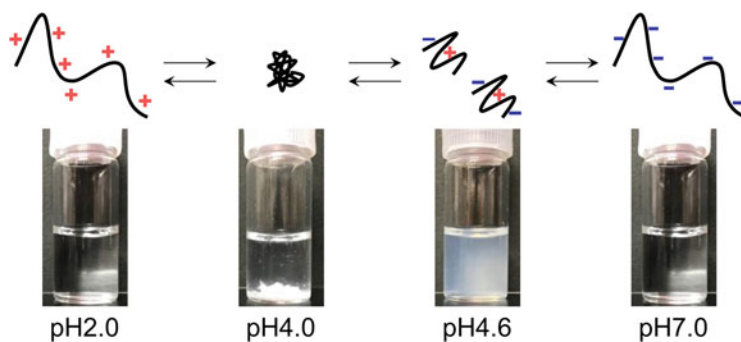


**Fig. 17** Structures of EDTA-linked chitosan (ED-ch) (a) and its chelation complex with Cu(II) (b)

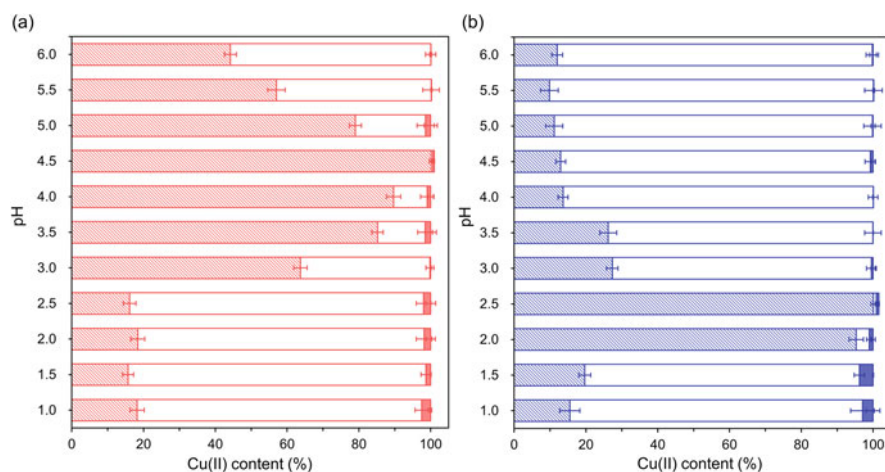


**Fig. 18** pH dependent solubility of ED-cd observed by transmittance at 600 nm (a) and its zeta potential (b)

conditions, respectively. The amphoteric property of ED-ch with D.S. 39 and 70% was confirmed by relation between pH and zeta potential (Fig. 18b). Furthermore, the potential curve suggested that charge neutralization of ED-ch with D.S. 39 and 70% occurred at around pH 3.5 and pH 2.5, respectively. Turbidity experiment shown in Fig. 18a revealed that ED-ch had good water solubility in both acidic and basic regions, whereas turbidity was increased at around the isoelectric pH and almost complete precipitation was observed at the narrow pH region. These pH



**Fig. 19** Schematic drawing of pH controlled flocculation of ED-ch 39 and photos of ED-ch samples



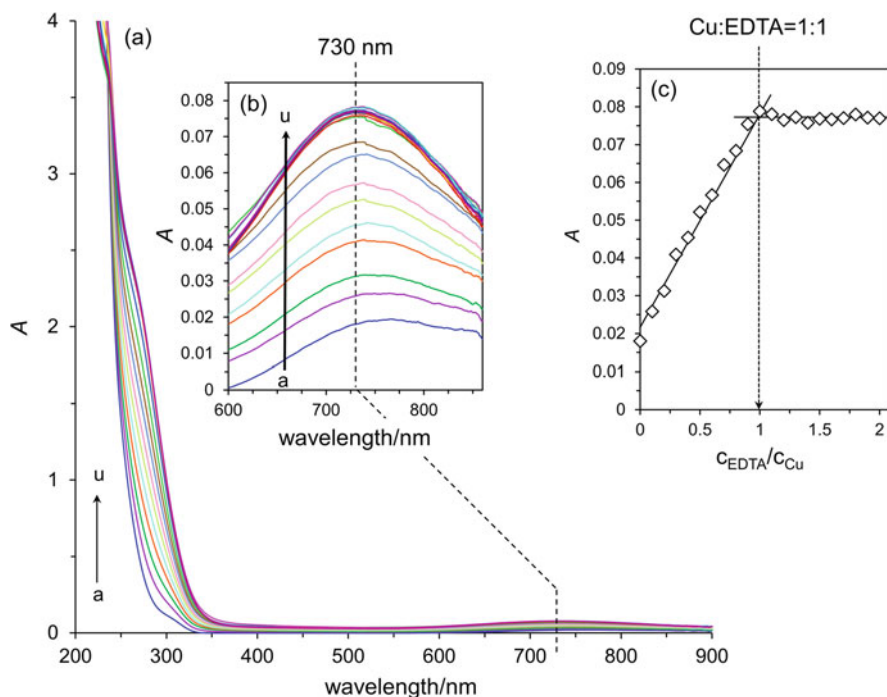
**Fig. 20** pH dependent Cu(II) distribution in the presence of ED-ch 39 (a) and ED-ch 73 (b) (closed bar: free Cu(II), open bar: chelated Cu(II) in solution, dotted bar: precipitated Cu(II))

dependence properties of ED-ch suggested that the flocculation occurs by charge neutralization of the polymers (Fig. 19).

### 5.3 Metal Ion Removal by ED-ch Flocculation

Using ED-ch that has pH dependent flocculation property, removal of Cu(II) was performed under various pH conditions. After mixing with ED-ch with D.S. 39% or 73%, each sample was separated by centrifuge to obtain precipitate, and then the resulting supernatant was fractionated into polymer gel and filtrate by ultrafiltration. Content of Cu(II) was estimated by atomic absorption and summarized in Fig. 20.





**Fig. 21** Spectroscopic titration of ED-ch with Cu(II). UV-vis spectrum with different amounts of Cu(II) (a), (b), and the titration curve (c)

**Table 4** Removal of various metal ions by ED-ch determined by atomic absorption spectrometry

	Cu (II)	Cd (II)	Pb (II)	Zn (II)	Ag (I)	Fe (III)	Hg (II)	Mn (II)	Cr (VI)	Ca (II)	Mg (II)
ED-ch 39	89%	84	94	82	94	90	95	85	35	20	3
ED-ch 73	96%	96	92	96	95	99	98	95	34	70	5

All filtrate fractions found to contain <5% of Cu(II) suggesting that almost all Cu (II) is captured by ED-ch. The ratio of Cu(II) containing the precipitate and the polymer gel was dependent on pH of the samples and the best removal by ED-ch 39 and ED-ch 73 was achieved at pH 4.5 and 2.5, respectively. Furthermore, spectroscopic titration of ED-ch with Cu(II) (Fig. 21) showed formation of EDTA-Cu(II) chelation complex in the ratio of 1:1.

The ability of metal chelation and flocculation abilities of ED-ch could be useful for the removal of various metal ions. ED-ch was added to a metal ion containing solution, and then pH was adjusted to form precipitate, which was separated by centrifuge. As shown in Table 4, Cu(II), Cd(II), Pb(II), Zn(II), Ag(I), Fe(III), Hg(II), and Mn(II) were successfully removed more than 90%. However, removal of Cr

(VI) was unsuccessful because of low chelation ability of its oxyanion. Since flocculation is one of the most efficient methods for the waste water treatment, the unique property of water-soluble ED-ch extends this procedure to metal ion removal.

#### 5.4 Some Applications of EDTA-Linked Chitosan

In order to extend applicability of the pollutant removal, further chemical modification of ED-ch was performed by several groups as shown in Fig. 22. Moreira et al. described introduction of two functional groups, EDTA and pyridyl amino, into chitosan skeleton increased its affinity toward Cr(VI) [64]. Reductive amination of chitosan was conducted with 2-pyridinecarboxaldehyde and NaBH<sub>4</sub>. Subsequently, the product was acylated with EDTA dianhydride (EDTAD) to give a cross-linked insoluble material (ED-py-ch). ED-py-ch has both cationic functional group of ammonium group and chelation site of EDTA group. The removal of Cu(II) and oxyanion of Cr(VI) from a single aqueous solution using the novel bifunctionalized adsorbent material revealed that the maximum adsorption capacities for Cu(II) 2.60 mmol g<sup>-1</sup> at pH 5.5, whereas that of Cr(VI) was 3.50 mmol g<sup>-1</sup> at pH 2.0. These results were explainable by consideration of the zwitterionic structure of the adsorbent. Presence of rich ammonium cations at low pH conditions enhances Q<sub>max</sub> for oxyanion of Cr(VI), while deprotonation of carboxyl group occurred at higher pH region stabilizes chelation complex of Cu(II) and EDTA.

Furthermore, biodegradable adsorbent for the heavy metal ion removal was synthesized by thermal condensation of three components, namely EDTA tosylate, chitosan, and carboxymethyl cellulose (CMC) [65]. This composite material (ED-ch@CMC) was insoluble in water, and efficiently removed Cu(II) from an aqueous medium. Washing ED-ch@CMC with an EDTA solution resulted in desorption of Cu(II), which means possibility of the repeated use of this adsorbent. As an excellent advantage, this material was shown to be decomposed when it was buried under the soil for 50 days.

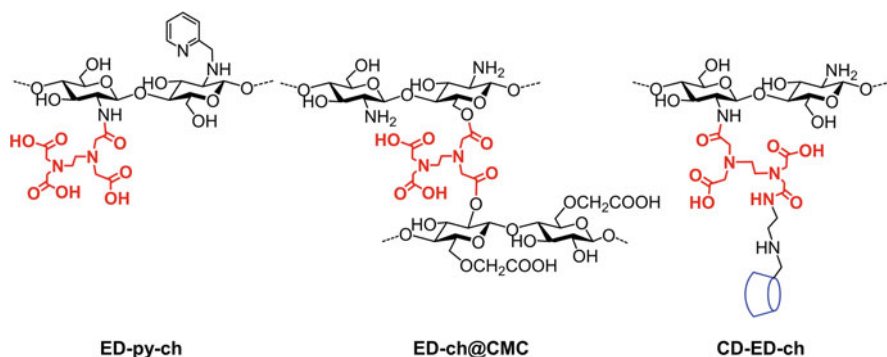


Fig. 22 Partial structures of multi-functional ED-ch adsorbents

The global contamination of water resources with inorganic and organic micropollutants, such as metals and pharmaceuticals, poses a critical threat to the environment and human health. Zhao et al. reported on a bio-derived trifunctional adsorbent (CD-ED@ch), which consisted of chitosan, EDTA, and  $\beta$ -CD [66]. They fabricated via a simple one-pot synthesis method, which involves cross-linking chitosan and 6-amino- $\beta$ -CD derivative using EDTAD as a cross-linker. In this 3-component-system, chitosan chain is considered as the backbone, the immobilized  $\beta$ -CD cavities capture the organic compounds via host-guest inclusion complexation, and EDTA-groups form chelation complexes with metal ions. CD-ED@ch displayed a monolayer adsorption capacity of 0.803 and 1.258 mmol g<sup>-1</sup> for Pb(II) and Cd(II), respectively. While a heterogeneous adsorption capacity of 0.177, 0.142, 0.203, 0.149 mmol g<sup>-1</sup> for BPS, ciprofloxacin, procaine, and imipramine, respectively. Importantly, the adsorbent performed an effective role in the simultaneous removal of metals and organic pollutants at environmentally relevant concentrations.

Chitosan derivative with pendant EDTA showed potential chelation ability toward various metal ions, and its zwitterionic property resulted in pH dependent dynamic morphology change, which could apply to the removal of heavy metals by flocculation. Further chemical modification of ED-ch provides multi-functional adsorbents for simultaneous removal of different types of pollutants.

## 6 Conclusion

Over the past few decades, the biological systems represent a successful strategy for the design of materials. Highly organized structures and functions in living organisms have been a source of inspiration of new materials, of which properties are beyond the artificially synthesized materials. This chapter describes important consideration in designing and synthesizing new adsorbents mimicking remarkable biological system of molecular recognition, and also highlights recent advances in biomimetic adsorbents for the selective and efficient removal of target pollutants.

Utilizing the inclusion ability of CDs, new type of adsorbents have been synthesized by CD derivatives and polysaccharide, chitosan, and shown to have a high affinity toward various organic and hydrophobic pollutants with appropriate molecular sizes. In these studies, employing soft, flexible, and swelling polymer such as polysaccharide scaffolds of CD demonstrated their high selectivity and high adsorption capacity of CD-based adsorbents. The importance of the soft scaffold is also shown in the preparation of biomass-immobilized adsorbents. Chitosan and calcium alginate hydrogel beads have flexible and highly swelling property and they act as a scaffold of a large number of living or dead biomass, which have an ability of pollutant accumulation and degradation. Their biocompatible nature helps the growth of various bacteria and fungi with pollutant degradation ability, and their multi-functionality is useful for structural modification such as introducing molecular recognition sites and cross-linking.

Furthermore, adsorbents having intercalation and chelation ability are designed. DNA-immobilized materials inspired by interaction between DNA and genotoxins are shown to be useful for the removal and the detoxification of water containing various polycyclic aromatic pollutants. Chitosan derivative with pendant EDTA showed potential chelation ability toward various metal ions, and its zwitterionic property resulted in pH dependent dynamic morphology change, which could apply to the removal of heavy metals by flocculation. Further chemical modification of ED-ch provides multi-functional adsorbents for simultaneous removal of different types of pollutants.

Although the efficiency of novel synthetic adsorbents designed based on biomimetic approaches is still far away from that of our request, further improvement of adsorbent structures will possibly surpass conventional adsorbents. Further investigations on fundamental comprehension of supramolecular chemistry and study on mechanism of action of pollutants would be necessary.

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